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COLLOID CHEMISTRY

THEORETICAL AND APPLIED

BY SELECTED INTERNATIONAL CONTRIBUTORS

COLLECTED AND EDITED BY

JEROME ALEXANDER

GENERAL PRINCIPLES AND SPECIFIC INDUSTRIES

SYNTHETIC POLYMERS AND PLASTICS

REINHOLD PUBLISHING CORPORATION

330 WEST FORTY-SECOND ST., NEW YORK, U. S. A.

1946

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Preface

It is hoped that the six volumes of this series, by bringing into juxtaposition so many extensive reviews and bibliographies covering so many diversified but interrelated fields, are contributing to the advance, dissemination, and utilization of scientific knowledge.

Even as a boy, the great Scottish mathematical physicist, James Clerk Maxwell, when confronted with an interesting happening, would ask: "What is the *go* of it?" And his curiosity as to the causes of phenomena led him to such explanations as the electromagnetic theory of light While many papers in this series deal with or include theoretical aspects, others record merely observations which await explanation by or coordination with colloid theory. It must always be remembered that accurate observations are never vitiated by conflicting views as to the causes of phenomena. In fact, to avoid dogmatism, the Editor has in some cases deliberately sought out and included diverse theories, which, on comparison and analysis, generally turn out to be simply different aspects of the same phenomena, and not so conflicting as their sponsors imagine We continue the endless effort to understand the "go" of natural phenomena, so that in addition to the joy of understanding them, we may control, modify, and utilize them to further life, health, and happiness

The 71 papers in Vol VI are devoted mainly to applications of colloid chemistry involved in the processes and the products of industry, or of value to technology and technologists. Including a few theoretical papers, they fall into two groups: 38 papers dealing with specific industries or industrial operations; 32 papers centering about synthetic resins and plastics A general article on nuclear fission and atomic energy is also included The Editor expresses his profound thanks and appreciation to the many eminent contributors, whose cooperation has made possible so many informative and suggestive papers

Pedagogical convenience has led to the establishment of faculties in pure sciences and in applied sciences. As a consequence, some harbor the erroneous notion that "pure" science is sacrosanct. But with the exception of abstract mathematics, all sciences deal with material units and their interrelations, and thus constitute a physical and intellectual continuum. What is considered pure science today, may soon be of widespread public use It is said that when Faraday demonstrated to Gladstone the basic relations between a magnetic field and an electric current, the statesman remarked: "This is very interesting, Mr. Faraday, but of what use is it?" To which Faraday prophetically replied: "Some day you may be able to tax it."

Now that World War II has ended, we shall learn more of improvements in technology, public health and medicine, in addition to protective coatings, foam plastics (from plasma, starch, cellulose, etc.), petrol thickeners for flame throwers, smoke generators, and other novelties which the conduct of war has shrouded in secrecy. Great developments will loom in the near future, if human nature and politics will learn to utilize the powers of science fully for the good and happiness of mankind rather than for destruction.

This applies especially to the release of nuclear energy, as exemplified by the "atomic bomb" and several other matters made public by the end of the war which are considered in appendixes, or have been added in proof.

JEROME ALEXANDER

New York, N. Y.
July 23, 1945

To My Life's Companion

Gertrude Eleanor Alexander

Ideal Wife and Mother

December 25, 1945

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Part I

General Principles and Specific Industries

The Surfaces of Solids and Liquids and the Films That Form upon Them

Part II. Solids and Adsorption at the Surface of Solids or Liquids*

WILLIAM D. HARKINS AND GEORGE JURA

University of Chicago and The Universal Oil Products Company

INTRODUCTION

This chapter deals largely with the effects of adjacent liquids or adsorbed films upon the energy relations of the surfaces of solids as determined in the Laboratory of Surface Chemistry of the University of Chicago during the last fifteen years. The work has been based upon a general idea which has not been utilized sufficiently elsewhere. This is that the energy relations of interfaces with solids are the same as those of liquids, except insofar as they are modified by the more specific structure of the surface of the solid. However, the methods of investigation are, of necessity, very different.

A few of the differences in the characteristics of solids and liquids are as follows.

(1) While liquids exhibit the property of viscosity and, to a slight extent, of rigidity, a crystalline solid is distinguished by a rigidity of form which is usually extremely high by comparison. The lack of mobility in the surfaces of solids is responsible for some of the most important differences between the characteristics of films on solids and on water.

(2) In a perfect single crystal, the order in the arrangement of the molecules and atoms extends to the phase boundaries (surfaces) of the crystal. In a liquid this order extends to only the immediate neighbors. In a crystal the equilibrium positions of the atoms or molecules are considered as a space lattice, whereas in the surface of a crystal they may be considered as a surface lattice or network of points made up of rows of equidistant points which fall on two or more sets of straight lines, the lines in each set being parallel (Fig. 1). The surface exhibits an energy contour, which may be illustrated by Fig. 2. A space lattice is represented by a similar set of points in space (Fig. 3).[1]

(3) The state of the interior of a solid and of its surface as well, often depends at a given temperature upon the previous history of the solid; this is not true of a liquid. The differences in the methods which can be used for the investigation of the energy relations between a solid and either a liquid or a film are in general very great. These are due to the fact that the direct determination of the surface tension of a liquid or that of the two-dimensional pressure of a film on its surface is very simple; but no method is known for the determination of the surface tension of a solid. Though the film pressure can be obtained, very indirect methods must be used, as will be shown later.

Much can be learned of the characteristics of films on the surfaces of liquids by determinations of viscosity and of surface potential, but these methods are not ap-

* Part I of this chapter appears in Volume V of this series.

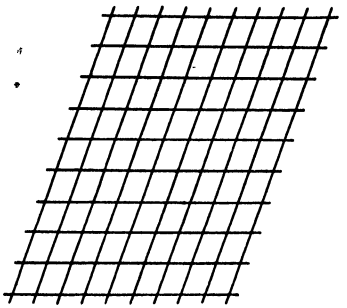

FIGURE 1. A surface lattice in which the intersection of the lines gives the mean positions of the atoms of a monoatomic solid or of the space group for molecular solids.

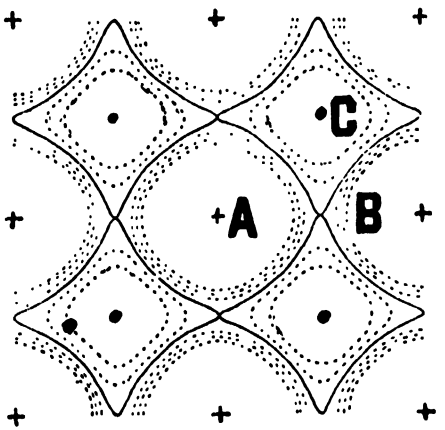

FIGURE 2. Schematic representation of the force fields on the surface of an ionic crystal as calculated by Lennard-Jones. *Trans. Faraday Soc.*, **28**, 333 (1932).

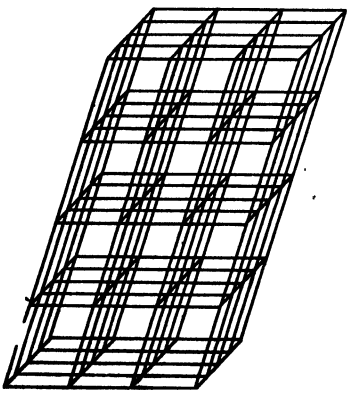

FIGURE 3. A space lattice, the same representation as for the surface lattice. The atoms or molecules, however, are found at the intersection of three lines.

plicable in general to films on solids. However, potential measurements have been made on conducting solids.

While the experimental work is much simpler with liquids, the reverse is true of theoretical calculations, since the model developed for solids is in a much more satisfactory state than that for liquids; in fact, there is at present almost no model for liquids.

Classes of Solids

From a consideration of their chemical, thermal, electrical and magnetic characteristics, solids have been considered to belong to five classes:[2]

(1) Metals
(2) Ionic crystals: sodium chloride, magnesium oxide
(3) Valence crystals: diamond, zinc oxide
(4) Semi-conductors: cuprous oxide
(5) Molecular crystals: nitrogen, hydrocarbons, other organic solids, etc.

In addition to solids and liquids as usually defined, there are other condensed states of matter which need to be classified separately. Among these are the resins, which have a high elasticity which disappears at a lower temperature, and the gels, which exhibit viscous, elastic, and plastic properties dependent upon specific types of structure.

The structure of glass is intermediate between that of a solid and of a liquid. While glass is often considered as an undercooled liquid, for the purposes of surface chemistry it may be classified as a solid. While glass does not exhibit the regular lattice structure of a crystal, the neighbors of any molecule, at not too high a temperature, are as permanent as in a crystalline solid.

At the present time, very little is known about the energy of the clean surfaces of solids; indeed, it may be said that neither the free nor the total surface energy for even a single solid is known with any certainty. Both experimental and theoretical approaches to this problem have been made, but in every case there has been at least one factor that makes the value questionable. On the other hand, the effects of adsorbed gases and of adjacent liquids on the energy of solid surfaces can be readily evaluated. It is the latter problem with which the major part of this discussion concerns itself.

Effect of the Subphase on Metallic Films

A subphase frequently imposes certain of its characteristics on a film deposited upon it. Thus G. P. Thomson[3] found that silver deposited on an etched (100) face of a copper single crystal followed the orientation of the copper, but with normal silver spacings. Gold sputtered on a glass surface, half of which was covered by sputtered platinum in (111) orientation, takes up a similar orientation on the platinum, but is random on the glass.[4] *

A thin aluminum film, when deposited on platinum,[5] is forced into a face-centered tetragonal structure with basal dimensions similar to those of platinum, but with a major axis equal to the length of side of a unit cube of normal aluminum. This basal plane pseudomorphism is the two-dimensional analog of the pseudomorphism of three-dimensional crystallography.

It is found that crystalline metallic films often dissolve in the surface of a metal, provided this surface consists of a Beilby layer due to polishing.[6] † Thus zinc crystals dissolve rapidly in this layer on copper, and somewhat less readily on polished mild

*The importance of catalyst (enzyme) templates in determining biological structures is obvious, an outstanding instance being the genes. J. A.

† See review paper with references by Sir George Beilby in J. Soc. Chem. Ind., 1903, **22**, 1166-77; also "Colloid Chemistry," by J. Alexander, p. 279 (D. Van Nostrand Co., 4th ed., 1937). J. A.

steel surfaces, at room temperature; but after the Beilby layer is removed by etching, the crystals will no longer dissolve. The Beilby layer may become saturated with zinc, after which further deposited layers retain their crystal structure indefinitely. The same effects were found with zinc, tin, lead, and silver flashed upon the surface of mild steel, lead, gold, or zinc, and with copper and lithium condensed on a Beilby layer on copper. While 30 seconds' electrodeposition at 0.1 amp per sq cm gave a permanent crystalline zinc layer on crystalline copper, a period of 3 minutes was necessary on a polished copper surface.

Statistical Calculation and Experimental Determination of the Surface Energy Values of Solids

Because of the difficulties involved, surface energy values have been calculated for certain ionic solids only and in addition for the diamond. Of these the simpler calculation is that of Harkins [98] for the diamond.

Since either the free or total surface energy of a liquid or solid is equal to approximately half the respective energy of cohesion involved in pulling the material apart to form two plane surfaces, the calculation of the surface energy and of the cohesion involve the same theory. If a solid is split in a plane which gives two unlike surfaces, then the factor is no longer one-half. Furthermore a correction for the "distortion" of the electrical fields in the surface is involved, and this in general reduces the value calculated from the cohesion obtained without an allowance for this distortion.

For homogeneous binding the total energy of a solid (E) is given by the relation

$$E = -aV + b\Sigma, \tag{1}$$

where V is the volume of the material and Σ is the area of the surface. The second term on the right has a sign opposite to the preceding term because the molecules are bound toward the inside, but not toward the outside, of the surface.

In the formation of surfaces the London dispersion forces must be taken into account, since they add to the surface energy ($+ b\Sigma$) of all surfaces, but they are relatively small in all of the solids considered here. The dispersion energy is additive, and decreases as the sixth power of the distance, so at the surface its contribution to the surface energy is almost altogether restricted to the adjacent molecules. The magnitude of the term $+ b\Sigma$ may be obtained by a calculation of the binding energy for those molecules which would be present adjacent to the plane of the surface if the solid or liquid were to extend beyond it, but which, on account of the existence of the surface, are not there. This is a general method of calculation applicable to all types of molecular, atomic, and ionic forces.

It is customary in surface chemistry to express the energy (ϵ) of a surface as that per unit area, so

$$\epsilon = b\Sigma/\Sigma = b. \tag{2}$$

Surface Energy of the Diamond

The diamond crystal is the hardest of known substances, and has an extremely high melting point (for graphite m.p. = 3800° K). Blom [7] considers the cohesion in elementary solids to be proportional to T_m / V, where V is the atomic volume. The diamond has both an excessively high melting point and the lowest of all atomic volumes. From these relations it is evident that the cohesion in the diamond should be excessively high, which indicates that the related surface energy should also be extremely high. A method which may be applied in order to determine the cohesional energy is to calculate the energy utilized in splitting a diamond crystal along some definite plane to give two surfaces. Since for each cm^2 of the plane two cm^2 of surface are formed the surface energy is one-half the cohesional energy, or

$$\epsilon_S = \epsilon_C/2.$$

Cohesional and Surface Energy in the 111 Plane. If the diamond crystal is split in the (111) plane, in a position equidistant from the carbon atoms on the two sides of the plane, only one carbon-carbon bond is ruptured for each carbon atom on one of the sides of the plane. Furthermore the bonds, before rupture, are perpendicular to the plane. The well-known arrangement of the bonds is represented in Fig. 4. The rupture may be assumed to occur in a plane parallel to the base of

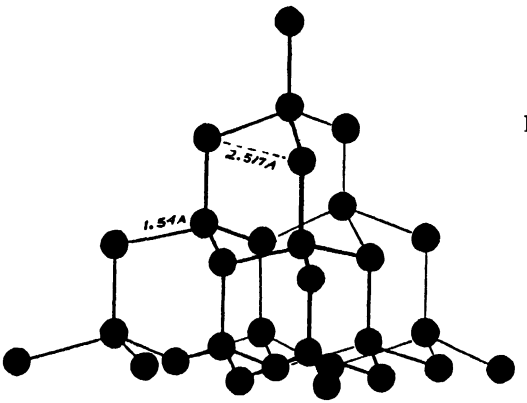

FIGURE 4. Structure of the diamond with the 111 plane horizontal. To obtain 111 faces the single vertical carbon-carbon bonds are broken.

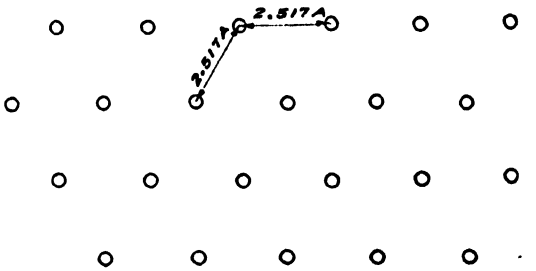

FIGURE 5. Arrangement of bonds in the 111 plane of the diamond; also the arrangement of the atoms at the ends of the bonds.

the figure. The arrangement of the atoms in the layer just above or just below the plane, is shown in Fig. 5. The length of the carbon-carbon bond is 1.54A, but the edge (a_0) of the cubic lattice cell is 3.560A in length. The distance d between adjacent atoms in the 111 plane is given by

$$d = 3.560/\sqrt{2} = 2.517\text{A},$$

from which the area per atom (σ) in the plane, or per bond projecting perpendicularly from the plane, may be obtained as follows:

$$\sigma = (2.517)^2 \sin 60° = (2.517)^2\sqrt{3}/2 = 5.48\text{A}^2.$$

The density (ρ) of atoms (or bonds) of the above type is:

$$\rho = 10^{16}/5.48 = 1.825 \times 10^{15} \text{ bonds cm}^{-2}.$$

If the energy required to break one mole of bonds is E_B ergs, the energy per bond is $E_B/6.06 \times 10^{23}$ ergs, and the cohesional energy is given by:

$$\epsilon_C = 3.00 \times 10^{-9} E_B \text{ erg cm}^{-2}$$

or

$$\epsilon_S = 1.50 \times 10^{-9} E_B \text{ erg cm}^{-2}.$$

Cohesional and Surface Energy Parallel to the Cubic Face. If the diamond crystal is pulled apart in a plane parallel to the cubic face (Fig. 3), the area of this face, $<3.560>_{Av} = 12.56A^2$, represents two atoms, and two bonds per atom are broken. Thus

$$\sigma = 12.67/4 = 3.167A^2 \text{ per bond}$$

and

$$\rho = 10^{16}/3.167 = 3.158 \times 10^{15} \text{ bonds cm}^{-2}$$
$$\epsilon_C = 5.21 \times 10^{-9} E_B \text{ erg cm}^{-2}$$
$$\epsilon_S = 2.10_5 \times 10^{-9} E_B \text{ erg cm}^{-2}.$$

The energy required to rupture a mole of bonds has been determined by different investigators to require an energy from as low as 62.5 to as high as 90 kcal, so the magnitude of the energy of the strength of the carbon-carbon bond is by far the most inaccurate part of the calculation of the surface energy. These values give E_B from 2.62 to 3.77×10^{12} ergs per mole of bonds. Thus the values all in erg cm^{-2} lie between the maximum values calculated below and the minimum values obtained when 2.62 is substituted for 3.77

$$\epsilon_{C(111 \text{ plane})} = 3.00 \times 3.77 \times 10^3 = 11310 \text{ to } 7860$$
$$\epsilon_{S(111 \text{ plane})} = E_C/2 = 5650 \text{ to } 3925$$
$$\epsilon_{C(100)} = 5.21 \times 3.77 \times 10 = 19640 \text{ to } 13650$$
$$\epsilon_{S(100)} = E_C/2 = 9820 \text{ to } 6900$$

The free energy of these faces has also been estimated. For the two extremes of the value (in erg cm^{-2}) of the energy of the carbon-carbon bond these are: Free energy of the (111) face = 5400 to 3750; of the (100) face = 9400 to 6520.

The values of the total and free surface energy are actually slightly lower than those given by the method of calculation, due to an effect not mentioned above. However, this is obscured by the large error in the energy of the carbon-carbon bond. This lowering is due to the breaking of the bonds which become a part of the surface, causing some adjustment of the energy of the unbroken bonds adjacent to the surface, in such a direction as to decrease the surface energy; but no attempt has been made to estimate the magnitude of the decrease, although it is probably greater than that because of long-range binding of the broken bonds.

Thus the magnitudes of the surface energy given in this paper may be considered as maximum values if considered from this point of view alone.

Calculation of Surface Energy of Ionic Crystals

The surface energy of ionic crystals was first calculated by Born [8] from his theory for the potential energy of ionic crystals and the relations of Madelung.

The potential energy ($-u$) released per ion pair on their approach from infinity to their position in the crystal, according to Born, is given by

$$-u = \frac{-a}{r} + \frac{b}{r^n}$$

in which a is the product of the ionic charges and the Madelung constant. If the crystals are those of the alkali halides, the constant n, which represents the variation of the repulsion, increases from 6 to 10 as the molecular weight increases, and the repulsive energy amounts to about 10 to 15 per cent of the total lattice energy. From Eq. (1) and this theory it is possible to calculate the surface energy for the (100) and (110) planes. The original theory and method have been refined by later workers whose data follow.

On the basis of the assumption that certain halide and other crystals are ionic, and that the repulsive force constants are similar to those for neon and argon, theoretical values for the surface energy have been calculated by Lennard-Jones and Taylor, and by Miss Dent,[9] and these are collected in Table 1. Unfortunately there are no entirely reliable data for the surface tension of molten sodium chloride. Jaeger,[10] by the use of the bubble pressure method found surface tensions of 113.8

dyne cm^{-1} at 803° C and 88 erg cm^{-1} at 1172° C. If it is considered that a linear extrapolation is justified, then at 0° K both the surface tension and the total surface energy would be 190 dyne cm^{-1}. Since Jaeger's value for the surface tension, even at the high temperature of 803°, is higher than that calculated by Miss Dent, it is evident that there is a serious disagreement between the calculated and the experimental values.

Table 1A. The surface energies of alkali halides and alkaline earth oxides and sulfides (erg cm^{-2}). (100 planes.) (Lennard-Jones, Taylor, and Miss Dent.)

F	Cl	Br	*I*		*O*	*S*
Na (304)	(96)			Mg	1362	357
265	77	76	79			
K (180)	(76.6)			Ca	1032	356
149	56	54	58			

Values in parentheses are uncorrected for distortion of the surface.

Table 1B. Surface energies of certain salts (0, 1, 1 plane)

011	*F*	Cl	011	*O*	*S*
Na	784	350	Mg	3940	1730
K	489	260	Ca	2850	1440

The total surface energy, $\Sigma\epsilon_s$, of a solid which Eq. 1 shows to be dependent on the area, can be determined experimentally. Thus the heat of solution of a very finely divided salt should be different from that of a coarse salt. Lipsett, Johnson, and Maas [11] have carried out such experiments with sodium chloride. They found the total surface energy to be 400 erg cm^{-2}. However they calculated the area of the salt from the dimensions of a small number of crystals. This general method was later shown to give, in general, too low values. Thus the 400 erg cm^{-2} should be higher than the true value. Their work, however, proves definitely the existence of a surface energy. J. E. Wertz, working in this laboratory, obtained a single value of 180 erg cm^{-2} for sodium chloride, but one determination is insufficient to show anything at all as to its accuracy.

Adsorption at Interfaces in Solid, Liquid, and Gaseous Systems

The extremely thin region in which any two of the phases solid, liquid, or gas, are in contact is designated as an *interface;* or as a *surface* when one of the two phases is a gas. One of the most important characteristics of an interface is that the concentration of any dissolved component is in general very greatly different at the interface than in either adjacent phase. For example, a two-phase system may be considered which (1) consists of water and water vapor and (2) water and oil. In each condensed phase the molecules are held together by electrical forces, and it may be considered that in water there is a general cohesional field, due to these electrical forces, of the general order of 12,000 atmospheres, and for simplicity an oil may be considered in which the value is 3,000 atmospheres. If the surface of either the water or the oil or the interface between them were perfectly sharp, the surface energy would be excessively high. However, no surface is entirely sharp and the amount of the surface energy may be considered to decrease, in general, as the thickness of the surface region increases. In passing from water into the vapor phase it may be said that there is a decrease of 12,000 atmospheres in the cohesional field. In terms of the surface this is represented at 25° by a free surface energy of 72 ergs per square centimeter. At the interface, however, the change from 12,000 to the general order of 3,000 atmospheres is represented in the special case of benzene by 34 ergs per square centimeter.

If, now, another component is added whose molecules are like water at one end and like the oil at the other, these exhibit a higher concentration at either the surface or the interface than either the water or the oil. If such molecules pass into the surface they thicken the interfacial region, thus reducing the free energy (also the total surface energy). It may be considered that either the surface or the interface acts as a trap for such molecules, since the decrease in the cohesional field is greater at the surface than at the interface between oil and water. It is to be expected that for any specific polar-nonpolar molecules the surface should trap the molecules better than the interface.

However, the following consideration indicates that this should vary with the concentration in either the aqueous, the vapor, or the oil phase. For example, consider butyric acid present in these various phases. At low concentrations, even neglecting the ionization, the concentration in an aqueous phase is greater than that in benzene, while at high concentrations the solubility is much greater in benzene than in water. This is due to the fact that in the nonpolar solvent the polar carboxyl groups attract each other much more than they do the oil, so that two or more molecules unite to form an aggregate which acts much more like a nonpolar molecule than the single molecules.

At very high concentrations of the adsorbed molecules at either the interface or the surface the molecules of butyric acid will be oriented with the polar group toward the water and the nonpolar group toward either benzene or vapor. The number of molecules at the two interfaces may be expected to be practically equal, since the number which can get into the film which is only one molecule thick depends almost entirely upon the cross-sectional area of the molecules in this position. However, at lower concentrations, where the packing is less tight, the number of molecules present in the surface should be much greater than in the interface, since the drop in intensity of the cohesional field is much greater and the molecules still maintain some part of their perpendicular orientation. As the film gets more and more dilute, the molecules in the surface appear to lie down and the magnitude of the drop in the cohesional field should no longer produce any appreciable effect upon the number adsorbed.

That these expectations are fulfilled is shown by Table 2A, which gives the ratio between the number of molecules adsorbed in the surface and in the interface at various concentrations. At 1/100 molal concentration for the aqueous phase the number of molecules adsorbed is the same in both the surface and the interface, while at 1/10 molal there are 70 per cent more molecules in the surface than in the interface and at 0.375 molal this has fallen to only 7 per cent. As the concentration increases, the number of molecules in the surface or the interface rises considerably above the number adsorbed, since the number in the surface before adsorption rises as the concentration of the solution increases.

Table 2A. Ratio (R) of Number of Molecules of Butyric Acid Adsorbed in Surface to Molecules in Interface (Water-Benzene) as a Function of Concentration of the aqueous Solution

Molality	*R*
0.01	1.0
.05	1.45
.10	1.71
.15	1.50
.20	1.36
.25	1.27
.375	1.07

Since the thickness of the adsorbed layer is not always known, it is more convenient to express the amount adsorbed as the number of molecules per sq cm. With some systems this amount may be determined by entirely experimental means; in others it is necessary to invoke the help of the methods of either (1) thermodynamics, or (2) statistical mechanics, to obtain the amount adsorbed.

The direct method is illustrated by an experiment [48] in which sodium oleate, with an excess of sodium hydroxide to decrease hydrolysis, was used to emulsify a paraffin oil in water. The amount of soap adsorbed in the whole interface was obtained by an analysis for soap of the aqueous phase before and after the emulsification. To obtain the adsorption in the desired units, it was necessary to determine the total oil-water interfacial area. In each experiment this was done by an accurate measurement of the diameters of from two to three thousand emulsion droplets by the use of an oil-immersion objective. Since the droplets are spherical it was possible to calculate the area distribution curve, and from this the total interfacial area. The precautions necessary to obtain accuracy are so extensive that for these the original paper should be consulted. The final result of this particular experiment was that each adsorbed sodium oleate molecule occupied an area of 27Å^2. With more concentrated solutions this area is very slightly smaller and with less concentrated, may be much larger.

In an experiment with a water-gas interface,[48] bubbles of nitrogen were passed into a long, nearly horizontal glass tube filled with a solution of *p*-toluidine. The bubbles were collected at the upper end. From an analysis of the liquid from the bubbles, and their total area, the areas per molecule of *p*-toluidine and isoamyl alcohol were found to be 21A^2 and 13A^2, respectively. The total area of the interface was taken as the number of bubbles multiplied by the area per bubble. The principal error was in obtaining the area of the bubble from measurements of its dimensions as an imperfect ellipsoid of revolution.

Adsorption of a Soluble Substance at the Surface of Water or the Water-Oil Interface

Gibbs has given an equation which may be used to calculate the amount of adsorption of a soluble substance at an interface. This has been expressed in the following form by Lewis and Randall: [12]

which may be written

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln a}\right)_T$$

$$\Gamma = -\frac{a}{RT}\left(\frac{\gamma}{\partial a}\right)_T \qquad (3)$$

Since it is easy to determine the surface tension of a solution, the only difficulty is that involved in the determination of the activity (a) of the solute. It is unfortunate that there is only one solution of an organic substance, that of *n*-butyl alcohol in water, for which the activity relations have been determined accurately. In this work, carried out by Harkins and Wampler,[44] the activities were calculated from the lowerings of the freezing point obtained from measurements made by a thermal-potentiometer system capable of measuring to 10^{-5}° C.

Table 2B. Films of Butyl Alcohol on Water

Molality	Activity	Surface tension	Moles per sq cm × 10^{10}	Number of molecules per sq cm: Adsorbed	Already present	Total	Area per molecule adsorbed (sq A)	Area per molecule, (sq Å)	Film pressure (π)
0.00329	0.00328	72.80							
.00658	.00654	72.26							
.01320	.01304	70.82	1.26	0.76	0.04	0.80	132	120	1.98
.0264	.02581	68.00	2.15	1.31	.06	1.37	76	73	4.80
.0536	.05184	63.14	3.54	2.14	.10	2.24	47	45	9.66
.1050	.09892	56.31	4.72	2.86	.15	3.01	35	33	16.49
.2110	.19277	48.08	5.26	3.19	.23	3.42	31.4	29.2	24.72
.4330	.37961	38.87	5.69	3.45	.37	3.82	29.0	26.2	33.9
.8540	.71189	29.87	6.03	3.65	.56	4.22	27.4	23.7	42.9

Surface tensions at 25°. Activities at 0°. It is assumed that the relative activities at 25° are the same as at 0°.

Table 3. Adsorption and Molecular Area for Organic Acids
Temperature, 0°

Moles per 1000 g of water	Area per molecule (Ångström units) Adsorbed	In film
	Propionic Acid	
0.1008	70.8	63.8
.2420	47.2	41.8
1.0167	32.4	26.4
2.3110	28.8	21.7
	Butyric Acid	
0.0211	98.0	93.0
.0503	62.5	59.3
.1049	43.2	40.4
.2510	34.6	31.5
.5088	30.2	26.6
1.095	26.5	22.2

The values of the molecular area indicate that the adsorbed film is monomolecular with respect to butyl alcohol. At the *highest* concentration used, 0.854 *M*, the area of the surface available for butyl alcohol molecules is 23.7Å², while the higher insoluble alcohols can be compressed to an area of 20.7Å² per molecule at the same temperature. The area per molecule in solid alcohols, as measured perpendicular to the molecular axis, is even smaller. The adsorbed film is probably a two-dimensional gas, though there is some indication that there may be a transition to the liquid expanded at an area of 33Å² per molecule. The data are not sufficiently accurate to make this certain. Other soluble films that have been studied give similar results.

The Gibbs equation can also be applied to insoluble films on the surfaces of liquids. Since the solubility and the vapor pressure of such films are both so low, the entire material spread on the surface can be considered to be the surface excess. Since the film pressure (π) is measured directly, the relative activity of the films at different areas can be calculated by integrating the Gibbs equation:

$$\ln \frac{a_2}{a_1} = \frac{N_0}{RT10^{16}} \int_{\pi_1}^{\pi_2} \sigma d\pi \qquad (4)$$

where N_0 is Avogadro's number and σ is expressed in Å² per molecule. This formula is the exact analog of that used for the calculation of the fugacity in three dimensions, since area is substituted for volume and film pressure for pressure. This equation was derived by Frumkin and Pankratov.[18]

Application of the Gibbs Equation to the Surfaces of Solids

Although no experimental procedure has been devised for the determination of the free surface energy or surface tension of a clean solid surface, the Gibbs equation can be used to calculate the decrease (π) of the free surface energy caused by the adsorption of a gas or vapor.

When the adsorption of a gas on a solid is determined, Γ and p are given by the data, and the fugacity of a vapor is so nearly equal to the pressure that the assumption of equality involves little error. Consequently, the lowering of the free surface energy can be calculated by integrating the Gibbs equation. The method of doing this is presented in a quotation from the *Journal of the American Chemical Society*:[110] Bangham [14, 15, 16] was the first to show that the reduction of the free surface energy of the surface of the solid could be obtained by the use of the Gibbs adsorption equation. The integration of this equation is expressed by the relation

$$\pi = \gamma_s - \gamma_{sf} = \frac{RT}{V\Sigma} \int_0^p \frac{v}{p} dp \qquad (5)$$

where R is the gas constant, T the absolute temperature, V the molar volume of gas, Σ the specific area of the solid, p the equilibrium pressure of the adsorbed gas, and v the volume of gas adsorbed per g.$^{-1}$ of solid. This equation has been discussed in a paper from this Laboratory by Boyd and Livingston.[17] However, their numerical results are open to question owing to their method of evaluating the integral, as considered later.

In a series of recent papers, Armbruster [18] and Austin have used the equation in the following form

$$\pi = \frac{RTv_1}{V\Sigma} + \frac{RT}{V\Sigma}\int_{\frac{p}{v}\text{ as }v\to 0}^{\frac{p_1}{v_1}} v/\mathrm{d}\ln\frac{p}{v} \qquad (6)$$

The authors attribute this equation to a development of Innes and Rowley.[19] If Eq. 6 is expanded, it is found to be identical with the integration of the Gibbs equation proposed by Bangham. Thus, in actuality, there is only one independent general

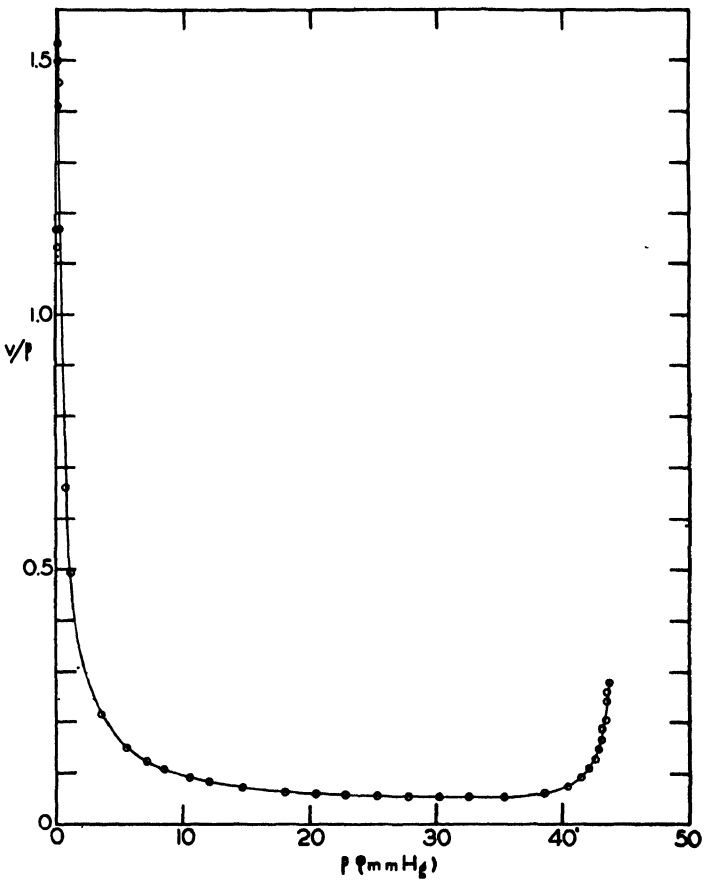

FIGURE 6. Curve for integration of Eq. 5. The total area below the curve up to any point on the curve gives the lowering of the free surface energy (π) at that pressure. The curve gives values for the adsorption of *n*-heptane on anatase.

method of obtaining the decrease in free surface energy of the surface of a solid. Other methods have been proposed.[20] These, however, depend upon an equation of state and cannot be considered suitable for general use.

The numerical evaluation of the integrals in Eqs. 5 and 6 presents certain difficulties. It is obvious that if an equation in v and p were known that would reproduce the isotherm the integrals could be evaluated analytically. Since this is not the case, graphical integration must be used. The greatest difficulty in the computation lies in the low pressure region. In the experience of the writers there is only one procedure which makes it possible to obtain the correct value of the integral. This is to take a large number of experimental points in the very low pressure region. Obviously, the method of measurement in this region must be made more sensitive than that necessary for the remainder of the isotherm. If this is done, it is found that at relative pressures below approximately 0.001 the film behaves like a gas. It is then simple to extrapolate the curve to zero pressure if Eq. 5 is used, or to zero volume if Eq. 6 is used. Frequently, the volume-pressure relationship observed is that of a perfect gas, for which

$$\pi = \frac{RT}{V\Sigma} kp$$

where $k = v/p$. Once the upper limit of existence of this region has been located, the remainder of the computation is simple, regardless of the shape of the isotherm.

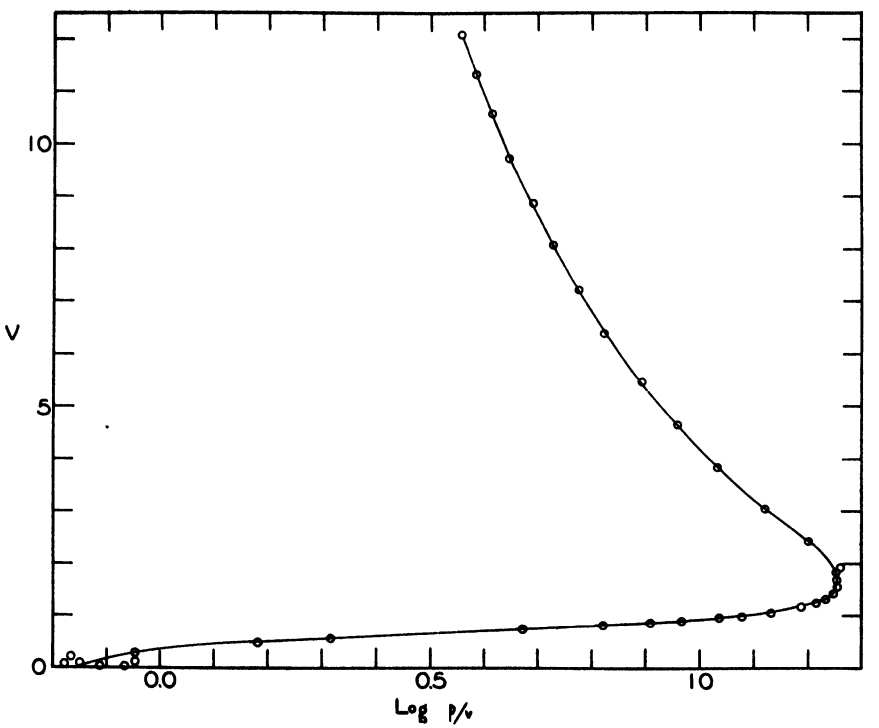

FIGURE 7. Same as Figure 6, except that it represents the integration of Eq. 6.

Figs. 6 and 7 exhibit the curves which need to be integrated when Eqs. 5 and 6, respectively, are used. The curves shown are for the adsorption of n-heptane on TiO_2 (anatase) at 25.0°, whose isotherm is shown in Fig. 8a. Obviously the shape of

the curve depends on the shape of the isotherm. In both cases, the integration must be carried out along the x-axis. An examination of the curves shows that Eq. 6 is simpler to use in the low pressure region, that is up to a relative pressure of about 0.4, whereas Eq. 5 is easier to use beyond this point. Independent integration by each

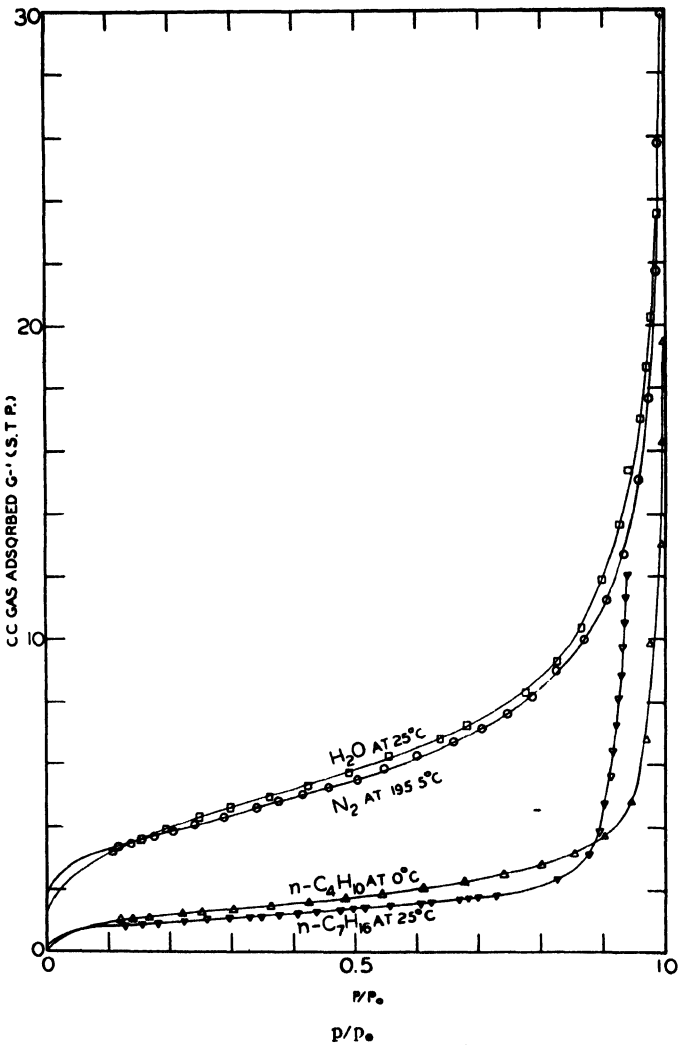

FIGURE 8a. Adsorption isotherms of water, nitrogen, n-butane, and n-heptane on crystalline TiO_2 (anatase).

equation, carried out over the entire range for this system, gave values of 39.3 and 39.2 ergs, respectively, per square centimeter at the maximum pressure measured. The values agreed equally well at intermediate points. The scattering of the points for low values of p in Fig. 6 and low values of v in Fig. 7 is within experimental error of the determination of the pressure, and the volume adsorbed in this region.

If the low-pressure data are lacking, the only increment of free surface energy which can be calculated is that in the range in which sufficient data have been ob-

tained. The methods of calculation used by Boyd and Livingston [17] gave values which agree with those obtained by the integration of the equation of Brunauer, Emmett and Teller.[21] However this equation, remarkably good over a certain range of pressures, is not at all valid at a relative pressure (p/p_o) below about 0.05. For the

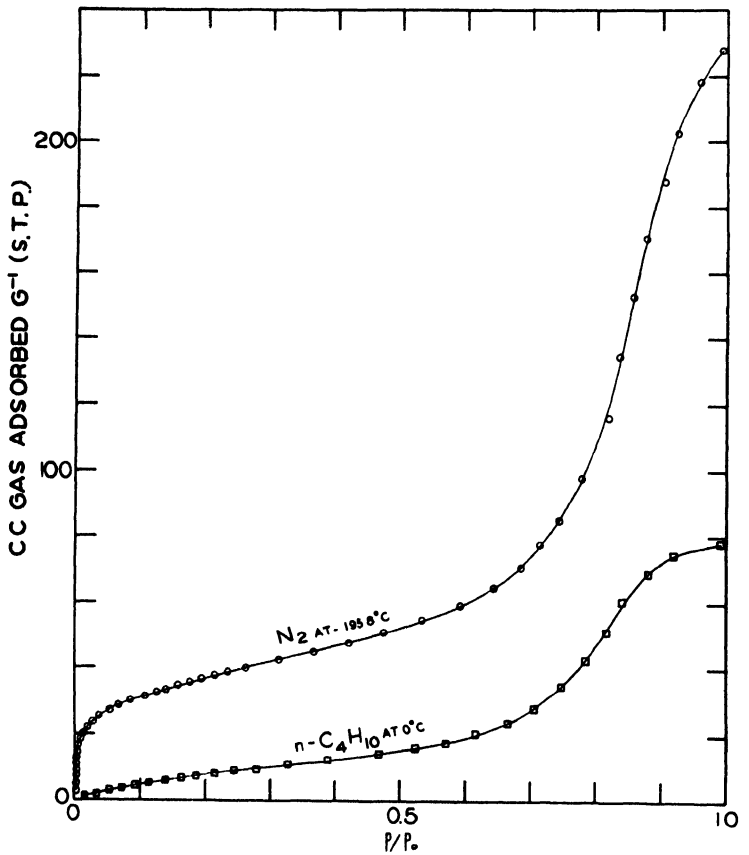

FIGURE 8b. Adsorption isotherms for a silica-alumina gel.

adsorption of nitrogen on several solids at a given pressure, the application of the equation gave 18, 17 and 16 ergs per square centimeter, whereas the correct integration gives 29, 23 and 21 ergs per square centimeter, a very large difference between the two methods. This shows that the equation of Brunauer, Emmett and Teller cannot be used for the integration in the *low* pressure region.

Figs. 8a and 9 exhibit the adsorption isotherms of nitrogen at −195.6°, *n*-butane at 0.0°, *n*-heptane at 25.0° and water at 25.0° on a sample of anatase whose area is 13.8 m^2g^{-1}. Fig. 10 shows the decrease in free surface energy (π) of anatase by the above adsorbates as a function of the equilibrium pressure. The lowering of the free energy for anatase by these gases is typical of those systems for which the contact angle is zero. The values of the lowering of the free energy for these vapors extrapolated to $p/p_o = 1.0$ are 190, 56, 43 and 46 erg cm^{-2} for water, nitrogen, *n*-butane, and *n*-heptane, respectively. The values thus far found with different polar solids, both porous and non-porous, fall between the following limits in erg cm^{-2}: water at 25°, 180-250; nitrogen at −195.8°, 35 to 56; *n*-butane at 0°. 30 to 45; and *n*-heptane at

25°, 25 to 69. These values, would not of course hold for a system such as water on graphite, where the contact angle is not zero. Investigation of this system, though it has been started, is not as yet complete. A sample of graphite containing 10 per cent ash gave a value of 58 ergs cm^{-2}, while the value for another sample containing 0.46 per cent ash gave 19 ergs cm^{-2} at saturation. A sample containing less than 0.004 per cent ash indicates that the maximum value for π is 19 ergs cm^{-2}.

In all the systems studied where the contact angle is zero, the films are polymolecu-

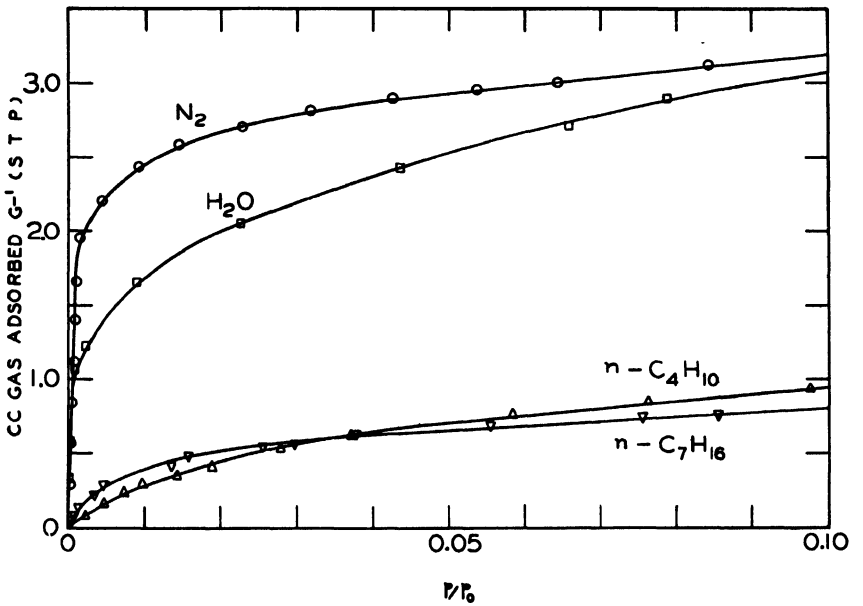

FIGURE 9. Low pressure region of Figure 8a.

lar. When nitrogen is the adsorbate it is found that the film pressure of the monolayer, as calculated by the theory of Brunauer, Emmett and Teller, is greater, the lower the vapor pressure of the adsorbed monolayer. The other gases seem to follow the same relationship, but the data are not sufficiently extensive to make the results certain. Fig. 11 illustrates the data for nitrogen.

In the section devoted to contact angles, it is shown how the above data can be used to obtain the spreading coefficient, the free energy of emersion, and the work of adhesion. The film-pressure data can also be used to study the state of the adsorbed films in the same manner that this quantity is used to study films on liquid surfaces.

Experimental Procedures for Solids

The determination of an adsorption isotherm requires the simultaneous measurement of two quantities: (1) the amount of material adsorbed, and (2) the equilibrium pressure of the adsorbed material.

There are many ways in which each of these quantities can be measured. For example, the amount adsorbed may be obtained by either gravimetric or volumetric methods. Among the best known of the gravimetric methods are the use of the McBain-Bakr balance,[22] which is merely a helix of quartz, or of a quartz beam balance.[23]

The volumetric methods depend on the measurement of the volume and pressure of the gas or vapor before and after adsorption. The difference calculated by the gas laws is the amount adsorbed.

The writers have found that the volumetric methods, as described below, are

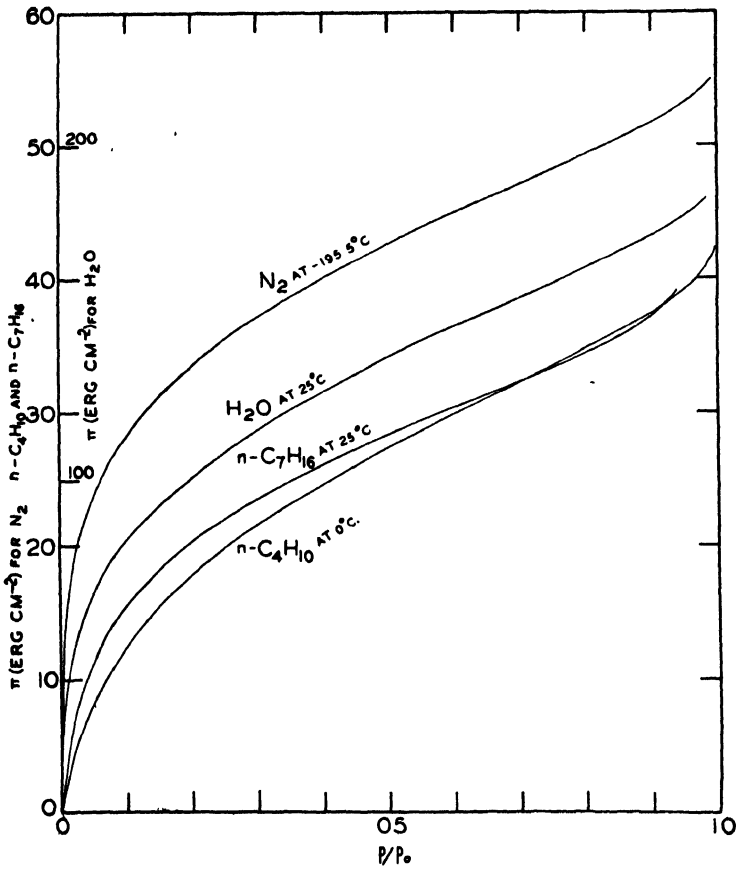

FIGURE 10a. Lowering of the free surface energy (film pressure π) for films on anatase as a function of the relative pressure. (Note that values on the Y-axis are four times larger for water than for the other vapors.)

sufficiently accurate, much more so than some gravimetric methods, and at the same time are more rapid. The McBain-Bakr balance is excellently adapted for use with porous solids of high area, but not with non-porous solids.

Two types of apparatus are now in use, one suitable for careful work for those liquids whose vapor pressure is between 20 and 100 mm, and the other from 100 to 1000 mm. The apparatus represented in Fig. 12 is used for the lower pressures. This is described in a quotation from the *Journal of the American Chemical Society*:[110]

The bulb B contains the adsorbent, while R, which holds the liquid whose vapor is to be adsorbed may also be used as a gas reservoir if it is desired to investigate only the very low pressure region of the isotherm. The mercury manometer M is made of 25-mm tubing, since the diameter should be large in order to allow the

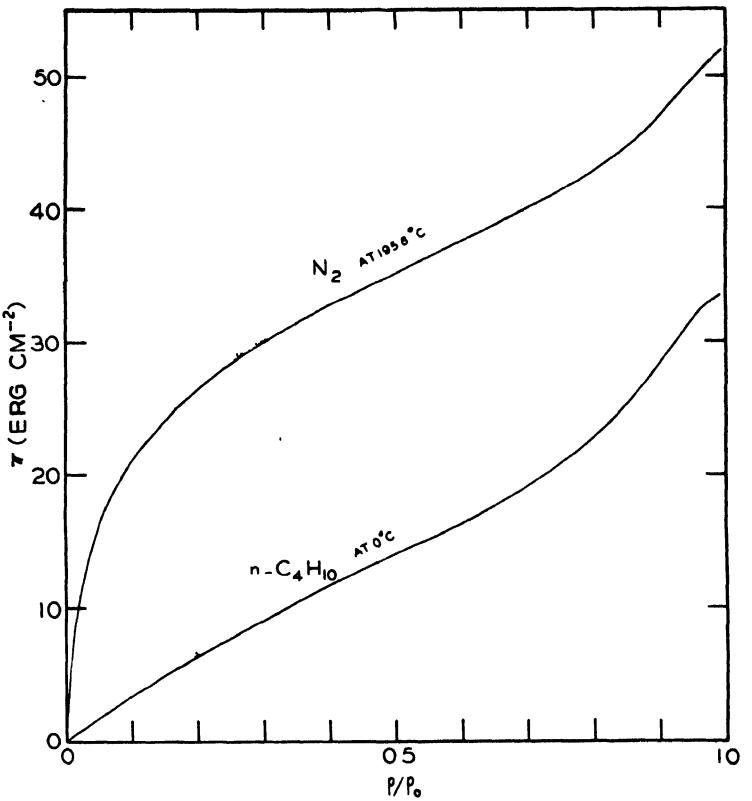

FIGURE 10b. Values of π for films on a porous silica-alumina gel.

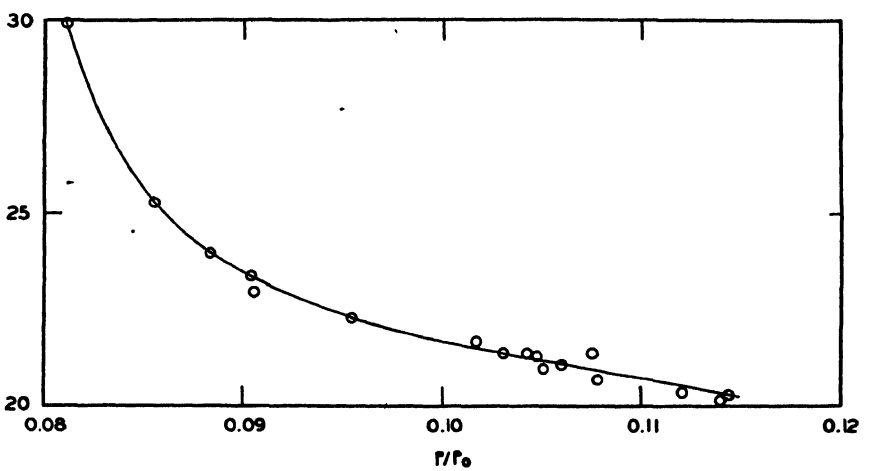

FIGURE 11. Values of the lowering of the free surface energy (π) on completion of a monolayer of nitrogen (as calculated by the theory of Brunauer, Emmett and Teller) and the relative pressure (p/p_0) of the nitrogen at that point.

meniscus to move freely. A set of calibrated bulbs G is employed to control and measure the volume of the gas adsorbed. A mark C is used in the determination of the volume of that part of the manometer which is in the adsorbing system. Stopcock 1, when open, permits the gas to enter the buret system and then to pass to the adsorption bulb.

The volume of the bulbs in G is determined by the weight of the mercury they

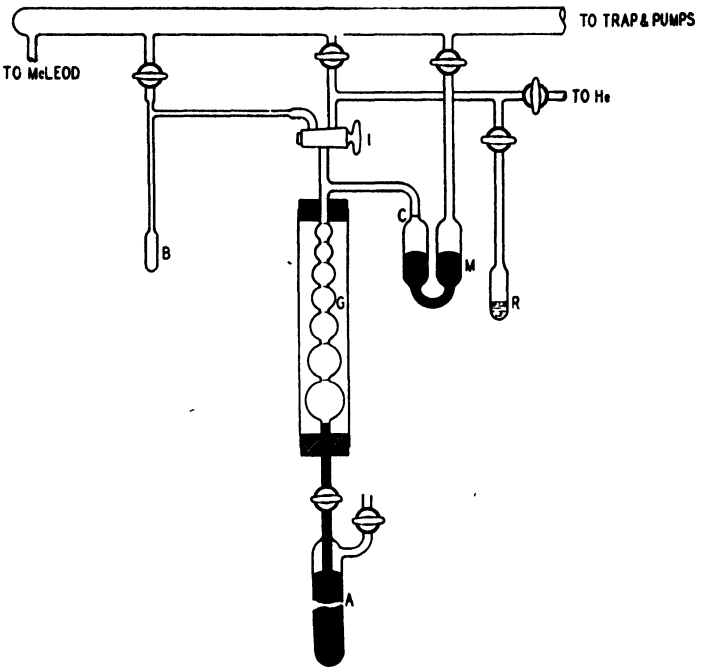

FIGURE 12. Apparatus for the determination of adsorption at pressures below 100 mm.

hold. Duplicate determinations of the volume of each bulb agree on the average to 0.005 cc. The volume of the left side of the manometer was determined as a function of the distance from the calibration mark to the level of the meniscus, and the volume of the tubing leading from the graduated bulbs was obtained by measuring the change in pressure as the volume in the bulbs is decreased by successively filling them with mercury from the reservoir A. For one system the volume of the tubing was 25.10 cc. The average deviation was 0.02 cc., or less than 0.1 per cent. The dead space in the adsorption chamber was determined with helium, by measuring the initial volume and pressure in the buret system, and also the final pressure after the gas had been allowed to expand into the dead space.

The difference in height of the mercury in the arms of the manometer was determined with a traveling microscope of a sensitivity of 0.001 mm, which was set on a transit mount so that it could be rotated. The average deviation of a given height when a series of readings were taken was found to be 0.002 to 0.003 mm, while that of a single reading from the average did not exceed 0.006 mm. The screw of the microscope was not in error by more than 0.010 mm, and its errors are known to 0.001 mm.

After the surface of the sample has been degassed, the dead space determined, and the sample thermostated, the helium is pumped out, and successive additions of

vapor are made. The initial and final volume and pressure of the vapor are measured, and the amount adsorbed is calculated from the gas laws.

Figure 13 shows two adsorption isotherms of water vapor on TiO_2 (anatase) as determined by this procedure. The circles are for a determination in which the total adsorbing surface was about 17 m^2, while the squares represent a determination in which about 12 m^2 was used. The agreement between the two is excellent. Each of these experiments required about fifty hours to complete.

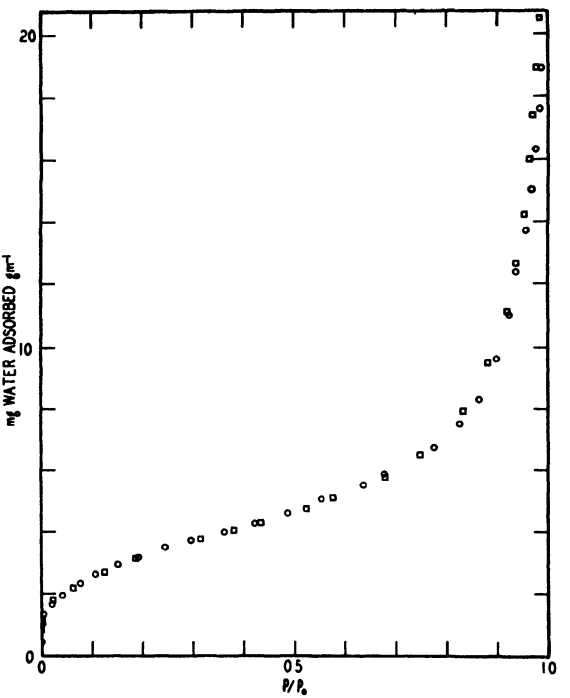

FIGURE 13. Represents two isotherms of water on anatase (TiO_2) as determined independently.

When the isotherm of some condensable liquid, such as water or heptane, is being determined, the work at high relative pressures is very difficult. Here in order to obtain any appreciable increment in the adsorption it is necessary to start with as much volume in the bulbs as possible, and then get the vapor into the adsorption bulb by filling the bulbs with mercury. The compression must be carried out with sufficient slowness so that the pressure of the vapor is kept less than the condensation pressure. Since the rate of adsorption in this region is moderately slow, the compression of the gas must of necessity be slow. It has not been feasible by this method to go to relative pressures above 0.985.

The low pressure at which the adsorption is carried out, when vapors such as those of water or *n*-heptane are used, permits good measurements on much smaller areas than could be used when the saturation pressure is as high as 700-800 mm. Determinations have been made with the apparatus when the total adsorbing surface was only 1 m^2. From the behavior in this case, it appears that moderately accurate isotherms could be obtained with as small an area as 0.25 m^2 for the sample in the adsorption chamber.

A diagram of the apparatus for the determination of the nitrogen isotherms is

exhibited in Fig. 13. The part of the apparatus used for the higher pressures is the same in its essential features as that of Emmett and Brunauer.[24] The variations in technique and design are not of a major type, but they contribute markedly to the

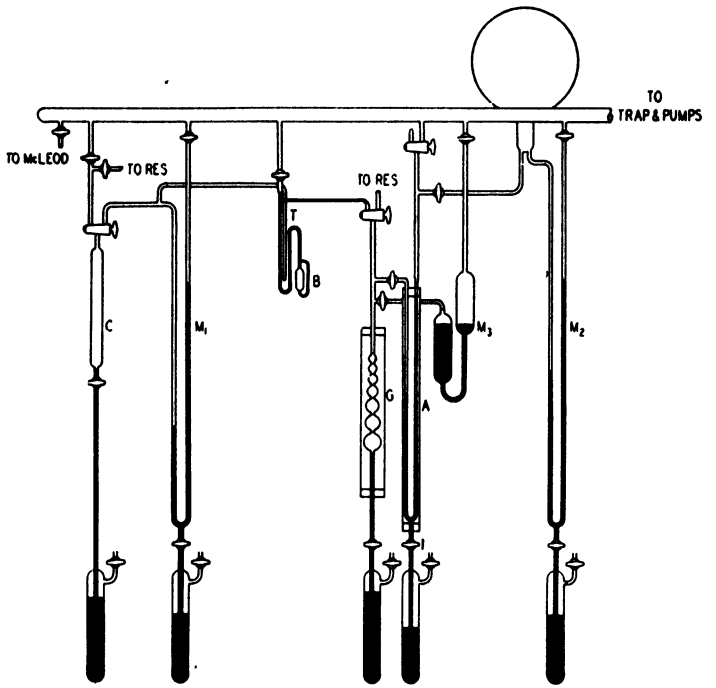

FIGURE 14. Apparatus for the determination of adsorption isotherms at pressures from 10 to 760 mm. Tubes labeled "To Res." lead to flasks, like L, not shown, used for the storage of helium and nitrogen, etc. Butane, heptane, water, etc., are stored as liquids in tubes.

precision of the results and are, therefore, important. The diagram shows also the attachment and necessary stopcocks for the use of either the low or higher pressure manometer. The changes in design are the addition of (1) a vapor pressure thermometer as described in the following paragraph, of (2) a wide bore, 25-mm diameter, manometer for low pressure work, and the use of (3) only one U-tube before the sample, thus decreasing the dead space.

A compression chamber C and the tube leading to the manometer M_1 are filled with the gas whose adsorption isotherm is to be determined. The gas is then compressed by filling C with mercury, thus condensing the vapor into liquid in T, which is immersed in the same bath as the adsorption bulb. The vapor pressure of the liquid is then read on the manometer M_1.

The buret system is composed of the bulbs G and the left-hand side of the mercury cut-off, A. The latter is a tube 60 cm long with a 5-cc capacity graduated in 0.01 cc. The graduations were checked by the volume of mercury delivered. For higher pressures, the manometer M_2 of an external diameter of 12 mm is used. The difference in height of the mercury is obtained either with a cathetometer or a meter stick. With the cathetometer no attempt is made to obtain the pressure to better than 0.1 mm. When the meter stick is used, a slide arrangement with projecting arms is used, which gives the pressure with an accuracy of 0.4 mm. The scale on the meter stick

was calibrated by that of the cathetometer. The pressure measured by M_2 is that of the gas in the 5-liter bulb, L, whose purpose is to permit ease in the variation of the pressure.

The pressure in the buret system is made equal to the pressure in L by the following procedure. The mercury in the cut-off A is pulled down and the cut-off is evacuated. After this the mercury is allowed to rise. On the left side the meniscus of the mercury is brought exactly to one of the graduation marks. The amount of mercury in the cut-off is maintained constant by closing stopcock 1. As long as the temperature remains constant, the pressures on the right and left hand sides are equal when the mercury is at the chosen graduation mark. When this method is used it is possible to reproduce pressures to 0.05 mm with a maximum deviation of 0.10 mm.

This method of determining pressures was chosen because, due to small internal diameter of the buret, small variations in diameter have a marked effect on the level due to capillary depression. In the system now in use, the difference in height of the mercury in the two arms with a vacuum on both sides is −2 to about +3 mm as the mercury is moved up. Thus, if it were assumed that the pressure on both sides is the same when the arms are level, an error of as much as 3 mm might be made. The per cent error would of course depend on the absolute value of the pressure. Working with nitrogen at −195.8° at a relative pressure of 0.2, the error in the pressure reading could be as high as 4 per cent. This error would obviously also be reflected in the calculation of the adsorbed volume of gas. The isotherm is obtained by successive additions of vapor.

This apparatus has been used primarily for nitrogen adsorptions at −195.8°. Figure 15 shows two sets of isotherms, of which the upper one is for a sample of

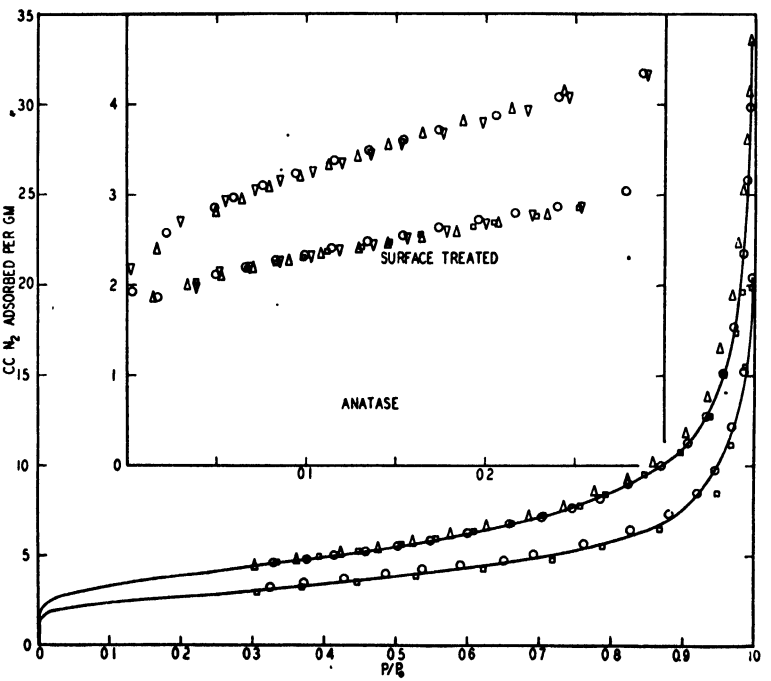

FIGURE 15. Nitrogen isotherms for anatase and surface-treated anatase.

TiO_2 with an area of 13.8 $m^2\ g^{-1}$ by our absolute method. The excellent agreement between the values for this sample in the three determinations shown is of interest

since they were made on three independent experimental units, each with an entirely independent calibration. The concordance in the three sets of measurements indicates high accuracy, as well as precision, in the results. The agreement among the three sets of data is shown by the fact that if 16.20 sq Å is used for the area of the nitrogen molecule in conjunction with the BET (Brunauer, Emmett, Teller) theory, the area is found to be 13.92 $m^2\ g^{-1}$, with an average deviation for the three of only 0.06 $m^2\ g^{-1}$. The lower curve shows the results of duplicate determinations of a sample of anatase, surface treated with aluminum oxide, whose area is 9.6 $m^2\ g^{-1}$. This curve represents the *least* precise set of measurements obtained in all of our work. The low precision is due to the low area of the sample. With a lower area the precision would be even lower.

Fig. 16 shows the precision obtained with a porous solid. The areas determined from these two isotherms were found to be 320.2 and 320.7 $m^2\ g^{-1}$. All of the above determinations were made on entirely different samples.

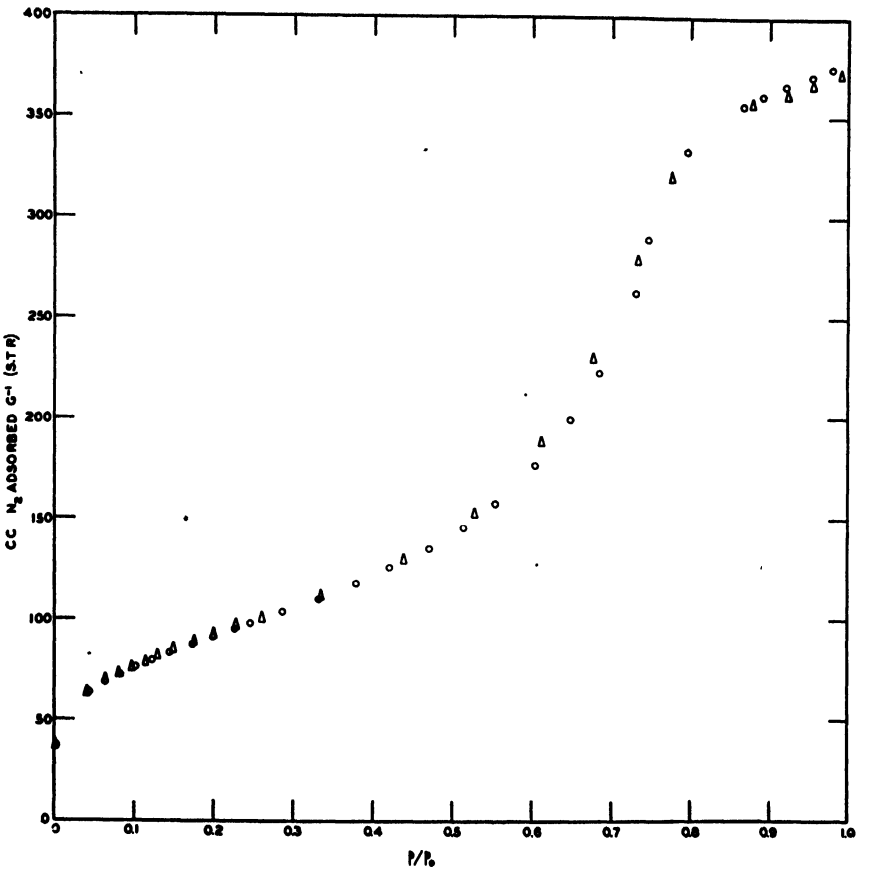

FIGURE 16. Nitrogen isotherms for a silica-alumina gel.

THE AREA OF SOLIDS FROM THE ADSORPTION ISOTHERM [112]

A knowledge of the area of a solid is an essential basis for the determination of its energy relations. The statement that the heat of emersion of a sample of titanium dioxide in water is 1.69 cal gm^{-1} is meaningless unless other information is given,

but that it is 510 erg cm^{-2} gives a basis of comparison with other solids. It is only recently that the determination of the area has been made accurate enough to be of use. Theoretically, the best method, the only one which is absolute, depends on the determination of the heat of immersion of the solid saturated with the vapor of the liquid. This method, described on p. 40 however, is exceedingly difficult and tedious and is not applicable to any but finely divided, non-porous solids. Thus recourse must be had to other, less difficult methods.

One of the simplest of all techniques for this purpose is the determination of the adsorption isotherm of a gas or vapor on the solid. The shape of the isotherm and the amount of gas adsorbed depends upon the area of the solid, its nature, the nature of the gas, and the temperature. The first theory of general applicability developed for the interpretation of the isotherm is that of Brunauer, Emmett and Teller,[21] which, however, does not give the area of the solid, but the number of molecules required to form a complete monolayer. Before the area can be obtained from their theory it is necessary to calculate the effective cross-sectional area per adsorbed molecule in the monolayer. They consider that this can be obtained by assuming that the molecules are close-packed in the surface and have the same density as either the three-dimensional liquid or solid at the given temperature. The areas obtained in this way are affected by the fact that the area per molecule is varied by the surface layer of the solid by ± 10 per cent when the determinations are made at temperatures of 77° K to 200° K and if the vapor pressures are sufficiently high. However, when other vapors are used at room temperatures, the molecular areas obtained by their method are commonly too low by 20 to 40 per cent. Now, from the general theory of solids, it is to be expected, as indicated above, that the mean area occupied by adsorbed molecules will be affected by the surface lattice of the solid.

Another method of determining areas from the adsorption isotherm is that due to the writers. This is based on an entirely different principle from that of Brunauer, Emmett and Teller, and in contrast gives the area directly.

Actually the method is a relative one, but gives the correct area when the constant is determined by our absolute method.

For any condensed film the isothermal equation of state is

$$\pi = b - a\sigma \tag{7}$$

This may be transferred by the methods given in a later section into the equation

$$\log (f/f_0) = B - A/v^2 \tag{8}$$

More accurately, what is involved in $\log f/f_0$; but the ratio of the pressures is so nearly the same that the equation is usually used in the form

$$\log (p/p_0) = B - A/v^2 \tag{8a}$$

If now, $\log (p/p_0)$ is plotted (Fig. 16) against the reciprocal of the square of the amount (volume at S.T.P., mass, moles or molecules) adsorbed, a linear relation is exhibited where the $\pi - \sigma$ relation is linear, *i.e.*, where the film is condensed. If the film is not condensed for any value of p/p_0 of the adsorbate employed, it is necessary either to lower the temperature, or else to change to an adsorbate which gives a condensed phase at a suitable temperature.

When the first set of isotherms for nitrogen obtained at −195.8°, was plotted in this way, it was at once noticed that as the area of the solid increases the numerical value of the slope, A also increases. It was then found very quickly that the area (Σ) of the solid is proportional to the square root ($A^{1/2}$) of this slope. Thus the area of the solid is given by the equation

$$\Sigma = kA^{\frac{1}{2}} = ks^{\frac{1}{2}} \tag{9}$$

where the slope is represented by A or by s.

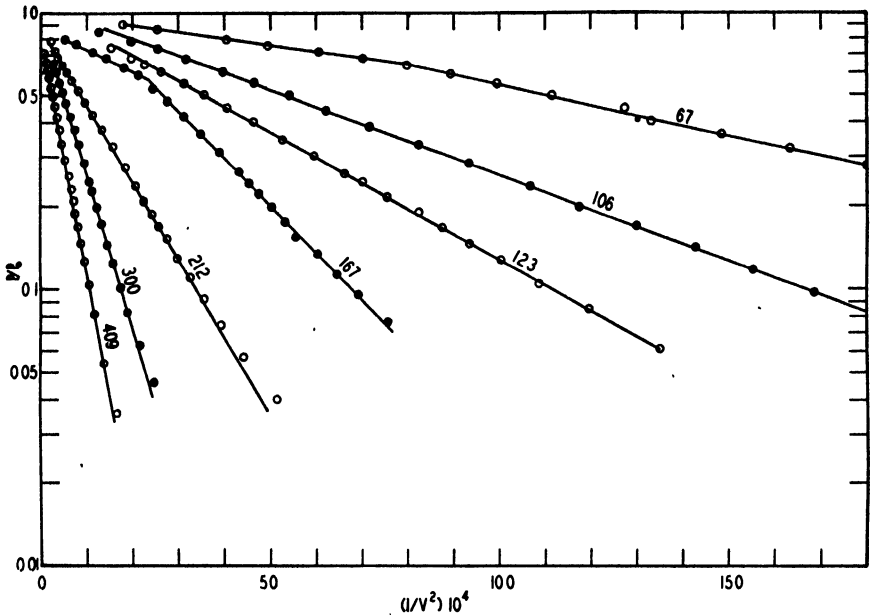

FIGURE 17. Nitrogen isotherms on porous solids. These areas (given in sq. meters per g.) are 4.06 times the square roots of the linear portion of the isotherm.

The way in which the square root of the slope becomes involved is as follows. The value of the constant A in Eq. 8 is

$$A = \frac{10^{16} V^2 a \Sigma^2}{4.606\, RTN_0}$$

where 10^{16} is the conversion unit from cm^2 to $Å.^2$ V is the molar volume of gas, a is the constant in Eq. 7, R the gas constant, T the absolute temperature, and N_0 is Avogadro's number. It has been observed that when the aqueous subphase under an insoluble film is changed, the area at which a phase appears may be altered, *i.e.*, the value of b in Eq. 7 is altered. However, there is no change, or only a very slight change, in the value of a. The assumption is made that this is also true of the films on the surfaces of solids. On this basis Eq. 9 follows. In some of the films studied, two condensed phases are present. When this situation exists, the slope of the phase appearing at the lower pressures should be used for the calculation of the area, inasmuch as this is the phase in which the monolayer is completely built up and a polymolecular film appears.

If, now, the area (Σ) of a single crystalline solid is determined by our absolute method the value of k is given by

$$k = \frac{\Sigma}{A^{\frac{1}{2}}} \qquad (10)$$

According to the usual convention the values of these quantities are those for one gram of the solid.

If nitrogen at −195.8° is the vapor adsorbed, then $k = 4.06$ and

$$\Sigma = 4.06 A^{\frac{1}{2}} \qquad (11)$$

gives the area (Σ) in square meters per gram. With other adsorbates or at different

temperatures, the constant is different. The values thus far obtained are: water at 25°, $k = 3.83$; nitrogen at −195.8°, $k = 4.06$; *n*-butane at 0°, $k = 13.6$; *n*-heptane at 25°, $k = 16.9$.

Fig. 18 exhibits some of the shapes the isotherm may assume for a given area.

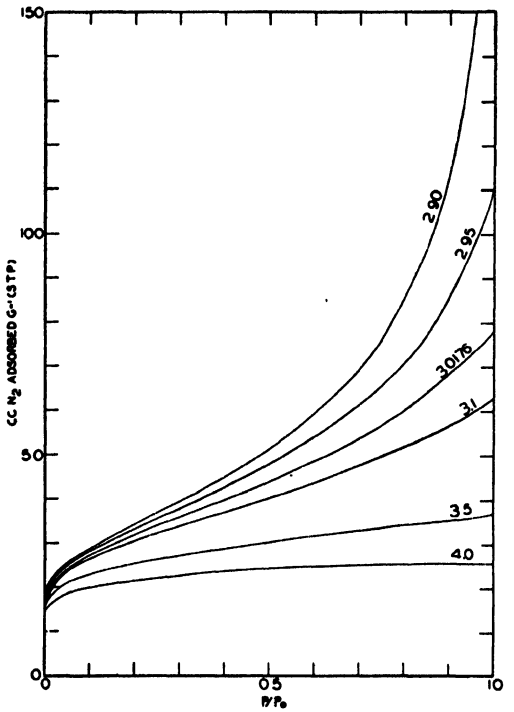

FIGURE 18. Effect of a change in the value of B (Eq. 7a) on the shape of the adsorption isotherm.

The curves were obtained by varying the value of the constant *B*. The curve marked 3.0176 is the actual curve obtained for an aluminum trioxide silica gel catalyst whose area is 118 $m^2 g^{-1}$.

Figs. 19 and 20 show the comparison between the calculated and observed values for the adsorption of nitrogen at −195.8° on a non-porous and a porous solid. It is to be noticed that for anatase at high relative pressures the calculated values lie below the observed values, while for the porous solid the reverse is true. This is discussed on p. 32.

The results obtained by this method can be checked in two ways: (1) by comparing the results with those obtained by the theory of Brunauer, Emmett and Teller and (2) by the consistency of the results when different gases are used with the same solids. If 15.4Å² is used as the area of the nitrogen molecule at −195.8°, the areas obtained by the two methods agree to within ± 9 per cent for (101) solids. Another method of comparing the results is to calculate the area of the nitrogen molecules from the area determined by the relative method and the number of molecules in the monolayer obtained from the theory of Brunauer, Emmett and Teller. The results of this comparison are shown in Fig. 21.

This figure shows a remarkable grouping of the value of the nitrogen area at three values; 14.05, 15.2 and 16.15 Å² per molecule. It is true that the comparison in only 101 cases is insufficient statistically to establish the existence of the three observed peaks. There is additional evidence, however, which indicates that the variation of molecular area is real.

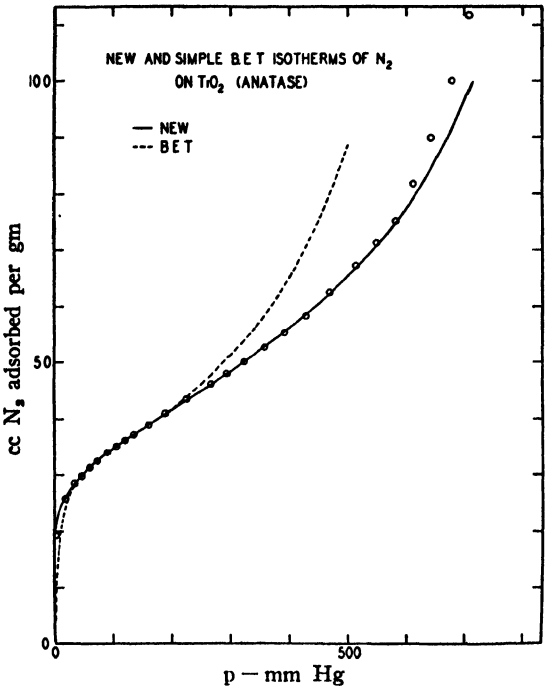

FIGURE 19. New and simple (two constant) BET isotherms of N_2 on TiO_2 (anatase).

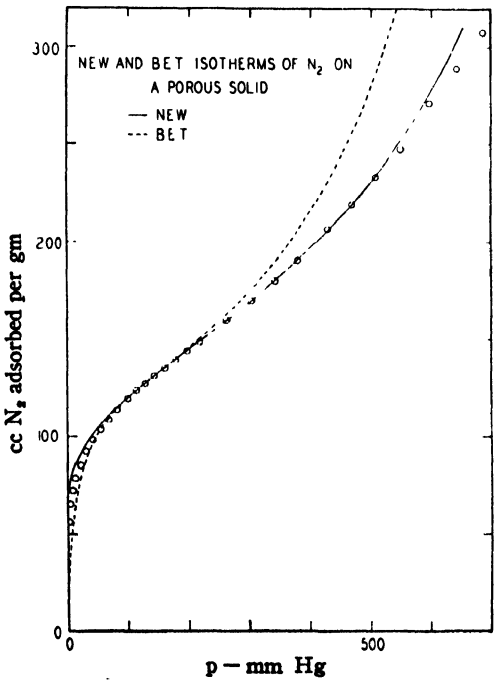

FIGURE 20. New and simple (two constant) BET isotherms of N_2 on a porous solid.

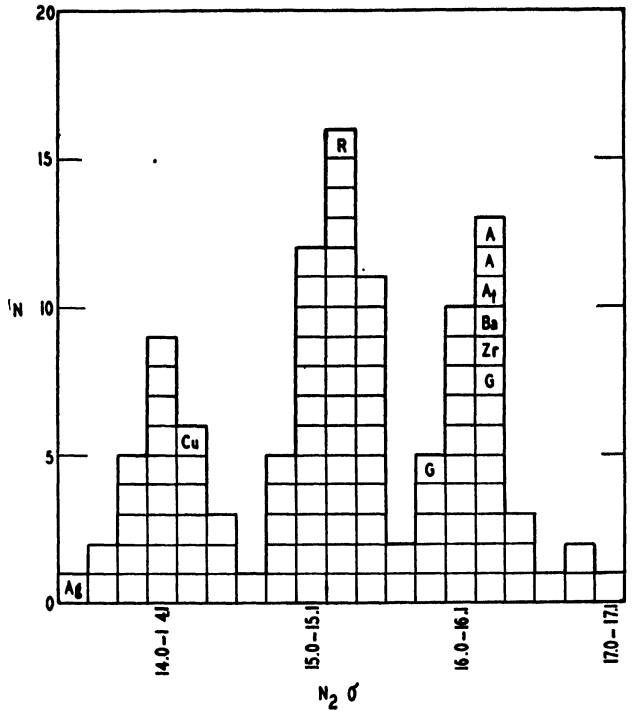

FIGURE 21. Molecular areas of nitrogen on 108 solids as calculated from the equations of Brunauer, Emmett and Teller, and of our new theory. The non-porous solids are marked by a symbol in the square: Ag, silver; Cu, copper; R, rutile; A, anatase; G, graphite; A_t, anatase treated with aluminum oxide; Ba, barium sulphate; Zr, zirconium silicate.

Unfortunately, we cannot publish all the detailed evidence which has been obtained in the experimental work. A typical example of a known change of surface is the following: a silica-alumina gel gave a molecular area for nitrogen of 14.1 Å.^{2} The surface was then coated with a carbonaceous deposit by exposing the solid to hydrocarbon vapors for a short time at an elevated temperature. The deposit reduced the area of the solid, but increased the area determined for the nitrogen molecule to 16.2 Å.^{2} After the deposit was removed, the area of the solid returned to its original value, and the area of the molecule was found to return to 14.2 Å.^{2}, its initial value within the limits of error.

Five such instances have been investigated. The values with the carbon deposit on the surface were found to be within the narrow range of from 16.0 to 16.3 Å.^{2}, regardless of the inital value exhibited by the solid without the deposit.

In one series of solids composed of two components, silica and aluminum oxide, the ratio of the two was varied at concentrations of aluminum oxide of 6 per cent or less. The area of the nitrogen molecule was found to be almost constant at 15.2 Å.^{2}, *but at 8 per cent or more this shifted to 14.0 Å.*^{2}

A second two component porous solid, of very different composition, gave a shift in the opposite direction. This exhibited an area of the nitrogen molecule of 15.2 Å.^{2} for all samples in which the content of the second component was 2, 4 and 6 per cent by weight, but with 10 to 12 per cent, shifted to 16.2 Å.^{2}

The x-ray analysis of this solid shows a certain structure at all of the lower percentages but indicates that at 12 per cent a partial change to a second crystal form

has occurred. Since x-rays are not sensitive to a small percentage change of structure, it is probable that the shift in the area of the nitrogen molecule was caused by this change in structure and detected the change at a lower concentration than the x-rays.

The most important criterion for the determination of the area, however, is the following: the same area should be obtained regardless of the molecule used. Table 4 shows the areas of five solids determined with nitrogen at −195.8°, water at 25°, *n*-butane at 0°, and *n*-heptane at 25°. The table also gives the values as determined by the theory of Brunauer, Emmett and Teller. The concordance of the results obtained by our relative method is very good, the maximum difference in the areas of the same sample being 7 per cent, while the areas given by the theory of Brunauer, Emmett and Teller exhibit a much greater variation.

Table 4. Areas of Solids Calculated by the New Method and by That of Brunauer, Emmett and Teller
(Areas in Square Meters Per Gram)
The data used for both sets of calculations are the same.
A. Crystalline Solids

	New Method				BET Method			
	N_2	H_2O	*n*-Butane	*n*-Heptane	N_2 $\sigma = 16.1$	H_2O 14.8	*n*-Butane 56.6	*n*-Heptane 64.0
TiO_2I (Standard)	13.8	13.8	13.8	13.8	13.8	13.8	13.8	13.8
TiO_2 II	8.7	8.4		8.7	8.6	11.7		8.7
SiO_2 (Quartz)	3.2	3.3		3.3	3.2	4.2		3.6
$BaSO_4$	2.4	2.3	2.2	2.3	2.4	2.8	2.7	2.4
$ZrSiO_4$	2.9	2.7			2.8	3.5		

The BET Method has been standardized here by our absolute method.

Also, the values given by their method are better than they would be if their method of calculating the cross-sectional area of the molecule were used. In general, though, both of these methods should be used for the calculation of the area.

Extension of the Attractive Energy of a Solid into a Liquid, and the Thickness of Adsorbed Films

One of the fundamental problems of physics and chemistry, entirely unsolved until the work described here was done, is that of the distance to which the molecular interaction between a solid and an adjacent liquid extends into the liquid. More exactly, since the interaction decreases rapidly with distance, this involves a determination of the energy of interaction as a function of this distance.

A related problem is that of the thickness of films adsorbed from vapors at vapor pressures below that of saturation ($p / p_0 < 1$). Heretofore the (unsuccessful) attempts to solve this problem have all been made on the basis of theory. Now, however, the determination of the area of a sample of anatase by our absolute method gives the basis of a simple, entirely experimental determination of the thickness of adsorbed films on this crystalline material.

Theories of Adsorption. For many years there have been two contradictory theories of the ultimate thickness of adsorbed films on the surface of a solid: (1) the *monomolecular* theory, the principle exponent of which is Langmuir, and (2) the *multimolecular* theory.

According to (1) the films do not grow to a thickness of more than one molecule, even at values of p / p_0 only very slightly below saturation. This is sometimes modified by the statement that if this is exceeded the second layer is only a partial one. The theory, as stated in 1940 by Langmuir,[24a] is expressed by the following quotation from his paper, which refers to films of argon, nitrogen, hydrogen and methane at liquid air temperatures: "the amount adsorbed increases about in proportion to the pressure, but at higher pressures reaches a limiting value which in every case studied corresponds to less than a monolayer. Evidently, therefore, even with

these cases of adsorption which involve merely van der Waals forces, the effective range of action of the forces responsible for the adsorption is less than the molecular diameter, so that we are still clearly dealing with forces which act between atoms or molecules in contact."

Many other investigators have adopted this general point of view, as expressed by Langmuir's adsorption isotherm.[24b]

The variation of the energy of interaction between anatase (TiO_2) and water with distance in the water is determined by obtaining calorimetric measurements of the energy of immersion in water of the dry crystals, and of the crystals covered by increasingly thick films. This procedure is described in the section on the relation-

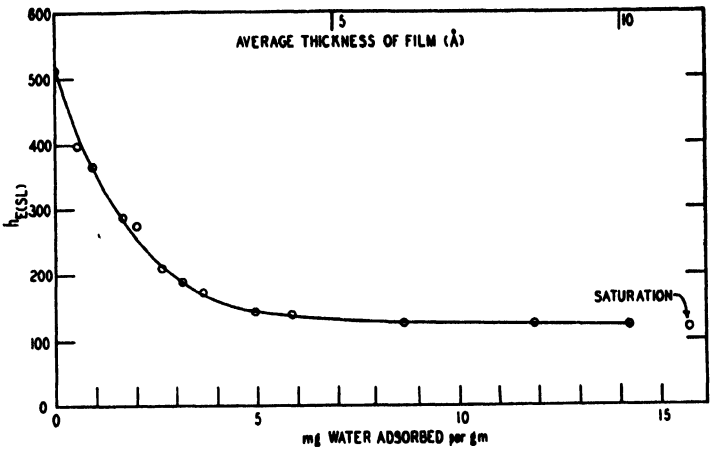

FIGURE 22. Thickness of the water film and the energy of emersion per sq cm of the surface of TiO_2 (anatase). The weight of water adsorbed per gram of anatase is also given.

Table 5. Energy of Emersion of Titanium Dioxide (Anatase) from Water at 25° as a Function of the Thickness of the Water Film with which it Emerges

1 mg H_2O g^{-1} in film	2 Mean thickness [a] of film in Å., T	3 Energy of erg cm^{-2} $h_{E(S/L)}$
0	0	512 [a]
0.548	0.4	399
0.953	0.7	366
1.68	1.2	289
1.99	1.4	279
2.60	1.9	210
3.15	2.3	190
3.68	2.7	172
4.95	3.6	142
5.86	4.2	139
8.66	6.3	127
11.86	8.6	125
14.20	10.0	122
Saturated	>15.0	119

[a] $h_{E(SL)}$

(1) This was determined by weighing the solid before and after adsorption.

(2) The mass obtained in (1) is divided by the density of the liquid, which gives the volume the film would have in the uncompressed state. The volume (V) divided by the area (Σ) of the solid gives T the thickness.

(3) This is the quantity of heat developed by immersion of the solid in water in the calorimeter, divided by the area (Σ).

ship between the heats of adsorption and of immersion, where Figs. 38 and 39 give some of the energy relationships found.

Fig. 22 shows that the specific energy of emersion ($h_{E(SL)}$) of the solid from the liquid decreases from 512 erg cm^{-2} for the dry crystals to 118.5 erg cm^{-2} at saturation. The variation of the energy of emersion with the thickness of the water film already present is shown in Table 5.

Variation of the Energy of Desorption with the Number of Molecular Layers. It is of interest to estimate the variation of the molar energy of desorption with increase in the number of molecular layers (Table 6).

The increase in the energy of vaporization of water by the presence of the adjacent solid is given in column 4. Thus the vaporization of the first molecular layer requires 6550, the second 1380, and the third 450 cal. $mole^{-1}$ more energy to vaporize than if water alone were present. Thus these values give the increase in molecular interaction due to the presence of the solid.

Table 6. Molar Energy of Desorption of Molecular Layers of Water from the Surface of Titanium Dioxide (Anatase)

1 Number of layer	2 Internal energy of desorption, cal $mole^{-1}$, $H_{D(VnS)}$	3 Internal energy of vaporization of water, λ_1	4 $H_{D(VnS)} - \lambda_1$ or $E_n - E_L$ determined	5 Theory of exponential decay
1	16450	9900	6550 [a]	6550
2	11280	9900	1380	1637
3	10350	9900	450	409
4	9980	9900	80	102
5	9940	9900	40 (?)	26
Sum of all above 5			30 (?)	

Column 2 gives the energy of desorption for a whole layer, when a 1 of the lower layers are complete.
Column 3 gives the internal energy of vaporization which does not include the work done.
[a] The BET theory gives a value for E_1-E_L of 2100 cal $mole^{-1}$.

The theory of Brunauer, Emmett and Teller was used to calculate the number (N) of molecules in the monolayer (1) next to the surface of the solid. It was assumed as the basis of the calculation that the number of molecules in each higher layer is also equal to N. The values obtained by the application of this theory indicate that the water molecules in the first layer (1) are somewhat loosely packed, at 25°, while at − 195.8° nitrogen molecules (which are larger) are more nearly in contact.

The values of column 4 suggest an exponential decay in the energy of desorption. In column 5 it is assumed that the value of 6550 cal. $mole^{-1}$, as given in column 4 is correct, and that the energy for any other layer is one-fourth of that of the layer just beneath it. In *general* this gives the same rate of decay as that exhibited by the experimental values but it may be noted that these latter are lower for even layers and higher for odd layers, than corresponds to the exponential decay. This is just what would be expected if the more polar part of the water molecules is turned toward the solid in the first layer, away from it in the second, toward it in the third, etc. This is exactly the type of orientation exhibited in built-up multilayers of polar–non-polar molecules. Unfortunately, the values of column 4 do not have sufficient accuracy to prove that this alternation in orientation actually occurs.

Discussion: Multimolecular Films. The important relation brought out above is that for water on a non-porous crystalline "polar" solid (anatase) the attractive energy exhibits a rate of decay which does not, for the first few layers, seem very far from exponential. However, the application of a different method, not described here, indicates that for the highest layers the rate is probably slower than this would indicate.

The term "polar" solid is used because a better term has not, as yet, been

introduced. It is used to designate solids, such as quartz, etc., whose molecular interactions may be considered to exhibit not too small *relative* intensities of both dispersion forces and those due to segregated electrical charges, in addition to repulsive forces. On such solids the curve which represents the decrement $(-\Delta\gamma = \Delta\pi)$ of free surface energy due to a film of nitrogen at − 195.8° has the same form (with smaller magnitudes) as that for water at 25°. The film of nitrogen attains, very slightly *below* saturation, a thickness of 36 Å., while for water, as cited earlier, the value is 15 Å. On the whole it does not seem improbable that nitrogen, a non-polar adsorbate, also may exhibit decay of the attractive energy, which is not at first extremely far from exponential.

The saturated film of butane at 0° on this same solid, is 64 Å, thick, so it is not essential to use a polar adsorbate in order to have a highly polymolecular film. However, it is true that the butane molecule has a high polarizability. While the water film attains a thickness of about 5, and that of nitrogen about 10 molecular layers, the number for butane cannot be specified, since in its first monolayer *the molecules lie flat,* while near the outer surface of the film they must have much more nearly the type of orientation exhibited by the surface of liquid butane. If the thickness of this film is to be specified in molecules as units all that can be said is that its thickness is of the same general order as that of nitrogen (10 molecules).

It is of interest to note in connection with the discussion of the two preceding paragraphs, that with the particular sample of titanium dioxide used for this work the adsorption isotherms for nitrogen at − 195.6° and water at 25° are practically identical except possibly very close to saturation, both in form and the volume of gas adsorbed (Fig. 9).

Thus the writers have obtained entirely definite evidence that adsorbed films of water, nitrogen, butane and *n*-heptane on titanium dioxide in the form of anatase are highly polymolecular, with minimum *thicknesses* of 15, 36, 64 and 72 Å, respectively, at pressures just below saturation. We believe that these are correct thicknesses for pressures *very* slightly below saturation, except that the thickness of the water film may be greater than 15 Å. As has been specified these values express the volume of the liquid at the given temperature divided by the area, as determined by the area of the surface of the solid. If the film has a density higher than the three dimensional liquid, then these values in actual ångström units are that much too high, but in terms of molecular diameters the values are not affected.

No uncertainty is introduced by the value of the area which is employed for the calculation, since the determination of area was made by our absolute method. This method is based upon the premise that water on anatase forms a film sufficiently thick to be *duplex, i.e.,* the surface of the film is sufficiently thick to give inappreciable (experimentally) interaction between the outermost layer of the film and the solid. Thus the surface energy of the outer part of the film is supposed to be the same as that of water at the same temperature. That this is true within the limits of experimental error is shown by the fact that as the thicker films thicken there is no detectable decrease in the energy of immersion. Thus, for the first time, certain evidence has been obtained for the highly polymolecular character of certain adsorbed films. As mentioned earlier, no attempt is made here to prove the *non-existence* of monomolecular adsorbed films at high values of p / p_0.

Monomolecular films of stearic acid are formed by adsorption of the acid at the interface between *dry* benzene and TiO_2 (anatase) such as that used in this investigation. In fact, even the monolayer is loosely packed, since only about 70 per cent as much stearic acid is adsorbed as the amount required for close packing.

All the measurements by various investigators of the contact angle of water against graphite agree that the angle is not zero. Since water does not form a duplex film on graphite, many investigators believed that the film would be monomolecular. This however, is not the case, since the water film attains a thickness

of 10Å, or three molecular layers, at a relative pressure of 0.97. The measurements on graphite are discussed in detail on p. 37.

The writers have considered it important to obtain *definite* evidence, already presented, which shows that by the adsorption process alone films taken up from vapors on the surfaces of solids become highly polymolecular at the higher values of p / p_0, provided the contact angle between the solid and the liquid is zero. That this point of view is not universal among specialists in the field of adsorption, is shown by a recent statement by Brunauer,[24c] who is, himself, an enthusiastic supporter of the theory of polymolecular (multimolecular) adsorption:

"Many advocates of the capillary condensation theory maintain that adsorption in porous bodies is largely due to capillary condensation, although they do not deny the existence of unimolecular adsorption. The two schools (unimolecular and capillary condensation) of thought meet on a common ground, namely, that adsorption on a plane surface where capillaries do not exist must be unimolecular."

Capillary Condensation Theory. The monomolecular theory of adsorption on solids receives support at the present time only because the apparent discrepancies which it introduces are explained away by the theory of capillary *condensation.* Undoubtedly this phenomenon is prominent in highly porous solids, but it does not contribute as much to the "sorption" as is assumed by the adherents of this theory.

Indeed, at high relative pressures, the total amount adsorbed is commonly *greater per unit area on a plane surface,* where the high value cannot be explained by the assumption of capillary condensation, *than the total amount of "sorption" for the same area exhibited by a porous solid.* The explanation of this fact is simple: the adsorption in pores is limited by the growth of the film from all sides of the pore. In the simple case of a pore with parallel plane walls the "film" cannot be thicker than half the distance between the walls. When the values for the thicknesses of films of water, nitrogen, and butane given in this paper are considered, it is evident that many of the smaller pores in a silica gel or a catalyst of high area, would become completely filled by adsorption even if capillary condensation were absent.

That capillary condensation, as suggested by Zsigmondy [25] plays an important part in the sorption, is undoubtedly true. However, the assumption by others than Zsigmondy that this phenomenon is responsible for all of the material taken up from a vapor by a porous body, with the exception of a single monolayer, is certainly false. If this assumption had not been made, the monomolecular theory of adsorption could not have survived up to the present time.

Monomolecular and Slightly Thicker Films on Solids. It is shown earlier in this paper that almost all of the films on non-porous solids thus far investigated begin to lose their monomolecular character at a relatively small value of p / p_0 which is of the order of 0.08 to 0.12 for nitrogen at − 195.6° and of 0.15 to 0.25 for *n*-butane at 0° and for water at 25°.

If it is desired to find a film which remains in the monomolecular state up to high values of p / p_0 when adsorbed on a polar solid, it would seem that the choice of a substance whose molecules are polar–non-polar, would be a good one. Thus molecules of an alchol should, in the first monolayer, be oriented with their long axis perpendicular to the surface of a polar solid and with the polar group toward the solid. This leaves the hydrocarbon chains, which resemble paraffin, and which exhibit little attractive energy, on the outside. It would seem that this would give a good chance of obtaining a film which remains monomolecular up to high values of p / p_0. However, the presence of the polar group makes the position of the molecule highly dependent on the surface lattice of the crystal used for adsorption, which should on this account give variations in the thickness of the adsorbed film.

As mentioned earlier the only system which the writers know, that exhibits monomolecular adsorption on a non-porous solid, is propyl alcohol on barium sulfate.

The area available per molecule of the alcohol, and the mean thickness of the films are given in Table 7 as a function of the relative vapor pressure (p / p_0).

Table 7. Propyl Alcohol Films; Monomolecular on Barium Sulfate up to $p/p_0 = 0.9$; do not Complete Their Second Layer on TiO_2 at $p/p_0 = 0.8$, and Complete Their Second Layer on Quartz at $p/p_0 = 0.7$

	$BaSO_4$		TiO_2 (Anatase)		SiO_2 (Quartz)	
p/p_0	Area per molecule, Å.²	Film thickness, Å.	Area per molecule, Å.²	Film thickness, Å.	Area per molecule, Å.²	Film thickness, Å.
0.15	...	..	...	..	End of monolayer	
.2	22.5	4.3	18.7	5.2	16.8	5.8
.4	21.6	4.5	17.3	5.7	14.3	7.0
.6	20.6	4.7	15.9	6.1	11.8	8.2
.8	19.6	5.0	14.5	6.7	7.6	12.8
.88	...	..	12.9	7.6	...	..
.90	19.1	5.1	Values calculated from the data of H. K. Livingston, Ph.D., thesis, University of Chicago, Dec., 1941.			
end of monolayer						
.95	16.6	5.9				
.99	11.2	8.7				

The lattice constants of these three types of crystalline solids indicate that the first monolayer of propyl alchol should exhibit at a given vapor pressure, the most loose packing on barium sulfate, the tightest on quartz, with that for anatase intermediate. That this is a fact is indicated by Table 7.

The end of the monolayer on the surface of the solid occurs at a relative pressure (p / p_0) of about 0.9 (which is very high) with barium sulfate, at about 0.2 with anatase, and about 0.15 with quartz. With quartz the second layer is completed at a relative pressure of about 0.7. Since there is no known method of determining at just what pressure the second layer is actually completed, it is assumed that when the first monolayer is completed the propyl alcohol molecules are closely packed, and the same assumption is made for the second layer. Thus where the area per molecule adsorbed is equal to that which a propyl alcohol molecule should exhibit in perpendicular orientation, it is considered that the film is a monolayer, and if the mean molecular area is half as large, the film is assumed to be two molecules thick.

While the literature contains a very great number of isotherms which represent the adsorption of vapors upon the surfaces of solids, it is unfortunate that most of these isotherms were obtained with porous solids, where adsorption and capillary condensation are inextricably mixed. It is also unfortunate that a large percentage of the work on non-porous solids has not been carried to saturation of the vapor. Thus the literature gives almost no data which help in the development of a theory of adsorption uncontaminated by the effects of capillary condensation.

The State of Adsorbed Films on the Surfaces of Solids

The states of insoluble films on liquid subphases have been studied extensively. Five different phases have been known to exist: the gas, the liquid expanded, the liquid intermediate, liquid condensed, and what is usually designated as the solid phase. Recently Harkins and Copeland [96] discovered a sixth phase, which exhibits extremely remarkable properties. Of the two liquid condensed phases one is so rare that it will not be considered here. The above conclusion is based on the concept of higher-order phase transitions as developed by Ehrenfest,[26] and applied by Dervichian [27] and by Harkins [28] and on experimental work on the π-σ, viscosity, and surface potential relationships as carried out in this laboratory.

Of the above experimental procedures the investigation of the pressure-area relationships is the only one applicable to the study of films on solids. Thus conclusions as to the existence of the various phases cannot be as certain as with insoluble films on liquids. The theory of higher-order phase changes, however, applies equally to

solid or liquid subphases. Thus the only uncertainty is in the identification of a specific phase.

The π-σ isotherms for films on solids can be readily obtained experimentally. The pressure (π) is obtained by the method given earlier. The area of the surface available for each molecule is found by dividing the total area (Σ) by the number (N) of adsorbed molecules. Figs. 23 and 24 illustrate the types of π-σ isotherms thus

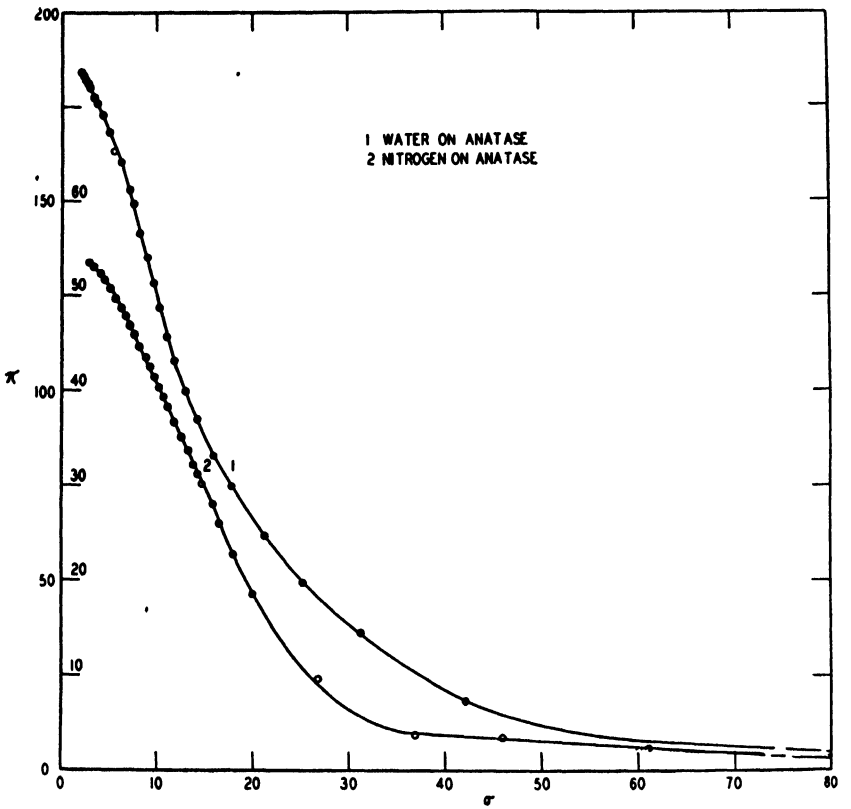

FIGURE 23. The pressure (π)-area (σ) isotherms of nitrogen and water films on anatase at −195.6° C and 25.0° C. Both films exhibit a long condensed region.

obtained. The similarity between these isotherms and those found on liquid subphases is remarkable. Fig. 23 which is the π-σ isotherm of nitrogen on anatase has the same general appearance as that of stearic acid on 0.01N HCl, while Fig. 24 for n-butane on a silica-alumina gel has its counterpart in the film of pentadecylic acid on 0.01N HCl.

The question naturally arises as to whether or not the phases obey the same relationships on both solid and liquid subphases. For this a quantitative criterion is essential and this has been taken as the isothermal equation of state.

Unfortunately, theoretical isothermal equations of state for insoluble films are not known except for the gas phase, even with liquid subphases. It is true that Langmuir [29] has proposed an equation for the liquid expanded state, but unfortunately, this does not agree well with the experimental data for this phase on a liquid subphase as obtained in this laboratory. Therefore, it is useless for the purpose of identifying a liquid expanded film on a solid.

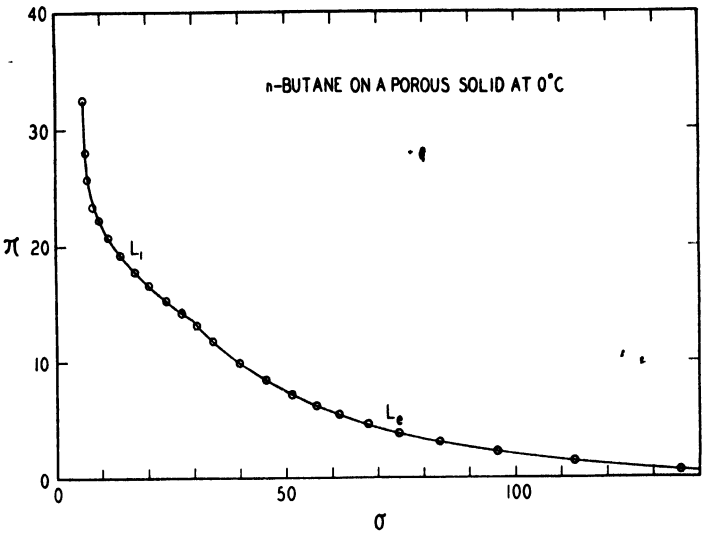

FIGURE 24. The pressure (π)-area (σ) isotherm of the *n*-butane film on an alumina-silica gel. The isotherm exhibits the liquid expanded and liquid intermediate states with a second order phase change between the two.

The equation of state of a perfect gas is [80]

$$\pi\sigma = kT \tag{12}$$

For condensed phases the equation is obvious, since π is a linear function of σ, so:

$$\pi = a - b\sigma \tag{7}$$

where a and b are constants which assume different values for each of the possible condensed phases. Thus, if equations of state can be found empirically for the liquid expanded and liquid intermediate states it becomes simple to identify the different phases.

Thus it is found that the following equation

$$\pi = c + \frac{\sigma}{a} + \frac{b}{a}\ln\sigma \tag{13}$$

is valid for the liquid expanded phase on water, while the liquid intermediate phase is represented by

$$\pi = c + \frac{1}{b}\ln(b\sigma + a) \tag{14}$$

Fig. 25 exhibits the excellent agreement between the calculated and observed values for the liquid expanded and intermediate phases of a film of pentadecylic acid on a 0.01*N* H_2SO_4 solution at 27.5°. The equations have been applied with equal success to this film at other temperatures, and also those of octadecynitrile and of several esters.

The application of the equation of state of the condensed film agrees with the experimental data for films on solids, as is shown by the excellent results obtained when it is used to calculate the area of the solid.

Fig. 24, which illustrates the similarity between the pressure-area relations of films on solids and on liquids, also shows the agreement between the equations for the liquid expanded and intermediate states and the experimental data. The solid

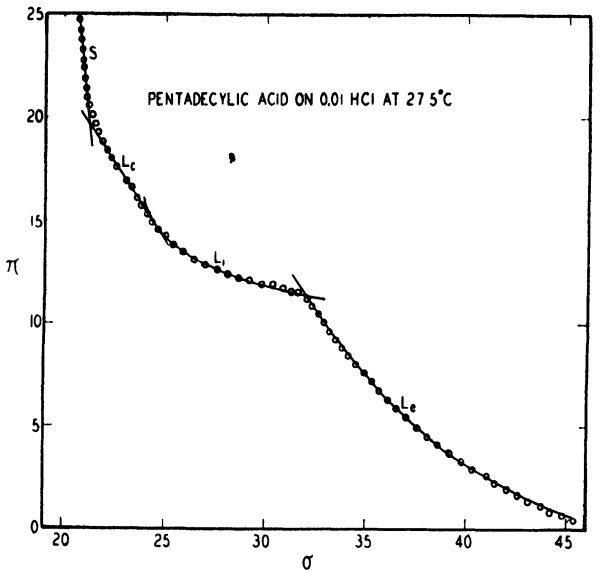

FIGURE 25. The agreement between the calculated (lines) and observed (circles) $\pi - \sigma$ values for the liquid expanded and liquid intermediate film of pentadecylic acid on $0.01N$ H_2SO_4 at 27.5° C.

lines are calculated values and the circles are experimental points. In the low-pressure region all films behave as gases, though not as perfect gases. The equation for a gas in two dimensions exhibits the same type of departure from the perfect gas as an ordinary gas in three dimensions. If the gas region does not extend to too low a molecular area (*i.e.*, below 200-300Å^2 per molecule), the following equation is usually satisfactory.

$$\pi(\sigma - \sigma_0) = kT \tag{15}$$

The two-dimensional equations of state can be transformed into corresponding $p - v$ equations, in which p is the vapor pressure of the adsorbed material and v is the volume of gas adsorbed. This is done by the use of the Gibbs equation. In general

$$\pi = \phi(\sigma) \tag{16}$$

By performing the necessary operations to substitute in the Gibbs equation it is found that

$$\left(\frac{\partial \ln p}{\partial v}\right)_T = -\frac{10^{16}(V\Sigma)^2}{RTN_0v^2}\phi'\left(\frac{10^{16}V\Sigma}{vN_0}\right) \tag{17}$$

The desired equation is obtained by integration of the equation by substitution of the proper form of ϕ'. Table 8 summarizes the results.

The application of $p - v$ equations for condensed films is illustrated in Figs. 15 and 16, and those for the imperfect gas, the liquid expanded and intermediate films in Fig. 26. This is the same system as that of Fig. 24. The agreement between the calculated and observed values is good except at the highest pressures, where the deviation is of the type expected from the porosity of the solid.

The order of the transitions of films on solids also has been investigated, but the experimental data are not yet as complete as is desirable. It can be shown that if a

Table 8. Equations of State

Film	$\pi - \sigma$ Equation	$p - v$ Equation
Perfect Gas	$\pi\sigma = kT$	$v = kp$
Imperfect Gas	$\pi(\sigma - \sigma_0) = kT$	$\ln p = \frac{V\Sigma}{V\Sigma - vN_0\sigma_0 10^{16}} - \ln \frac{V\Sigma - VN_0\sigma_0 10^{16}}{v}$
L_e	$\pi = c + \frac{\sigma}{a} + \frac{b}{a}\ln\sigma$	$\ln p = K + \frac{c}{2aDv^2} + \frac{b}{aDv}$
L_i	$\pi = c + \frac{1}{b}\ln(b\sigma + a)$	$\ln p = K - \frac{1}{bDv} + \frac{a}{b^2Dc}\ln\frac{bc + av}{v}$
Condensed $\left(D = \frac{RT}{V\Sigma}\right)$	$\pi = b - a\sigma$	$\ln p = -\frac{A}{v^2} + B$

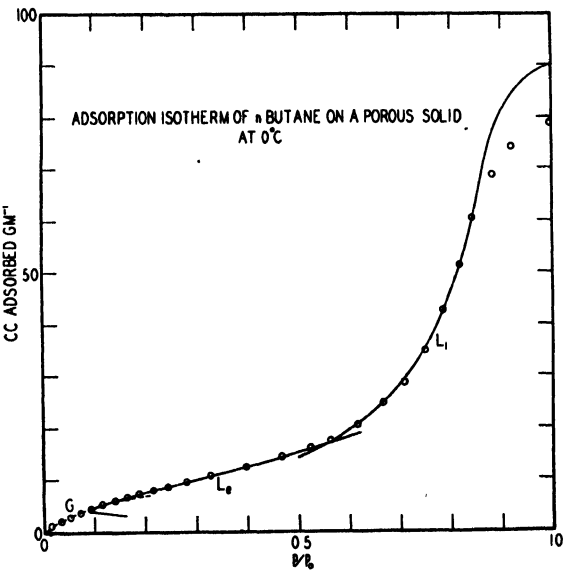

FIGURE 26. The calculated and observed pressure-volume isotherm corresponding to the $\pi - \sigma$ isotherm of Figure 24. Here three phases, the gaseous, liquid expanded, and liquid intermediate are shown. The agreement between the observed and calculated values is excellent except in the very high pressure region where the observed values deviate in the manner predicted from the porosity of the solid.

first-order phase change occurs, the amount adsorbed varies without a change in pressure; for a second-order change there is a discontinuity in $\left(\frac{\partial v}{\partial p}\right)_T$ and for a third order change in $\left(\frac{\partial^2 v}{\partial p^2}\right)_T$. Definite first- and second-order phase changes have been observed. In no case, however, has a third-order change been found. Fig. 27 shows a first-order phase change for the adsorption of water on a sample of graphite which contains 0.46 per cent ash, and a second-order change between liquid intermediate and liquid expanded phases is given in Fig. 24, while Fig. 28 exhibits the same order for a change from the gas phase in the case of an adsorbed film of *n*-butane on an aluminum oxide-silica catalyst. A second-order change between two condensed

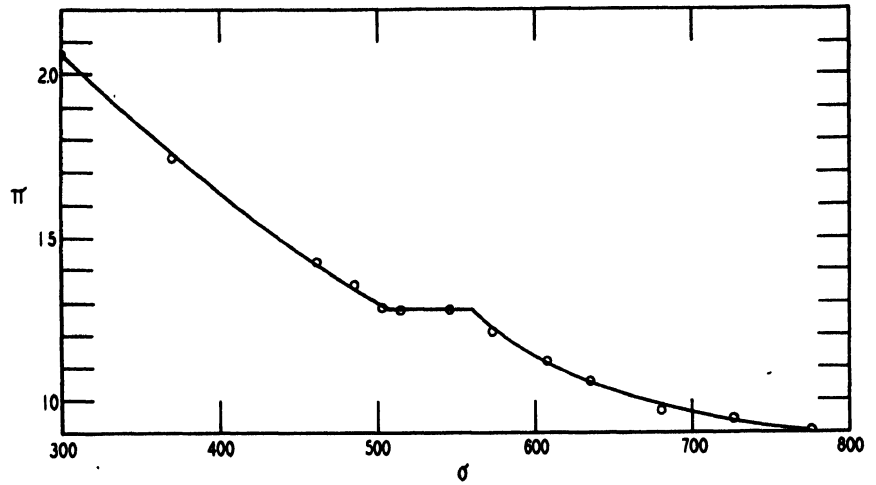

FIGURE 27a. The pressure-volume isotherm of water on a sample of graphite containing 0.46% ash illustrating a first order phase change in the water film. It is seen that the volume adsorbed changes without any change in pressure.

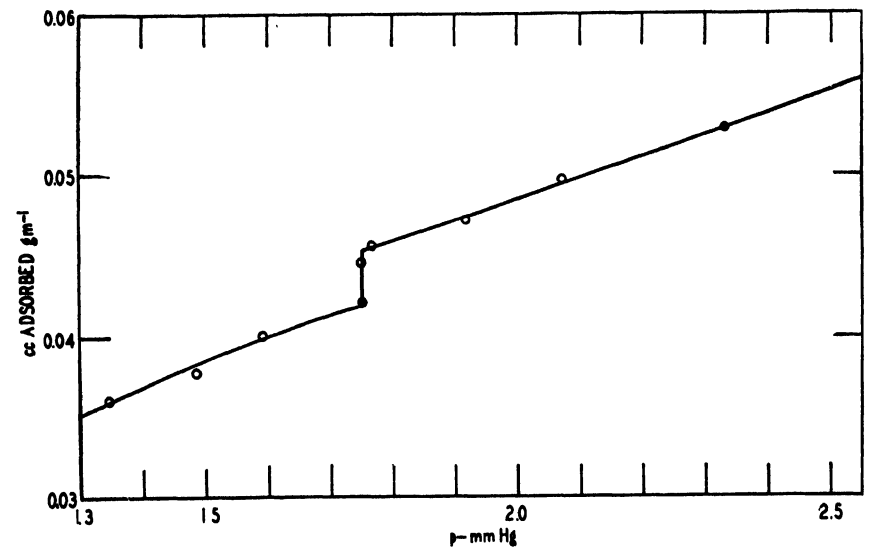

FIGURE 27b. The same as Figure 27a, but expressed in pressure (π)-area coordinates. This figure shows the characteristic "flat" found for all first order changes.

phases is exhibited in Fig. 29, while Table 9 summarizes the order of phase transitions for films on liquids and solids.

A first-order phase change in an adsorbed film on a solid was observed earliest by Edward H. Loeser of this laboratory while working under the direction of the writers. This occurs over a much longer range of σ and of v than the first-order change of Figs. 27a and b, but this specific change of state cannot be published at present.

From the agreement in the π-σ curves and the nature of the transitions it seems

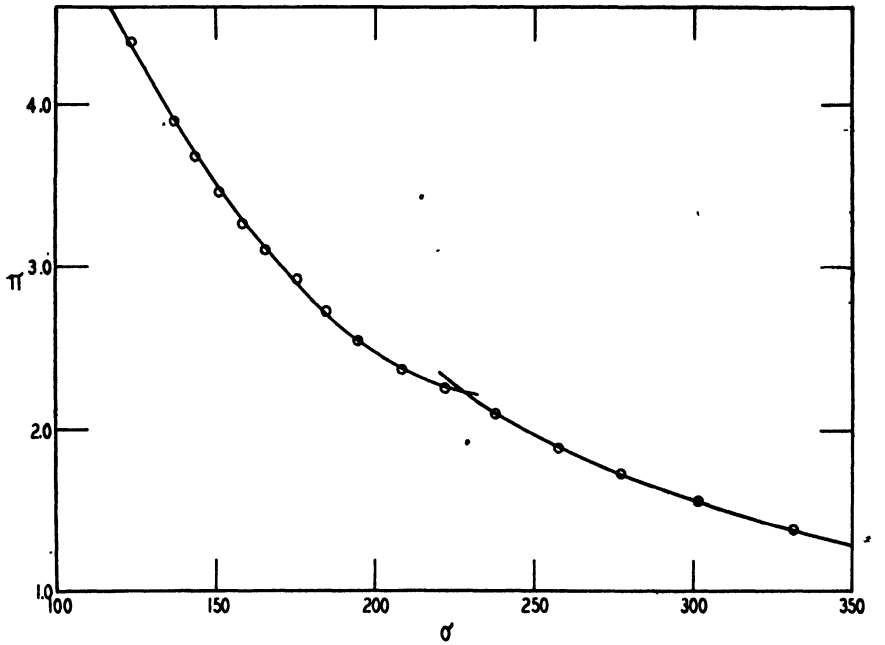

FIGURE 28a. The pressure-volume isotherm for *n*-butane on an alumina-silica gel at 25° C., which illustrates a second order phase change from the gaseous phase at the kink.

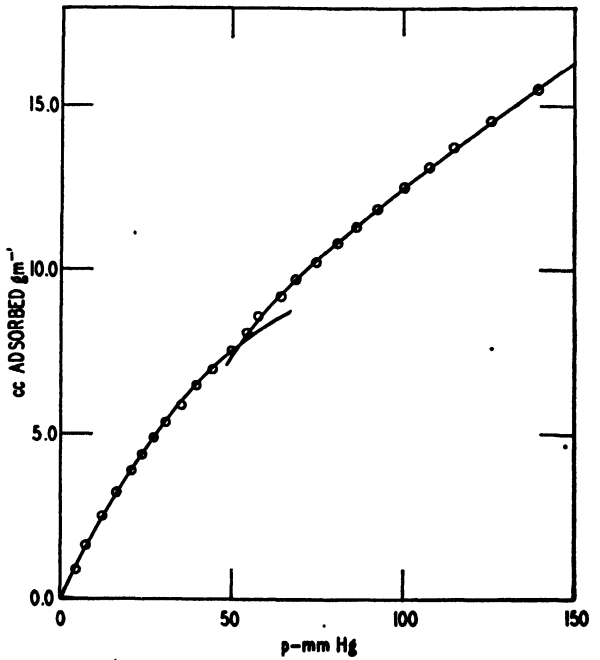

FIGURE 28b. The same as Figure 28a, but shown with pressure (π) and area as variables. The "kink" which is characteristic of second order phase changes in films is marked.

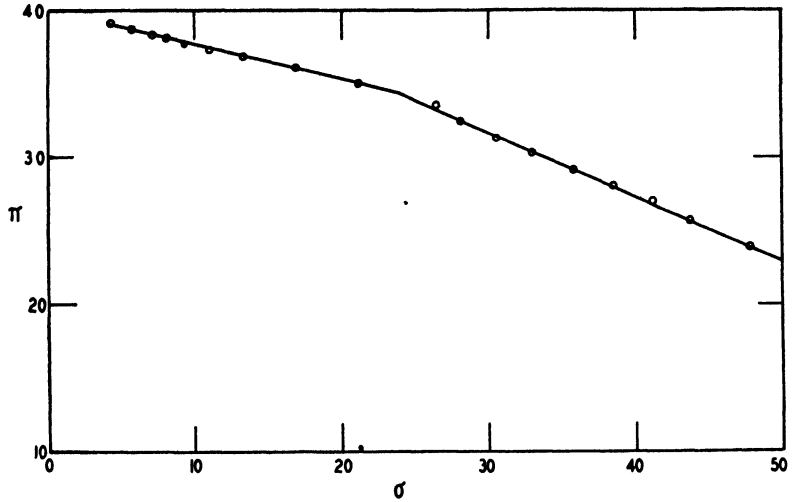

FIGURE 29. This illustrates a second order phase change between two condensed phases. The system is n-heptane-anatase at 25° C. Figure 17 shows similar effects for the adsorption of nitrogen on some porous solids.

probable that the films on solids behave in a similar manner to those on liquids. Obviously, there are striking differences. For example, the film pressures are much higher, the films polymolecular rather than monomolecular; in nearly all systems there is a reversal of the sign of $\left(\frac{\partial \pi}{\partial T}\right)_\sigma$; and in the transition between condensed phases the films on solids go to a film of higher compressibility while on liquids

Table 9. Order of Phase Changes in Adsorbed Films Found when Subphase is a Three-Dimensional (1) Liquid or (2) Solid

Two-dimensional film phase from which transition occurs	Three-dimensional subphase	
	Liquid	Solid
	Order 1 or 2	Order 1 or 2
Gas	2	2
L_E	3	Unknown
L_I	2 *	2
L_C		

* In one case the transition between condensed phases is first order.

they transform to a phase of lower compressibility. These differences, however, are not unexpected in view of the differences between solids and liquids previously listed.

THE HEAT OF IMMERSION

The fundamental method for the direct determination of the most important term used in the calculation of the total energy of adhesion, which is the area of the solid with other related quantities, involves immersion of the finely divided solid in the liquid contained in an extremely sensitive calorimeter. It is obvious that if the energy of immersion of the clean surface is desired, the solid should be outgassed at as high a temperature as can be employed without affecting the surface. In the determination of the area the solid is then put into contact with the vapor of a liquid before immersing in the same liquid.

Of all the possible calorimetric determinations which yield information about the

surface of solids, the most highly developed, both from the technical and theoretical points of view, is that of the heat of immersion. By performing the proper simple auxiliary experiments, the data obtained can be used to give (1) the energy required to separate a solid from a liquid (energy of adhesion); (2) the integral and differential heats of adsorption; (3) the decrease in total surface energy caused by the adsorption of a vapor or liquid on the surface of the solid; (4) the true area of a solid; and (5) the free energy change at any temperature, when it is known at one temperature. To obtain the energy of adhesion, it is necessary to measure the heat of immersion of the clean solid in the pure liquid; for the determination of the heats of adsorption and decrease in surface energy, the heat of immersion must be known as a function of the amount of vapor adsorbed. The area of a solid is obtained from the heat of immersion of the solid saturated with the vapor of the liquid, while the free energy at any temperature may be obtained from the temperature variation of the heat of immersion and the knowledge of the free energy at one of the temperatures.

Experimental Methods

From the theoretical point of view, the ideal solid to use would be a single sheet on which one crystal face is so predominant that all the other faces give only a negligible contribution to the total observed effect. The heats measured, however, are so small that the effects could not be observed even in the most sensitive calorimeters yet built. Thus, the best solids for the purpose are finely divided, non-porous, and crystalline. Although the heats of immersion of porous solids have been measured extremely often, the interpretation of the results is difficult, since they depend both on the composition and structure of the solid. At the present time, there is no way in which every factor involved with porous solids can be exactly evaluated. The effects of porosity are discussed in the section on adsorption.

The value obtained for the heat of immersion is highly sensitive to a number of factors: (1) temperature, (2) impurities in the liquid or on the solid; and (3) degree of solubility of the solid in the liquid. The effect of temperature is easily controlled and is discussed later.

The effect of impurities in the liquid may be very large. This is especially true when the system consists of a polar solid and a non-polar organic liquid, in which the most common impurity is a small amount of water. For example,[42] Harkins and Dahlstrom found the heat of immersion of a sample of titanium dioxide in the form of anatase to be 1.15 cal gm^{-1} in water and 0.390 cal gm^{-1} in thoroughly dried benzene; but with 0.03 per cent of water by weight present *initially* in the benzene this value rose to 1.12 cal gm^{-1}, only 3 per cent lower than the high value found with water. Fig. 30 exhibits the effect of water and butyric acid on the heat of immersion of titanium dioxide in benzene. In both cases it is evident that traces of water or butyric acid, which for most other purposes are insignificant, produce a greater effect than the 3000 times larger amount of benzene present. Marked effects are noted if the solid is initially contaminated by a film. For example, Harkins and Jura [104, 109] found that when 0.548 mg of water was initially adsorbed on a gram of anatase of area 13.8 sq meters the heat of immersion was reduced from 1.689 to 1.316 calories. Lastly, it is apparent that if the solid is appreciably soluble in the liquid, the heat of solution is usually sufficiently large to render the results completely invalid, unless the heat of solution and the amount of solid dissolved are known. The foregoing effects must be considered in any experiment on the heat of immersion. Care should be taken in the preparation of the sample and the liquid and in the prevention of contamination during the course of the experiment.

Preparation of Samples. The preparation of the solid is relatively simple. If it is desired to obtain the value for the clean sample, the solid, after washing by a suitable solvent, is heated in a high vacuum (10^{-5} mm Hg) at as high a temperature as can be used without changing the nature of the solid. With titanium dioxide, 24

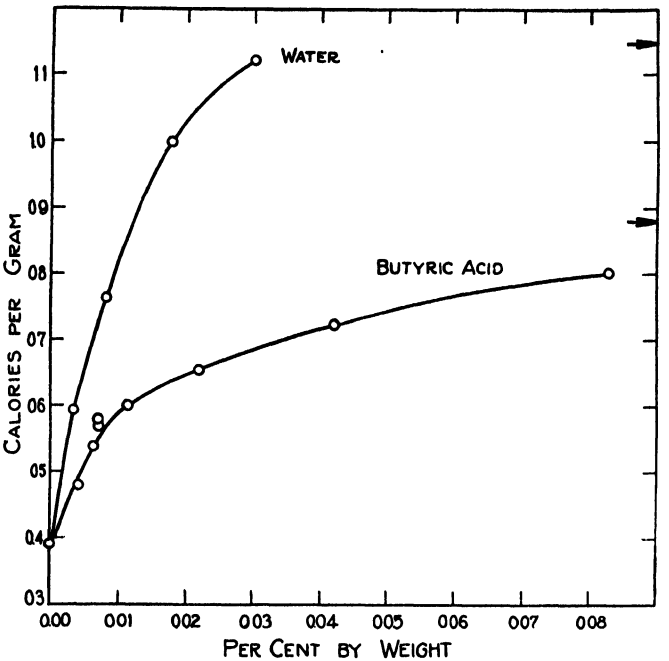

FIGURE 30. Energy of immersion of titanic oxide in benzene which contains water or butyric acid. The arrows give the values for pure water or pure butyric acid.

hours at 500° has been found sufficient. If lower temperatures are used, then in general longer periods of heating are required. The samples, after heating and evacuation, are sealed off while the tube is either completely evacuated or filled with a purified, dried inert gas, preferably helium.

If it is desired to adsorb some of the vapor of the liquid on the surface of the solid, the latter is evacuated as described and then the vapor is adsorbed. A satisfactory apparatus for this type of work is represented by Fig. 31. The powder and the liquid are both weighed out and, after the solid is outgassed, the liquid is allowed to vaporize and to be adsorbed by the solid.

Purification of Liquids. The chemical nature of the liquid determines the method of its purification. If water is employed, it should be very pure. As an example of the preparation of an organic liquid, the procedure for benzene is as follows: The liquid is dried by immersing in it considerable quantities of sodium wire which has a fresh surface. Every few days additional sodium wire is added, and at the end of 2 weeks the benzene is refluxed over sodium for 3 hours. The benzene is then transferred, without contact with the atmosphere, into a distilling flask connected with a closed distillation system. This system, including the flask, is dried for 2 days before putting the liquid into it, by passing through it air dried by bubbling through sulfuric acid and passing through a very long tube over phosphorus pentoxide. The calorimeter is dried in the same way. Finally, the benzene is distilled and is used in the dry calorimeter.

The Calorimeter. A satisfactory calorimeter for the determination of the energy of immersion of a powder in water is that of Harkins and Dahlstrom (Fig. 32). In its use the clean, dry powder which has been immersed inside a sealed glass tube for a long period in the thermostat, is poured into the Dewar used as a calorimeter, through the opening I. If it is desired to keep the powder inside the calorimeter

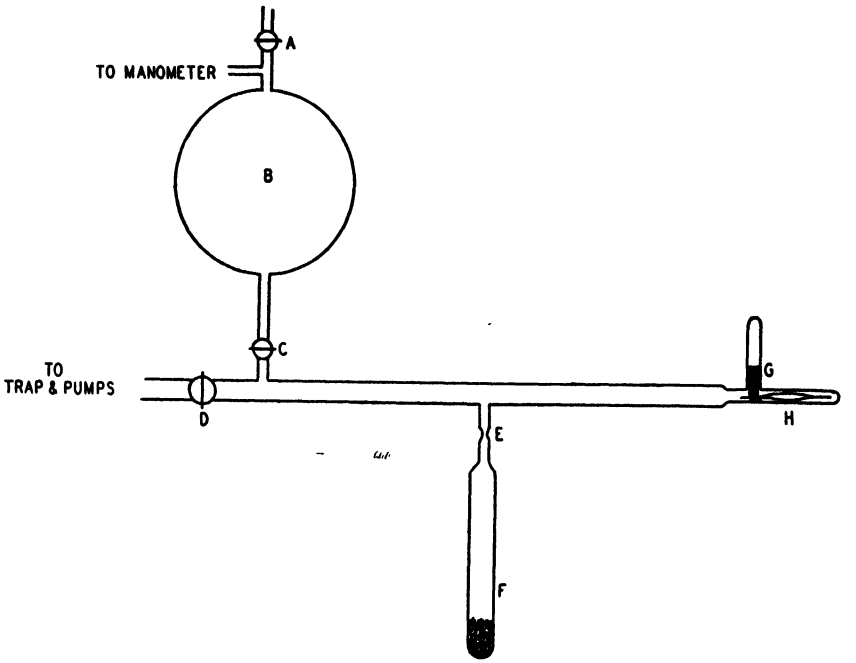

FIGURE 31a. Simplified diagram of apparatus for the adsorption of water vapor on a finely divided crystalline solid in *six* bulbs (F). The water is weighted in the tube H before adsorption and adsorbed on the solid in the bulbs. G is a piece of soft iron used for breaking off the point of the tube H, and B is a gas filled bulb used for the determination of the free volume of the remainder of the apparatus up to the stopcocks C and D.

while it attains the equilibrium temperature, or if a non-aqueous liquid is employed, then modifications made in the work of this laboratory should be introduced (Fig. 33).

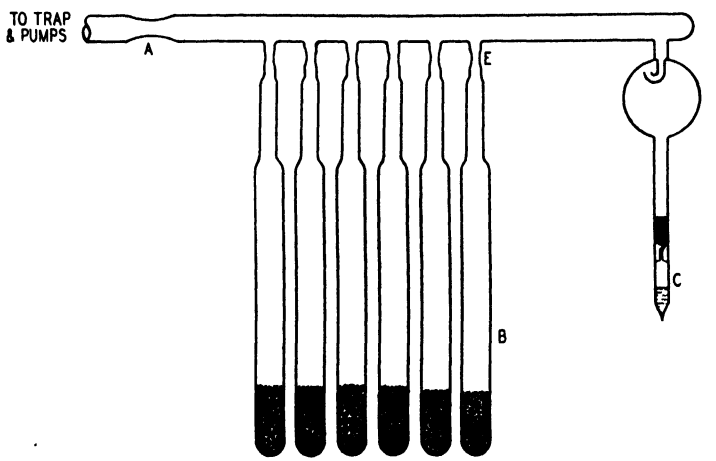

FIGURE 31b. Apparatus for the adsorption of an equilibrium film on a powder. C indicates the liquid. The six tubes are filled with the powder.

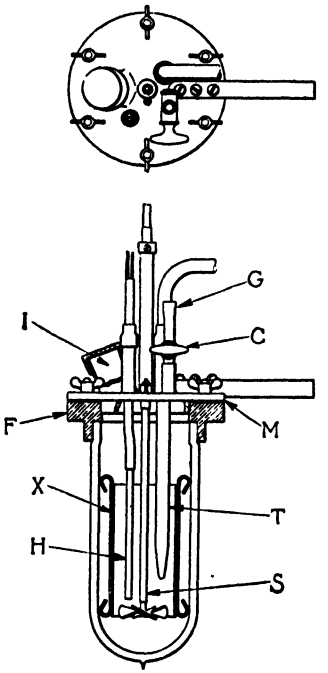

FIGURE 32. Calorimeter. T, 36-junction thermel; H, heating element; G, inlet for liquid; C, stopcock; X, chimney to give better circulation of powder; I, opening for introduction of powder.

The technique of its use is described in a quotation from the *Journal of the American Chemical Society*.[94]

The calorimeters consist of 800 cu cm wide-mouth silvered Dewar flasks (Fig. 33) cemented by litharge-glycerol cement to brass rings to which the calorimeter top is bolted. The 36-junction copper-constantan thermel (T), the stirrer (S), the heater (H), and all-glass cooler (C), the glass tube for filling the calorimeter (G), and the support (B) for the wire basket in which the thin-walled glass bulb filled with powder is contained, are all admitted by vapor tight tubes through the cover. The bulb is broken by the action of a screw. A small correction is introduced by the heat of breaking, but the use of the bulb allows the powder to come into thermal equilibrium with the liquid before contact.

The following factors were found to be of primary importance: type and rate of stirring; high accuracy of the measurement of change of temperature; rigorous drying of solids, liquids and the calorimeter, and the transference of liquids under anhydrous conditions; reduction of the error due to evaporation; accurate determination of the electric energy equivalent; and rapid attainment of thermal equilibrium with the calorimeter.

Stirring. The stirrer should be so designed as to cause the rapid disintegration of the aggregates of powder, and to bring the whole interior of the calorimeter to constant temperature, with the minimum production of heat due to stirring itself. The use of the inner tube (X) (Fig. 33), and of two propellers of proper design aided in attaining these ends. To aid in obtaining complete wetting only 5 to 10 g of powder was used in 650 cu cm of liquid. The liquid and powder were usually made to flow upward through X, but with powders which tend to float on the surface, this direction was reversed.

The best rate of stirring was decided upon in each instance by the use of a preliminary experiment with an unsilvered Dewar which permitted observation of the

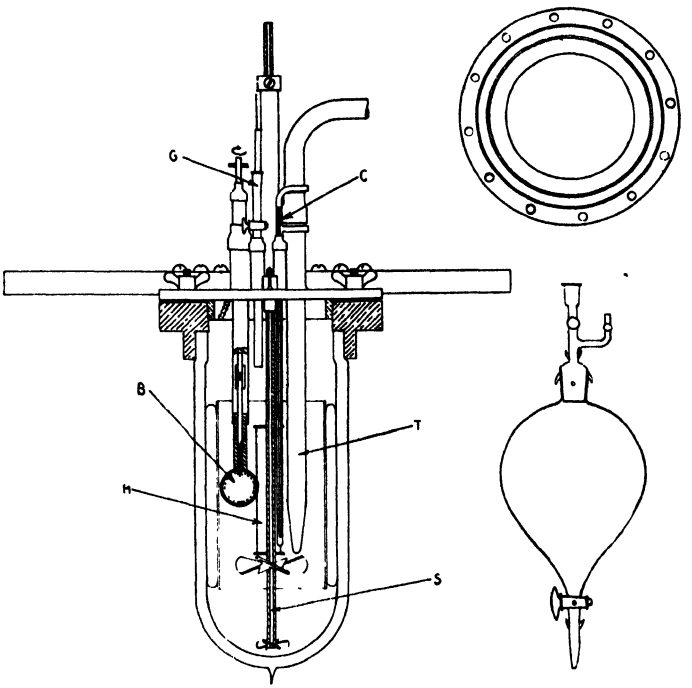

FIGURE 33. Calorimeter for use with anhydrous liquids. Also shown is a top view of the brass ring to which the top of the Dewar flask is cemented and the funnel used to add the dry liquid at G.

rate of dispersion, together with a calorimetric test of the lack of superheating effects upon immersion of the powder. If the stirring was adequate, it was observed that the heat of immersion, expressed as calories per gram, was independent of the total mass of powder immersed over ranges of mass up to 15 g in 650 cu cm of liquid.

Temperature Measurement. Owing to the necessity of using small amounts of powder and to the small magnitude of the heat of immersion itself, the apparatus for the temperature measurement was made so as to give a high sensitivity. Thirty-six junction copper-constantan thermocouples were utilized with a White double potentiometer and a galvanometer of high voltage sensitivity. One mm on the galvanometer scale placed at 250 cm corresponded to 0.00005°. One end of the thermel was fitted tightly into a small, narrow-mouthed Dewar of about 300 cc capacity which was shielded externally by means of a thin-walled copper cylinder. Since this vessel remained in the thermostat and was filled with water, it afforded a very constant environment and any rapid slight changes in the thermostat temperature were lagged out. The thermostat was a 250-liter bath of light-bodied oil controlled to within 0.0005° by means of a large mercury regulator used in conjunction with a vacuum tube relay heating circuit.

Calorimeter Calibration. The temperature change in the calorimeter generated by the immersion of the powder was compared with the temperature increase caused by a known amount of electrical energy which was introduced by a heater (H, Fig. 33). In the experiments reported the agreement between successive values of the electric energy equivalent (calories per microvolt) was within 0.15 per cent. The heating procedure was so arranged that the heater resistance and the heating current could be determined at the time of the heater rating.

Auxiliary Features. Owing to the unusual sensitivity of the heat of immersion to minute amounts of impurities, experiments were usually performed as soon as the calorimeter and its contents could be brought to thermal equilibrium. Often the wetting liquid was initially at a temperature far removed from the thermostat temperature; so if it was inconvenient to wait a sufficient time for the excess heat to leak out through the Dewar jar walls, artificial cooling (cooler C, Fig. 33) was employed. Usually the experiment was begun within one hour after the contents of the calorimeter had been brought to temperature equilibrium.

In order to exclude water, which for this work is without doubt the most important impurity likely to occur in ordinary organic liquids, several precautions were taken in addition to the rigorous purification and drying of the liquid itself. To exclude the possibility of contamination by water vapor, the calorimeters were dried thoroughly by passing dry air through them for forty-eight hours. The air, which had been passed previously through towers containing successively soda lime, calcium chloride, anhydrone, sulfuric acid and a five-foot column of phosphorus pentoxide was led into the assembled calorimeter through the glass stirrer shaft, which was a piece of capillary tubing. The air escaped through the glass filling tube (G, Fig. 33). When the stopcock on this tube was closed, sufficient air pressure was built up inside the calorimeter to stop the passage of air entirely. This test served to indicate the tightness of the calorimeter assembly. By use of interchangeable ground glass joints, the calorimeters were filled with the organic liquids without contact with the air at any time after the final distillation. Sometimes, when the purified liquid had been in storage for a length of time previous to the experiment, it was passed over a column of activated silica gel into the calorimeter.

The Energy of Adhesion (Fig. 34)

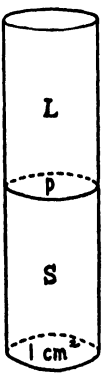

FIGURE 34. The work of adhesion (W_A) and the energy of adhesion (h_A) are, by definition, the increase of free and internal energy, respectively, involved in the separation of the liquid L from the solid S, at the interface of unit area between the two when no trace of adsorbed film is left on the surface of the solid. The actual process is always carried out in the reverse direction beginning with the clean solid in a vacuum.

The total surface energy (E_s) or enthalpy (H_s) of a clean, dry solid is given by the relation

$$H_S = \Sigma_S\left[\gamma_S - T\left(\frac{\partial \gamma_S}{\partial T}\right)_p\right] \tag{18}$$

If the non-porous solid is immersed in a liquid, the solid surface with its energy disappears and is replaced by a solid-liquid interface with an enthalpy of

$$H_{SL} = \Sigma_{SL}\left[\gamma_{SL} - T\left(\frac{\partial \gamma_{SL}}{\partial T}\right)_p\right] \tag{19}$$

Since the area (Σ_s) of the surface of the solid and that of the interface (Σ_{SL}) are equal, the enthalpy of emersion is

$$H_{E(SL)} = \Sigma\left[\gamma_S - \gamma_{SL} - T\left(\frac{\partial\gamma_S}{\partial T} - \frac{\partial\gamma_{SL}}{\partial T}\right)_p\right] \tag{20}$$

or per unit area

$$h_{E(SL)} = \frac{H_{E(SL)}}{\Sigma} = \gamma_S - \gamma_{SL} - T\left(\frac{\partial\gamma_S}{\partial T} - \frac{\partial\gamma_{SL}}{\partial T}\right)_{p,\Sigma} \tag{21}$$

Now, the change of enthalpy is related to the change of internal energy by the equation

$$\Delta h = \Delta\epsilon + \Delta(pv) \tag{22}$$

or at constant p

$$\Delta h = \Delta\epsilon + p\Delta v \tag{23}$$

Since Δv is so small [95] that within the limits of experimental error it cannot be detected

$$h \cong \epsilon \tag{24}$$

that is, the change in enthalpy is equal to the change in internal energy; both are given by Eq. 21.

Two quantities of great importance are the work and energy of adhesion as defined by Harkins.[6] The energy of adhesion is the change in internal energy involved where a liquid is separated from a solid at their interface to give clean surfaces of both the solid and the liquid. Thus, the energy of adhesion $\epsilon_{A(SL)}$ is

$$\epsilon_{A(SL)} = \epsilon_S - \epsilon_{SL} + \epsilon_L = \epsilon_E + \epsilon_L \tag{25}$$

That is, the energy of adhesion is simply equal to the heat of emersion plus the surface energy of the liquid. This latter quantity is obtained from the surface tension and the temperature variation of the surface tension of the liquid.

Some values of heat of emersion and energy of adhesion for solid-liquid systems are given in Table 10a and b, respectively.[95]

Table 10. Energy of Separation of a Liquid from the Surface of a Crystalline Solid. (Erg-Cm.$^{-2}$) at 25° (Values for Liquid Mercury for Comparison)

Solid....	$BaSO_4$	TiO_2	Si	SiO_2	ZrO_2	SnO_2	$ZrSiO_4$	Graphite	Hg
Liquid	A. Energy of Emersion (h_E or ϵ_E)								
Water	490	520	580	600	600	680	850	175	
Ethyl alcohol		500		520					
Ethyl acetate	370	360		460		530			
Butyl alcohol	360	350		420		500			
Nitrobenzene		280			310		430		
Carbon tetrachloride	220	240			270	320	410		
Benzene	140	150		150	190	220	260		123
Isoöctane		105			110	120	190		
	B. Energy of Adhesion (h_A or ϵ_A)								
Water	610	640	700	720	720	800	970	295	
Ethyl alcohol		550		570					
Ethyl acetate	430	420		520		590			
Butyl alcohol	410	400		470		550			(195)
Nitrobenzene		360			390		510		
Carbon tetrachloride	280	300			340	380	470		
Benzene	210	220		220	260	290	330		193
Isoöctane		155			160	170	240		160

The energy of separation of the hydrophilic solids exhibits the two important relations: (1) If the solids are arranged in the order of increasing energy of separation from water, they are also arranged in this order for all of the other liquids. An

apparent exception for butyl alcohol with barium sulfate and titanium dioxide is within the limits of experimental error. (2) If the liquids arranged in order of decreasing energy with respect to one of these solids (as titanium dioxide) they are arranged in this order for all of the other solids.

These factors can be shown in a more striking way by taking the heat of emersion from water as unity and recalculating the other values (Table 11).[94]

Table 11. Heat of Immersion of Powders in Liquids: Relative Values (Water = 1.00)

Liquids	TiO_2	ZrO_2	SiO_2	SnO_2	ZnS	$BaSO_4$	$ZrSiO_4$
Water	1.00	1.00	1.00	1.00	(1.00)	1.00	1.00
Ethyl alcohol	0.97	..	0.87	..	..	..	..
Butyric acid	.77	..	..	..	..	..	..
Ethyl acetate	.69	..	.78	0.77	..	0.76	..
Butyl alcohol	.67	..	.70	.74	..	.73	..
Nitrobenzene	.55	0.52	..	.69	..	..	0.50
Carbon tetrachloride	.46	.45	..	.48	..	.46	.48
Benzene	.28	.32	.25	.32	(0.46)	.28	.31
Isoöctane	.20	.16	..	.17	..	.17	.23

These relations are non-specific or physical, rather than specific or chemical. However, the presence of a dipole in the molecule of the liquid causes the energy of binding, as measured for immersion or adhesion, to be high.

It is obvious that the number of dipoles of the liquid, present at unit area of the surface of the solid, depends upon the area per molecule of liquid; and this is dependent upon the orientation in the first monolayer of liquid. If the molecules are polar-nonpolar it is not difficult to show that the probability is extremely high that they are oriented with their dipole group toward the surface of any of the hydrophilic (polar) solids.

Determination of the Change in Surface Energy Caused by Adsorption of a Gas or Liquid

If a liquid or its vapor is adsorbed on the surface of a solid, the free surface energy changes from γ_s to some lower value γ_{sf}, and the total surface energy from

$$\gamma_S - T\left(\frac{\partial \gamma_S}{\partial T}\right)_p \text{ to } \gamma_{Sf} - T\left(\frac{\partial \gamma_{Sf}}{\partial T}\right)_p.$$

The heat of emersion per unit area of the sample with the film adsorbed from the vapor is

$$h_{E(Sf/L)} = \gamma_{Sf} - \gamma_{SL} - T\left(\frac{\partial \gamma_{Sf}}{\partial T} - \frac{\partial \gamma_{SL}}{\partial T}\right)_{p,\Sigma} \tag{26}$$

Substraction of Eq. 26 from Eq. 21 gives

$$h_{E(SL)} - h_{E(Sf/L)} = \gamma_S - \gamma_{Sf} - T\left(\frac{\partial \gamma_S}{\partial T} - \frac{\partial \gamma_{Sf}}{\partial T}\right)_{p,\Sigma} \tag{27}$$

But $h_{E(SL)} - h_{E(Sf/L)}$ is the reduction of the total surface energy, and the right-hand side of Eq. 27 has the same form as the expression for the heat of spreading of an insoluble monolayer on a liquid subphase, as defined by Harkins, Young, and Boyd.[89] To obtain the change in surface energy brought on by adsorption, it is thus necessary to measure at least two heats of emersion. The variation of the energy of emersion from water as a function of the amount already adsorbed is exhibited in Fig. 22. The heat of emersion of the clean sample was found to be 512 erg cm^{-2} and decreased to 119 erg cm^{-2}. Thus the maximum reduction of the surface energy was 393 erg cm^{-2}. The decrease in total surface energy is shown in Fig. 35 together with the variation in free surface energy and surface entropy.

Relationship between the Heat of Adsorption and the Heat of Emersion

The heat of adsorption of a vapor upon the surface of a solid can in general be calculated more accurately from heats of immersion and condensation than by any direct or indirect experimental adsorption method. It is, therefore, unfortunate that the equations used in the literature to express the relationship between the energies of adsorption and immersion are universally incorrect.

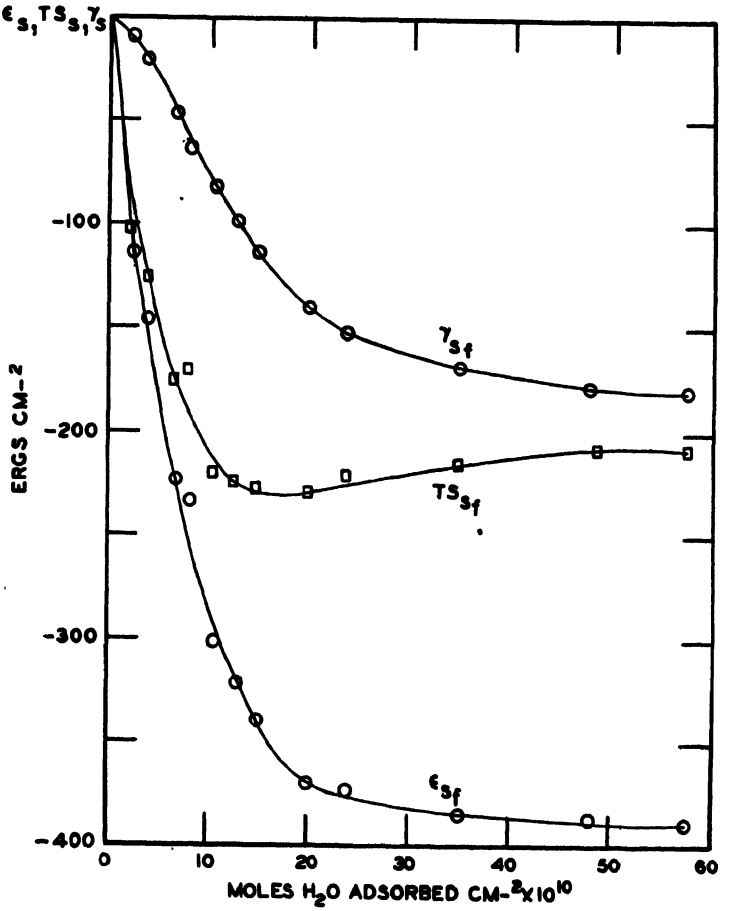

FIGURE 35. Lowering of the surface energy of TiO_2 (anatase) by an adsorbed water film. The lowering of the total surface energy is $\epsilon s - \epsilon s_f$, of the free energy $\pi = \gamma s - \gamma s_f$, and of the latent heat $l = T(s_s - s_{sf})$, where s is the entropy per unit area. The top line represents the surface energies of the clean solid which are not known.

Consider a non-porous solid with an area of 1 cm^2 and a negligible volume. The following processes may be imagined to occur:

1. The solid is emersed from n_1 moles of liquid into a vacuum. Here n_1 is assumed to be large in comparison with the n moles considered in the next step.

$$\Delta H = h_{E(SL)}. \tag{28}$$

2. The solid is emersed from n_1 moles of liquid into the vapor of the liquid at the pressure p_1 carrying with it a film of just the correct thickness to give it equilibrium

with the vapor *at this pressure*. The amount of liquid removed in this film is n moles.

$$\Delta H = h_{E(SfL)}. \tag{29}$$

3. Of the n_1 moles of liquid left in (1), evaporate n moles, leaving $(n_1 - n)$ moles, which is the amount of liquid left in 2.

$$\Delta H = n\lambda. \tag{30}$$

Subtract 29 from 28 + 30, since this will give the increase in the value of the heat function when the film of n moles is vaporized (desorbed) from the surface of the solid.

$$h_{D(VSf)} = h_{E(SL)} - h_{E(SfL)} + n\lambda. \tag{31}$$

Now,

$$h_{E(SL)} = h_S - h_{SL} \tag{32}$$

$$h_{E(SfL)} = h_{Sf} - h_{SL}. \tag{33}$$

So,

$$h_{D(VSf)} = h_S - h_{Sf} + n\lambda \tag{34}$$

and since in general

$$h = \gamma - T(\partial\gamma/\partial T)_{p,\,\Sigma} \tag{35}$$

where γ is the free surface energy per sq cm

$$h_{D(VSf)} = \gamma_S - \gamma_{Sf} - T[(\partial\gamma_S/\partial T) - (\partial\gamma/\partial T)]_{p,\,\Sigma} + n\lambda. \tag{36}$$

It has been customary to express the heat of adsorption either in cal g^{-1} or cal $mole^{-1}$. If it is wished to express the heat in cal g^{-1} the result is

$$H_{D(VSf)} = H_{E(SL)} - H_{E(SfL)} + n\lambda, \tag{37}$$

where $H_{E(SL)}$ and $H_{E(SfL)}$ are the heats of emersion in cal g^{-1} of adsorbent and n is

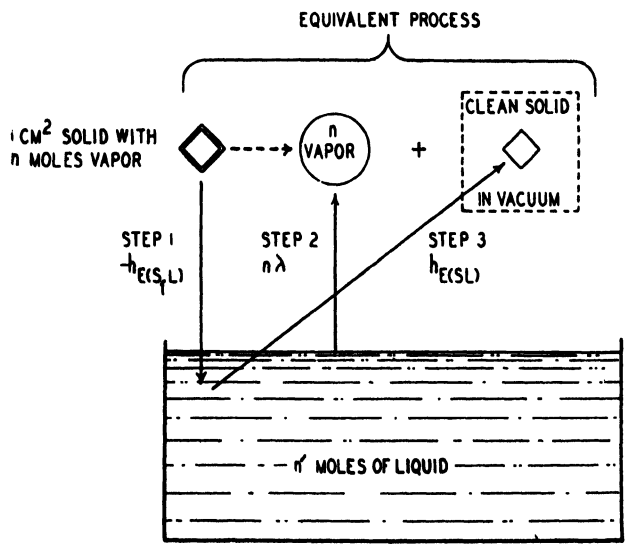

FIGURE 36. Steps 1, 2, and 3, by means of which a solid with an area of 1 sq cm, with n moles adsorbed on the surface, is transformed into n moles of vapor and the solid in a vacuum. The equivalent process involves merely the desorption of the n' moles from the surface.

the number of moles of vapor adsorbed g^{-1}. If it is wished to express the result in cal $mole^{-1}$ of vapor adsorbed, the equation becomes

$$H'_{D(VSf)} = (1/n)[H_{E(SL)} - H_{E(Sf L)}] + \lambda. \tag{38}$$

Fig. 36 gives a graphic representation of the necessary steps in the derivation of Eq. 31. Although the equation has been derived for a non-porous solid, it is evident that it is equally true for one which is porous.

The incorrect expression in general use is, however,

$$H_{D(VSf)} = H_{E(SL)} + n\lambda$$

This omits the term, $-H_{E(Sf L)}$, which is not zero. That heat of emersion of the solid covered by the film in equilibrium with the saturated vapor of the liquid is considered in detail in the next section. Eq. 31 is true for any solid regardless of the amount of vapor or liquid adsorbed.

From the nature of the derivation of Eq. 31 there is no doubt of its validity. There is only one type of system for which sufficient data are given in the literature to make it possible to compare the heats calculated from data on heats of emersion

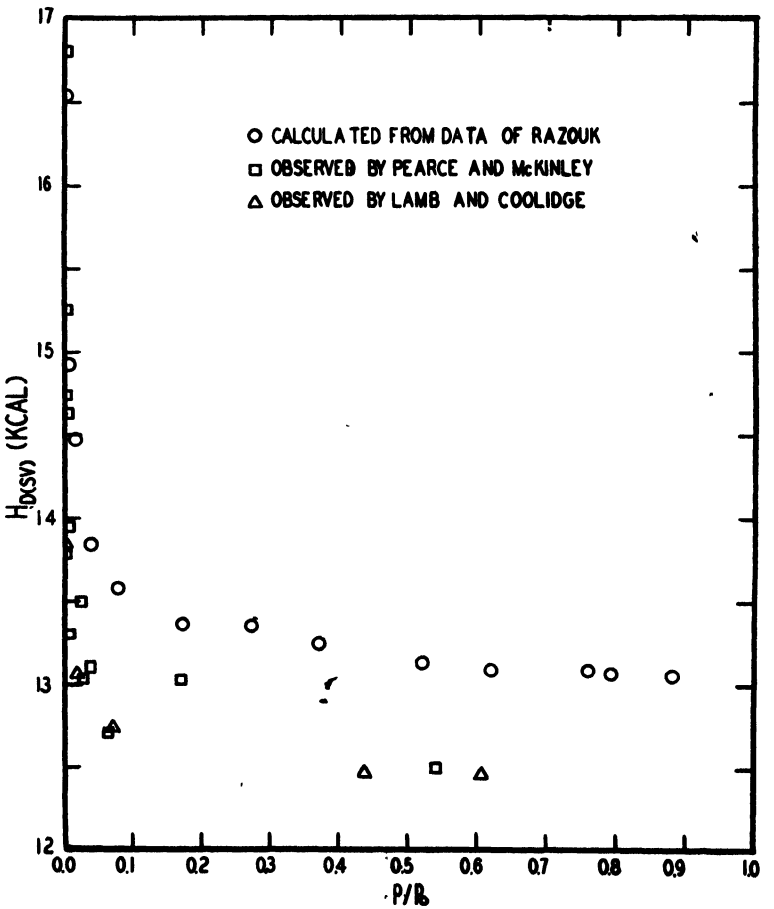

FIGURE 37. Shows the comparison between the calorimetrically measured integral heats of adsorption with those calculated from heat of emersion data.

with experimentally observed heats of adsorption. Razouk[31] measured the necessary heats of emersion of charcoal from methyl alcohol, while Lamb and Coolidge[32] and

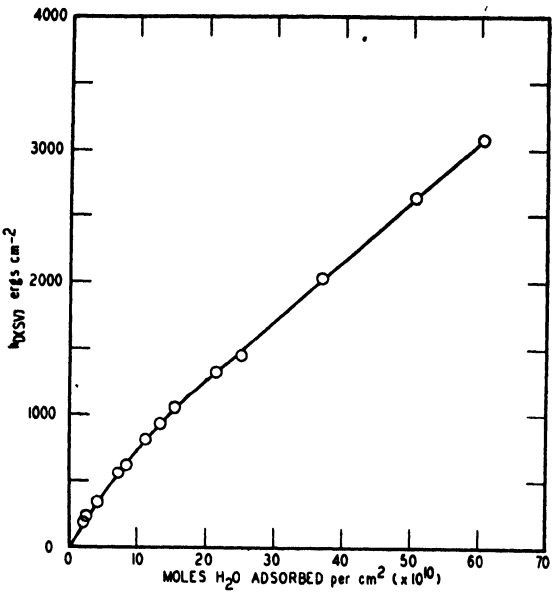

FIGURE 38. Variation of the heat of adsorption per sq cm of area of TiO_2 (anatase) with the weight of water vapor adsorbed.

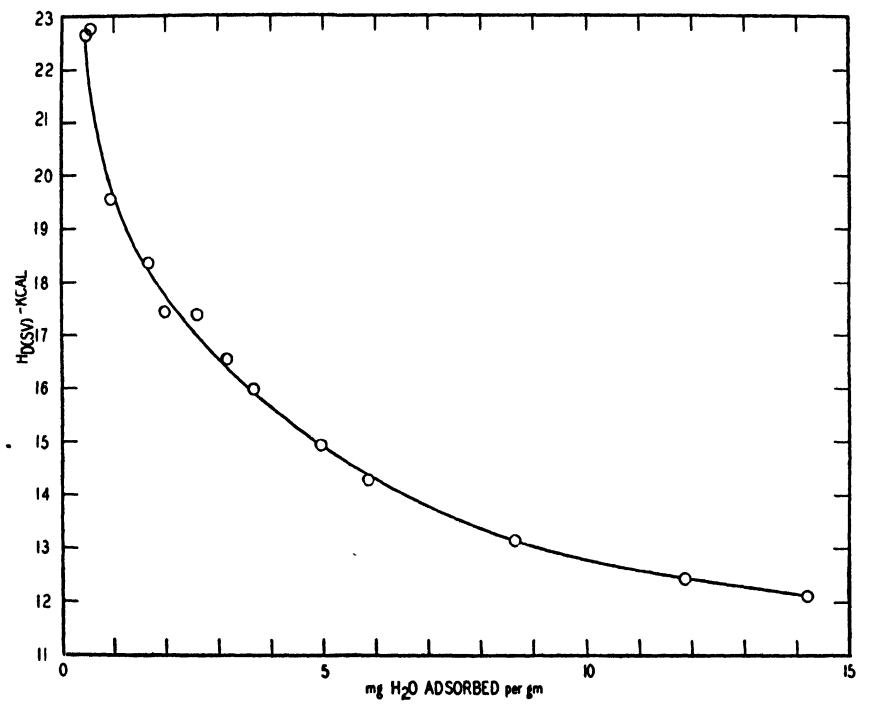

FIGURE 39. Decrease in the energy of desorption, in calories per mole of water, from the surface of TiO_2 (anatase) as a function of the weight of water adsorbed.

Pearce and McKinley[33] made direct calorimetric measurements of the heat of adsorption of this alcohol on charcoal. The comparison between them is shown in Fig. 37. It is seen that when the differences in the charcoals and temperatures is taken into consideration the difference between the results (maximum, 6 per cent) is surprisingly small. Figs. 38 and 39 exhibit the values of the heat of adsorption of water vapor on anatase in erg cm^{-2} and in cal $mole^{-1}$ of vapor. These values were calculated from the heats of emersion shown in Fig. 22.

This method of determining heats of adsorption is at the same time the most tedious and the most accurate thus far developed. The accuracy is due to two factors: (1) in general, heats of vaporization of liquids are either known or can be measured accurately, and the heat of adsorption is obtained by adding to this a quantity measured in a calorimeter for an interaction which in general becomes complete in only a very few minutes; and (2) experimental conditions can always be so arranged that equilibrium between the solid and vapor is attained. This last factor is especially important in the very low and very high pressure regions. The precision obtained in the heats calculated from heats of emersion obviously depends on the accuracy with which each individual heat of emersion can be measured. Thus, for the adsorption of water on anatase the precision increased from a deviation of 4.5 per cent at the lowest pressure to only 0.3 per cent at the highest pressures.

The relationship between the heats of emersion and adsorption, as expressed by Eq. 31, is exceedingly important and valuable. Some of the consequences of the equation are outlined below.

This equation, for the first time, clearly indicates the heat changes that take place in the process of physical adsorption, namely, the *change in surface energy of the solid* and the *heat of condensation of the gas.* This shows that the generally accepted development of Hückel [34] is erroneous. In the development of his equation he assumed that the change in the surface energy is zero. As a consequence, he defined the integral heat of adsorption as the change in energy of the gas. This error necessitates a redefinition of the integral heat of adsorption, which may be expressed as follows: the integral heat of adsorption is the heat change when n moles of gas are adsorbed per gram of solid, or even better, per unit area of the surface of the solid. The differential heat of adsorption can then be obtained in the usual manner.

Eq. 31 also shows clearly why the integral and differential heats of adsorption approach the heat of condensation of the vapor as the amount adsorbed per unit area increases. The integral heat of adsorption in cal $mole^{-1}$ of vapor is given by Eq. 38. The results of Razouk, and of Harkins and Jura, show that the heat of emersion changes most rapidly when only small amounts of vapor are adsorbed, and the quantity $H_{E(SL)} - H_{E(S/L)}$ varies only slightly when n becomes large. Thus $\frac{1}{n}[H_{E(SL)} - H_{E(S/L)}]$ becomes smaller and smaller as n increases. Thus $H'_{D(V_n/)}$ approaches λ as a limit as n increases. The same reasoning applied to the differentiation of Eq. 31 with respect to n demonstrates why the differential heat of adsorption approaches the heat of condensation.

Another result of Eq. 31 is that for those systems in which the heat of adsorption is less than the heat of condensation the heat of emersion increases as the amount of adsorbed material is increased, as with charcoal or graphite and water. If $H_{E(SL)} - H_{E(S/L)}$ is calculated from the heat of adsorption of water on charcoal from the data on Keyes and Marshall,[35] it is found that $H_{E(S/L)}$ increases by more than 3 cal gm^{-1} over $H_{E(SL)}$. Since the heat of emersion of clean charcoal in water is around 10 cal gm^{-1}, the increase is easily measurable. Such experiments have not as yet been performed.

The relationship between the heats of emersion and adsorption possesses a large number of other properties. However, since the experimental verification is not available and difficult to obtain, they will not be given here.

Fig. 40 shows the changes in the heat content, the free energy, and the product of the temperature and entropy for the adsorption of water on anatase as a function of the equilibrium pressure of the gas for the following process. One mole of water vapor whose pressure is such that it would be in equilibrium with the liquid is ad-

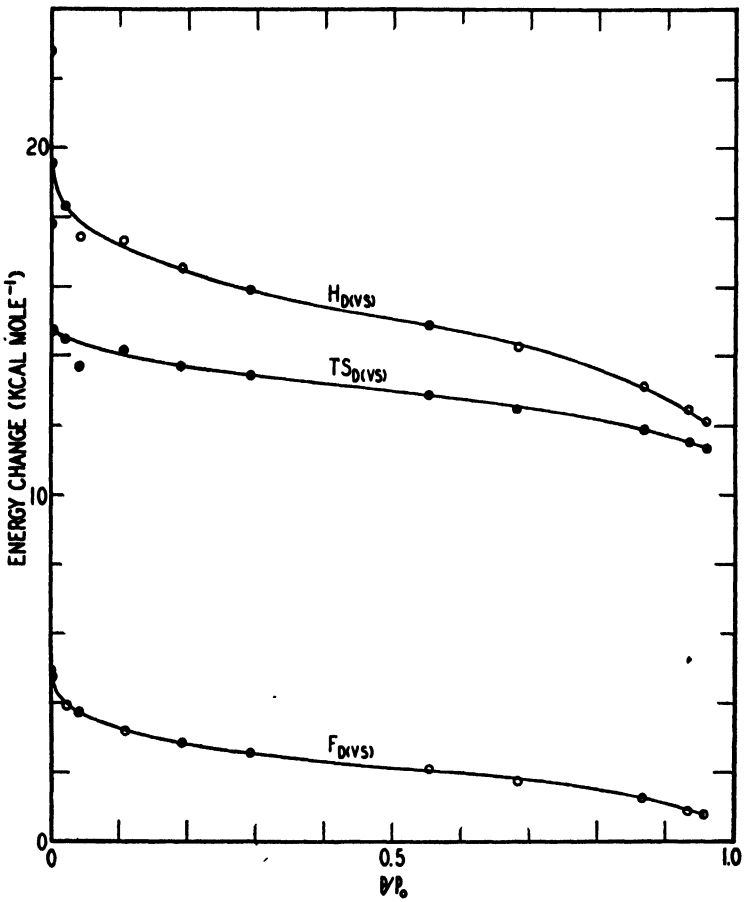

FIGURE 40. The same as Figure 39, but given as a function of the relative pressure. The free energy and the product of the temperature and entropy are also given for the "standard" process.

sorbed on the correct amount of clean solid to give the plotted equilibrium pressure. Fig. 41 exhibits the same changes in erg cm^{-2} as a function of the amount of adsorbed water is varied. These graphs indicate that the entropy term contributes much more than the free energy to the heat change. The process that has been used is such as to make the free energy change as large as possible.

Absolute Method for Determining the Area of a Finely Divided Solid from the Energy of Emersion

Under proper conditions the heat of emersion can be used as an absolute method for the determination of the area of a finely divided crystalline solid. If a single clean plane surface of a solid is exposed to the vapor of a liquid, the solid continues to adsorb the vapor until the vapor pressure of the adsorbed material is equal to that

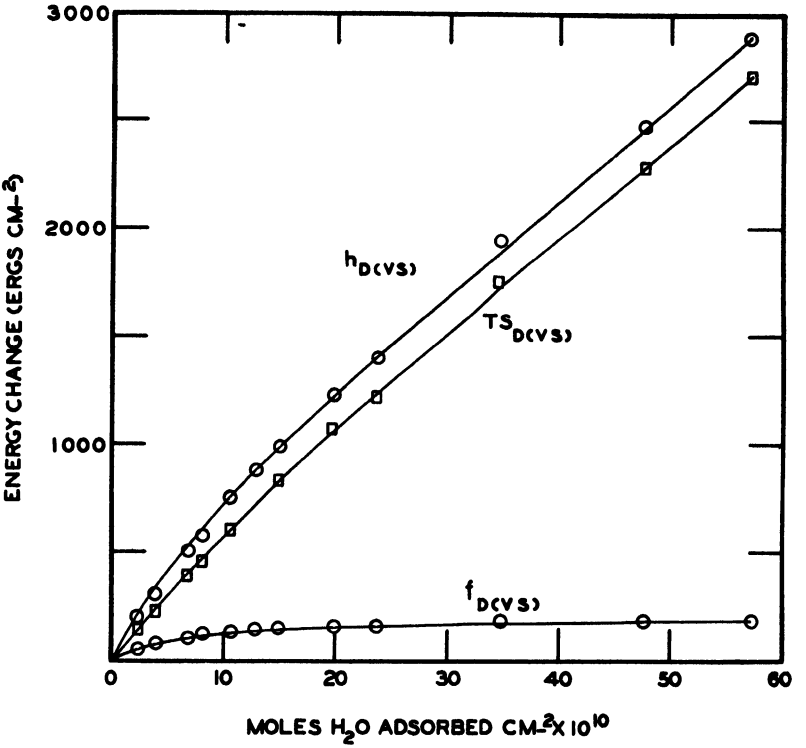

FIGURE 41. The same as Figure 39 with the inclusion of the free energy and product of the temperature and entropy for the "standard" process.

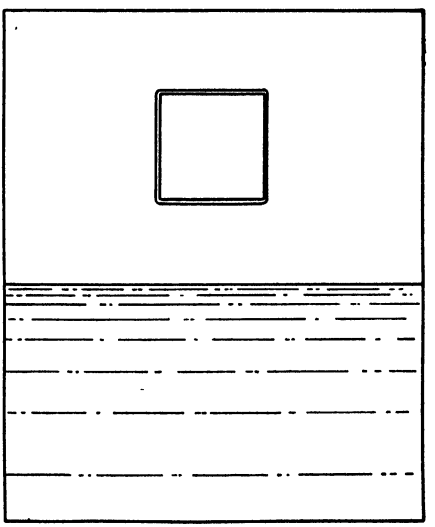

FIGURE 42. Crystal in equilibrium with the vapor of a liquid: to be immersed in the liquid and thus lose the surface energy of the duplex film of liquid.

of the liquid. If a duplex film [91] is formed, the free surface energy of the film is equal to that of the liquid whose vapor has been adsorbed. Since the free surface

energy is equal to that of the liquid for all temperatures in the neighborhood of the temperature at which the work is being done, the total surface energy of the film on the surface is equal to that of the liquid. Thus, if the solid is immersed in the liquid (Fig. 42), each square centimeter gives off heat corresponding to that which would be given off if many small drops of liquid of a total area of one square centimeter were immersed in a body of the same liquid. Since this quantity can be determined for the liquid from its surface tension and the temperature variation of its surface tension, it is apparent that the area of the solid can be determined if the relationsip between the area of the solid and that of the film is known.

The heat of emersion of the clean solid is given by Eq. 21. If the solid is exposed to the saturated vapor of the liquid until the adsorbed film attains equilibrium with respect to the vapor, the free surface energy changes from γ_s to γ_{s_e} while the surface enthalpy is changed from $h_{E(SL)}$ to $h_{E(s_eL)}$. The heat of emersion of the solid saturated with the vapor then becomes

$$h_{E(S_eL)} = \gamma_{S_e} - \gamma_{SL} - T(\partial\gamma_{S_e}/\partial T - \partial\gamma_{SL}/\partial T)_{p,\,\Sigma} \tag{39}$$

Eq. 39 may be simplified by the use of the relationship

$$\gamma_{S_e} = \gamma_L + \gamma_L \cos\theta \tag{40}$$

If Eq. 40 is substituted in Eq. 39, it is found upon simplification that

$$h_{E(S_eL)} = \left(\gamma_L - T\frac{\partial\gamma_L}{\partial T}\right)\cos\theta + T\gamma_L \sin\theta \frac{\partial\theta}{\partial T} \tag{41}$$

where θ is the contact angle of the liquid on the solid. If it is assumed that $\theta = 0$, it is found that

$$h_{E(S_eL)} = \gamma_L - T\partial\gamma_L/\partial T = h_L \tag{42}$$

The right-hand side of Eq. 42 is simply the heat content of the surface of the liquid used. This quantity can be obtained from the surface tension and temperature variation of the surface tension of the liquid.

The outer area of the film (Σ'), in equilibrium with the saturated vapor of the liquid is not much larger than that (Σ) of the clean solid. The value of Σ' is given by the relation

$$\Sigma' = 4.185 \times 10^7 H_{E(S_eL)}/h_L \tag{43}$$

where $H_{E(s_eL)}$ is the heat of emersion of the film-covered powder in cal g^{-1}. This is the same relation obtained in the general discussion of the previous section.

If it were possible to work with a single plane surface, Σ' would be equal to Σ, the specific area of the clean solid surface. If the material is porous, it is apparent that Σ' will be much less than Σ. This is due to the filling up of the pores, thus greatly reducing the surface area exposed. The measured value for the heat of emersion may then be so small as to appear to be zero, as reported by Razouk, who found that charcoal saturated with methyl alcohol gave a zero heat of emersion.

If, however, the solid is non-porous and crystalline, the area of the clean solid surface, Σ, can be obtained from the area of the film-covered surface. The method is illustrated below by data obtained by the immersion of a sample of anatase of high area in water, the adsorption isotherm of which is given in Fig. 9 (untreated). The area obtained for this powder is 13.8 sq meters per gram, as given in Table 12.

Table 12. Area (Σ) per Gram of Anatase (TiO_2) by the Absolute Method

$H_{E(SL)}$	$h_{E(SL)}$	$H_{E(S_eL)}$	Σ'	Σ
1.69 cal	510 ergs	0.409 cal	14.4	13.8

Here Σ' is the area of the powder coated with the excessively thin (about 17Å) film of water when in equilibrium with liquid water. The area (Σ') is obtained by

converting 0.409 cal into ergs and dividing this by 118.5, the surface energy of water at 25°. This gives 14.4×10^4 cm^2 per gram.

The thickness of the water film is obtained by dividing the total volume of liquid water adsorbed by this area (14.4×10^4 cm^2). The assumption was made that the density of the adsorbed water in the duplex film has a mean value of unity. The weight of the film was taken as the weight of the sample plus the film, minus the weight after drying, as obtained on an analytical balance. This gave 20Å as the thickness of the water film. The only uncertainty of any moment is that involved in the shape and distribution of sizes of the particles of anatase, but, since the *whole* correction is small (4.0 per cent) the error in its calculation is not important. The form of the particles is shown in Fig. 43, as obtained by an electron microscope.

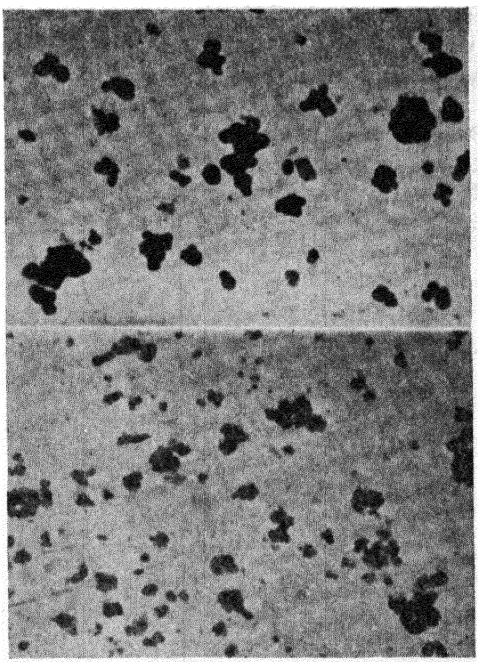

FIGURE 43. Electron microscope photograph (× 14,600) of a TiO_2 (anatase) powder of area 13.8 mg^{-1} by our absolute method, and 13.9 sq mg^{-1} by the method of Brunauer, Emmett and Teller on the basis of the assumption that the mean area per N_2 molecule is 16.2 A^2 (Emmett). (Photographs by E. F. Fullam, Interchemical Corp.).

This area, 13.8 m^{2}g^{-1} is the most accurate ever obtained for a fine powder. It is of interest that from a nitrogen adsorption isotherm, which we determined with great care, and by the use of the theory of Brunauer, Emmett and Teller for calculation, the value of 13.9 m^{2}g^{-1} was obtained when Emmett and Brunauer's favorite value of 16.2Å^2 was taken as the area occupied per nitrogen molecule. The area thus obtained (13.9 m^{2}g^{-1}) is almost identical with the absolute value given above. However, this seems to be because fine crystals of anatase (TiO_2), cause nitrogen molecules to occupy this area, as is true of zirconium dioxide or silicate, or of barium sulfate while on some crystalline metals it packs much more closely.

The Temperature Coefficient of the Heat of Emersion

The temperature coefficient of the heat of emersion has not been investigated extensively. The few experiments which have been made show that the temperature coefficient may be zero, positive or negative. The determinations show, however, that the temperature coefficient is not very large. The largest thus far observed is that of Harkins and Jura,[36] who determined the heat of emersion of a sample of

titanium dioxide coated with aluminum oxide and obtained 1230 ergs cm^{-2} at 11.70° and 1130 ergs cm^{-2} at 24.97°.

Very little has been done theoretically with the temperature coefficient of the heat of emersion. The only detailed investigation that has been made is that of Jura,[87] who investigated only the relationship of the temperature coefficient of the heat of emersion to the free energy of emersion.[88] The results of this investigation show that the usual integration of the free energy equation is valid for emersion of solids from liquids and that

$$\Delta\left(\frac{f}{T}\right) = -\int_{T_1}^{T_2} \frac{h}{T^2} dT$$

The various possible methods of variation of the free energy of emersion were considered. The general results of this investigation are represented by Figs. 44 and 45. Much work still remains to be done on this subject.

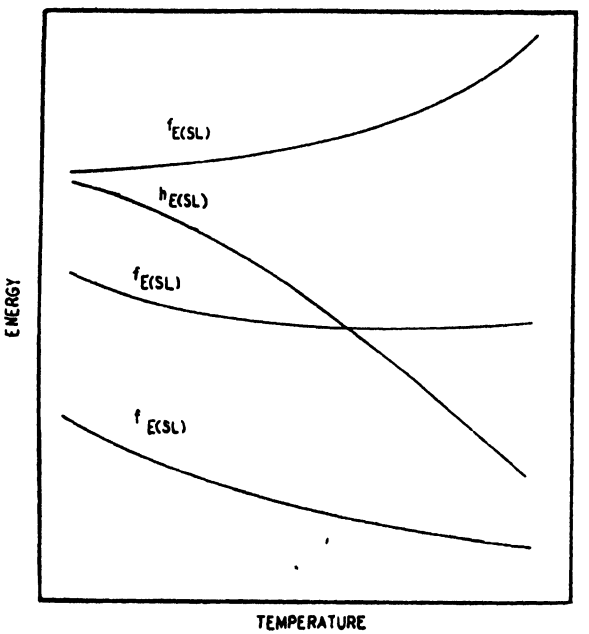

FIGURE 44. Modes of variation of free energy of emersion.

THE CONTACT ANGLE

Experimental Methods

If a liquid is in contact with a clean surface of a solid, there is a solid-liquid interface between the solid and the liquid, while any bare surface of the solid absorbs the vapor of the liquid until the fugacity of the adsorbed material is equal to that of the vapor and of the liquid. The angle, equal to or greater than zero, between the liquid and the solid, is designated as the angle of contact. This is the angle at the line of contact between the solid and the liquid as measured in the liquid phase (Fig. 46).

Although many methods are used for measuring this angle, the most suitable found thus far is that of the tilting plate advocated by Adam and Jessop [89] as modified in this laboratory.[88] Fig. 47 shows the apparatus, as developed by Harkins and

Fowkes, but without the cover, which should fit as tightly as possible in order to keep the vapor at its saturation pressure. Perhaps the most important additions were: (1) the use of glass barriers to clean the surface, (2) the inclusion of a film balance which makes it possible either to detect the presence of impurities on a supposedly clean water surface or to determine the surface tension of the solution simultaneously with the measurement of the contact angle, and (3) in work by Harkins and Jura, the addition of a tight cover.

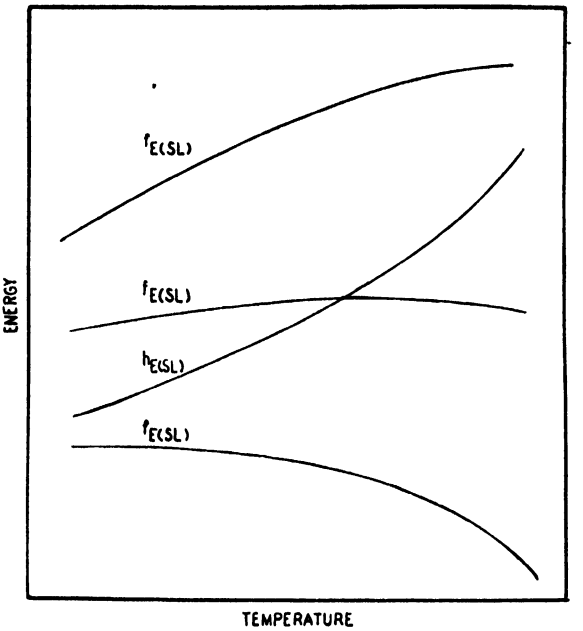

FIGURE 45. Same as Figure 44.

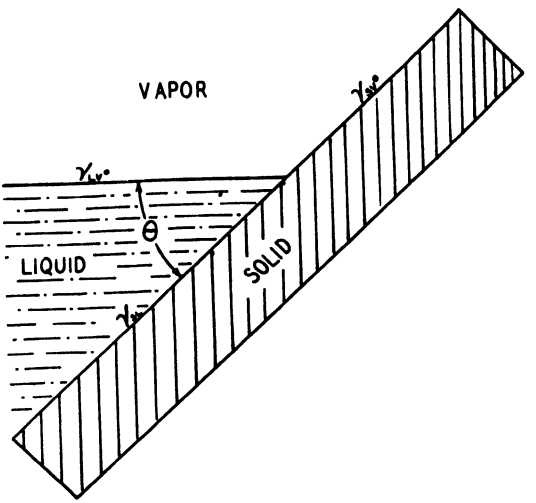

FIGURE 46. Angle of contact between a solid and a liquid.

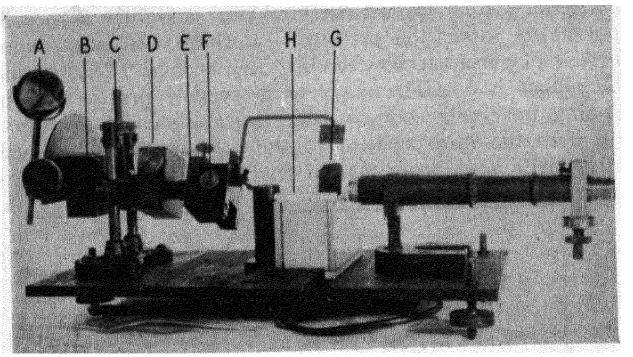

FIGURE 47. Instrument for measuring contact angles.

The main requirements of an accurate instrument for the measurement of contact angles by the tilting plate method are three-fold. First, the surface of the liquid must be kept clean during the period of measurement. This is the condition most often neglected. Secondly, the observed edge of the solid-liquid intersection must lie on the axis of rotation of the solid surface.[40] Thirdly, there should be a mechanism to move the slide up and down in the liquid, and also in a direction parallel to the length of the slide. The apparatus used in this investigation and shown in Fig. 47 was designed to meet all these requirements. There are two rotational movements consisting of a forty-tooth worm gear and a worm for each unit. There are also two centering devices with rack and pinion movements. The rotating worm (B) turns the slide during a measurement. The corresponding worm gear is fastened to the main shaft, to which the pointer (A) shown in the mirror is also fastened. The main shaft is raised to the proper height by means of the adjustable-height bearing (C). Fastened to the main shaft is the calibrating worm gear box (D), the worm gear of which rotates an inner shaft to which the two mutually perpendicular centering movements are attached. By means of the first centering movement (E) the slide of solid (G) is moved perpendicular to its length, and by the second, (F) parallel to its length. This latter movement dips the slide in and out of the water during measurements. Paraffined glass barriers (H) are used to sweep the surface of the liquid in the paraffined glass trough. A small Wilhelmy type surface tension balance is used to check for surface contamination. The intersection of the solid and liquid surfaces is observed through a microscope which has a 32-mm objective, and an eyepiece with a fixed vertical crosshair and a traveling horizontal crosshair.

The temperature coefficient of the contact angle of pure water on either graphite or paraffin is +0.06° per degree C. Therefore temperature control of better than plus or minus one or two degrees is unnecessary, so the room temperature was kept between 23 and 27° while taking measurements for calculations at 25°. A metal box with a glass window for observation was kept over the trough and slide during measurements in order to keep out air currents and contamination from the air.

Theory and Data

Reference to Fig. 46 shows that the relationship between the surface tensions of the liquid, the solid-liquid interface, and the surface of the solid covered by its adsorbed film is expressed by:

$$\gamma_{S_e} = \gamma_{SL} + \gamma_L \cos \theta \qquad (44)$$

This equation is said to have been developed by Young,[41] but no such equation is to be found in his paper, where he expresses the relations in words whose significance is not clear. According to Adam, it was given by Dupré.[42] Although extremely

simple, both in meaning and derivation, this equation has been incorrectly interpreted until recently, as is shown in a later section. It is evident, if equilibrium is attained, that for a given solid and liquid there can be only one value of the contact angle. The "advancing" and "receding" angles [48] obtained by nearly all investigators other than those in this laboratory is due to improper preparation of the surface, and poor techniques in making the measurements. Harkins and Fowkes and later workers, who used their apparatus, were able to secure the same value of the angle whether the angle was obtained by having the liquid advance or recede before the masurement was made.

The general thermodynamic theory of spreading has been developed by Harkins.[91] This theory is applicable to both solids and liquids. The contact angle is thus far the only available method for determining whether a duplex or non-duplex film has been formed. If a duplex film is formed, the contact angle must be equal to zero; but if a non-duplex film, whether mono- or polymolecular, is formed, the angle is greater than zero. These conclusions are obvious from the definitions of duplex and non-duplex films and Eq. 44. It has been observed that in the majority of cases pure liquids on the clean surfaces of solids exhibit zero contact angles. A solid on which water gives a contact angle greater than zero is designated as hydrophobic. Table 13 gives accurate contact angles for four such solids as determined by Fowkes and Harkins.

Table 13. Contact Angles (Σ) Greater than Zero with Water

Substance	θ	
Ceylon graphite	85.7	
Talc	87.8	
Stibnite	84.2	
Paraffin	108-111	(Varies according to composition of the paraffin)

The values for paraffin are in good agreement with those obtained by other investigators. Much lower values for graphite have, however, been reported by Rehbinder [44] and his associates. A repetition of the determination of the contact angle for graphite was made by Jura,[45] who employed the apparatus of Fowkes and Harkins, but with the addition of a tight cover. The bottom of the apparatus was flooded with water in which filter papers were suspended, since it is essential to bring the vapor pressure as close to that of water as possible, because the thickness of the water film near saturation is highly dependent on the vapor pressure of the water (Fig. 23). After one-half hour the contact angle was found to be 85.5°, which agrees with the result obtained by Fowkes and Harkins within experimental error. The angle did not change for the following six hours. The values of these contact angles should be determined in a vacuum, with the same pre-treatment of the sample as that used for the determination of the adsorption isotherm.

The Work of Adhesion and the Contact Angle

The work of adhesion, as defined by Harkins for a solid and a liquid, is

$$w_{A(SL)} = \gamma_S - \gamma_{SL} + \gamma_L \tag{45}$$

γ_L either is known or can be readily determined. The problem is then to determine $\gamma_S - \gamma_{SL}$. Eq. 44 can be written

$$\gamma_S - \gamma_{S_e} = \gamma_S - \gamma_{SL} - \gamma_L \cos\theta \tag{46}$$

The quantity $\gamma_S - \gamma_{S_e}$, which is π_e, can be determined from the adsorption isotherm (see page 10). Thus,

$$\gamma_S - \gamma_{SL} = \pi_e + \gamma_L \cos\theta \tag{47}$$

or

$$w_{A(SL)} = \pi_e + \gamma_L(1 + \cos\theta) \tag{48}$$

The equation used prior to the paper of Harkins and Livingston [99] was

$$w_{A(SL)} = \gamma_L(1 + \cos\theta) \tag{B}$$

This differs from the correct equation by the omission of the term, π_e. On the basis of Eq. B, the work of adhesion would be limited to values lying between 0 and $2\gamma_L$, which is absurd. Table 14 gives the correct values for the work of adhesion for several liquids against titanium dioxide. In the next section some values are given for graphite. The spreading pressures of these liquids on the solids are also given.

Table 14. Work of Adhesion, Spreading Coefficient and Free Energy of Emersion between TiO_2 (Anatase) and Various Liquids (erg $cm.^{-2}$)

Liquid	Spreading coefficient $S_{L/S} = \pi_e = \gamma_S - \gamma_{SL} - \gamma_L$	Free energy of emersion $f_E = \gamma_S - \gamma_S$	Work of adhesion $w_A = \gamma_S - \gamma_{SL} + \gamma_L$
H_2O	190	262	334
N_2	56	64	72
n-C_4H_{10}	43	58	73
n-C_7H_{16}	46	66	86

None of the values in Table 14 agree with those obtained by the use of the usual incorrect Eq. B, valid only if $\pi_e = 0$, which can be true only if the solid adsorbs none of the vapor of the liquid. The system that most nearly approximates this is paraffin and water. If it is assumed that solid paraffin adsorbs the same amount of water as the liquid hydrocarbons, then within the experimental error of the determination of θ, $\pi_e \cong 0$. This conclusion is based on the work of Harkins and Ginsburg,[35] who found the surface tension of pure dry benzene to be 28.88 dynes cm^{-1}, while that of benzene saturated with water was only very slightly lower, 28.82 dynes cm^{-1}. In general, however, the correct equation should be used.

Effect of a Solute and of Solute Concentration on the Contact Angle

The values of the contact angles for pure water against paraffin, graphite, talc, and stibnite are given in Table 13. The presence of solutes in the water has a marked effect on the contact angle. For example, the addition of n-butyl alcohol to water to form an 0.818 molar solution reduces the contact angle of water against paraffin from 111.0° to 55.3°. Solutions of n-butyl amine, n-butyric acid, n-propionic acid, n-acetic acid, and sodium n-butyrate have the same general effect. The lowering of the contact angle is the least marked with sodium n-butyrate. The influence of these solutions on the contact angle for the other solids is similar. Table 15 gives data for n-butyl alcohol on paraffin and graphite.

Table 15. The Effect of N-Butyl Alcohol on the Contact Angle of Water against Paraffin and Graphite

Paraffin				Graphite			
m	Log a_2	γ	θ	m	Log a_2	γ	θ
0	....	72.4	111.0 ± 0.2°	0	....	72.0	85.7 ± 0.2°
0.00674	−2.175	72.0	109.7 ± .2°	0.0135	−1.876	69.0	84.4 ± .4°
.01629	−1.795	69.5	109.2 ± .1°	.0330	−1.493	64.3	84.5 ± .1°
.02959	−1.541	66.5	108.5 ± .1°	.0564	−1.266	60.6	82.5 ± .2°
.0606	−1.237	60.7	105.7 ± .1°	.1095	−0.987	54.1	76.3 ± .2°
.1222	−0.943	53.5	100.1 ± .2°	.2297	− .680	45.5	67.5 ± .3°
.2269	− .687	46.4	91.6 ± .3°	.4362	− .418	37.0	52.5 ± .5°
.4565	− .400	37.0	78.0 ± .4°	.947	− .107	27.5	0
.8180	− .165	29.2	55.3 ± .5°				

A question still remains as to the validity of the theory for which the above data were used by the authors for solids other than paraffin.

Orientation in Monomolecular Films on Liquid Subphases and the Contact Angle

The technique of built-up films, *i.e.*, depositing insoluble monomolecular films from liquid subphases on either glass or metal slides, gives a method for studying the orientation of molecules in these films. The basis on which such decisions can be made by use of the contact angle is that the contact angle against a pure paraffin would be 109°, while the angle against the polar groups would be zero. If the surface contains both polar and non-polar groups, the contact angle should lie between these limits, its exact value depending on the ratio of polar to non-polar groups.

Most of the investigations have been carried out [46] with the barium, calcium, and magnesium soaps of the *n*- long-chain paraffin acids. It was found that if it is assumed that the polar group is next to the water, the contact angle was either 0 or 100°, depending on whether an odd or even number of layers had been deposited on the slide.

An investigation has been made of the variation [47] of the contact angle of a built-up film of egg albumin with its film pressure. The egg albumin was spread on an acetate buffer of pH 4.67, the isoelectric point. After the film was deposited on the slide and dried, the contact angle was measured. The deposition was such that the side of the film away from the subphase was the side on which the contact angle was measured. It was found that the contact angle increased linearly with the film pressure, reaching a value of 56.4° when the pressure rose to 23.08 dyne cm^{-1}. The work shows that the ratio of polar to non-polar groups on the top side of the film decreases as the pressure increases. The present results indicate that if the contact angle remains a linear function of the film pressure, the film pressure would have to go to 50 dyne cm^{-1} before the angle reaches 109°, or the film becomes as non-polar as paraffin. However, the film collapses before this pressure is reached.

Unfortunately, not enough is known about the variation of the contact angle with the ratio of polar to non-polar groups. The above work does show that, as the film pressure is increased, more of the polar groups in the protein molecule turn to the liquid subphase. The work also indicates that at no time are all of the polar groups oriented to the water. It is possible that the collection of more such data as the above may help in the elucidation of the structure of the denatured protein molecule. The results are exhibited in Fig. 48.

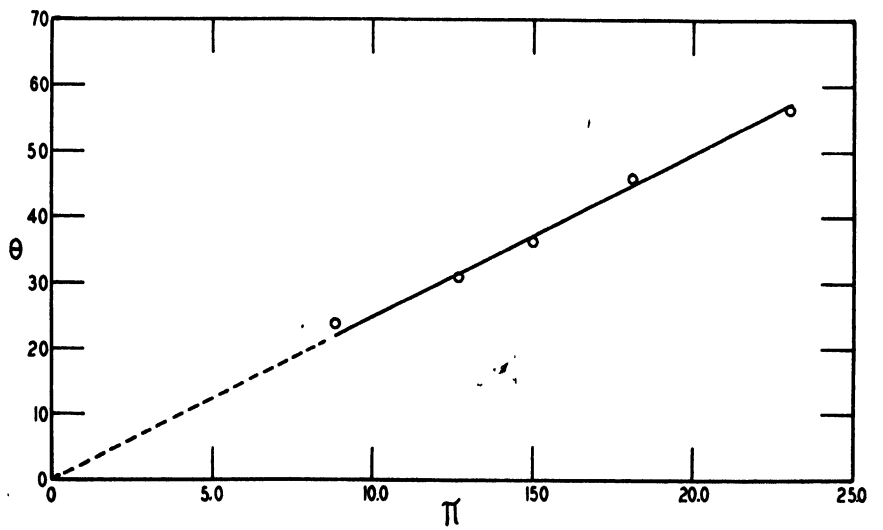

FIGURE 48. The contact angle Θ of a deposited egg albumen film against water.

The Contact Angle and the Films Adsorbed at the Solid-Liquid Interface

The surface tension or free surface energy of hydrocarbons is only very slightly, if at all, affected by the addition of other compounds. For example, the surface tension of dry benzene at 20° is 28.88 dynes cm^{-1}, while saturating the benzene with water reduces the surface tension to only 28.82 dyne cm^{-1}. From the orientation theory it is apparent that a compound such as butyl alcohol would have a similarly negligible effect.

If it is assumed that solid paraffin behaves in the same way, the adsorption at the paraffin-aqueous solution interface can be obtained from the variation of the contact angle. If the contact angle of the solvent is θ_1 and that of a solution is θ_2, then the following equations hold,

$$\gamma_{S_1} = \gamma_{SL_1} + \gamma_{L_1} \cos \theta_1 \tag{49}$$

and

$$\gamma_{S_2} = \gamma_{SL_2} + \gamma_{L_2} \cos \theta_2 \tag{50}$$

Now, for a solid such as paraffin

$$\gamma_{S_1} \cong \gamma_{S_2}$$

Subtraction of Eq. 50 from 49 gives

$$\gamma_{SL_1} - \gamma_{SL_2} \cong \gamma_{L_2} \cos \theta_2 - \gamma_{L_1} \cos \theta_1 \tag{5}$$

But $\gamma_{SL_1} - \gamma_{SL_2}$ is the decrease, π, of the interfacial energy; and since γ_{L_1}, γ_{L_2}, $\cos \theta_1$, and $\cos \theta_2$ can be determined, π can be calculated. It is evident that this decrease can be due only to the adsorption of the solute at the interface. The amount of solute adsorbed can be obtained by the use of the Gibbs adsorption equation. Fig. 49 shows the $\pi - \sigma$ curves for *n*-butyl alcohol, *n*-butyl amine, *n*-butyric acid, propionic acid, and acetic acid at the water-paraffin interface, as determined by the con-

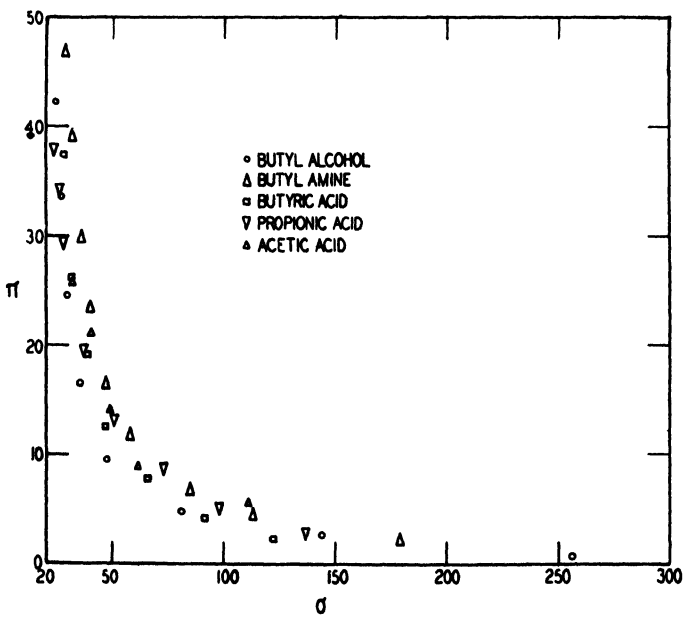

FIGURE 49. The pressure (π)-area (σ) isotherms of various films adsorbed at the paraffin-water interface.

tact-angle method. These films all behave as imperfect gases, as expressed by the equation

$$\pi(\sigma - \sigma_0) = ckT \tag{52}$$

The values of the constants σ_0 and c are given in Table 16.

Table 16

Solute	σ_0	c
n-Butyl alcohol	17.6	0.602
n-Butyl amine	21.5	1.012
n-Butyric acid	16.7	.955
Propionic acid	10.1	1.280
Acetic acid	23.1	0.875

Considering the assumptions made and the errors in determining π and σ, the values are as good as can be expected. The value for σ_0 should be on the order of 20Å^2, while the values for c are not too far from unity. The results also show that the films are monomolecular.

This method, however, would not work if the solid were graphite, for which even though the free energy decrease due to water is small, that due to organic acids or alcohols may be large.

Graphite as an Example of a Hydrophobic Solid *

The (001) face of a crystal of Ceylon graphite was found by Fowkes and Harkins (Table 13) to give a contact angle of 85.7°, while talc, stibnite, and paraffin exhibited angles of 87.8°, 84.2°, and 108° to 111°. Such surfaces are designated as hydrophobic. The contact angle with a paraffin oil appears to be zero, and the surface is considered as oleophilic. When these relations are considered, it is to be expected that the adsorption isotherms of water and of paraffin oils on these surfaces should be of entirely different types. In fact, it has been considered that the water film does not become thicker than a monolayer, even at values of p/p_0, nearly as high as unity. However, the experiments described here show that actually it attains a thickness equivalent to several monolayers.

Now, the presence of a complex of oxygen on the surface of graphite or of ash may reduce the contact angle and also increase the amount of water adsorbed at any given vapor pressure. To overcome these difficulties an adsorption isotherm has been determined with a sample of graphite whose surface is free from oxygen and with a three-dimensional content of less than 0.004 per cent of ash, specially prepared for this work by the National Carbon Company.

For comparison, isotherms were obtained with graphites which contain 0.46 and 10 per cent of ash. The oxygen content of their surfaces is unknown. In the order listed, the areas of these samples are, respectively, 4.18, 6.17, and 27.6 sq meters per gram.

The water isotherms of these different samples of graphite are exhibited up to $p/p_0 = 1.0$ in Fig. 50 and at lower pressures up to 0.1 in Fig. 51. It may be seen that the amount of water adsorbed is very much larger on the surface of the graphite of high (10 per cent) ash content. At low vapor pressures the sample free from oxygen and with the lowest ash content (<0.004 per cent) adsorbs less water than that with 0.46 per cent. However, it seems strange that this is reversed at high vapor pressures.

Two important results were obtained in this work: (1) the water film is polymolecular at high relative pressures, and (2) in the low-pressure region $\frac{d^2v}{dp^2}$ is negative. The fact that the water film on graphite is polymolecular is important, because

* The effect of carbon chemically fixed in surfaces appears in the paper on silicones in this volume. J. A.

this is the first example of a *polymolecular non-duplex* film. All the polymolecular films thus far observed have been duplex (stable only on solids), whereas the non-duplex films have always been monomolecular (all films on water). At present, it is not known how extensive the group showing this characteristic will be found to be.

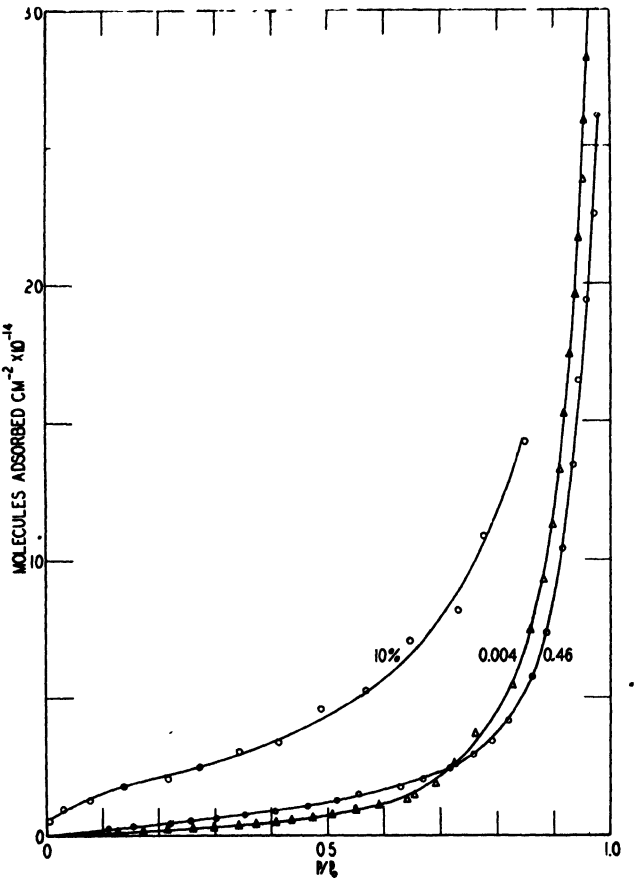

FIGURE 50. Adsorption isotherms of water on three graphites which contain 10 per cent, 0.46 per cent, and less than 0.004 per cent ash, the last without an oxygen complex on the surface.

An examination of Fig. 50 shows that if the lowest pressure region is neglected the isotherm would be considered to be of Type III (Brunauer's classification[48]), in which the isotherm is concave to the pressure axis, even at $p = 0$, *i.e.*, $\left(\frac{\partial^2 v}{\partial p^2}\right)_T$ is positive. However, Fig. 51, which gives the low-pressure region on an expanded scale, shows that this is not the case in the low-pressure region where $\left(\frac{\partial^2 v}{\partial p^2}\right)$ is negative, *i.e.*, the curve is at very low pressures of the same type as those which give at higher pressures a duplex film with the following two differences: the point of inflection occurs (1) at a lower relative pressure and (2) when only a small fraction of a monolayer has been adsorbed, while, when duplex films are formed at high values

of p/p_o, the inflection occurs after more than a monolayer has been adsorbed. Careful work in the low-pressure region would be necessary to establish the above as a general feature of this type of isotherm.

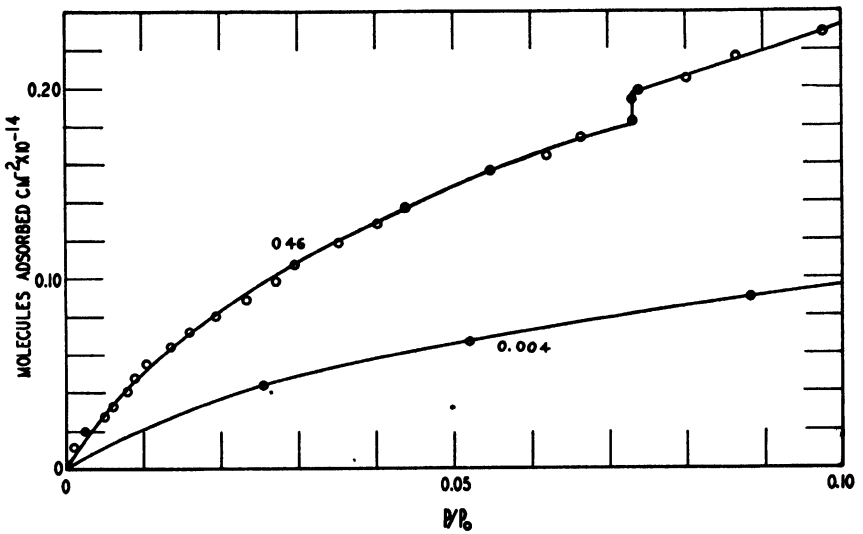

FIGURE 51. Same as Figure 50 for graphites with 0.004 per cent and 0.46 per cent ash, except that the low pressure region $0 \leqq p/p_o \leqq 0.1$) has been greatly expanded to show the form of the curve in this region.

The behavior of graphite toward hydrocarbons is different from that of water, in that the isotherms show the formation of duplex films. Fig. 52 exhibits the isotherms of water and *n*-heptane on the graphite with 0.46 per cent ash. It is observed that the isotherm of *n*-heptane is of the same type as those obtained for all films on anatase which have been investigated.

The integration of the adsorption isotherms to obtain the decrease in free surface energy gives striking results, as summarized in Table 17.

Table 17. Lowering of the Free Surface Energy (π) of Graphite by *n*-Heptane and by Water at 25°

Ash content of graphite (%)	H_2O	*n*-Heptane
10	58 *	60 *
0.46	19	69
less than 0.004	19	—

* Probably low because of method of integration and absence of values for adsorption at low pressures.

The values for *n*-heptane are, except for magnitude, the same as those obtained for the oxides. The contact angle is zero, and the free energy of emersion and the work of adhesion can be obtained by adding γ_L and $2\gamma_L$ respectively to π_e. It is then found that for the graphite with 0.46 per cent ash the free energy of emersion and work of adhesion are 89 and 109 erg cm^{-2}, respectively.

The spreading pressure, free energy of emersion, and work of adhesion of water on graphite depend upon the contact angle. If the value of 85.5° obtained in this laboratory for the contact angle is used, the spreading pressure, free energy of emersion, and work of adhesion are found to be −47, 25, and 97 erg cm^{-2} for each of the two low ash content graphites.

Because of the thickness of the water film on graphite and the discrepancy between the reported values by other observers of the contact angle, the question arises, Would it be possible for water to form a duplex film on graphite, that is, what would be the necessary value of the contact angle so that $\gamma_s - \gamma_{sL} \geqq \gamma_L$? Using the value of 19 erg cm^{-2} for π_e, it is found that for $\gamma_s - \gamma_{sL} \geqq \gamma_L$, $\theta \leqq 42.6°$.

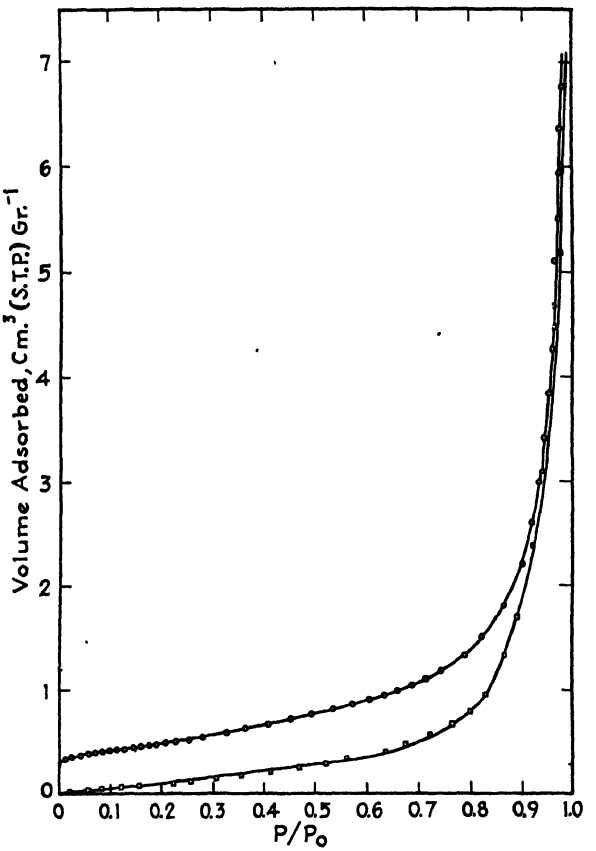

FIGURE 52. The adsorption isotherms of *n*-heptane (○) and water (□) at 25.0° C on a sample of graphite which contains 0.46 per cent ash. In spite of the much greater size of the *n*-heptane molecule, many more of these molecules are adsorbed at a given relative pressure than of the much smaller water molecules.

This is lower than any value thus far reported for the contact angle of water against graphite. Thus, it may be concluded from the data available at present, that water cannot form a duplex film on graphite. This system is then analogous to the spreading of a liquid such as methylene iodide on water, where the initial spreading coefficient is negative.

A partial study has been made of the heat of emersion of graphite in several liquids. The results, as far as available, do not follow the same pattern as that observed for the oxides and inorganic compounds as illustrated in the earlier Table 11. The values for the different graphites are summarized in Table 18.

All the data for adsorption and thermal effects with graphite as given in this section were obtained in this laboratory. Those for the adsorption on the graphite

Table 18. The Heats of Emersion of Graphite in erg cm^{-2}

Ash content of graphite (%)	H_2O	CCl_4	C_6H_6	n-C_7H_{16}
10	265	195	225	—
0.46	225	—	215 *	165
less than 0.004	175	—	—	145

* This determination was made with undried benzene. Preliminary work on dry benzene indicates a lower value.

with 10 per cent ash were found by Dr. H. K. Livingston; the water isotherm on the sample with less than 0.004 per cent ash and the *n*-heptane isotherm on that with 0.46 per cent ash were obtained by Edward H. Loeser; the work on the heat of emersion of the two low ash content graphites is that of Paul R. Basford, and the heat values for the graphite containing 10 per cent ash are those of Harkins and Boyd.[95]

Topochemistry: Chemical Changes at Crystal Corners, Edges, and Interfaces *

In all the work on adsorption and energy relations for the surfaces of solids no account was taken of the possible effects of different crystal faces, edges, or corners. The observed effects are the statistical sum of the effects of all the faces, edges, and corners present. Since the energy is different for the different crystal faces, an edge, or a corner, it is apparent that the actual concentration of adsorbed material, and the energy relations would be different at the different crystal positions. Thus, it is within the realm of possibility that one face of a crystal may catalyze a reaction, whereas a different face of the same crystal may not. These effects are most strikingly shown by the topochemical reactions described in this section.

Harkins [49] has calculated that a rather sharp edge of a lens of a heavy paraffin oil in air would have an edge energy of the order of 3×10^{-6} erg cm and a tension of 3×10^{-6} dyne. Such an edge, however, would not be stable, and edges of oil lenses on water would have an energy less than this. Even more important and more definite are the edge energies of crystals as calculated by Born and Stern [50] as 2.16 for NaCl and 1.73 for KCl in units of 10^{-6} erg. By the use of more elaborate equations Lennard-Jones and Taylor [51] found, in the same units: 5.13 for NaF, 3.97 for NaCl, 3.95 for KF, 3.06 for KCl, 27.0 for MgO, 20.8 for MgS, 20.5 for CaO, and 16.8 for CaS. The method used in calculating the energy of the *sharp* edge of a heavy oil is entirely different from that for the salts, but it may be noted that both values are about 3×10^{-6} erg, if KCl is the salt.

The lattice energies of ions in the surface of a crystal, at edges, on surfaces, and at corners or points (Fig. 53) have extremely different energies. The energy in these positions is also very different for water of hydration, the carbon dioxide of carbonates, ammonia, and other constituents which may escape as gases. In some instances the energy is greatly affected by scratching or by breaking the surface of a crystal. The classical instance of this is that observed by Faraday,[52] who found that without such a process perfect crystals of sodium sulfate, carbonate, or phosphate sometimes remain stable for years; but if the surface is scratched or broken, efflorescence immediately begins to spread from the line or point of injury and soon covers the whole crystal. In Table 19 ϕ is the electrostatic attraction constant for such a position, ϕ_2 is the repulsive force, and $\phi = \phi_1 + \phi_2$, the resultant energy. ϕ' is the same as ϕ, except that the value refers to the energy of separation of a neutral NaCl molecule.

An example of the inverse of this is that too strongly heated lime, or plaster of paris, take up the first traces of water only with the greatest slowness, because the crystal surface takes up water much more readily adjacent to a position in which water is already present.

* See paper on "Adsorption and Crystal Habit Modification" by Wesley G. France in Vol. V of this series. J. A.

Another very early illustration [53] is that of crystals of ferric xanthate, which decomposes along the edges of the crystals to form ferric oxide. Preferential adsorption at edges and corners occurs with radioactive indicators.[54]

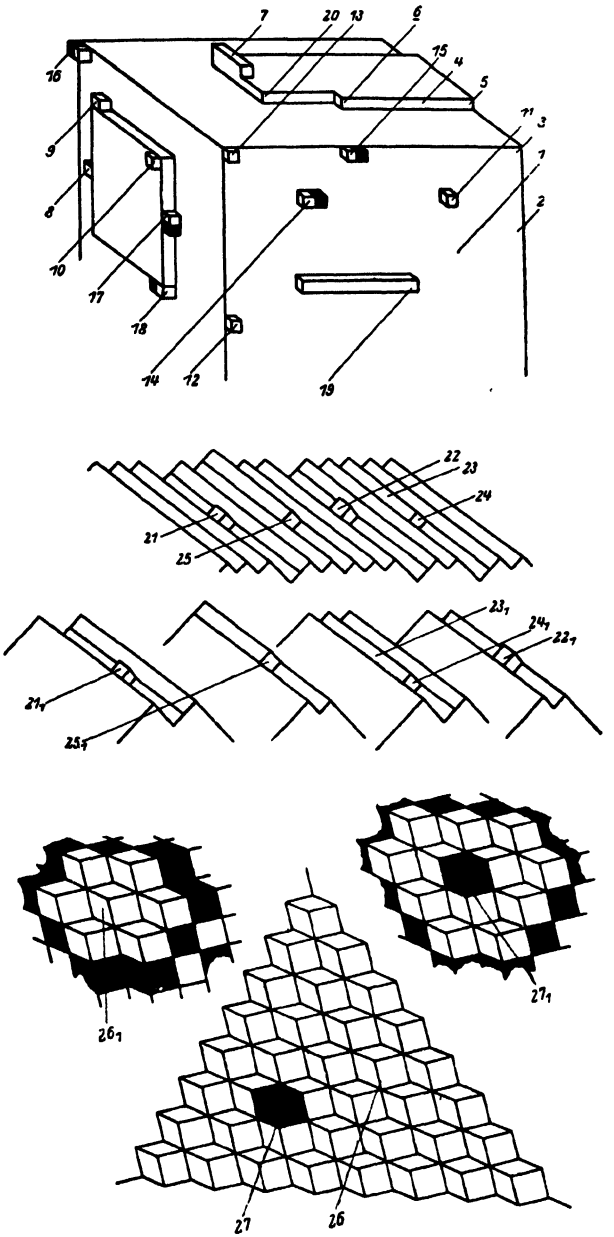

FIGURE 53. The energies of removal of ions (ϕ' of molecules) in the different positions on the surface of a sodium chloride crystal according to I. Stranski, *Zeit. Phys. Chemie*, **136**, 259 (1928).

In a great number of the reactions of the surfaces of solids the reaction begins adjacent to nuclei of a second phase, and spreads outward so regularly as to allow the determination of a linear velocity of reaction. Such reactions have been designated by Kohlschütter as "topochemical."

Table 19. Energy of Separation of Ions from a Sodium Chloride Crystal

Position of the Ion	$\varphi_1 \frac{\delta}{\epsilon^2}$	$\varphi^2 \cdot \frac{\delta}{\epsilon^2}$	$\varphi \cdot \frac{\delta}{\epsilon^2}$	$\varphi' \frac{\delta}{\epsilon^2}$
0	3.487(6)	−0.387(7)	3.100	1.868
1	3.355(9)	−0.316(6)	3.039	1.746
2	3.175(8)	−0.248(2)	2.928	1.524
3	2.682(7)	−0.184(7)	2.498	1.251
4	3.127(3)	−0.252(6)	2.875	1.418
5	2.369(7)	−0.187(7)	2.182	1.034
6	1.743(8)	−0.193(8)	1.550	0.709
7	2.949(6)	−0.185(1)	2.765	1.198
8	0.360(3)	−0.134(9)	0.225	0.709
9	0.937(8)	−0.132(3)	0.806	0.545
10	0.591(2)	−0.064(5)	0.527	0.266
11	0.131(7)	−0.070(9)	0.061	0.709
12	0.180(2)	−0.067(5)	0.113	0.650
13	0.493(1)	−0.064(5)	0.429	0.536
14	2.131(7)	−0.129(7)	2.002	−0.328
15	2.180(2)	−0.126(4)	2.054	−0.224
16	2.026(8)	−0.126(4)	1.900	−0.062
17	2.360(3)	−0.193(7)	2.167	0.000
18	2.104(4)	−0.190(3)	1.914	0.380
19	1.515(2)	−0.129(7)	1.386	~0.381
20	2.321(3)	−0.191(6)	2.130	~0.981
21	<0.305(9)	−0.138(4)	<0.168	~0.593
22	>0.408(8)	−0.131(5)	>0.277	~0.702
23	<3.072(3)	−0.256(0)	<2.816	<1.300
24	<1.689(4)	−0.197(2)	<1.492	<0.593
25	>1.792(3)	−0.190(3)	>1.602	>0.813
26	<−1.362(8)	−0.201(6)	<−1.564	——
27	>7.122(4)	−0.186(0)	>6.936	~2.981

φ: (0) > (1) > (2) > (4) > (7) > (3) > (5) > (17) > (20) > (15) > (14) > (18) > (16) > (6) > (19) > (9) > (10) > (13) > (8) > (12) > (11); (22) > (21); (25) > (24)
φ': (0′) > (1′) > (2′) > (4′) > (3′) > (7′) > (5′) > (20′) > (6′) = (8′) = (11′) > (12′) > (9′) > (13′) > (19′) ~ (18′) > (10_γ) > (17′) > (16′) > (15′) > (14′)

In an interesting investigation large single crystals of $CuSO_4 \cdot 5H_2O$ were prepared, and the surfaces of these coated with nuclei of $CuSO_4 \cdot H_2O$ in a finely powdered form by rubbing the two together in a fine bag of silk.[55] At 46° the pentahydrate changes into the monohydrate, and the rate of reaction, for a known surface area of the original crystals can be determined by placing the crystals in a vacuum. The boundary between the two phases moves into the crystal at a constant rate, so it keeps parallel to the initial face of the crystal. The rate of reaction was found to be constant, and was little affected by the thickness of the outer monohydrate layers.

Another early example [56] is the reduction of copper oxide by hydrogen, where the formation of the linear interface is made visible by the difference in color between the copper oxide and the metal. The reduction begins by the formation of a red speck which spreads rapidly over the whole surface.[57] The reaction is autocatalytic and water retards the formation of the red patches.

Other reactions of this type are that in which silver oxide changes to silver and oxygen with a rate which increases with the amount of silver.

Interfaces of this type are of great importance in that autocatalytic reactions may become explosive. Impurities, formed by slow decomposition, often accelerate the decomposition.[59]

In some instances the spreading of a reaction may be watched through a microscope. Potassium acid oxalate as the hemihydrate, $2KHC_2O_4 \cdot H_2O$, may be prepared

at 0° and loses water at room temperature. The reaction begins with the appearance of dark microscopic dots,[60] and the dark areas spread in such a way as to keep the boundaries parallel to the crystal edges. The rate is constant for parallelism to any given edge, but vary for different edges.

Nuclei which start transformations, such as that of yellow into red mercuric iodide practically always begin at an edge, preferably at a corner, but rarely at a face.[61]

The details of other reactions which proceed from surface nuclei or scratches may be found in the literature. These include the escape of ammonia from $CuSO_4 \cdot 5NH_3$ and similar salts,[62] the escape of carbon dioxide from calcium carbonate [63] and other carbonates,[64] and the decomposition of silver oxalate,[65] and of permanganates.[66]

Certain reactions similar to these occur at a linear interface between solid and liquid. Thus, Adhikari and Felman [67] found that in a vacuum iodine molecules which impinge on a glass ball are reflected directly from the surface, while on a drop of mercury they spread without chemical action, and then evaporate. Also, if an iodine crystal is touched to the surface, the iodine spreads and then evaporates. However, if the drop is touched anywhere by a HgI_2 crystal, chemical action begins at the line of contact, and HgI_2 rapidly forms and grows over the surface.* The advance of a colored band sharply defined and parallel to the edges of the crystal may also be seen under a microscope when good potassium chromate crystals are immersed in sulfuric acid, or crystals of copper, or of nickel sulfate in an alcoholic solution of nickel sulfide. The coloring of nickel sulfate by dimethyl glyoxime, of potassium ferrocyanid by ferric chloride in ether, and the bleaching of the edges of copper sulfate by potassium cyanide, have all been observed by a trio of investigators.[68]

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* In some batch processes a small residue of an earlier batch is often left as a "starter" for the desired reaction. It is interesting to note that non-living units may serve this purpose. J. A.

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Addendum

The relations between the nature of a heating surface and the boiling of a liquid in contact therewith, are discussed by R. H. Larson in *Ind. Eng. Chem.*, 1945, **37**, 1004 *et seq.* Nucleate and film boiling are considered. L. A. Philipp and B. E. Tiffany (*Refrig. Eng.*, 1933, **25**, 140) corrected evaporator trouble by choice of a suitable "ebullator" surface, at which superheating did not occur. See also W. Swietoslawski, "Ebulliometric Measurements" (Reinhold, 1945). J. A.

Nature of Strength and Failure in Brittle Solids

EUGENE F. PONCELET

Owens-Illinois Research Fellow, Preston Laboratories, Butler, Pa.

The Physical Nature of Solids, Particles, and Bonds

It is well established that solids in general have a particulate structure, that is, that they consist of particles of definite size held at certain spacings by fields of force. In spite of this fact, theories of the behavior of solids under stress do not take such structure into consideration. In these theories it is still assumed that solids are of a continuous nature, consisting of homogeneous matter indefinitely divisible.[1, 2, 3]

Such an assumption lends itself admirably to treatment by continuous mathematical functions. It has achieved outstanding success in elasticity,[4] the study of elastic deformations and stresses, and considerable success in rheology,[5] the study of permanent deformation and flow. Its success has been much less pronounced in the study of fracture and strength of solids.

This is not surprising. Such phenomena as elastic strain and stress, and to a certain degree viscous flow, have external forces as immediate causes. The effects of these relatively distant forces on two adjoining particles are practically identical, and each particle influences the others in a continuous manner. These effects are therefore susceptible to treatment by continuous mathematical functions as if the solid were of a continuous nature.

The phenomena of fracture and plastic flow, on the contrary, have local stress concentrations as their immediate causes, and the response of these particles to these stress concentrations is most abrupt. Furthermore, this abrupt reaction influences the local stresses surrounding the neighboring particles in a decisive manner. The first particle to move abruptly thus sets the pattern for the continuation of the process.

The indeterminacy connected with the behavior of each of the separate particles is thus not blended into an average with neighboring particles to form a nicely continuous process, but on the contrary is enhanced to such a degree that it controls the succession of phenomena.[6]

Consequently, we may visualize an ideal brittle solid as composed of a collection of identical particles held together at definite spacings by bonds of an electrostatic character. These bonds may be pictured as the resultant of electrostatic attractions and repulsions existing simultaneously between the particles and represented as a function of the spacing between particles by a graph, usually referred to as a Morse curve.[7] (Fig. 1.)

Electrostatic attractions between two particles must exist, since the positive charge of the nucleus of one particle is attracted to the negative charges of the swarm of electrons of the other; electrostatic repulsions must exist between the nuclei of both particles and also between the electrons of both particles.

The Morse curve reveals that when the spacing is reduced below its equilibrium value, the Morse resultant is a very steeply increasing repulsion, and when the spacing is increased beyond its equilibrium value, the resultant is an attraction, which

increases to a maximum value and then decreases asymptotically to zero. This equilibrium is stable, since the Morse resultant of their bond urges the particles back toward their equilibrium spacing, no matter what their actual spacing may momentarily be.

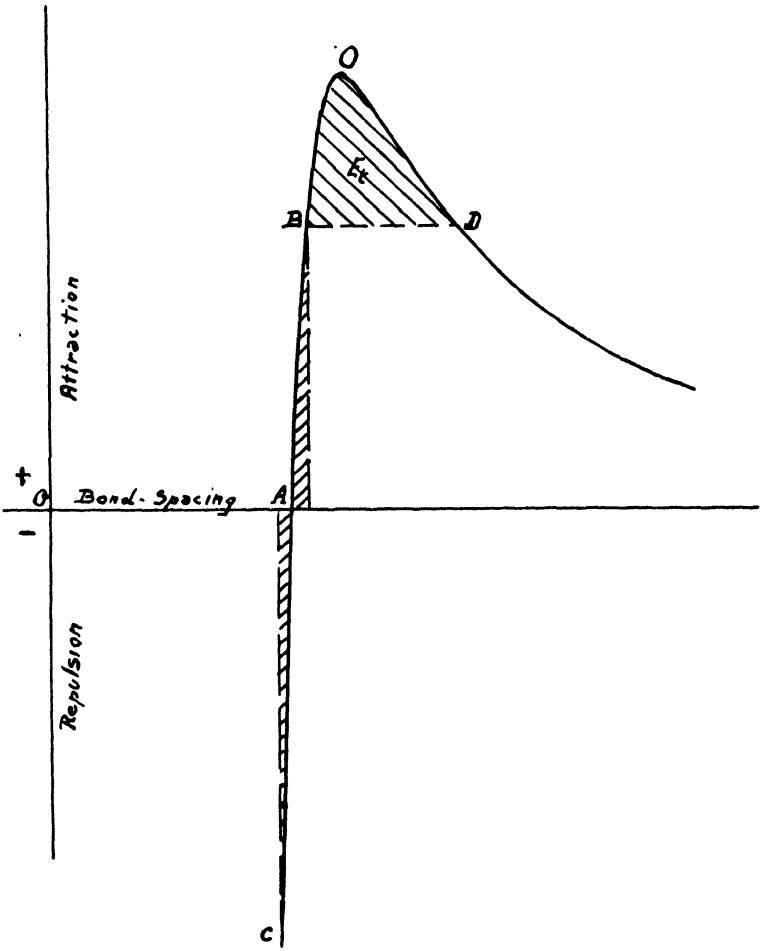

FIGURE 1. Morse curve, $t = (1/s)^2 - (1/s)^{10}$ giving Morse resultant "t" as a function of bond spacing "s."

Under the influence of such restoring bonds the particles vibrate, and their spacings pulsate about their equilibrium A, between two values represented, for example, by B and C on the Morse curve. The energy involved in these oscillations is represented by the area subtended by the arc AB or AC of the Morse curve and is usually referred to as the thermal-energy level of the particles.

While the energy levels of the various particles are changing continually and independently as the particles bump into and otherwise interfere with one another, the distribution of the various energy levels amongst the particles of a solid in thermal equilibrium follows a well determined pattern, usually referred to as the Maxwell-Boltzmann law.[7] As this law is usually stated it gives the number of particles having

at any given instant an energy level higher than an arbitrary one in proportion to the total number of particles, or the time during which any particle has an energy level higher than an arbitrary one in proportion to the total duration of the period of time considered.

Since any particle in a solid is at a finite distance from any of the other particles, it is joined to all of them by innumerable bonds. The computation of the energy level of a particle is consequently a very complicated matter. It can be simplified by using the artifice of assigning the various energy levels to the bonds instead of to the particles: each bond joins but two particles. Both bonds and energy levels being abstract quantities, there is no difficulty in doing so. The energy level of any particle is then represented by the half-sum of the energy levels of all the bonds joining it to the other particles.

The vibrations and energy levels of the various bonds of a particle do not depend solely on the vibration and energy level of the particle considered, but also on the vibrations and energy levels of the other particles to which the particle in question is bound. It follows that the vibrations and energy levels of any one bond vary independently of any other bond. The vibrations and energy levels of the various bonds can therefore be considered independently, that is, one at a time.

The Physical Nature of Stresses

The notion of force is simple and usually clear, since it is universally and continually experienced by all in most varied forms. The notion of stress, however, is much more complicated, and sometimes is confused with that of force.[4]

Any forces acting on a solid at one point can be reduced to a resultant force having definite direction and magnitude. Therefore, like all other quantities involving one definite direction and magnitude, it can be represented by a vector, which is merely a composite of these two elements. Unless it is balanced by some other forces at other points of the solid, the effect of the resultant force is to cause the solid to accelerate in the direction of the resultant.[5]

The state of stress at any point in a solid cannot be reduced to a resultant force, as a state of stress never causes an acceleration. Any vector which would attempt to represent a state of stress must therefore be accompanied by a second vector equal to the first one and directly opposed to it. Such a vector-pair cannot represent the independent components of the stress existing in orientations perpendicular to itself. To do this requires two more vector-pairs perpendicular to each other and to the first one.

Elasticity teaches us that any state of stress can be reduced to three independent partial stresses, usually referred to as principal stresses, oriented in the three principal directions perpendicular to each other, and can therefore be represented by a composite of three vector-pairs oriented in these directions.[4] Such a composite is usually referred to as a principal tensor, and consists of six independent variables. The vector-pairs can be positive to represent tensile stresses, or negative to represent compressive stresses, their magnitude being that of either vector.

To picture and distinguish the three principal directions, we shall call "up-and-down" the direction of the most positive stress, "fore-and-aft" the direction of the most negative stress, and "to-and-fro" the direction of the middle principal stress.

If two of the principal vector-pairs are nil, we have the state of simple stress. If only one of the vector-pairs is nil, we have the state of plane stress. If the algebraic sum of all the vector-pairs is nil, we have the state of pure distorting stress, which includes as a special case the state of pure shear if one of the vector-pairs also is nil. If the three vector pairs are equal in value, we have the state of "hydrostatic" stress, better described as pantothenic * stress, as the presence of no liquid is required, and the stress may be dynamic instead of static.

* From the Greek meaning "from all directions."

As parallel principal stress tensors can be added or subtracted simply by adding or subtracting their corresponding vector-pairs, it is apparent that any state of stress can be regarded as the sum of a pantothenic stress and a distorting stress. This leads us straight to the Brandenberger theory of elasticity.[9]

Since a principal stress and a bond are composed of the same elements, *i.e.*, direction and magnitude of the stress or of the Morse resultant, the three principal stresses may be represented by three bond-pairs around a particle, oriented in the three principal directions. We shall call these six bonds the principal bonds.

Since the various bonds keep pulsating, and the principal stresses do not, the latter must be represented by the principal bonds while all the bonds are at the equilibrium spacing, about which they vibrate.

The fact that the nearest neighbors to a particle in an amorphous solid may only accidentally be oriented in the direction of the principal stresses, is unimportant: the stress-tensor being continuous, its variation from a particle to its neighbor is necessarily very small compared to the magnitude of the tensor itself. It follows that in a small finite volume of the solid a large number of particles having their nearest bonds oriented at random are subjected to virtually identical stress-tensors. The size of this volume can always be chosen to include one particle having its neighbors in the desired directions. As the three principal stresses include the two extreme stresses, this latter particle is the one most likely to start the failure, and is therefore the one we are interested in. It matters little, therefore, whether the other particles in this small volume have their bonds oriented in the principal directions or not. Consequently, it can be assumed that they have.

The closest neighbors to a particle may not necessarily be six in number. As we need examine the stability of but one bond at a time, it matters little whether the other bonds are five in number or not, provided they balance the other five vectors of the prevailing stress-tensor, which they obviously do, as the solid is presumed to hold together. It may thus be assumed that there are five of them.

Besides the six principal bonds linking a particle to its nearest neighbors, there are other bonds between the particle considered and the more distant particles. These bonds are all much longer than the principal bonds. Since all of the particles in even an unstressed body are in equilibrium and do not move toward one another, the shorter bonds separating the particles, that is the principal bonds, must be repulsive in character and balance the attractive longer bonds. The effect of these weaker "long" bonds is consequently the same as that of an undetermined pantothenic compression applied to the whole solid. We shall call this apparent compression the pantothenic cohesion, and consider its effect separately from that of the principal bonds proper.

Physical Nature of Failure in Brittle Solids

Since we may consider the principal bonds as representing the principal stresses in a solid, it is plain that as long as these principal bonds remain stable the solid cannot fail. As it is patent that solids do fail, the principal bonds must become unstable when subjected to specific stress-tensors, as they reach certain spacings during their vibrations.

To obtain this result it is sufficient for the principal bonds to have one other equilibrium spacing besides the original stable one. The resultants of the bonds about the stable equilibrium are necessarily of a restoring character, and they cannot change sign and urge the bond away from its stable equilibrium spacing without becoming nil at some definite spacing. This particular spacing corresponds to a second equilibrium, which must perforce be unstable as the resultants urge the bond-spacing away from it. Since the very steeply falling negative Morse resultant precludes the continued contracting of the spacing of bonds, unstable bonds must perforce keep on expanding. Such bonds we shall call broken bonds.

There may be nothing to prevent the bond from reaching a third equilibrium spacing while expanding, which equilibrium would be again a stable equilibrium, since the resultants would urge the bond-spacing toward it. On reaching such a third equilibrium, the bond starts oscillating about it, and becomes then a "long" bond. It consequently ceases to be a principal bond, some other bond becoming principal in the process. We shall call such bonds "swapped" bonds.

The failure of a solid caused by broken bonds we call *fracture*, and the failure caused by swapped bonds, *flow*. Since brittle solids do show other phenomena than fracture when submitted to stress-tensors, there is no alternative to accept-

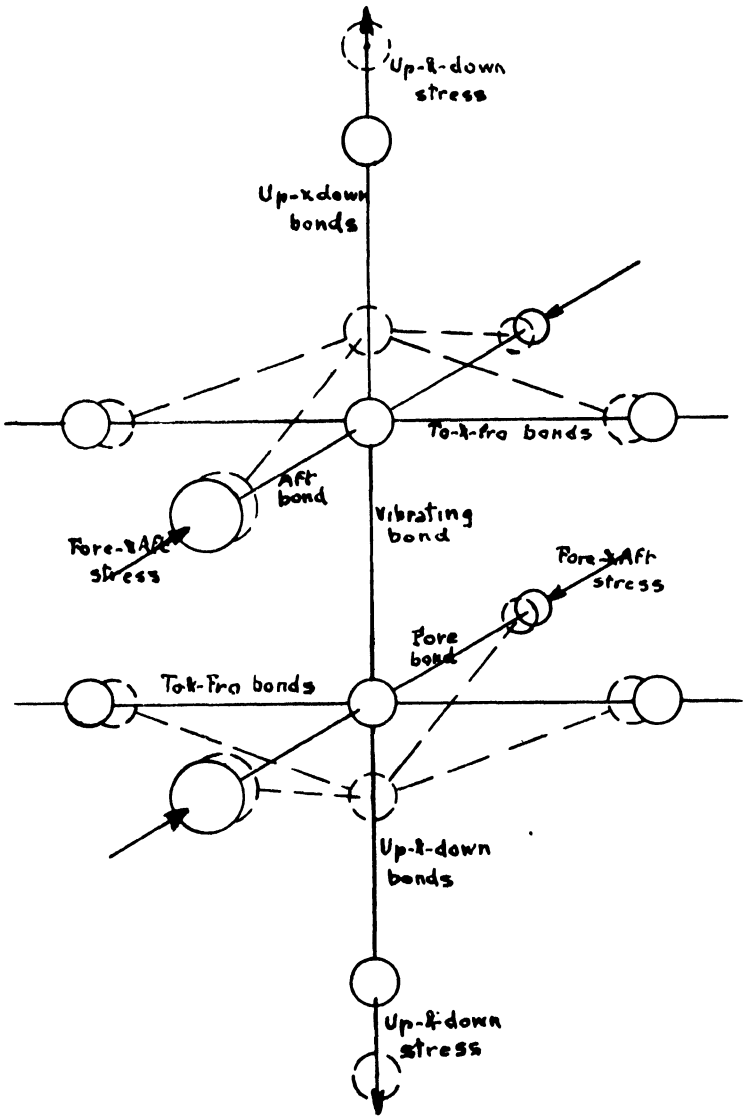

FIGURE 2. Model of a vibrating bond surrounded by adjacent principal bonds.

ing the possibility of flow, although not necessarily of viscous or plastic flow.[10]

As all these secondary equilibrium spacings are to be found in stretched spacings, we need only examine the stability of the most positively stressed principal bond, that is, the up-and-down bond, while it oscillates toward longer spacings from its stable primary equilibrium spacing.

The two up-and-down bonds beyond these two particles, representing the up-and-down stress, are assumed not to vary and they consequently follow bodily the motions of the two particles united by the vibrating bond (Fig. 2).

It is considered that the remaining bond-pairs acting upon each of these two particles do not oscillate independently, but assume such spacings as to balance the corresponding stress-vectors. Since the two particles in question vibrate up and down, and since the other eight particles which these bond-pairs join to these two vibrating particles are not assumed to vibrate in unison with the latter, these bond-pairs become symmetrically oblique to the up-and-down direction. Hence each of these bond-pairs has a resultant oriented in the up-and-down direction which plays its part in the equilibrium of the vibrating bond.

We are thus led to investigate the equilibrium of: (1) the Morse resultant of the vibrating bond, (2) the up-and-down resultant of the fore-and-aft bond-pairs, (3) the up-and-down resultant of the to-and-fro bond-pairs, and (4) the up-and-down bond-pair beyond the vibrating bond. We shall examine these equilibria in the case of tension, of compression, and of mixed stresses.

Failure under Tension

In the case of simple tension, the up-and-down stress is positive and both fore-and-aft and to-and-fro stresses are nil. At equilibrium spacing the vibrating bond must consequently be attractive, urging a contraction of the vibrating bond, equal to the up-and-down stresses urging it to expand. The state of this bond may be represented at this position by point B on the Morse curve.

As the vibrating bond reaches spacings greater than this primary equilibrium spacing, its Morse resultant urging a contraction at first increases from its value at point B with increasing spacing until a maximum represented by point O is reached. For still greater spacings, the Morse resultant decreases asymptotically to zero, as represented by points D and beyond.

Similarly, the fore-and-aft and to-and-fro bonds, becoming oblique, must necessarily acquire a greater spacing as the vibrating bond lengthens. It follows that their Morse resultants, and with them their up-and-down resultants, at first gradually increase to a positive maximum and then decrease asymptotically to zero, urging a contraction of the vibrating bond at any of these spacings.

The sum of all the resultants thus urges a contraction of the vibrating bond, and at the primary equilibrium spacing equals and opposes the up-and-down stress urging it to expand. As the spacing of the vibrating bond increases under the influence of its thermal energy, the sum of all these resultants at first increases from its primary value, then decreases asymptotically to zero; the up-and-down stress does not vary. It follows that there is one, and only one, spacing greater than the primary for which the resultants and the stress are again in equilibrium: this may be schematically represented by point D on the Morse curve. As explained before, this is an unstable equilibrium, and when the bond exceeds this length it becomes a broken bond.

To reach this unstable equilibrium, the bond must be excited to a sufficient thermal-energy level. The required energy can be calculated with the help of the Morse curve and may be represented schematically by the subtended area E_t. This required energy level varies with the tensile stress applied, and can therefore be expressed as a function of the stress.

The Maxwell-Boltzmann distribution law gives us immediately the time during which any bond possesses sufficient thermal energy to meet the above energy require-

ments, in proportion to the total duration of the tensile stress. As this time must on the average be one-quarter period of the bond vibration to enable the bond to reach the state of unstable equilibrium, the number obtained by the Maxwell-Boltzmann distribution law is inversely proportional to the average duration of stress required to break a bond.

It is found that the duration required varies extremely steeply with the stress A reduction of 20 per cent in the stress increases the required duration more than 20-fold, while a reduction of 30 per cent in the stress increases this duration more than 500-fold. Theoretically, the smallest tensile stress is sufficient to break a bond, but the required duration might equal geological epochs.[11]

Should one of the bonds be non-existent, as is the case when the vibrating bond under consideration is part of the outside surface of the solid, it is clear that the required energy level is appreciably less than if all the bonds contributed their quotas to this requirement. Under normal conditions, therefore, the first bonds to break will always be surface bonds.

There is another position in a solid at which the stability of a bond is at a disadvantage: it is the position at the tip of a crack, where the bond is oriented perpendicularly to the crack-plane, which plane we will call "horizontal." When the vibrating bond is in this position, the "aft"-principal bonds of the two particles united by the vibrating bond cannot remain perpendicular to the vibrating bond when an up-and-down stress is applied to the solid. The link between the far-particles of the two aft-bonds has been broken by the crack, and the up-and-down stress will cause these particles to separate. As a result, the aft-bonds will become oblique to the up-and-down direction, and their up-and-down resultant will add itself to the up-and-down stress. It follows that when simple tension is applied, such bonds will break much sooner even than surface bonds. In other words, a fracture normal to the prevailing tension, once started, will propagate to the catastrophic limit.

In the absence of obvious fractures or surface cracks, such as the scratch of the glazier's diamond, re-entrant angles of suitable orientations have a similar, though less pronounced, effect. It is immaterial whether the re-entrant angles occur at external surfaces (*e.g.*, a die mark) or at internal surfaces (*e.g.*, about an included impurity). Even in the absence of such re-entrant angles, a broken surface bond may be considered as an initial fracture perpendicular to the axis of tensile stress.

The above simplified picture of fracture disregards the effect of the pantothenic cohesion, which plays a minor part, as will be seen later.

It can be readily seen that the treatment of the general case of tension, in which all the stresses are tensile, is in all ways identical to the particular case of simple tension, and that consequently the conclusions are the same, although the numerical values may vary somewhat in different cases.

Fracture under Compression

In the case of simple compression, the up-and-down and the to-and-fro stresses are nil, while the fore-and-aft stress is negative. At equilibrium spacing of the vibrating bond, assumed in the up-and-down direction, the Morse resultant of the vibrating bond is nil, and the Morse resultant of the fore-and-aft bonds is negative, as represented by point *C* on the Morse curve, to balance the fore-and-aft stress.

As the vibrating bond exceeds the primary equilibrium spacing, its Morse resultant increases at first from zero to a maximum represented by point *O* urging a contraction of the vibrating bond, and for spacings exceeding this latter value decreases asymptotically back to zero.

Similarly, the up-and-down resultant of the to-and-fro bond-pair also increases from zero at the primary equilibrium spacing to a maximum at a certain greater spacing, urging a contraction of the bond, and decreases asymptotically back to zero for spacings exceeding this latter value.

The fore-and-aft bond-pairs become more and more oblique to the direction of the fore-and-aft compressive stress as the vibrating bond exceeds the primary equilibrium spacing. The compressive Morse resultants of these bonds must consequently increase, while their spacing shrinks accordingly. Also, the up-and-down resultant of these bond-pairs rises at first very slowly, then more and more steeply, as the bonds become more oblique, to reach great magnitudes, urging an expansion of the vibrating bond. There must come a vibrating-bond spacing we shall call X, for which the spacing of the fore-and-aft bond becomes too great to be compatible with the necessary fore-and-aft bond magnitude to oppose effectively the fore-and-aft compressive stress, which of course has not changed either in orientation or magnitude. The fore-and-aft bonds consequently cease to oppose these stresses, which are being automatically taken care of by the "long" bonds, that have become shorter in the process, between the particles at the far ends of the fore and of the aft bonds.

Thus further lengthening of the vibrating bond beyond X causes a lengthening of the fore-and-aft bonds, resulting in their Morse resultants rising past zero and becoming positive again. The up-and-down resultants of these bonds similarly pass through zero to change direction and urge a contraction of the vibrating bond as the latter widens beyond X.

The vibrating and the to-and-fro bonds consistently urge a contraction of the vibrating bond, while the fore-and-aft bonds at first urge its expansion, with an intensity which rises from zero to a very high value, then drops again to zero for a finite spacing of the vibrating bond. It follows that there are two and only two secondary equilibrium spacings for which the urge to contract the vibrating bond matches the urge to expand it. As we have seen, the shorter of the two secondary equilibrium spacings corresponds to an unstable equilibrium, the longer one to a second stable equilibrium. When a vibrating bond exceeds this shorter unstable equilibrium it becomes a swapped bond.

It must be noted that the result of such a swap amounts to a crumpling and consequent shortening of rows of particles in the direction of the compression, with corresponding lengthening of the rows of particles in other directions.

To become a swapped bond, a bond must be excited to a sufficient thermal energy level to reach the spacing of unstable equilibrium, as was the case in the event of becoming a broken bond. The Maxwell-Boltzmann relation gives us immediately the number of bonds becoming swapped bonds in proportion to the total number of bonds during the time required for the swapping to take place, or about one-quarter period of the bond-vibration. Thus this number is proportional to the rate at which the bonds will swap when subjected to a given stress-tensor.

If we suppose that the lattice itself is unchanged by the swap, as is the case for liquids, for instance, it is clear that the rate at which bonds will swap has no cause to change, and the resulting flow will consequently take place at a constant rate, provided the stress-tensor is kept constant. Such a flow we shall call "viscous flow." It follows that viscosity and so-called "internal friction" are merely effects of the fact that in order to swap, bonds must be excited by a sufficient thermal energy, depending on the stress-tensors applied.

In brittle solids, the particles are usually ions of various characters, the short bonds uniting two particles of different characters. It follows that the characters of the two particles to form the new bond are incompatible with the formation of a short bond, thus precluding the restoration of the original lattice after the swap has taken place. The new lattice, stable while the stress-tensor is maintained, is less stable than the original lattice when the stress-tensor is removed.

From the above is readily seen that a swapped bond does not regenerate a bond ready for further swapping, so that the number of bonds available for further swapping decreases as the flow proceeds. It follows that the rate of flow decreases asymptotically to zero as the flow proceeds while the solid is subjected to a constant stress-

tensor. Upon release of the stress-tensor, the swapping of the bond and consequently the flow, reverses toward the primary equilibrium, and consequently to the former lattice, at a rate which also falls asymptotically to zero, as the progress of the flow reduces the number of bonds available for reverse swapping. Such a flow, able to reverse, we shall call "elastic flow." [11]

Prolonged elastic flow in brittle solids must result in the absence of short bonds across certain small surfaces throughout the solid.[6] Such flaws in the lattice of the solid are comparable to small cracks. Griffith [1] has shown mathematically that the edges of such small cracks in solids subjected to any distorting stress-tensor are seats of local tensile stresses oriented almost perpendicular to the plane of the flaws or of the small cracks. Such local tensile stresses urge these small cracks to propagate to the catastrophic limit if the stress-tensor and the duration of its application are sufficient.

In most solids the character of the various particles, and consequently of the bonds, is such that both viscous and elastic flow take place simultaneously. Under such conditions it is clear that the reverse elastic flow, upon release of the stress-tensor, is inhibited by the viscous flow, and can take place only partially if at all. The viscous flow gradually restores the original lattice, or "heals" the solid, at an asymptotically decreasing rate, while the shape of the body remains permanently deformed. Such a flow we shall call "plastic" flow.

It can be readily seen that the treatment of the general case of compression, in which all the stresses are compressive, is in all ways identical with the case of simple compression, and that consequently the conclusions are the same, although the numerical values may differ somewhat in the different cases. In the case of pantothenic compression in particular, the shortening of any row of particles at the expense of rows perpendicular to it takes place at the same rate and simultaneously for all rows in all directions, and consequently cancels out. The net result is that no pantothenic compression can conceivably cause flow of any description, unless possibly in hastening the "healing" of plastically deformed solids. All deformations due to pantothenic compressions are consequently elastic without theoretical limit.

Failure under Mixed Stresses

In the case of mixed stresses, the up-and-down stress is necessarily positive, and the fore-and-aft stress necessarily negative, while the to-and-fro stress is either, or nil. At the primary equilibrium spacing of the vibrating bond, assumed in the up-and-down direction, the Morse resultant of the vibrating bond is equal to the up-and-down stress, balancing the urge of the latter to expand the bond.

As the vibrating bond exceeds the primary equilibrium spacing, its Morse resultant, urging its contraction, increases to a maximum represented by point O, and for spacings exceeding this value, decreases asymptotically to zero as it did under simple tension. The up-and-down resultants of the to-and-fro bond-pairs follow a similar pattern, unless the latter stress is negative, that is, compressive.

The fore-and-aft bond-pairs holding the fore-and-aft stress in equilibrium follow the same pattern as they did in simple compression. As the vibrating bond exceeds the primary equilibrium spacing, the up-and-down resultants of the bond-pairs, urging the vibrating bond to expand, increase but very slowly at first. As the fore-and-aft bonds become appreciably oblique, their resultant increases very steeply to reach a very high maximum at a certain spacing, X, of the vibrating bond. As the vibrating bond spacing exceeds X, the bond-pairs' resultant falls steeply back to zero, changes sign, and urges the vibrating bond to contract. At a certain vibrating bond spacing, Y, the resultant of the bond-pairs attains a maximum comparable to the maximum reached by the vibrating bond at point O, and for vibrating-bond spacings beyond Y both the bond-pairs and their resultant decrease asymptotically to zero. The to-and-fro bond-pairs and their up-and-down resultant follow the same pattern if the to-and-fro stress is negative.

Thus, at the vibrating bond spacing represented by point O, the resultants urging a contraction of the vibrating bond are greater than those urging an expansion, the latter having hardly begun to make themselves felt, while the former have increased beyond the magnitude of the up-and-down stress which they equalled at the primary equilibrium spacing. It follows that the primary equilibrium is stable. At the vibrating bond spacing, X, the resultants urging an expansion of the vibrating bond are much greater than all others. It follows that there is between vibrating bond spacings O and X an unstable equilibrium. At the vibrating bond spacing Y all the resultants urge a contraction of the vibrating bond, and their total is greater than it was at point O. It follows that between spacings X and Y there is a second stable equilibrium. At vibrating bond spacings beyond Y all the resultants fall asymptotically to zero, except the up-and-down stress, which therefore becomes paramount. It follows that beyond spacing Y there is a second unstable equilibrium.

Bonds excited by a sufficient energy level to exceed the first unstable equilibrium, but not the second, start vibrating about the second stable equilibrium and become swapped bonds; bonds excited by a sufficient energy level to exceed the second unstable equilibrium continue to expand, and become broken bonds. The process of fracture under mixed stresses is therefore identical with that under tensile stress, with the exception of the added elastic flow, which in normal brittle solids is of minor importance.

When considering the effect of the pantothenic cohesion together with other stresses it becomes apparent that the process of fracture is normally accompanied by the process of elastic flow. If the tensile stresses are smaller than the pantothenic cohesion, prolonged elastic flow results in the formation of flaws with high tensile stresses at their edges which ultimately develop into catastrophic fractures.

Physical Nature of Strength in Brittle Solids

The strength of solids is usually assumed to mean a limiting stress which may be applied to the solid, above which the solid fails. Since elastic flow in brittle solids is a failure so slight as to be hardly noticeable, strength in brittle solids normally refers to the fracture of the solid.

That fractures normally start at a surface of the solid and propagate perpendicular to the most positive principal stress follows from the above analysis in the case of tensile stress. It has been amply verified experimentally.[12, 8] That the tensile strength of brittle solids cannot have a fixed value, but must decrease with the duration of the stress, follows immediately from our analysis of failure. That this is so also has been proved experimentally.[2]

That identical brittle solids in identical tests will not give identical strengths follows from the indeterminacy of the energy levels of the various particles, and from that of the time at which a definite particle will reach a specified energy level. From an average time determined for a great number of samples an average strength may be computed on a statistical basis. Since the first bond to break sets the fracture phenomenon in motion, the duration of a specific stress required to fracture identical individual solids may vary greatly. Since tensile tests are normally performed at a slowly increasing stress, the "strength" of the various specimens varies too. That this is actually the case has also been established experimentally.[2]

That the strength of brittle solids depends considerably on the condition of the outside surface follows immediately from our discussion of tensile failure. It is also a well established experimental fact.[2, 8]

It is well known that the strength of glass fibers is much greater than that of glass rods.[1] That this must be so follows from the consideration of the pantothenic cohesion. It is clear that the pantothenic cohesion must be considerably greater in a rod than in a thin fiber as the number of bonds of any given length about a specific

particle is considerably greater in the rod than in the fiber. It follows immediately that the mean period of vibration of the various particles and of their energy levels is much shorter in the rod than in the fiber. Therefore, the duration of identical stresses to obtain fracture of rods and fibers, which is proportional to this period of vibration, must be much shorter for rods than for fibers. Tests at an increasing rate of stress consequently will give greater strengths for fibers than for rods.

It is another well established fact that the surrounding atmosphere has a considerable influence on the strength of brittle solids,[18, 2, 3] and that the strength of the latter is greatest in a vacuum, or in an atmosphere which has no affinity for the solid. We have not considered the surrounding atmosphere in our analysis so far, and we have assumed tacitly that surface particles of an unstressed solid always returned toward their points of equilibrium in the lattice, no matter how far away their vibrations may momentarily cause them to be. Since the atmosphere is also of a particulate nature, it would be surprising if those particles of the atmosphere having an attraction for particles of the solid did not take the place in the lattice of some of the more errant particles of the solid during their absence, and remain there. Such bonds formed between the "gaseous" particles and the "solid" particles are necessarily weaker, that is, involve less energy, than the bonds between the original "solid" particles. They may be considered as equivalent to broken bonds, cracks, or flaws in the most vulnerable part of the brittle solid, namely, its surface.

On account of all these variations in the tensile strength of brittle solids, it has become general to refer to a "compressive" strength of brittle solids, although it is clear that no particulate solid can fracture directly from application of compressive stress. Griffith,[1] Smekal,[2] Orowan [3] and others have assumed that brittle solids contained "flaws" or cracks of minute dimensions scattered at random. Griffith has established mathematically that the greatest tensile "flaw-stress" generated in a solid under simple tension is eight times the greatest tensile "flaw-stress" that would be generated under simple compression of the same magnitude.[1] It was deduced from these results that the strength of brittle solids in simple compression should be eight times the strength of brittle solids in simple tension. In glass and other brittle solids in which such flaws could not be detected, the compressive strength was found to be much higher, between nine and fifty times the tensile strength.[2]

In our analysis of failure under compression, we did not need to assume the pre-existence of flaws, but we did show that prolonged elastic flow does generate such flaws; in the case of failure under tension, such "flaws" were generated instantly with the first broken bond. Hence it can be readily understood that a greater duration of stress is required in the absence of these flaws than when they already exist, and that tests at an increasing rate of stress must indicate in the former case greater strengths than in the latter.

Conclusion

It appears from this provisional and qualitative discussion that it is quite unnecessary to resort to such time-honored hypotheses as the pre-existence of flaws in order to explain the behavior of homogeneous brittle solids under stress. The simple application of the laws of mechanics and elasticity to the fundamental physical concept of the particulate structure of matter and of the electrostatic character of its particles appears to suffice.

On this basis alone straightforward explanations are presented for the following phenomena:

(1) A fracture in brittle solids begins perpendicular to the most positive principal stress, usually at a point situated on the outside surface of the solid, and, once started, tends to propagate farther.

(2) The condition of the outside surface, the composition of the atmosphere in

immediate contact with the solid, and the duration of the stress have a great influence on the tensile strength of brittle solids.

(3) The tensile strengths of identical solids show a scattering of values instead of showing identical, reproducible values.

(4) The tensile strength of fibers is greater than that of rods.

(5) Brittle solids show evidence of very slight elastic flow at a decreasing rate when subjected to a steady, prolonged stress. This flow is reversed upon removal of the stress.

(6) The "compressive strength" of flawless brittle solids is more than eight times their tensile strength.

This discussion also brings out the fundamental difference between viscous flow and plastic flow.

A similar treatment of solids with an ordered or crystalline structure no doubt would offer explanations for the splitting along cleavage planes, sliding along glide planes, work-hardening, crystal plasticity, and other crystalline phenomena.[14] Applied to polycrystalline solids, it may throw further light on such phenomena as gliding fractures.[15]

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See also paper on "Cohesion and Adhesion" by J. W. McBain and J. Alexander, in Vol. III of this series.

The Mass Spectrometer and Its Applications

NORMAN D. COGGESHALL
Gulf Research & Development Co., Pittsburgh, Pa.

and

JOHN A. HIPPLE
Research Laboratory
Westinghouse Electric & Manufacturing Co., Pittsburgh, Pa.

Introduction

Unlike some instruments to be found today the present mass spectrometers are not the result of a few years of very intensive research by a fairly large number of technical men. The roots of this type of instrument may be said to be in the positive ray parabola experiments of Sir J. J. Thomson and in the first mass spectrographs of Aston.[1] A short history describing some of the various types of instru-

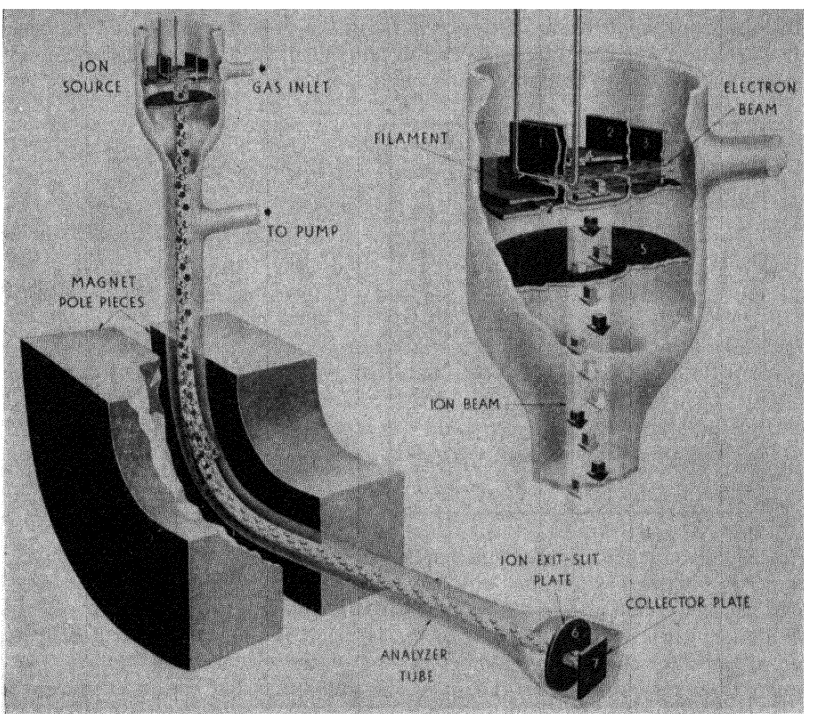

FIGURE 1. Pictorial representation of the mass spectrometer ion source, magnetic analyzer and ion collector.

ments developed over the last thirty-five years is to be found in an article by Jordan and Young.[2] For many years mass spectrometers were, with few exceptions, to be found only in the research departments of large universities, and the research done with them was of a fundamental nature. Now the research laboratories of many industrial companies are equipping themselves with this powerful research and analytical tool.

In the barest terms the primary processes involved in a mass spectrometer are: the creation of ions; the formation of these ions into a beam by electric fields; the sorting out by a magnetic field of the ions in the beam according to their momentum; and the measurement of the ion current in each momentum class. The perspective views in Fig. 1 show the spatial arrangement of parts and the manner of separation of the ion beams. The electron current from a hot filament is caused to pass between the system of electrodes 1, 2, 3, and 4. In this region there is a low pressure of the gas being investigated and the electrons create ions by impact on the gas atoms or molecules. The electric potentials on electrodes 2, 3, and 4 are so adjusted that the positive ions are drawn down through a slit in the bottom of electrode 2. A further difference of potential between electrodes 2 and 5 results in the ions being drawn down to 5 and the slit in 5, cut to match the one in 2, defines a ribbon-like beam of ions. In the figure, different ions are represented by differently shaded arrows. As all the ions formed in the ion source and drawn into the beam travel through the same electric fields, their kinetic energies will be essentially equal. Since the different types of ions have different masses, several momentum classes result. The magnetic field into which the ion beam passes sorts the ions according to their momentum, and the result is that the initial beam is split into as many separate beams as there are different ionic masses. The ion exit slit is located to catch the central ion beam; the ions pass onto a collector plate and the resulting minute current is measured by a special arrangement of a high resistance and suitably designed electronic amplification circuit.

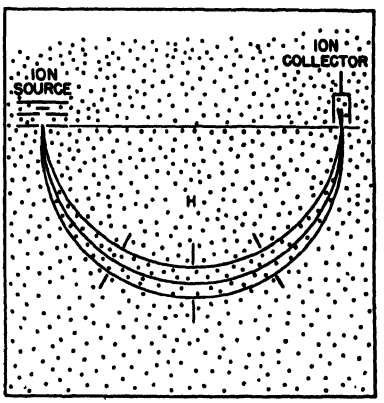

FIGURE 2. Schematic diagram of focussing in the 180° magnetic analyzer.

Fig. 2 shows schematically one focussing scheme in common use today. Here focussing is obtained when the ions are projected by an ion source in a region of uniform magnetic field and in a direction perpendicular to the lines of force. In such a case all ion paths will be portions of circles, and the ion source and collector are located at opposite ends of a diameter of one of the circular ion paths. The three dissimilar lines represent paths of ions of the same mass but slightly different angles of emergence from the ion source. Any type of ion desired may be caused to pass into the collector by varying either the accelerating voltages in the source or the magnetic field, H. Ions of masses different from that of the ions selected will travel

in arcs of different radii of curvature and will therefore not enter the collector slit. This type of instrument is sometimes called the 180° type.

Another type of focussing, sometimes called the sector type, is shown in Fig. 3. As is seen here, a diverging beam of ions leaving the ion source is focussed at the collector slit. The geometric relations governing this focussing are: that the ion source, ion collector and apex of the triangle, formed by the edges of the magnetic

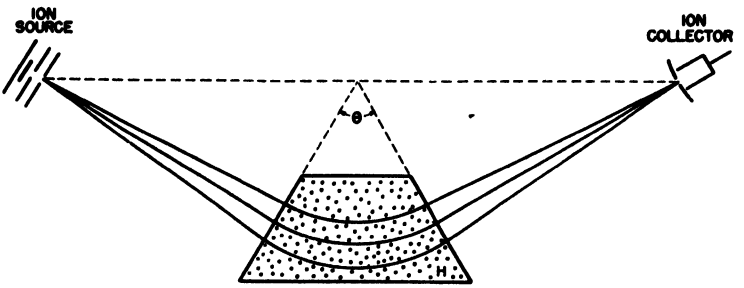

FIGURE 3. Schematic diagram of focussing in the sector type magnetic analyzer.

field, must lie on a line perpendicular to the bisector of the angle θ, which can be any desired angle. Focussing of any particular ion beam is achieved when its central ray enters the magnetic field perpendicular to the boundary and when the ion source voltages and the magnetic field strength are adjusted to give the ion path in the field a radius of curvature equal to the distance from the apex of the triangle to the point of entry of the central ray.

In both types of instruments described above it was stated that in a uniform magnetic field the ion paths are portions of circles. The equation relating this motion to the various physical parameters involved is easily obtainable from the two equations:

$$F = \frac{mv^2}{r}$$

which expresses the force F, necessary to keep a body of mass m moving in a circle of radius r, with velocity v, and

$$F' = \frac{Hev}{c}$$

which expresses the force F' acting on a charged particle of charge e moving with velocity v perpendicular to the magnetic field H. The quantity c is the velocity of light and enters as a units conversion factor. The force F' is perpendicular to both the velocity of the charged particle and the direction of the magnetic field. Combination of the two equations and simplification leads to the single equation:

$$\frac{c(mv)}{e} = rH.$$

If the velocity of the ion is expressed in terms of the accelerating potential V, the above equation becomes:

$$c\sqrt{\frac{2mV}{e}} = rH.$$

At this point we might indicate the functional difference between a mass spectrograph and a mass spectrometer. A mass spectrograph is an instrument operating on the same general principles, but carefully constructed to allow the research worker to correlate very accurately the positions of the ion beams with the ionic masses. It

is then an instrument designed primarily to measure, directly or indirectly, the atomic masses of the elements. The mass spectrometer, on the other hand, is designed for the measurement of the intensities of the ion beams. In the literature the designation "mass spectrograph" has often been used, although the investigator was really working with a spectrometer.

Operation

In Figs. 4 and 5 may be seen in more detail the geometrical and functional arrangement of the principal components of a mass spectrometer. Fig. 4 shows the

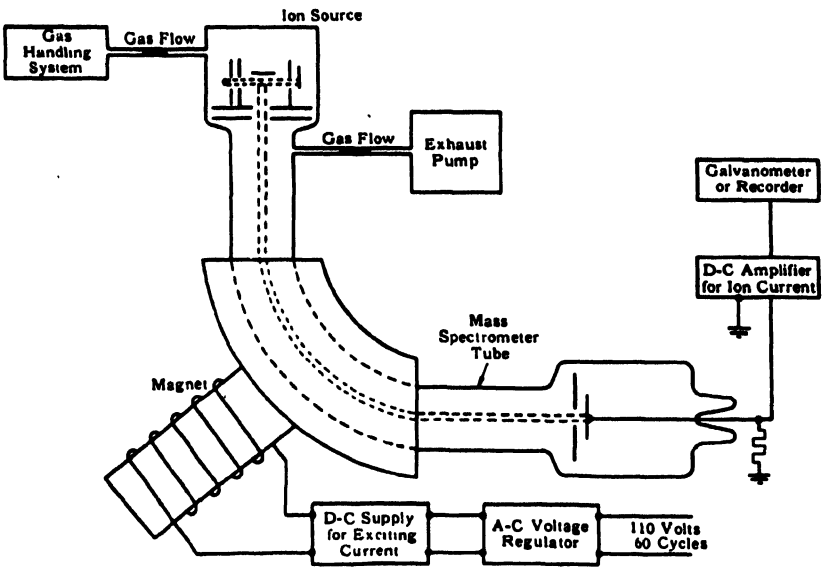

FIGURE 4. Schematic layout of main components involved in a mass spectrometer.

means provided for the entry of the gas being studied, etc. Fig. 5 gives a typical arrangement of electrical components and distribution of potentials needed in the operation of an ion source. Electrons emitted by the filament are accelerated by electrode 1, in which there is an aperture so that an electron stream passes through both 1 and 2, in which is also an aperture, into the ionization region. This ionization region is bounded by electrodes 2 and 4, between which there is a fairly weak electric field which draws the positive ions created by electron impact down toward a slit in electrode 2. After the ions pass through the slit in 2 they are further accelerated by the strong electric field between 2 and 5, and they emerge in a beam from the slit in 5. As may be seen, means are provided for maintaining all the electrodes at proper potentials. The function of electrode 3 is to collect the electrons that pass entirely through the ionization region.

When a monatomic gas is admitted into the ionization region the number of distinct ion peaks will be that of the number of isotopes of that element. When a polyatomic gas is being studied there results a multiplicity of peaks due mainly to the fact that a molecule may dissociate into various types of ionized fragments upon impact by an electron. The different ions may be brought into the collector by suitable adjustment of either or both the accelerating voltages in the ion source or the magnetic field strength. When the ion currents are plotted against either of these

two quantities there results a peak in the curve, called an ion peak, when the values are correct for focussing. Fig. 6 shows some of the ion peaks obtainable when *n*-butane is subjected to electron bombardment. Here the peaks are plotted against ionic mass. Such a curve is ordinarily referred to as a mass spectrum.

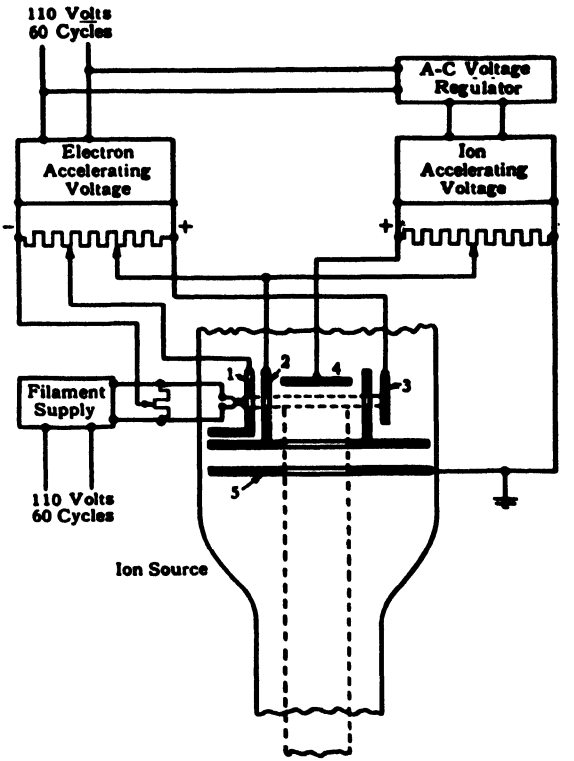

FIGURE 5. Schematic diagram of an ion source showing interrelation of electrical components.

In the utilization of this instrument for research and analytical problems the intensity of the ion beams, or the equivalent, the height of the ion peaks, is a problem of paramount importance, as will become clear later in the discussion of the applications. Consequently the operating parameters of the instrument which affect the ion intensities must be subject to close control so that they can be relied upon for constancy of operation.

Among these important variables are the filament current, the electron accelerating voltages, the positive ion accelerating voltages, the rate of inflow of gas to the ion source, and the temperature of the ion source. The magnetic field needs close control also, as fluctuations in it will cause the ion beam to fluctuate over the region of the collector slit. In recent years the great growth of the electronic art has benefitted the users of mass spectrometers enormously. Now amplifiers and voltage-stabilizing circuits are available which make it possible to dispense with some of the former equipment, which was both cumbersome and difficult to use.

In the ionization region a pressure of the order of 10^{-3} mm of Hg is often used. This allows ion beams of sufficient intensity to be obtained without the complications

of higher pressures. In the region of the magnetic analyzer, *i.e.*, between the ion source and the collector, it is important to have a considerably lower pressure. A vacuum of 10^{-5} mm of Hg or better is desirable to reduce scattering, which would weaken the ion beam intensities and harm the resolution. The pumping arrangement shown in Fig. 4 achieves the desired pressure differential.

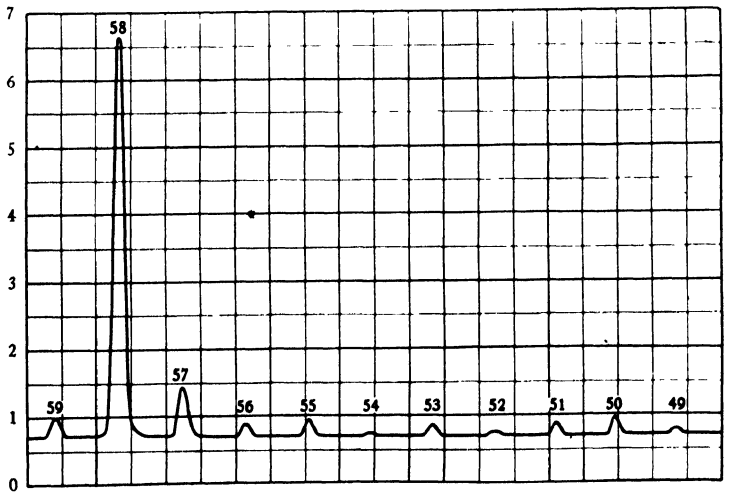

FIGURE 6. Mass spectrum of normal butane. The ordinate represents recorder deflection and the abscissa numbers refer to ionic masses.

At the present time the mass spectrometer has proven its value as a research and analytical tool to such an extent that such instruments are available commercially. Fig. 7 shows the spectrometer and its auxiliary equipment as built by the Consolidated Engineering Company.[3] In Fig. 8 may be seen the Westinghouse Electric & Mfg. Company's mass spectrometer and part of the auxiliary equipment.[4] Both these

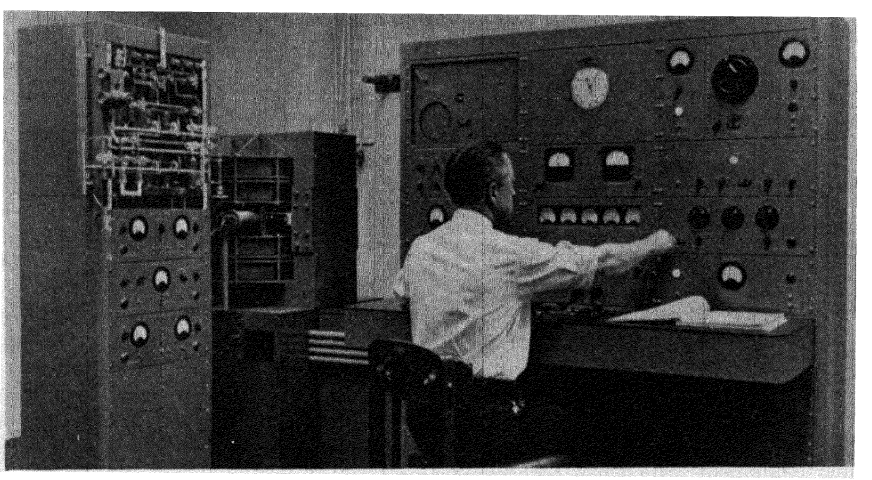

FIGURE 7. Mass spectrometer and auxiliary equipment built by Consolidated Engineering Corporation.

instruments are highly engineered devices utilizing some of the latest advances in electronics, and both are equipped to provide automatic recording of the mass spectra of the materials being studied. They are built to measure mixtures or compounds that have appreciable vapor pressures at room temperature. The material is generally introduced into the ion source through a small leak.

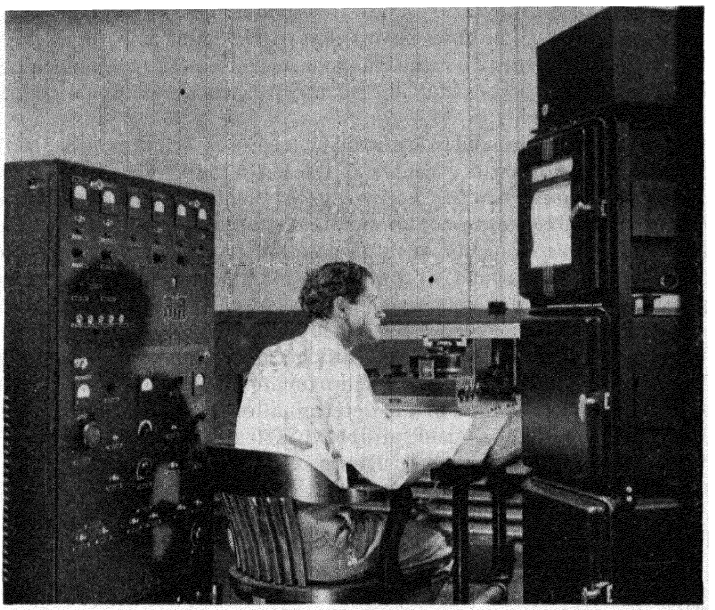

FIGURE 8. Mass spectrometer and part of the auxiliary equipment built by Westinghouse Electric and Manufacturing Co.

By virtue of the unique characteristics of the data obtainable with a mass spectrometer, it is very suitable for certain research and analytical problems. How the unique characteristics are utilized for specific problems will become more evident in the material which follows and which is devoted to a discussion of various applications. The applications are not discussed in any order of importance for either academic or industrial research.

Research and Analytical Applications

Natural Isotopic Abundances.* Ever since the concept of isotopes clarified itself to Rutherford, Soddy, and others about 1913, it has been a matter of vigorous interest to know definitely which of the elements are composed of isotopes, and in such cases, to know the isotopic weights and the relative abundances. It was for the job of studying isotopic abundances that many of the earlier instruments were built.

In the mass spectrographs of Aston and in those built by others the separate ion beams were focussed as thin lines on photographic plates. This resulted in a blackening at the lines of focussing, and the density of the blackening was used as a measure of the individual ion intensities. These studies resulted in some assignments of relative abundances being given to the isotopes of certain elements. However, the accuracy was none too good and more accurate figures have generally been obtained with mass spectrometers.

* A complete table of known isotopes of all elements, by Robley D. Evans, is printed as an Appendix to Vol. V of this series. J. A.

When neon, a monatomic gas, is introduced into a mass spectrometer it is possible to obtain ion peaks for the isotopes of mass numbers 20, 21, and 22. If it is assumed that no appreciable fractionation of the isotopes takes place at the small leak or orifice by which they are introduced into the ion source, the peak heights for the different isotopes will represent the relative abundances of the three isotopes.

For a diatomic molecule like N_2, measurements can be taken of the peak heights of ions of atomic mass 28 and 29. These ions would be N^{14} N^{14+} and N^{14} N^{15+} respectively. Alternatively, the ions beams due to N^{14+} and N^{15+} could be measured, the latter arising from both dissociation and ionization of the molecules. In this manner, all the gases may be studied and the percentage distribution of the constituent isotopes evaluated.

In the case of materials which are solid at ordinary temperatures, various techniques have been used to produce vapors in the ion source. One method suitable for some elements and compounds has been to use a small furnace or oven near or integral with the ion source to project an atomic or molecular beam through the ionization region.[5] For some elements, such as potassium, an ore or salt of the material may be deposited on a filament or heated disk.[6] When the temperature of such mountings is sufficiently high, positive ions are given off which may be drawn directly into collimating slits to form the ion beam.

At the present time, there is fairly satisfactory information as to the isotopic constitution of most of the elements. Unfortunately, there still exists considerable doubt as to the accuracy of some of the determinations. This doubt is caused by the fact that different investigators using different instruments have not always checked one another's results to within the consistency of their individual studies. The complete reasons for the errors are not as yet fully known, but doubtless will clear up as the parameters affecting the performance of an ion source are better understood.[7]

The information as to the existence of the various isotopes and their relative abundances is of value for a variety of applications. Nuclear physicists are greatly interested in the theoretical implications of which combinations of neutrons and protons form stable nuclei. The relative abundances can be used with the mass values obtained with the mass spectrograph to establish a set of physical atomic weights based on O^{16} having an atomic weight of 16.000000, in contrast with the chemical system of atomic weights based on the natural mixture of oxygen isotopes having an atomic weight of the same. Also, as will be brought out later, it is possible to enrich certain isotopes in some of the elements and use them as chemical tracers. Obviously, the abundance ratios for the naturally occurring isotopes must be known. Tables giving the latest information of the relative abundances have been published by Livingood and Seaborg [8] and by Seaborg.[9]

As a tool in following the progress and success of various methods of isotopic enrichment, the mass spectrometer has, of course, been an invaluable tool. A review of various methods of separating isotopes has been made by Urey.[10]

Isotopic Enrichment by Natural Processes. It is an intriguing question as to whether geological processes, organic processes, long-term chemical processes in the earth's crust, etc., can or have been effective in achieving any change in isotopic abundances in minerals, plants, etc.

Brewer [6] made an early study of the potassium isotopes found in various minerals and plants. The specimens were pulverized or ashed, and the powder applied to a platinum disk which, when heated, gave off potassium ions. Brewer determined the K^{39}/K^{41} ratio and, after a large number of determinations, he concluded that there is small difference in this ratio for minerals; that plants sometimes show a marked variation, kelp giving the most pronounced; that the variations in plants depended upon such factors as age, soil, species, and section of the plant.

More recently Cook [11] made a quite extensive investigation of the K^{39}/K^{41} ratio as depending upon the source of material. His technique in generating positive po-

tassium ions was, in general, similar to that of Brewer, although he fused some of his material into a salt on the filament in some cases. He used a method whereby the samples were compared to a standard filament without appreciably affecting the operation of the instrument. Also, he used a double collector system in a 180° instrument so that the ratio was directly obtained from potentiometer readings. After examining some thirty-seven kelps, minerals, and rocks of varying geologic age, he formulated the following conclusions: (a) the K^{39}/K^{41} ratio for most Pacific kelps does not vary more than 1 per cent from that of rocks; (b) the ratio for the fossils examined does not vary definitely from that of rocks; (c) rocks of different geological age show no definite change in the ratio; (d) the observed fluctuations in the K^{39}/K^{41} ratio are apparently due to isotope effects in the ion source. That such conclusions are the result of the elaborate work done underlines the difficulty of obtaining completely definite data.

An investigation of the isotopes of oxygen from meteoric sources has been made by Manian, Urey and Bleakney.[12] Their results were negative in that no differences were found from terrestrial oxygen. Nier [13] and his collaborators have made extensive studies of the variations in the carbon isotopes, and have found what appear to be significant differences. The results can be regarded as indicating a preference for C^{13} in limestones and for C^{12} in plants. In this work, the carbon was converted to carbon dioxide for admission to the ion source. Some of the results are shown in Table 1.

Table 1. C^{12}/C^{13} Ratio For Various Carbon Sources (From Murphy and Nier[13])

Source	No. of Samples	Average ratio for samples in group
Limestone	10	89.2
Coal (humic origin)	10	91.8
Wood	7	91.8
Petroleum	6	92.5
Bituminous shales	7	92.5
Torbinite and kerosene shales	3	91.7
Meteoric carbon	7	91.3
Graphite	1	90.2
Zeolitic calcite	1	89.9
CO_2 in air, Minneapolis, Minn. 3/1/41	1	91.5
Lycopodium spores	1	93.1
Balkashite algae	1	92.8
Marine shell	1	89.5
Sea water	1	89.3

Variations in the relative abundances of the lead isotope have been studied by Nier [28] and the results used to determine the geological age of various minerals. If lead is contaminated by naturally radioactive materials, the lead isotopic ratios will be changed, as some of them are the end products of particular radioactive decay processes.

Enriched Isotopes as Tracers. As we have seen, the natural isotopic ratios for the elements are fairly well known. If, then, it were possible to change the isotopic ratio artificially for a sample of some material, it would serve as a tracer in chemical studies. At the present, there has been considerable success in the separation of isotopes by electrolysis, exchange reactions, and thermal diffusion [10] which has made possible the utilization of this new tracer technique. As the mass spectrometer can distinguish between ion peaks representing different isotopes, it is the desired instrument for the analytical work. Except for the case of the light elements, in which density measurements can be used, it is the only instrument capable of satisfactorily distinguishing the different isotope ratios.

A good review of the application of enriched isotopes as tracers has been given by Rittenberg,[14] in which he describes some experiments of his own and others. Of chief interest here is the isotopic dilution method which is designed to make possible the quantitative analysis for organic compounds which are very difficult to determine by customary means. An example of such a compound is any one of the amino acids. Although it is virtually impossible to isolate all of one in a pure form from a protein hydrolyzate, it is possible to isolate a fraction of it which will be pure.

In the application of the isotope dilution method, a portion of the amino acid being studied is synthesized from nitrogen with N^{15} enriching it. A weighed amount of it is added to the protein hydrolyzate and then from this mixture is isolated a small amount of the same amino acid in pure form. The N^{14}/N^{15} ratio is determined for this sample; and from a knowledge of the same ratio for naturally occurring nitrogen, the same ratio in the enriched material, and the portion of synthesized material added, the amount of the amino acid existing in the original protein hydrolyzate can be calculated. This technique has been applied with considerable success by Rittenberg and others, and Table 2 shows a typical set of results obtained with it.

Table 2. Determination of Amino Acids in Fibrin
(From Rittenberg[14])

Protein hydrolyzed (g)	Amino Acid Added		N^{15} Excess (atom %)	N^{15} excess in compound isolated at successive stages of recrystallization (atom %)	Amino Acid in protein found (%)
	Compound	Weight (g)			
4.002	Glycerin	0.1315	2.00	0.781 0.784 0.782 0.782	5.12
4.995	*dl*-Glutamic acid	0.1266	2.10	0.182 0.186 0.185	13.2
5.382	*dl*-Glutamic acid	0.1152	2.10	0.162 0.161 0.157	13 0
5.034	*dl*-Glutamic acid	0.1222	2.10	0.185 0.176	12.9
7.675	*dl*-Glutamic acid	0.4005	2.10	0.356 0.355	12.8
	dl-Aspartic acid	0.4000	2.00	0.374 0.383	11.2

For biological studies the use of enriched isotopes also offers a powerful approach to problems of food assimilation. Animals which have been fed a diet one component of which consists of material with a changed isotopic ratio may be dissected and the same ratio determined for tissue from the various organs. This allows a determination of selective and time-dependent assimilation.

The application of C^{13} as a tracer in heterotrophic carbon dioxide assimilation processes has been made by Wood, Werkman, Hemingway, and Nier.[15] The purpose of the investigation was to determine the distribution of fixed carbon dioxide in the products of bacterial fermentation. In this work, $NaHCO_3$ was enriched with C^{13} and added to a medium in which a substrate with a cell suspension was fermented. Their general conclusions were: Carbon dioxide fixed in the permentation of galactose, pyruvic acid, and citric acid by *coli* occurs solely in the succinic and formic acids; in the fermentation of glycerol and glucose by *Propionibacterium*, the fixed carbon dioxide is in the succinic acid, propionic acid and propyl alcohol. Their results also had significant implications with respect to the specific intermediate reactions.

As new developments in the separation of isotopes become practical, it is to be

expected that great activity in the use of enriched isotopes as tracers in the biological field will follow.

Study of Chemical Reactions. The use of the mass spectrometer to study gaseous reactions is one field of application that has as yet not received a great deal of attention. The advantage of this instrument for such studies is its ability to measure the partial pressures of the constituent components as the reaction occurs. Hagstrum and Tate,[16] for example, have studied the thermal activation of the oxygen molecule in this manner.

When a study of the dissociation of a particular molecule by electron impact is made, the instrument must be carefully designed to insure that there is no appreciable thermal dissociation by the hot filament. In their electron impact studies of the oxygen molecule, Hagstrum and Tate noticed that the abundances of the ions representing CO_2, CO, and H_2O relative to O_2 depended on the temperature of the tungsten filament supplying the ionizing electrons. They then investigated this effect by inserting a platinum filament in the gas inlet line to the mass spectrometer and by replacing the tungsten filament by an oxide-coated one for the source of electrons in the ion source. When the platinum filament was run at 1600° K, the O_2 peak was found to decrease and the other peaks increased. After a short time with the filament at this temperature, the O_2 peak increased to its original value. It was suggested by the authors that the process involved activated adsorption of the oxygen molecules on the hot platinum surface. This would account for the bulb containing the platinum filament acting initially as a sink.

It was further suggested that the oxygen molecules were excited to a metastable state and evaporated, reacting with the very low vapor pressure material on the walls to produce CO_2, CO, and H_2O. The disappearance of the effect may then be explained by this "clean up."

Eltenton [17] has employed the mass spectrometer to detect free radicals and other intermediate products of chemical reactions. In his apparatus a thermal reaction chamber was placed adjacent to the ionization region in such a manner that a fraction of the products could escape through a small orifice in a thin diaphragm and be analyzed by the mass spectrometer. The electron voltage was set at a value below appearance potential of the free radicals arising from the dissociation by electron impact in C_2H_4, C_2H_6, and C_3H_6, but above the ionization potential of the free radical itself. In one series of experiments the methyl radicals were produced from lead tetramethyl, and their interaction with the three carrier gases mentioned above was studied. It was found that the reaction was greatest between CH_3 and C_3H_6. Methyl and ethyl radicals have been detected from ethane up to pressures as high as 120 mm.

In a study of the kinetics of the thermal decomposition of dimethyl ether and acetaldehyde, Leifer and Urey [18] used a mass spectrometer of the Bleakney type to detect intermediates and to measure their intensities. In this work the dimethyl ether or acetaldehyde was introduced into a hot reaction chamber into which intruded a capillary leak. This leak communicated to a line leading to the ion source of the mass spectrometer. Also, attached to the reaction chamber was a manometer by means of which they could measure the change of pressure with time and correlate this with the change of peak heights of the various ions measured. In Table 3 may be seen the ions resulting either from dissociation and ionization of the parent molecules or from ionization of the intermediates of the thermal decomposition. The voltages given here are the appearance potentials for these ions when produced from the parent molecules by electron impact. The electron voltages necessary to produce these ions from intermediates will be less. In this case the minimum energy required is that to produce ionization only, while the minimum energy mentioned above must be enough to produce both dissociation plus ionization as the ions are produced from parent molecules. Thus by using the proper voltage for the ionizing voltages, Leifer and Urey could be sure the ions they were producing were from the intermediates.

Table 3
(From Leifer and Urey [18])

Dimethyl ether			Acetaldehyde		
Mass	Ion	Acc. voltage (volts)	Mass	Ion	Acc. voltage (volts)
30	$HCHO^+$	14.5	28	CO^+	16.0
28	CO^+	18.5	16	CH_4^+	14.5
16	CH_4^+	18.0			
2	H_2^+	20.0			

To determine the dependence of ion peak height on pressure behind the leak, preliminary tests were made which indicated the peak heights to be directly proportional to the pressure. This allowed the data for the ion peaks to be used at any time to determine the pressure in the reaction chamber.

The decomposition process was indicated from a consideration of the intermediates formed and their dependence on time to be:

$$CH_3CHO = CH_4 + CO$$

for acetaldehyde, and:

$$(CH_3)_2O = CH_4 + HCHO$$
$$HCHO = CO + H_2$$

for dimethyl ether. Also Leifer and Urey used the indicated pressures to determine rate coefficients for the processes. The rate coefficients were found to be dependent upon initial pressures and to fall off as decomposition proceeded. Also by using unpacked, partially packed and fully packed reaction vessels, the rate coefficient for dimethyl ether was found to be a function of the surface volume ratio. Other very interesting results were obtained from this work but space does not allow their discussion here. It is to be expected, as mass spectrometers become more common and as their ease and reliability of operation increase, that more fundamental studies of this sort will follow.

Dissociation of Molecules by Electron Impact. During the last twenty-five years, many research workers have employed the mass spectrometer in the study of the processes involved in the production of ions from molecules by electron impact. This was a natural outgrowth of the early Franck and Hertz experiments on the one hand, and the development of the techniques of the positive ray analysis on the other. A review of this field up to 1931 has been written by Smyth.[19] The work up to this point was concerned primarily with the simpler molecules, composed of very few atoms. Since then, the experimental methods have been improved greatly, with the result that many of these molecules have been restudied and, in addition, some interesting interpretations have been made of the ionization processes of much more complex molecules. This advance has been largely made possible by the greatly increased sensitivity of the mass spectrometer due to instrument refinements, and more sensitive means of measuring the ion currents. The development of electrometer tubes has been a great impetus here. Now it is possible to operate the mass spectrometer at lower pressures and smaller electron currents, insuring that primary processes alone are being studied.

This instrument is able to obtain information not only on the appearance potential of the various fragments, but also on their relative abundances. The appearance potential for a particular ion formed by electron bombardment of gaseous molecules is the value of the ionizing electron voltage at which the ion may first be detected. It then serves as a lower limit for the energy sufficient to produce both the dissociation and ionization necessary for the ion to be formed from the parent molecule. In the study of appearance potentials, a particular mass is kept focussed on the exit slit and the current to the ion collector is studied as the electron energy is varied. The

same technique also furnishes ionization efficiency curves. The measurement of the relative abundances of ion fragments (or "cracking patterns") was usually considered of secondary interest until the recent application of the mass spectrometer as an analytical tool for routine analyses. The result of the application to this very practical problem has temporarily shifted the emphasis almost entirely to a study of the "cracking patterns." This will be discussed in a later section.

Methane was the first rather complicated molecule for which a serious attempt was made to interpret the process of ionization. A preliminary report of this was made by Bleakney, Condon, and Smith [20] and a more complete study was made by Smith.[21] This molecule serves as a nice example to illustrate the type of data obtained with the mass spectrometer, since a general review of the field would be out of place in this paper. Table 4 is from Smith's article and is a resume of the data on methane and its interpretation in terms of the most probable processes involved.

The most abundant ions in methane are those of masses 16 (CH_4^+) and 15 (CH_3^+). However, practically all possible ions are found to occur. For example, at a single electron impact all the hydrogen atoms may be stripped from the methane molecule, leaving the C^+ ion to be detected when the instrument is set to collect ions of mass 12. Such a rich spectrum is rather typical of all the hydrocarbons. There is one important change exhibited by heavier hydrocarbons: that the ionized parent molecule is no longer the most abundant one. The mass 28 peak ($C_2H_4^+$) is the largest peak in the ethane spectrum; however in the isobutane spectrum,[22] for example, the peak at mass 43 ($C_3H_7^+$) is more than ten times as abundant as the parent ($C_4H_{10}^+$) ion at mass 58. In some molecules such as tertiary butyl chloride, a parent peak cannot be detected. This may limit the complexity of the molecules that may be handled with the mass spectrometer. Thus far the chief reason why more complex molecules have not been studied is because of the difficulties of interpretation of the actual processes from the great number that one might assume for the production of the various fragments.

The interpretations shown in Table 4 were obtained by using thermochemical data in conjunction with the measured appearance potentials. In this way, additional information about the ionization and chemical bond energies may be inferred. The mass spectrometer cannot measure changes in the excitational energy of the molecule or kinetic energy of the neutral fragments. In many processes it has been found that these energies are small in the vicinity of the appearance potential. For instance, from the appearance potential of CH_3^+ Smith inferred that the ionization potential of CH_3 should be equal to or less than 9.9 volts. That is, this ion appears at 9.9 volts, and if the dissociation fragments possess no excitational or kinetic energy then it may be said that the ionization potential of the free radical CH_3 is 9.9 volts. If the more recent value $D(CH_3 - H) = 4.4$ volts (instead of 4.5 volts) is taken for the strength of the $CH_3 - H$ bond, then the deduced value for the ionization potential of CH_3 becomes 10.0 volts. Hipple and Stevenson [23] measured this ionization potential directly by thermally dissociating lead tetramethyl to produce the free methyl radicals in the ionization chamber of a mass spectrometer. This experiment yielded a value of 10.0 $\pm$, 0.1 volts, in excellent agreement with the value obtained with methane, assuming no excitational or kinetic energy.

Besides the question of the excess energy in the reaction which the mass spectrometer cannot detect, there is one other limitation in its application to the determination of the heats of dissociation of molecules. This is the inaccuracy due to the spread in velocity of the electron beam since the source of the electrons is a hot filament. The situation is improved somewhat by the use of an oxide-coated filament instead of one of tungsten, permitting the uncertainty to be cut down to 0.1 volt. However, from the viewpoint of the chemist, 0.1 volt is a large inaccuracy. There is a possibility of using a velocity filter on the electrons, but experimentally this is quite complicated and has not been attempted in this particular application.

Table 4. Ions Formed in Methane
(From Smith,[21])

Observed Ion	% of Total Ionization (Electron Energy 50 volts)	Observed Appearance Potentials (volts)	Probable Process $CH_4 \rightarrow$:		Calculated Minimum Energy (volts)	Additional Energy Required or Ionization Energy Deduced (volts)
			Positive Ions			
H^+	3.0	22.7 ± 0.5	$H^+ + CH_2 + H$	(1)	21.6	1.1
			or $H^+ + CH + H_2$	(2)	20.6	2.1
		29.4 ± 0.6	$H^+ + C + 3H$	(3)	28.6	0.8
H_2^+	0.3	27.9 ± 0.5	$H_2^+ + C + 2H$	(4)	26.0	1.9
H_3^+	0.005	25.3 ± 1.0	$H_3^+ + C + H$	(5)	$24.1 - D(H_3^+)$	$1.2 + D(H_3^+)$
			or $H_3^+ + CH^-$	(6)	$20.6 - D(H_3^+) - E(CH)$	$4.7 + D(H_3^+) + E(CH)$
C^+	0.6	26.7 ± 0.7	$C^+ + 4H$	(7)	26.3	0.4
CH^+	1.7	23.3 ± 0.6	$CH^+ + 3H$	(8)	$11.6 + I(CH)$	$I(CH) \leq 11.7$
			or $CH^+ + H_2 + H$	(9)	$7.1 + I(CH)$	$I(CH) \leq 16.2$
CH_2^+	4.2	15.7 ± 0.5	$CH_2^+ + H_2$	(10)	$3.7 + I(CH_2)$	$I(CH_2) \leq 12.0$
		22.9 ± 0.8	$CH_2^+ + 2H$	(11)	$8.1 + I(CH_2)$	≤ 2.8
CH_3^+	39.5	14.4 ± 0.4	$CH_3^+ + H$	(12)	$4.5 + I(CH_3)$	$I(CH_3) \leq 9.9$
CH_4^+	50.7	13.1 ± 0.4	CH_4^+	(13)	$I(CH_4)$	$I(CH_4) = 13.1$
			Negative ions			
H^-	0.04	6.1 ± 0.3	$H^- + CH_3$	(14)	3.8	2.3
		6.9 ± 0.8	$H^- + CH + H_2$	(15)	6.4	0.5
		7.3 ± 1.0	$H^- + CH_2 + H$	(16)	7.4	~ 0
		18.0 ± 0.6	$H^- + CH^+ + H_2$	(17)	$\lesssim 18.1$	~ 0
			or $H^- + CH_3^+$	(18)	$\lesssim 13.7$	4.3
C^-	0.003	27.4 ± 0.6	$C^- + H^+ + 3H$	(19)	26.7	0.7
CH^-	0.005	10.2 ± 0.3	$CH^- + 3H$	(20)	$11.6 - E(CH)$	$E(CH) \geq 1.4$
		24.5 ± 0.5	$CH^- + H^+ + 2H$	(21)	$25.1 - E(CH)$	≥ 0.8
			or $CH^- + H_3^+$	(22)	$20.6 - D(H_3^+) - E(CH)$	$3.9 + D(H_3^+) + E(CH)$
CH_2^-	0.002	8.9 ± 0.3	$CH_2^- + 2H$	(23)	$8.1 - E(CH_2)$	$0.8 + E(CH_2)$
		23.4 ± 0.6	$CH_2^- + H^+ + H$	(24)	$21.6 - E(CH_2)$	$1.8 + E(CH_2)$
			$CH_2^- + H_2^+$	(25)	$19.0 - E(CH_2)$	$4.4 + E(CH_2)$

In his paper on the study of butene-1 with the mass spectrometer, Stevenson [24] has summarized the heats of dissociation obtained from electron impact data. This summary is given in Table 5:

Table 5
Heats of Dissociation, D(R′ – R″), in E. V., for the Reactions R′ – R″ = R′ + R″ – D
(From Stevenson [24])

R″	R′ = H	CH_3	C_2H_5	C_3H_5	Cl
H	4.502	...	...	..	...
CH_3	4.40	3.62	...	...	...
C_2H_5	4.20	3.52	3.43	...	...
C_2H_3	3.95	3.43	3.30	3.32	...
Cl	4.46	3.50	3.45	3.1	2.50
I^a (R′)	13.5	10.07	8.67	9.9	12.9

Molecular Potential Energy Curves. In the discussion of the dissociation of molecules by electron impact, the fact that the kinetic energy of the fragments is unknown places a limitation on the method. No instrument has yet been designed that will provide information concerning the kinetic energy of the neutral fragments, but some fruitful investigations have been made on the kinetic energy of the ionic fragments. Information concerning the potential energy curves may be obtained in this way.

Bleakney [25] was able to demonstrate with his mass spectrometer the existence of the repulsion curves in hydrogen, predicted by quantum mechanics. The voltages in the ion source were so adjusted that only ions possessing greater than selected minimum kinetic energy could leave the ion source and enter the analyzer. Under these conditions no ions were observed when the electron accelerating voltage was below 26 volts. Above this voltage, however, atomic hydrogen ions possessing considerable kinetic energy were observed. These resulted from an electronic transition to a repulsion state in which the hydrogen atom and the ion fly apart with considerable kinetic energy. The Franck-Condon principle also predicts the formation by single electron impact of atomic hydrogen ions with little kinetic energy at an electron voltage of approximately 18 volts. These ions were observed. Lozier [26] investigated the velocity distribution of the high-speed ionic fragments in greater detail.

More recently a very interesting study of molecular potential energy curves as related to mass spectrometer peak shapes has been done by Hagstrum and Tate.[27] In this work they considered the collection efficiency of the usual ion source for ions of different initial kinetic energies. They obtained a curve of collection efficiency versus initial kinetic energy from a consideration of the manner in which the ions are collected by the first collimating slit and passed by the second. Also they considered the distribution of kinetic energy in the ions formed when certain diatomic molecules are dissociated and ionized by electron impact.

The theoretical distribution of initial kinetic energy of the ions was obtained by applying both the Franck-Condon principle and the quantum-mechanical wave functions for probability distributions as dependent upon internuclear separation. The Franck-Condon principle states that an electron impact with a molecule causes no significant change in internuclear separation because of the small mass and momentum carried by the electron. Excitation of a molecule to an ionized state may lead to dissociation if the minimum of the potential energy for the ground state is at a smaller internuclear distance than the minimum for the energy curve for the excited state. If the relative locations of the potential energy curves are known, the statistical distribution of ion velocities can be calculated by application of the square of the wave function representing the ground state. The product of the efficiency of collection function times the density distribution as a function of initial kinetic energy gives a curve representing the distribution of ions as a function of initial kinetic energy as they emerge from the slits of the ion source.

Depending upon the relative displacements of the potential energy curves of the ground and ionized states there may result any one of four distinct types of ion peaks. The difference is mainly in the shape, especially on the high mass side. They were able to explain the reason for satellite peaks and to demonstrate how the peak shapes can be used to deduce qualitative information concerning the potential energy curves for the excited ionized states giving rise to the ions.

This mode of attack is very interesting and has promise of more quantitative results if the conditions of ion collection can be more exactly controlled. A more precisely determined collection efficiency curve has been reported [7] but the complete processes are not yet entirely understood.

Analysis of Mixtures with the Mass Spectrometer. A natural outgrowth of the studies of ionization and dissociation by electron impact was the application of the mass spectrometer to analytical problems. The early analyses were very simple ones, such as the determination of the purity of inert gases. The measurement of traces of impurities in gas samples remains a very important field of application today, but in the last few years the method has been extended successfully to the analysis of rather complex gas mixtures.[29]

During the analysis the sample flows through the mass spectrometer tube at a constant rate. This is conventionally accomplished by bleeding the sample into the instrument through a flow-restricting device from a large reservoir at a rather high pressure (perhaps one millimeter of Hg). In maintaining a relatively constant flow rate in this manner, it is important that the "leak" have a linear flow characteristic, *i.e.*, the flow rate of each component must be a linear function of its partial pressure in the reservoir. There are a great many other problems to be solved in the successful application of the instrument, such as the design of a suitable pumping system, surface contamination of the electrodes, and thermal cracking of the molecules by the hot filament.

In obtaining the data for an analysis in routine operation a fast recording system is practically a necessity. This recorder should be able to record to an accuracy of 1 per cent ion currents differing in magnitude by a factor of several hundred because of the wide range of intensities in the spectra. This problem has been solved in the case of a photographic recorder by employing several galvanometers of different sensitivities.[29] Thus, the spot from the most sensitive galvanometers may be far off the scale, but under this circumstance a less sensitive galvanometer will be deflected sufficiently to provide an accurate reading. The required extended scale has been obtained with a pen and ink recorder by employing a logarithmic response coupled with an automatic change in sensitivity when the pen reaches the top of the scale.[30] By these methods a spectrum may be recorded accurately in about ten minutes.

Before making an analysis the mass spectrometer must be calibrated. This involves the recording of the spectra of the pure components in the mixture as well as a determination of the relative sensitivity of the instrument to each component. The simplest method of calibration is that of simply employing a pressure standard. For each component, the spectrum is obtained for a known pressure in the reservoir behind the leak. With this information available the analysis of a mixture of these components may be made. Recalibrations are necessary from time to time as the spectra are sensitive to changes in the surface conditions of the electrodes and changes in geometry, voltages and temperature of the tube. By careful control the effect of these variables may be minimized. In spite of the difficulties involved, the mass spectrometer has an important role in gas analysis because of its speed, the wide range of masses that may be covered, and its ability to detect without ambiguity small traces of impurities. For complex mixtures, the calculations require much greater time than that consumed in obtaining the data with the instrument when automatic recording is employed. They involve the solution of a set of linear equations similar in form to those employed in the infrared method of analysis.

Application to Photochemistry. One research field for which it is potentially quite valuable but to which the mass spectrometer has not as yet been very widely applied is that of photochemistry. One limitation to its use, of course, is that only photochemical processes that give ions or radicals easily ionized can be studied.

A direct application to the study of the products of the photo-dissociation of diatomic molecules into ions has been made by Terenin and Popov.[81] In their studies they observed that it was possible to get quite large photo-currents when the vapors of certain salts such as TlI, TlBr, and TlCl were subjected to ultraviolet radiation. By a series of tests they were able to conclude that the effect was truly one of photo-ionization of the molecules in the gas phase. For example they found that the current was independent of the change of the polarity of the electrodes, that it reached a saturation value as the potential between the electrodes was increased, and that it was proportional to the amount of light falling in the ionization region.

The source of ultraviolet light was a spark which could be of any one of the three materials: Al, Cd, and Zn. Using a monochromator made of fluorite and quartz Terenin and Popov were able to separate out various spectral lines and to study the dependence of the photo-current upon still another parameter, the wave length of the radiation.

As the studies on mere photo ionization of the Tl-halides did not indicate whether the process was:

$$TlX \longrightarrow TlX^+ + e^-$$

or

$$TlX \longrightarrow Tl^+ + X^-$$

a mass spectrometric study was made of the photo-ionization products. The ionization region was so constructed that an electric field would draw out the charged particles into a magnetic analyzer. By calculations as to the effective potential of these particles and by using a calibration of magnetic field as a function of their exciting current, Terenin and Popov were able to identify the ions and to demonstrate that the photo-ionization process was of the latter type, shown above. TlI, for example, was dissociated and ionized by the process:

$$TlI \longrightarrow Tl^+ + I^-$$

Further fundamental information concerning the process was obtained by using the equation:

$$U = D + J - E$$

where U is the total energy necessary to produce dissociation and ionization, D is the dissociation energy of the molecule into neutral atoms, J is the ionization energy of Tl, and E is the electron affinity of the halogen atom. By correlating U with the energy of ultraviolet light in each case, which produced maximum ionization, and by using known values of D, J and E, they discovered that the kinetic energy of the dissociation products was of the order of 0.5 electron volt. Further work on photo-ionization confirming that of Terenin and Popov as well as investigating the process for other compounds was done by Wehrli and Halg.[82]

There is another type of study which may yield to mass spectrometric techniques: that of identifying photo-dissociation products. Recent work [17, 18] has demonstrated the feasibility of detecting radicals by using lowered ionizing electron voltages.

Ionization Studies. The reversal of ionization, *i.e.*, change of sign of the ion upon striking a metallic surface, has been studied by Arnot and his collaborators for several different types of ions.[33, 34, 35, 36] In their investigations of the formation of diatomic Hg molecules they found negative ions of Hg in appreciable quantities. Using a mass spectrometer with special design of ion source they uncovered several significant facts about the production of Hg^-. In this ion source the filament was

located in line with the exit slits and, with the electric fields such as to draw negative ions from the region of the filament out of the source, the Hg^- ions were found. From their energies it was apparent that they were formed on or near the filament. The Hg^- ions were found to be proportional to the Hg^+ ions over a fair pressure range. The Hg^- ions have a quite large energy spread. Also it was found that ions of the same type appeared to be originating in the ion source at or near a metal gauze which served as an electrode for accelerating potentials. The recognition of the place of origin could be made by the electrostatic potential relations in the ion source and the correlation with the energy of the ions as determined using the magnetic analyzer.

From the above observations it was concluded that Hg^- ions are formed when a Hg^+ ion strikes the metal filament or electrode, that is, a certain fraction of the Hg^+ ions rebound in the form of Hg^-. Also, it was reasoned from the energy spread that the Hg^- ions have, on leaving the metal surface, some of the original energy which the Hg^+ ion carried. Further studies were made on a number of other gases showing atomic negative ions. As in the case of Hg^-, the investigations in each case indicated the negative ions to be the result of direct impact of the positive ion on a metal surface. Table 6 shows some of the results obtained.

Table 6. Probability of Conversion of 180-Volt Positive Ions into Negative Ions on a Nickel Surface
(From Arnot [34])

Negative Ion		Positive Ion From Which Formed	Probability of Formation on Units of 10^{-4}
Hg^-		Hg^+	6.4
H^-		H_2^+	0.104
N^-		N^+	1.07
O^-		O_2^+	1.10
O_2^-		O_2^+	0.42
CO_2^-		CO_2^+	2.31
O_2^-		CO_2^+	2.51
CO^-	77.4%	CO_2^+	10.8
O^-	+22.6%	CO^+	3.37
C^-			(0.1)

The mass spectrometer has been used by Hogness and his collaborators in studying ions formed by collisions of the second kind.[39] In mixtures of NO and A and of NO and He, increase in the relative intensities of NO^+ with increase in pressure gave definite evidence of collisions of the second kind, that is:

$$NO + A^+ \longrightarrow NO^+ + A$$

and

$$NO + He^+ \longrightarrow NO^+ + He$$

A similar magnetic analyzer study has been made by Harnwell,[38] who studied the ratio of He^+/Ne^+ and of He^+/A^+ under various pressure conditions. The ionization of gases by collisions of their own accelerated molecules has been studied by Berry.[39] In this work, he accelerated ions which were then neutralized before producing the further ionization. His selection of velocities was by an electrostatic velocity selector.

A mass spectrometer arrangement has been used by Scott [40] to measure and identify the different ions produced in an ion source designed for high intensity ion currents. His ion source was one in which the ions were formed by bombarding a region of gas with a beam of focussed electrons. From this source he obtained hydrogen ion beams as high as 4 ma.

The complex processes involving multiple collisions at higher pressures have not received as much attention during recent years, although some interesting studies of ion sources of high current output employing the mass spectrometric measuring

method have been made by Schütze.[41] In this work the intensity of H^+ was studied under different operating conditions of the ion sources.

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Direct Enrichment of Isotopes

Since the mass spectrometer is able to sort out the various masses of ions, an obvious application is that of collecting samples of the separated isotopes of the elements. Unfortunately the usual mass spectrometer must be operated at very small currents (10^{-9} amperes or less). This means that the sample collected is very minute. For example, with a current of 10^{-9} amperes it would require 700 hours to collect 1/10 microgram of potassium. For some applications, instruments have been specially designed to increase this current Such an instrument was that described by Smythe, Rumbaugh and West [42] with which it was possible to operate with a current of 10^{-4} amperes of K^{30} ions. This apparatus was later employed to show that the radioactivity associated with potassium was due to K^{40} and that of rubidium [44] due to Rb^{87} confirming in the latter case the conclusions of Hahn, Strassman and Walling [45] and of Mattauch [46]

More recently, Nier, Booth, Dunning and Grosse [47] were able to collect enough U^{235} to prove that this isotope was the one responsible for the fission of uranium when bombarded by slow neutrons. This was confirmed by Kingdon, Pollock, Booth and Dunning.[48]

In his War Department Report, Smythe discloses that a mass spectrometric method was used in collecting appreciable quantities of U^{235} for use in the atomic bomb.[49] It may be that in the future the technical details of these separators will be made more known to the public.

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The Geiger-Muller X-ray Spectrometer

FRANCIS G. FIRTH

North American Philips Co., Inc.

Introduction

Ever since the first report of Von Laue [1] that crystals can act as three-dimensional diffraction gratings when irradiated by an x-ray beam, the science of x-ray diffraction has progressed as fast as available instrumentation would permit.

The development of the Debye-Scherrer powder camera [2] simplified the technique of identification of polycrystalline powder aggregates, in which form most materials are usually found. By this technique it was possible to take an unknown sample and obtain a diffraction pattern that could be compared with other patterns that had been previously obtained from a variety of known substances. When the patterns matched, the presence of an identity of the same composition as the standard pattern could be assumed. If more than one substance or phase were present in the unknown, that could also be ascertained, since each substance present in the sample would give a pattern as though it alone were present. The intensity of the diffraction maxima, however, would be in proportion to the amounts of each substance in the sample. This method of identification was, and still is, being used to identify unknowns.

However, Hanawalt, Rinn and Frevel [3] simplified this procedure of identification and made it unnecessary to have a large library of x-ray diffraction patterns on hand as standards, by publishing diffraction data of a large number of substances, in the form of tables in a way that makes the identification of an unknown comparatively simple.

This index has also been published by the American Society for Testing Materials in the form of individual cards for each substance, and a whole new series of cards for other substances has been collected from a number of other workers in the field and will be available as supplements from time to time.

This makes available to x-ray workers an extremely valuable method of identification for unknown samples and enables x-ray diffraction techniques to take a position comparable with spectroscopy and chemical methods in the analytical field.

The Debye-Scherrer camera, while valuable for this work, is somewhat inadequate when quantitative analyses are required. It is necessary to prepare the specimen with care, load the camera with film and make an exposure that may last from 15 minutes to 25 hours. The film must then be developed, fixed, washed, and dried, and then measured to determine shrinkage. A microphotometer is required for quantitative work to measure the intensity of the maxima, and the diffraction line position must be measured to determine the Bragg angle. The interplanar spacings can then be calculated and the film indexed. This whole procedure involves skilled attention and the use of expensive equipment.

The Geiger-Muller X-ray Spectrometer has been designed to simplify this procedure and to give superior results to that obtained by the ordinary methods of x-ray diffraction.

The Spectrometer

In 1921 W. H. Bragg [4] published a description of a spectrometer that employed a two-crystal focussing system, and which was employed for the determination of precision lattice constants and wave-length data. This instrument, however, was extremely costly and required considerable skill to keep it in operation.

These facts precluded its acceptance for normal use. J. C. M. Brentano,[5] in a series of papers published between 1925 and 1937, described the use of a camera employing the Bragg focussing principle which can give superior resolution in x-ray powder diffraction studies. The recording means, however, was x-ray film, with all its drawbacks from a quantitative and time-consuming viewpoint.

A similar focussing principle is employed in the Geiger-Muller X-ray Spectrometer, except that a Geiger-Muller tube is used as the recording instrument. The focussing system employed is shown diagrammatically in Fig. 1. The asymmetric

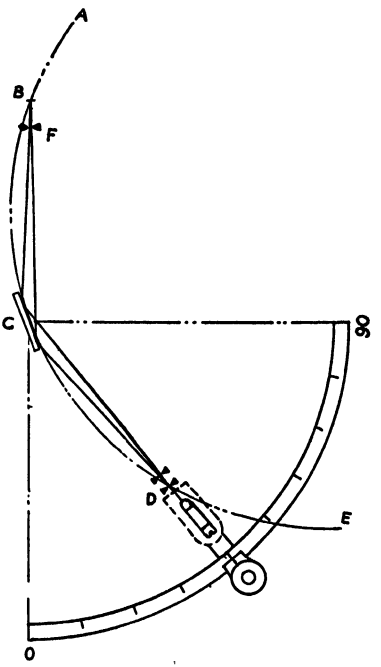

FIGURE 1

focussing circle is shown (*ABCDE*) with the x-ray focal spot (*B*), the specimen surface (*C*), and the Geiger-Muller tube entrance slit (*D*) on the same arc of a circle. An essential requirement for the focussing condition is that the distance between the x-ray focal spot and the specimen is the same as the distance between the specimen and the Geiger tube slit.

A divergent beam from the x-ray tube, whose divergence is limited by an adjustable slit system (*F*), is permitted to fall on the specimen, which is normally a flat surface of the powder sample. A convergent beam of diffracted radiation is emitted from the specimen when the Bragg law conditions are satisfied and enters the Geiger-Muller tube slit (*D*), if located correctly. The Geiger tube and slit system are mounted together in a housing and are attached to a goniometer arm that can rotate around the specimen center; the arm is so geared to the specimen mount that the sample will rotate at half the speed of the Geiger tube analyzer arm. In front of

the Geiger tube slit is another slit that prevents the bulk of the non-coherent radiation from the sample from entering the slit (*D*).

The goniometer is graduated in degrees and the arm has attached to it a vernier, which permits the position of the analyzer system to be read within 1/100th of a degree of arc. The total angular range of the goniometer is 90° and a reading in degrees obtained from it actually gives a value equal to twice the Bragg angle.

The Geiger-Muller Counter

Counter tubes have been known since 1908 when Rutherford and Geiger developed a simple design for a point counter that would indicate the presence of ions when connected to an electroscope. Later the proportional counter and the tube counter of Geiger and Muller were developed at about the same time. These were an improvement over the point counter because of their higher resolution at greater radiation intensities.

Most of the earlier counters described in the literature were somewhat unstable in operation, and their life was somewhat unpredictable. Reproducibility of response after following identical manufacturing procedure was unknown; consequently, Geiger-Muller tubes were then unsuitable for precise measurements. The Naval Research Laboratory,[7] after work on improving the counter, succeeded in making counters that were quite reproducible in response, and of a very high efficiency, particularly with x-radiation of long wave length (0.7 to 2Å).

These counters were so-called fast counters; they required no external electrical quench and could be used for resolving quanta that initiated up to 20,000 counts per second. The construction of a counter suitable for x-ray diffraction work is shown in Fig. 2b. (A picture is given in Fig. 2a). A metallic cylinder (*A*) with glass (*B*)

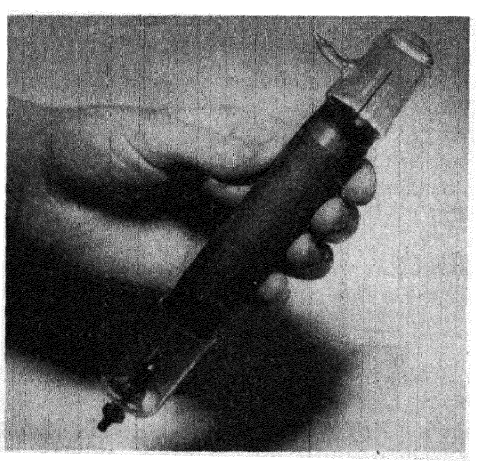

FIGURE 2a

sealed to each end, supports at one end a wire (*E*) that is concentric with the cylinder and a lead brought out from the wire at (*F*). The other end of the glass attached to the cylinder is closed off by a very thin window (*C*) of Lindemann glass, which has high transmissibility to soft x-rays. The tube can be exhausted and filled through the seal-off at (*D*). The counter is filled with a rare gas such as argon or krypton along with an organic gaseous quenching agent to make it a fast counter.

The length of the counter is so designed that the filling gas will completely absorb any long wave-length x-radiation entering the window within the length of the cylindrical electrode. If a suitable direct current voltage between 1100 and 1500 volts

is maintained between the central wire which serves as the anode and the cylinder which is cathode, a circular equipotential field will exist between the wire and the cylinder. If x-radiation enters the counter window it is strongly absorbed photoelectrically and each quantum may be expected to produce an ion pair. Since the wire is at positive potential, the electron will move toward the wire and will be accelerated as it approaches it, due to the increase in intensity of the field. Near the wire the electron gains sufficient velocity to excite a gaseous atom whose electron is ejected and accelerated, and bombards another gas atom. Thus this series of bombardments gives rise to the movement of a large number of electrons toward the wire. The positive ion moves relatively slowly in the field because of its greater mass, and as more positive ions are formed they eventually set up a space charge around the wire in the interelectrode space; this shuts off the accelerating field, and stops further electron formation.

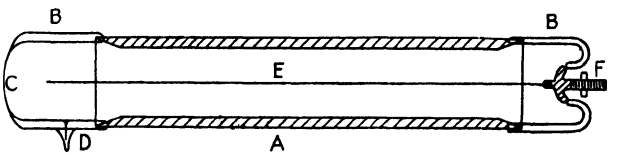

FIGURE 2b

This whole event is regarded as a count initiated by a single quantum, and can be completed within a time period of the order of 10^{-8} sec. The function of the organic vapor present is to prevent re-ignition of the discharge by secondary effects.

The voltage between the electrodes is of great importance in considering the performance of a counter. With a constant source of radiation the response of a typical diffraction counter is shown as a function of the voltage in Fig. 3. The region be-

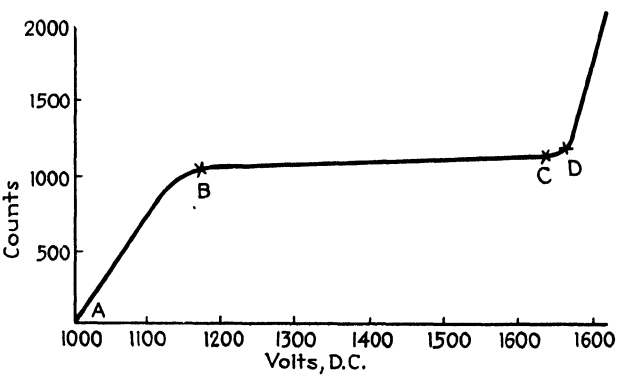

FIGURE 3

tween (*A*) and (*B*) on the curve is known as the proportional range. The tube will count between the corresponding voltages essentially in proportion to the voltage applied, until it reaches a voltage corresponding to the neck of the curve at (*B*), known as the Geiger threshold, which is a critical value for any one tube geometry and filling.

The curve then becomes essentially flat and linear for a considerable range of voltage until it reaches region (*C*), when it again shows an upward tendency. Increasing the voltage beyond (*C*) brings this curve to (*D*) at which point the tube discharge is not quenched but remains in a state of discharge. This point (*D*) is

known as the breakdown voltage, and the voltage range between (B) and (C) as the plateau.

This length and slope of the plateau is a measure of the quality of the tube; the counters used for the spectrometer have a plateau with a slope of about 5 per cent and length around 700 volts. The threshold voltage is usually 1100 volts. Such counters have a quantum efficiency of about 96 per cent for radiation of 1.54Å and resolution time better than 0.0005 sec.

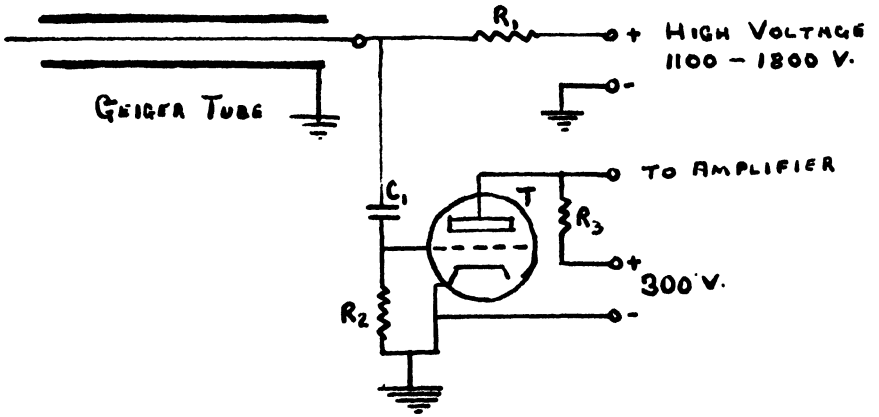

FIGURE 4

Circuit Description

Since the Geiger tube is operated at high potentials it is necessary to couple it to suitable circuits so that the number of counts can be measured; these, of course, are a function of the intensity of the radiation passing the window. This may be achieved by the use of a coupling circuit such as the simplified preamplifier shown in Fig. 4.

The center wire of the tube is connected through a high resistance, R_1, to the high voltage DC source while the cathode or cylinder is grounded. A mica condenser connects the anode to the grid of a triode which has also a suitable grid leak resistor, R_2, connected to ground.

When the Geiger tube is in a quiescent condition, no voltage will pass C_1. If a particle enters the tube and initiates a count, the voltage drop across R_1 will be transmitted through C_1, to the grid of the triode and alter the voltage on the plate of the triode. This is further amplified in other circuits until a usable signal is obtained.

The number of counts obtained, which is the measure of intensity, can be indicated in three ways; (1) by direct counting with an electromechanical counter, (2) by an integrating meter circuit that measures frequency, (3) by automatic recording. The use of the direct counting method is obviously the more accurate, providing the circuits have sufficient resolution. The main limiting factor in such a case is the electromechanical counter, presently available models of which will resolve up to 60 counts per second. The intensities obtainable with the spectrometer, however, can give counts in excess of 3000 per second for strong diffraction lines.

In order to overcome the limitation of the electromechanical counter, scaling circuits are employed that enable a selection of scaling factors of 2, 4, 8, 16, 32 or 64, in the counts supplied to the mechanical indicator. The scaling circuits make use of a series of similar circuits that will cut down the number of pulses passed on to the counter by a factor of 2 for every one employed. The length of time over which the electromechanical counter will operate is controlled by a variable range timer that

shuts it off after the preset time has elapsed. The ranges usually employed are 15, 32, and 60 seconds, and the intensity can thus be recorded as counts per second or counts per minute, as desired. A test pulse generator is incorporated and is synchronized with the 60-cycle input line so that the functioning of the various parts of the circuit can be checked independently of the Geiger tube.

A block diagram for the whole measuring unit is shown in Fig. 5. Typical cir-

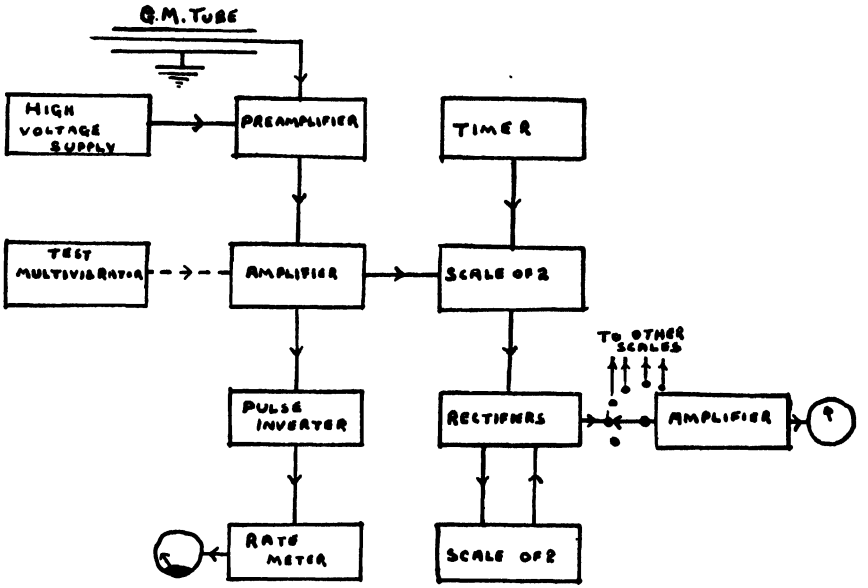

FIGURE 5

cuits employed for the scaling, mechanical counter, amplifier and timer sections are shown in Fig. 6; the frequency meter circuit is shown in Fig. 7.

Circuit Operation

In the frequency meter circuit the negative pulses from the Geiger-Muller tube are amplified by the preamplifier and following stage, and passed on to an inverter circuit that equalizes and differentiates the pulses. The equalized pulses are then introduced into the pentode rate meter circuit that averages the frequency of delivery of the counts, over a time interval dependent on the size of the damping capacitor employed in the plate circuit.

The scaling circuits in Fig. 6 are so arranged that each scale of two represents a regenerative feedback two-stage balanced amplifier, with two states of stable equilibrium. If a pulse is passed to the grids it is regeneratively amplified and the conductance of one triode is increased while the other triode approaches cutoff; this condition prevents further amplification and the circuit is then in a stable condition. If another pulse is then impressed on the grids the current flowing to the plate of the other triode is increased and amplification again ceases when cutoff conditions are attained.

This characteristic of two states of stable equilibrium enables alternate pulses to be taken off the plate on one side of the triode pair, thus giving a scale factor of two. The output pulses from one triode pair are then passed on to another triode amplifier biased to cutoff, so that pulses of the correct polarity and voltage are available to the next stage of two. A selector switch enables the scaling factor to be selected and

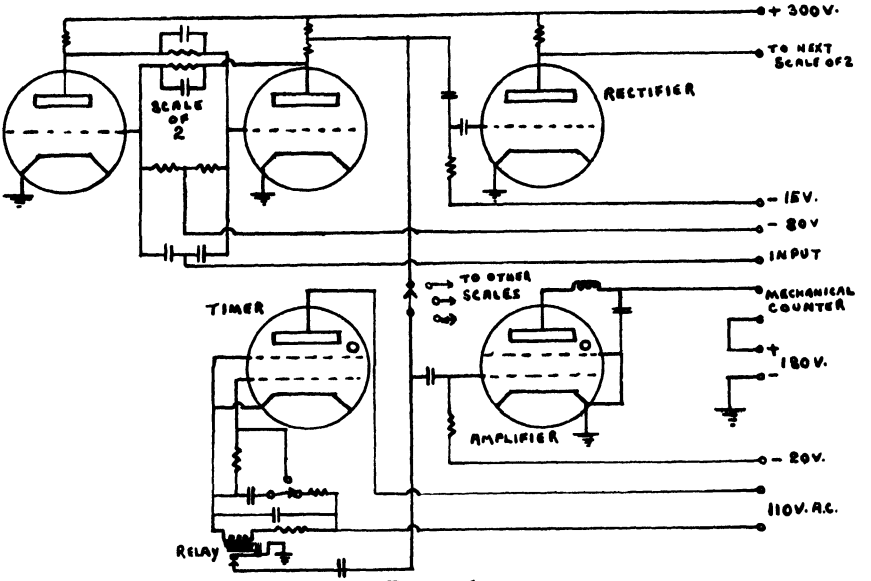

FIGURE 6

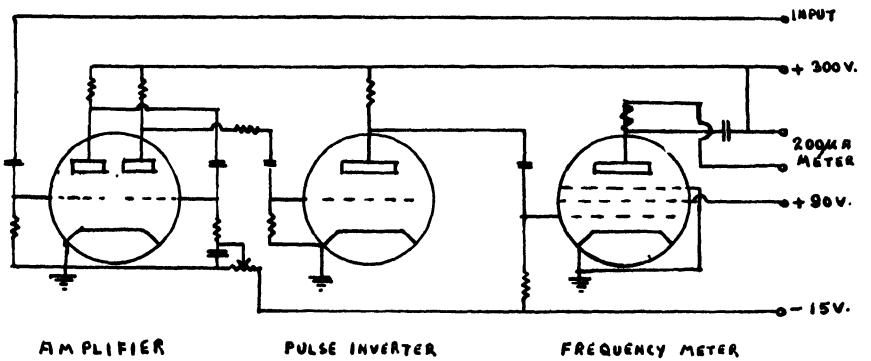

FIGURE 7

passes the pulse on to a thyratron biased to cutoff, so that when a signal does arrive the plate current in the tube will be sufficient to operate the electromechanical counter. The automatic timer is driven by a synchronous electric motor that operates a relay after the preset time interval, and by-passes to ground the pulses from the first scale of two.

X-ray Source

The x-ray tube is of a special line focus design encased in a protective shield. The normal operating conditions are 35 kv and 6 ma, which supplies adequate energy to operate the spectrometer. Alternating current is fed to the x-ray tube and the whole unit is stabilized by a built-in voltage regulator of the saturable type.

In order to insure constancy of x-ray output, a specially designed compensator is added that automatically compensates for the drift in tube milliamperage that occurs before stability is reached. These precautions result in a constancy in x-radiation

output energy that is better than 1 per cent under normal power line conditions. The x-ray tube is readily interchangeable within a matter of a few minutes, when it is desired to change the type of radiation. Provision is made to insert suitable absorption filters in the x-ray beam to remove the unwanted β-radiation.

Operation

If automatic recording is desired it is achieved by attaching the drive of a small synchronous motor, to the goniometer vernier dial, and by the connection of the frequency meter terminals, to the input of a fast response strip recorder. A microswitch is actuated by a cam on the motor for each degree, and by means of a solenoid-actuated pen on the recorder the angular position of the analyzer arm can be indicated along the chart length. The alternate method of using the instrument is to rotate the vernier knob by hand and watch the frequency meter dial. Whenever a diffraction maximum is received by the Geiger tube system a sharp rise in the meter reading will be noticed. Adjustment of the angular position of the analyzer arm will enable the maximum intensity on the meter to be determined.

The goniometer angle reading can then be obtained, and will indicate a value in degrees which is equal to twice the Bragg angle. The intensity of the line is read off the meter scale. This method has the advantage of being fast and the accuracy of the intensity value will depend on the meter accuracy, which is usually 2 per cent.

If weaker lines are sought or greater accuracy of intensity data is required, a point-by-point plot of intensity against Bragg angle can be obtained by using the scaling circuit in such a way that a suitable number of counts are obtained on the mechanical counter to obtain good proportionality.

Specimen Preparation

Either solid or powder specimens may be employed, and though the preparation is critical in some cases it is usually quite simple. Powders, for reasons of uniformity, are reduced to 200-mesh size, and may be pressed into a hole in a glass slide about 12 mm in diameter, with or without the addition of a binder, as required. The surface is then leveled off so that the powder layer is in the same plane as the glass surface. The slide may then be placed in the specimen holder and is ready for use. In cases where preferred orientation would result from such pressing of powders, the specimen can be mixed with a small amount of binder and smeared on a suitable plate of a material that will not give rise to an interfering pattern of its own, such as a glass microscope slide. Solid specimens, such as metallic samples, can be prepared by making flat discs about one inch in diameter and up to ¼ inch thick. These are given a rough polish on one side with emery cloth, electrolytically etched to remove the effects of cold working, and are then ready for use.

For optimum conditions it is required that the specimens shall have a curvature of the same radius as the arc of the focussing circle. Since this radius changes with the angle at which the goniometer arm is set, a perfect focussing condition is difficult to attain for all parts of the angular scale.

However, if a series of curved specimen mounts is prepared, each to cover a range of 10° of the 90° quadrant and of the same curvature as the focussing circle for each increment, it is possible to obtain optimum focussing conditions. By this procedure components present in a mixture to a value of less than one per cent can be quantitatively and qualitatively evaluated. In most instances it is unnecessary to do this, since sufficient accuracy can be obtained for usual purposes with a flat specimen.

A great variety of techniques may be successfully employed, such as orientation studies, where a vertical goniometer is inserted in the specimen mount position. For fiber studies the intensity data of the pole figures may be quantitatively studied. Within recent years great attention has been focussed on the x-ray method of particle size determination for the range where the average crystallite size is below 1000Å.

Recent reports in the literature[9, 10] give full details on the method which employs an evaluation of the half intensity breadth of a diffraction maximum.

The simplicity and reproducibility of specimen preparation simplifies the whole

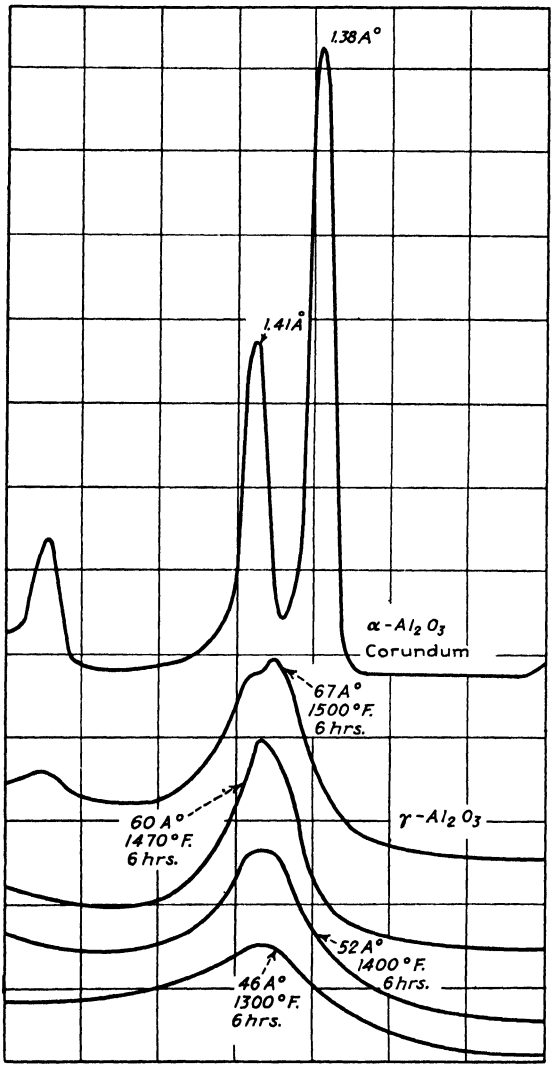

FIGURE 8. Set of curves showing the effect of various heat treatments of gamma alumina. The sharpness of the line increases with greater particle size. Prolonged heating at high temperatures will produce alpha Al_2O_3 or corundum.

procedure, and by keeping the spectrometer geometry fixed, accuracy of the determination can exceed 5 per cent for the range below 300Å.

Fig. 8 shows a typical set of curves obtained from samples of γAl_2O_3 that have been heated at different elevated temperatures for the same period of time. As the temperature of treatment becomes higher the diffraction lines become more sharp,

until signs of the formation of αAl_2O_3 can be seen in the pattern of the material heated to 1500° F for 6 hours. A pattern may be obtained from a powder sample of αAl_2O_3 within a total sample preparation and scanning time of 35 minutes, which represents a considerable factor over the time taken to obtain comparable results from any film technique.

An overall picture of the apparatus is given in Fig. 9.

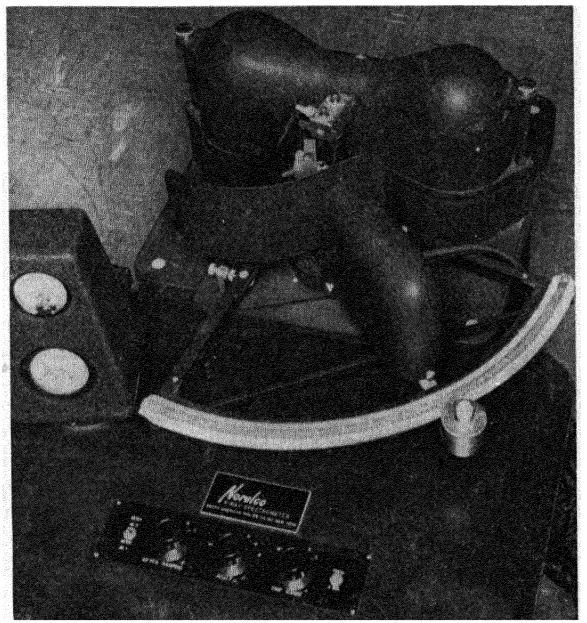

FIGURE 9

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Some Practical Aspects of Electron Microscopy

V. K. Zworykin and J. Hillier

RCA Laboratories, Princeton, N. J.

It is likely that the electron microscope would have been developed even if the wave nature of the electron had never been discovered; natural scientific curiosity would have insured that. However, when the possibility of producing an electron lens was realized [1, 2] the knowledge that a wave, much shorter than that of light, was associated with the electrons led very soon to the hope of using electron lens systems to observe submicroscopic entities. This provided an impetus which led to an unusually rapid development, not only of a new instrument but of a whole new science.

In the preceding volume of this series Prebus [3] has provided an extensive review of the theory of the electron microscope, including in particular, the theory of the electron lens and the structure of the image. He has also discussed, relatively briefly, the applications of the instrument. In the present paper, it is the intention of the authors to attempt to add to the value of the above mentioned paper by discussing the electron microscope from the point of view of its user—in particular of the user interested in technological problems. The discussion will include the basic theory of the operation of the instrument, many of the difficulties and an itemized list of applications.

Introduction

Shortly after Busch showed mathematically that electrostatic or magnetic fields possessing rotational symmetry behaved as lenses for electrons a great volume of theoretical mathematical analysis was published which firmly established the exact equivalence of geometrical electron and light [4-9] optics. However, such theory has had only a slight effect on the design of electron microscopes and even less on their use. In fact, three basic facts which appear in the first work of Busch are sufficient to explain all the first order phenomena that can be observed in the operation of an electron microscope. First, the well-known simple lens formula:

$$\frac{1}{v} - \frac{1}{u} = \text{const.} = \frac{1}{f} \tag{1}$$

must apply to an electron lens, where u and v are object and image distances, respectively, measured in the same direction from the center of the lens. Secondly, the imaging process is exact only for the single ray coinciding with the axis of symmetry of the lens. The further a ray departs from coincidence with the axis the further the image departs from an exact representation of the specimen. Thirdly, there is associated with imaging by a magnetic lens, a rotation of the image which is proportional to $\int_{z_0}^{z_i} H(z)dz$ where $H(z)$ is the value on the axis of symmetry of the magnetic field component parallel to the axis and z_o and z_i are the axial coordinates of the object and image respectively.

Accurate measurements would show the first of these statements to be only a first approximation in the case of any usable electron lens. Actually, if the thickness of the lens is of the same order of magnitude as the focal length (f), the object and image distances must be measured from certain fixed planes, called principal planes. Furthermore, it is possible for the object, image or focal points to be situated within the field of an electron lens, that is, within the lens itself in which case even the principal planes are not fixed. Since such departures from the simple formula make themselves apparent to the operator of an electron microscope only through unusual tests and very accurate measurements they will be considered as being of only incidental interest in the following discussion.

In a transmission electrostatic electron microscope where the lenses usually have a fixed focal length Equation (1) can be used directly. However, most of the electron microscopes being used at the present time are transmission instruments using lenses of the magnetic type. The whole evolution of such instruments has centered about the fact that it is possible to vary the strength of a magnetic type electron lens merely by varying the current flowing in the exciting coil. That is,

$$\frac{1}{f} = F(Ni) \tag{2}$$

Where Ni is the number of ampere turns used to excite the lens. The function $F(Ni)$ depends on the magnetic field distribution along the axis of symmetry of the lens and is seldom a simple function. In fact, when the lens system contains iron the magnetic field distribution is itself a complicated function of (Ni). At present these complexities prevent analytical methods from producing accurate practical results.

One type of magnetic field which can be solved analytically [10] and which approximates the fields found in actual lenses,[11, 12] is given by the expression

$$H(z) = \frac{H_o}{1 + (z/a)^2} \tag{3}$$

where H_o is the maximum value attained on the axis by the component of the magnetic field parallel to the axis and $2a$ is the half-value width of the distribution. If the complete field is used for imaging, that is, the lens is used as a projector, the refractive power can be shown to be given by the expression

$$\frac{1}{f} = -\frac{1}{a(k^2+1)^{\frac{1}{2}}} \sin\left[(k^2+1)^{\frac{1}{2}}\pi\right] \tag{4}$$

where

$$k^2 = \frac{eH_o^2a^2}{8mc^2\Phi} = \frac{0.022}{V} H_o^2a^2$$

Φ is the potential through which the electrons have been accelerated and c, m and e represent the velocity of light, the mass of the electron and its charge respectively. In the practical expression V represents the accelerating potential in volts. If the thin lens formula as given by Busch [2] is used for the refractive power of such a lens, the following expression is obtained

$$\frac{1}{f} = \frac{e}{8mc^2\Phi}\int_{z_o}^{z_i} H^2(z)dz = \frac{0.022}{V} H_o^2a\frac{2\pi}{2} \tag{5}$$

After converting H_o into ampere turns through the expression

$$\frac{4\pi Ni}{10} = \int_{-\infty}^{\infty} H(z)dz = H_oa\pi \tag{6}$$

the expressions in (4) and (5) are plotted in Fig. 1 as well as the refractive power of an actual lens. It can be seen that over a large part of the range of currents used

in the practical case Equation (4) gives a good approximation to the experimental value. Equation (5) which is simpler for computation gives a value which is satisfactory for most work. However, as soon as iron of the pole pieces approaches saturation the experimental curve departs radically from both the others. In the following Equation (5) will be used almost exclusively because of its simplicity. The errors introduced by the use of this equation are an order of magnitude smaller than the effects to be considered.

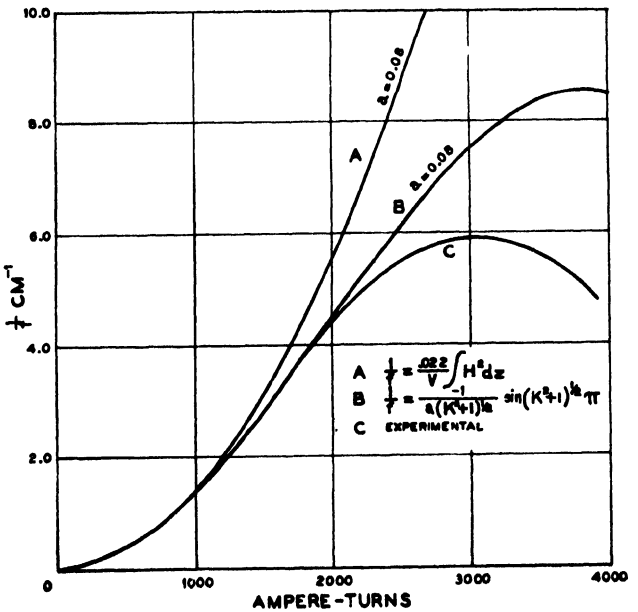

FIGURE 1.

The Electron Microscope

Fig. 2 is a simplified ray diagram of the electron microscope which can be seen to be a complete electronic counterpart of a high power compound light microscope. (See also Fig. 3.) Fig. 2 applies equally well to electrostatic or magnetic systems, though some of the more recent of each type are not arranged in quite the same way.

The electron gun produces somewhere on the axis of the instrument an image of the emission from the microscope filament. This image is marked in Fig. 2 as the electron source of diameter d_k situated a distance u_c from the condenser lens. The condenser lens situated a distance v_c' above the specimen images the electron source at some position along the axis of the instrument and thus controls the irradiation of the specimen. The rays in the vicinity of the specimen and objective are represented on a larger scale to the right of the encircled region.

All points of the specimen are irradiated by similar pencils of electrons. On traversing the specimen each of the pencils is altered by interaction with the specimen in a way which depends on certain physical properties of the specimen points. The action of the objective is to select from each pencil a certain group of electrons and to focus them to a point which occupies a position in the image geometrically similar to that occupied by the point of origin of the pencil in the specimen. Thus the image is seen to consist of intensity variations arranged according to a geometrical representation of the specimen. In discussing resolving power and image inter-

pretation, it must always be remembered that there can be no image without variation in intensity, regardless of the perfection of the imaging system.

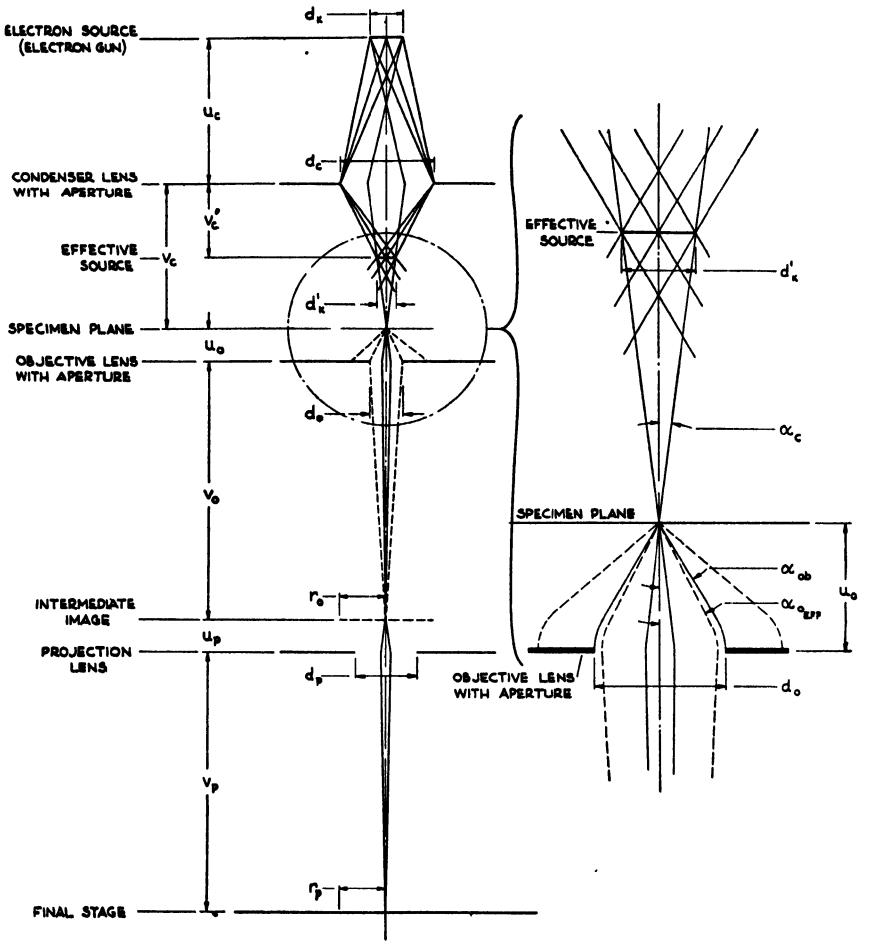

FIGURE 2. Ray diagram of the electron microscope.

Actually the sharply defined cone of electrons which irradiates each point of the specimen is scattered so that on leaving, it is diffused into a somewhat larger and less sharply defined cone. The aperture of the objective, actual or effective, prevents the more widely scattered electrons from reaching the image point and hence causes a reduction in intensity of that point. Since the scattering at the specimen point depends on its physical properties there is a correlation between the intensity of the image and the nature of the specimen. While this phenomenon is responsible for the intensity variations which constitute the electron microscope image, it is now well known that little use can be made of it in the interpretation of those images.

The Illuminating System. In light microscopy the lens systems are of such high quality that the most important aberration is that which is inherent in the nature of the light itself, namely, diffraction. In order to minimize the diffraction defect, the apertures of the lenses are made as large as possible. In electron microscopes, how-

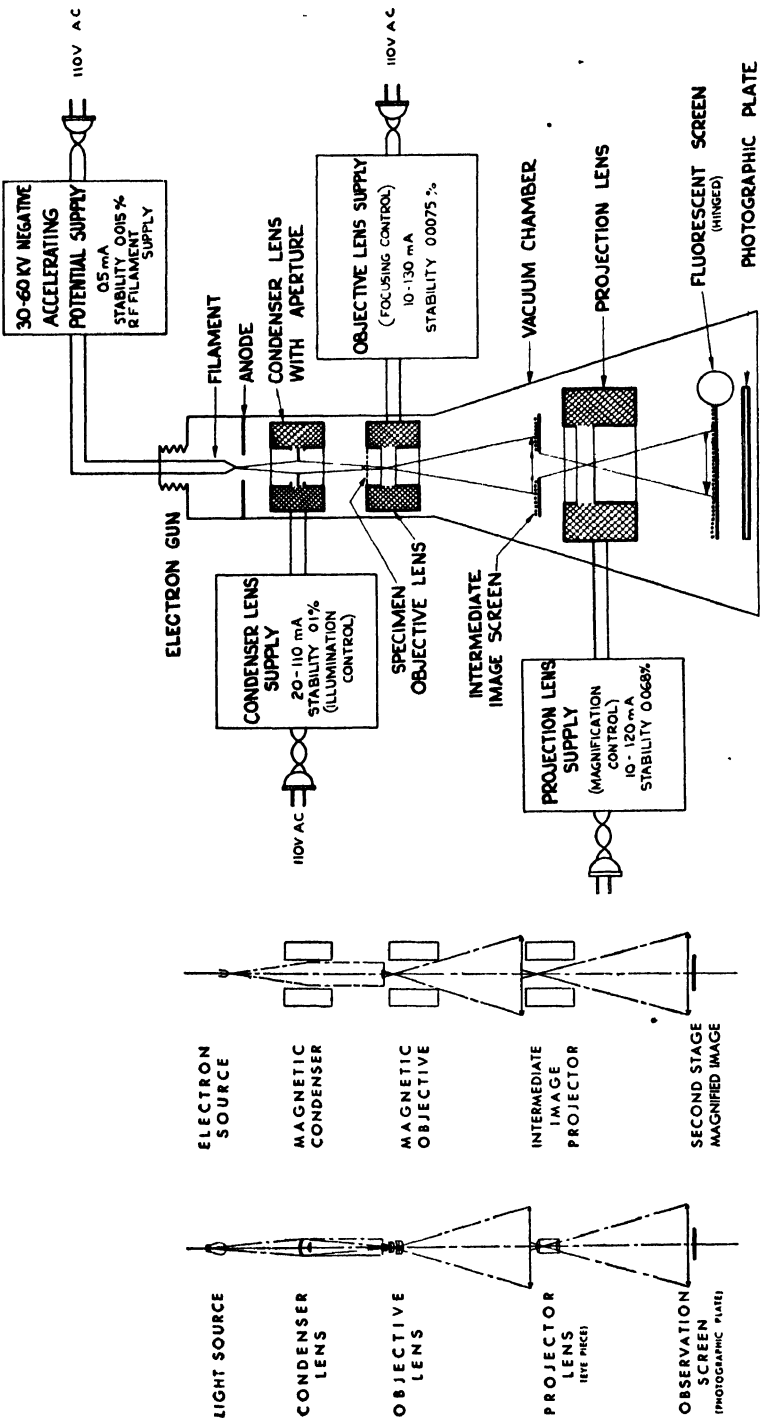

FIGURE 3. Simplified diagrams comparing light and electron microscopes and a more complete diagram showing the arrangement of a magnetic electron microscope.

ever, the opposite is true at present. The lens aberrations are all quite large requiring the use of extremely small apertures if high resolving power is to be obtained. While it is usually pointed out in articles on the electron microscope that for optimum results the objective aperture should have a value for which the resolving power, as limited by the lens aberrations, and the resolving power, as limited by the diffraction defect, are approximately equal, it is seldom—if ever—carried out in practice. The technical difficulties of placing a perfectly clean aperture of exactly the right dimensions at the exact *electron optical center* (not mechanical) of the objective lens have never been satisfactorily overcome. Furthermore, tests in this laboratory have shown that such an aperture gives an improvement, in practice, in only very special cases.[13]

Large aperture operation in which the objective aperture is very large relative to the optimum is more commonly used. The aberrations that would normally accompany such a mode of operation are reduced almost to their minimum value by using illumination which has a very small angular aperture. The theory of this type of operation is beyond the scope of the present paper [14] but it should be pointed out that in the thin specimens which are suitable for the electron microscope the diffusion of the imaging pencils is slight, so that the rays leaving a point of the specimen do not fill the entire aperture of the objective but only a small part of it. This provides, with regard to the aberrations, an effective angular aperture which is only slightly larger than that of the illumination.[15] Of course this effective angular aperture varies with the properties of each specimen point; for thicker parts of the specimen it is larger. Even in this case the effective angular aperture does not become indefinitely large because the action of the aberrations themselves provide a diaphragming effect by diffusing the widely scattered electrons over the entire image plane. It is obvious from this that the control of the aperture of the *illumination* is the most important single factor in the operation of the present day electron microscope.

In the electron microscope as in any lens system, the intensity and angular aperture of illumination are inseparably related. The temperature of the emitter is the only method of independently controlling the intensity of illumination of the specimen which is given by

$$I_s = 4I_k\left(\frac{u_k}{d_k}\right)^2\alpha_c^2 \tag{7}$$

where I_k is the specific emission controlled by the temperature of the emitter. (See Fig. 4.)

The important role played by the angular aperture of the illumination in producing good quality electron micrographs was realized quite early, and while the part played by the condenser was worked out, it is only recently that the part played by the electron gun itself has been investigated thoroughly.

We shall first consider the case represented in Fig. 2. Then the angular aperture of irradiation is half the angle subtended at a specimen point by the effective source of diameter d_k'. That is

$$\alpha_c = \frac{d_k'}{2(v_c - v_c')} \tag{8}$$

Since the magnification of this system is given immediately by the ratio v_c/u_c the expression for the angular aperture of the illumination can now be written

$$\alpha_c = \frac{-d_k}{2\left(\frac{u_c v_c'}{f_c} + v_c' - u_c\right)} \tag{9}$$

where u_c and d_k are considered constant for the present. This expression becomes infinite for one value of $\frac{1}{f_c}$ if the electron source is above the condenser as indicated

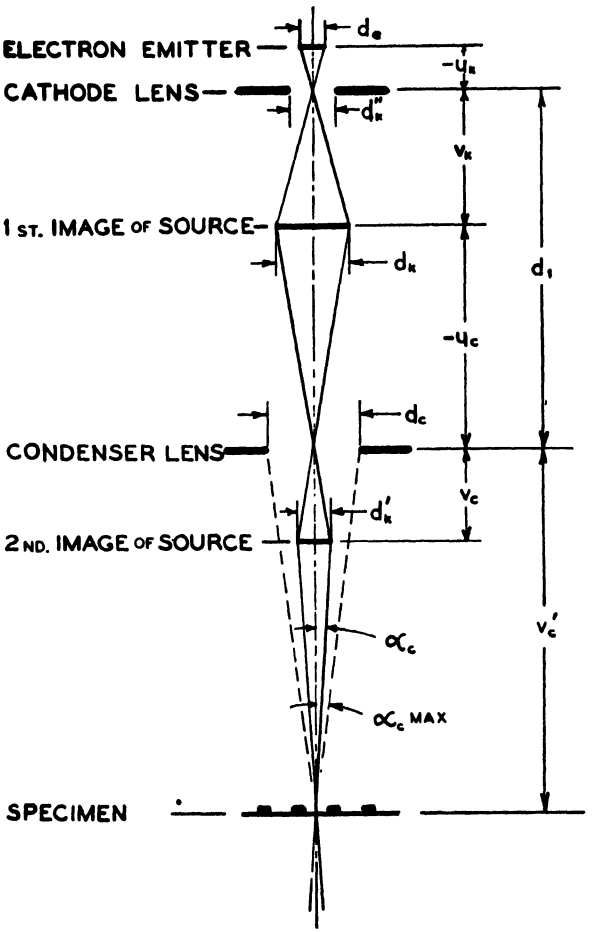

FIGURE 4. A diagram of the illuminating system of an electron microscope illustrating the meaning of the symbols used in the text.

in Fig. 2, that is if u_c is negative. However, the aperture in the condenser lens sets a maximum value to α_c:

$$\alpha_c(\max) = d_c/2v_c' \tag{10}$$

Substituting a set of practical values: $d_c = 1.0$ mm, $d_k = 0.030$ mm, $u_c = -160$ mm, and $v_c' = 160$ mm, leads to the expressions

$$\alpha_c = \frac{5.4 \times 10^{-7}}{\frac{1}{80} - \frac{1}{f_c}} \text{ for } \alpha_c \gg 3.12 \times 10^{-3} \text{ radian} \tag{11}$$

This is plotted in Fig. 5 to show the variation of the angular aperture of the illumination with condenser power.

The above discussion is the one usually found in descriptions of an electron microscope illumination, but it does not represent the situation as it occurs in actual practice. Normally, instead of the single lens system described here the electron microscope source includes two lenses, the condenser and the cathode lens formed by the shield or apertured diaphragm placed in front of the emitter of the electron gun. The

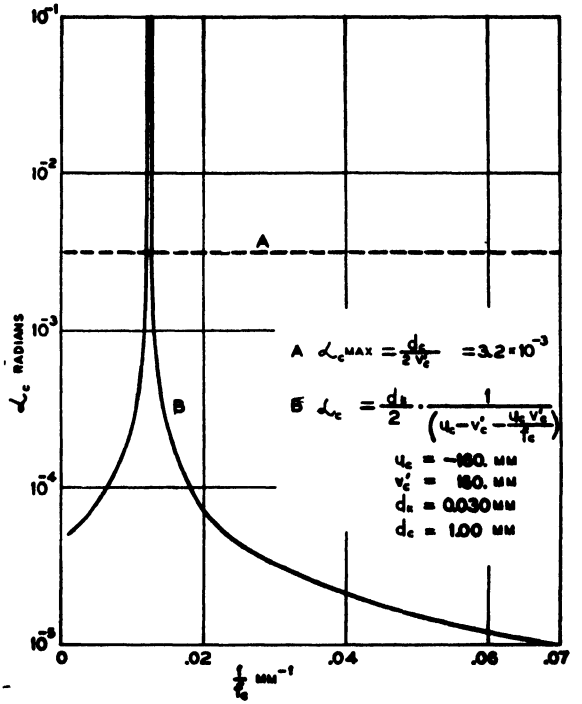

FIGURE 5. Angular aperture of illumination plotted as a function of the power of the condenser lens where it is assumed that the illumination originates from a source of diameter d_k situated above the condenser lens.

application of a negative potential to this shield or the use of a mechanical adjustment of the position of the emitter has always provided a means of adjusting the electron beam but the idea that this adjustment involves the control of the strength of a lens at the cathode position does not seem to have been ever brought out clearly.

If, in the following discussion, the concept of a lens at the cathode position of variable strength $1/f_k$ of aperture d_k'' and of object distance u_k is introduced, the dependence of α_c on $1/f_c$ will be found to change radically according to the value of $1/f_k$. Other dimensions and symbols are represented in Fig. 4. For simplicity in the following discussion the position of the image formed by the cathode lens and represented by v_k will be taken as the independent parameter. In this way the only discrepancy introduced by the lack of knowledge of the behaviour of the cathode lens will be a constant magnification factor determining the value of d_k.

The angular aperture of the illumination is determined by the smallest of three factors: (1) Half the angle subtended at the specimen by the condenser aperture. This is constant and represents the maximum possible value of $\alpha_c \gtrless \alpha_{c(max)}$ as given in (11). (2) Half the angle subtended at the specimen by the image of the cathode aperture d_k'' produced by the condenser. In this case

$$\alpha_c \gtrless \frac{-d_k''}{2\left(\frac{u_c v_c'}{f_c} + v_c' - u_c\right)} \tag{13}$$

(3) Half the angle subtended by the image of the electron emitter as produced by the combined action of the condenser and cathode lenses. In this case, if d_e is the diameter of the emitter

$$\alpha_c \leqq \frac{d_e}{2} \cdot \frac{v_k}{u_k} \cdot \frac{v_c}{u} \cdot \frac{1}{v_c - v_c'}, \tag{14}$$

where $u_c = v_k - d_1$ and the simple lens formula holds so that

$$\alpha_c \leqq \frac{d_e}{2} \cdot \frac{v_k}{u_k} \frac{1}{v_c'} \cdot \frac{1}{(v_k - d_1)\left(\frac{1}{f_c} - \frac{1}{v_c}\right) + 1} \tag{15}$$

these curves have been plotted, for various values of v_k and d_k'', in Fig. 6. It can be

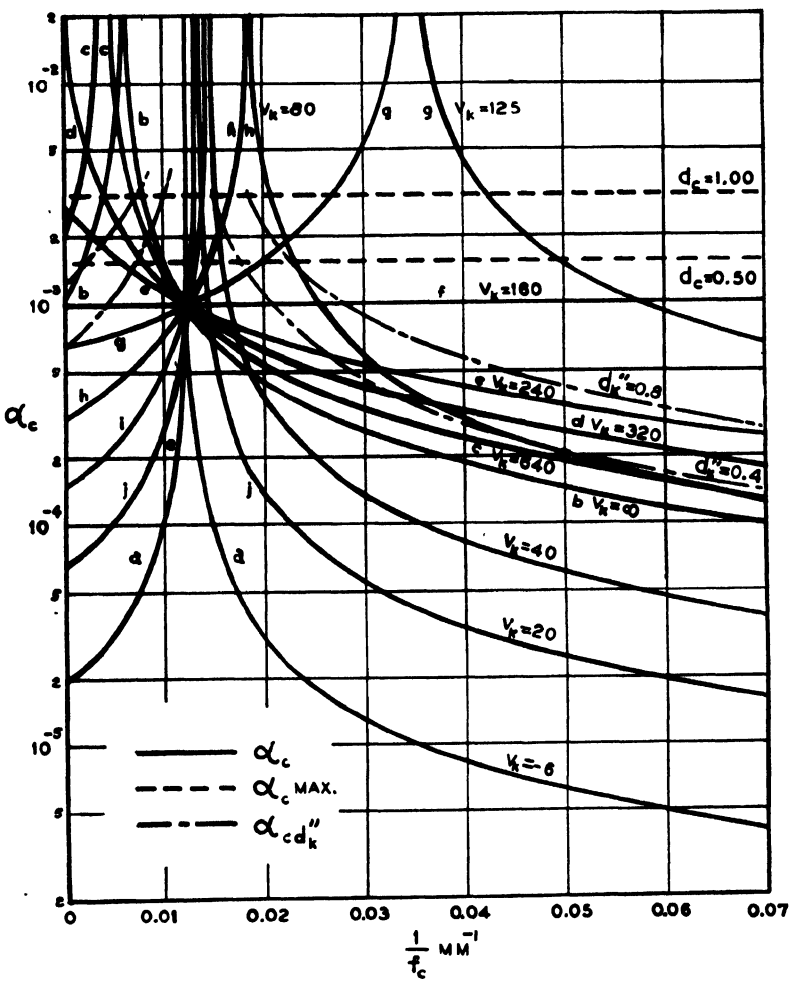

FIGURE 6. The angular aperture of the illumination plotted as a function of the power of the condenser lens where it is assumed the illumination originates from an image of the actual source produced by the cathode lens system. The position of this image on the optic axis, relative to the cathode lens, is the variable parameter. Other factors which control the angular aperture are also indicated.

seen that changes in the gun adjustment can produce radical changes in the way in which α_c depends on $1/f_c$. In fact for values of v_k lying between d_1 and $d_1 + v_c'$ the

image of the source cannot be made to coincide with the specimen plane for any condenser power. Furthermore, when $v_k = d_1$, that is, the image of the source coincides with the plane of the condenser, the value of α_c as determined from (15) is constant, the condenser having no effect whatever on the position of the image of the source. In these special cases (13) and (14) control the actual value of α_c.

The microscopes used in this laboratory have been found to agree quite well, qualitatively, with these curves. For instance, if the maximum intensity is measured for different cathode lens powers (as u_k increases for one type of electron microscope) the curve shown in Fig. 7 is obtained. The second minimum occurs naturally

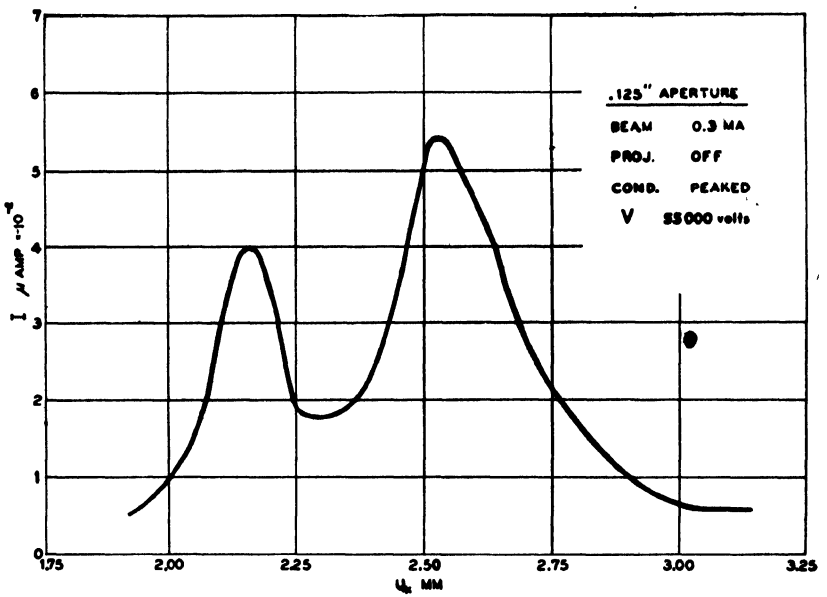

FIGURE 7. An experimental curve showing the relationship between the maximum intensity of illumination for various adjustments of the cathode lens.

as a result of dependence of α_c on $\frac{1}{f_k}$ as demonstrated by the maximum permissible values of α_c on curves a, b. . . . j taken in that sequence. According to (6) I_s should increase as the square of u_k. In the actual case, however, it reaches a maximum value and then decreases rapidly for larger values of α_c. Space charge can account for this last effect.

Figure 8 is a sequence of enlarged images of the electron distribution on the specimen plane for a number of qualitatively defined values of $1/f_k$ corresponding to approximately 2.2, 2.25, 2.35, 2.50, 2.60 and 2.75 mm respectively for the value of u_k. These patterns are normally observed at the intermediate screen of conventional electron microscopes. The specimen is removed and the objective current lowered sufficiently so that the magnification is reduced and the entire pattern made visible on the screen. The value of $1/f_k$ which is chosen as the optimum is that for which the intensity for $\alpha_c(max)$ is a maximum. (See Fig. 7.) Fortunately, this value corresponds to one which gives a satisfactory curve for α_c *vs* $\frac{1}{f_c}$. (See Fig. 6, curve (j), and Fig. 8d.)

The origin of the ring of secondary sources Figs. 8 (d-f) appears to be in a total

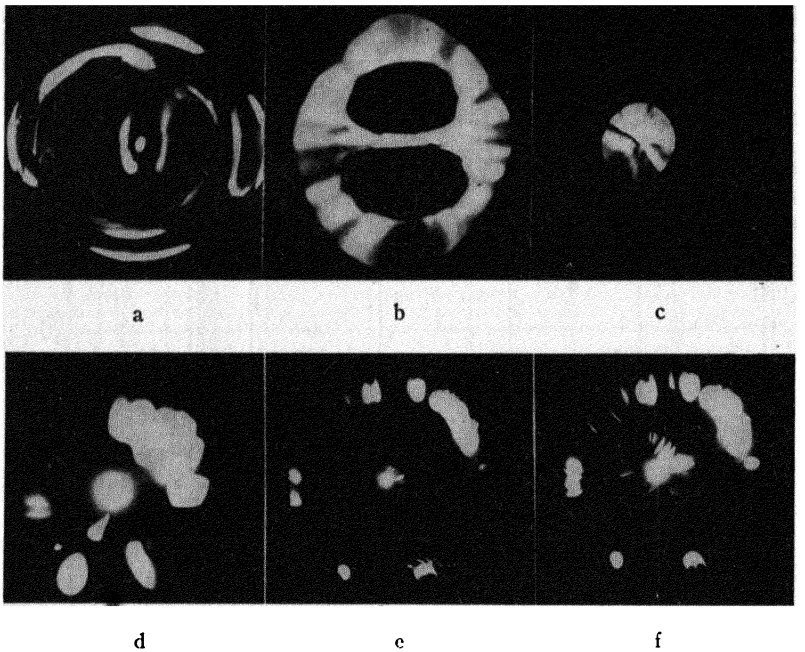

FIGURE 8. A sequence of enlarged images of the illumination of the specimen for various adjustments of the cathode lens system. In each case the power of the condenser was adjusted to give the maximum intensity at the center of the pattern.

reflection phenomena produced by the equipotential surfaces near the edges of the shield aperture. These secondary sources can be a source of many image defects in the electron microscope and must be eliminated. The irregularities are known to be due to the corresponding irregularities in the emission over the surface of the emitter and not due to irregularities in the edge of the aperture. It is known that the coating of semi-insulating carbonaceous material which forms on bombarded electrodes in demountable systems greatly enhances the intensity of this ring. This contamination can produce the spurious sources in an otherwise satisfactory gun, and it requires that the shielding aperture be cleaned and polished periodically. It is also known that for 50-kv electrons the diameter of the shield aperture must exceed a certain minimum dimension (3.0 mm in RCA electron microscopes) if the spurious sources are to be eliminated even with a clean system. Finally, it is necessary for the wires of the filament to run directly back from the bent tip. Fig. 9 (a) and 9 (b) show diagrammatically the essential features of a satisfactory and an unsatisfactory electron gun of the type used in electron microscope.

The Objective Lens. The objective lens of an electron microscope is often referred to as the heart of the instrument though like its living counterpart, it can hardly function without the supporting action of the remaining components. The quality of an electron microscope objective is determined by the design and precision of manufacture. Thus, the operator has little control over the ultimate resolving power attainable with his instrument and so has little more than an academic interest in the design factors which control that resolving power. He is vitally concerned, however, with the techniques of continually attaining that resolving power in his images. One of the most important of these techniques has been described above.

The operator's most direct contact with the objective is through the focusing of

the instrument which he does visually (usually) on the final fluorescent screen. If, for the present, it is assumed that the objective is a hypothetically perfect lens then the only possibility of a poor image arises in the possible inaccuracies of focusing. The range of adjustment over which a satisfactory focused image is obtained is defined as the depth of field.

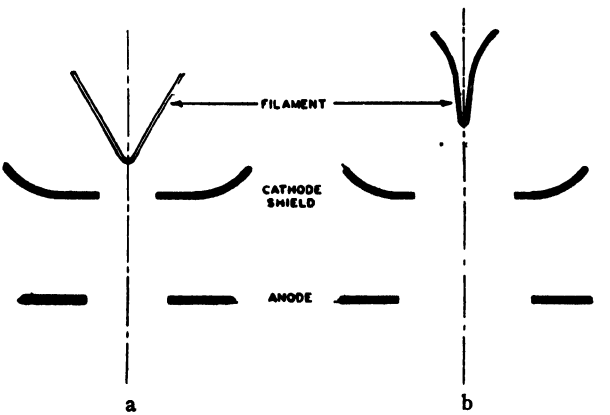

FIGURE 9. A diagram comparing the qualitative features of a bad (a) and good (b) arrangement of an electron microscope filament. In the good arrangement the filament has been pinched so that the wires run close together—almost parallel to the axis of the system and the cathode shield aperture has been made considerably larger.

The objective lens is a lens of variable focal length f_o producing an image on a fixed image plane at v_o.

Thus, the plane imaged by the objective varies with change in objective power according to the simple lens equation applied to the objective:

$$\frac{1}{v_o} - \frac{1}{u_o} = \frac{1}{f_o} = \frac{k_o(N_o i_o)^2}{V} \tag{16}$$

for the case where $v_o >> u_o$. In other words, the image at v_o will consist of an enlarged reproduction of the electron distribution in the conjugate plane at $u_o \cong -f_o$ providing, of course, that none of the electrons in that distribution make angles with the axis greater than the acceptance angle of the objective. Now, if the objective current is adjusted so that the imaged plane at u_o is displaced by an amount Δu_o from the actual object plane the electron distribution, of which the image is formed, is the shadow cast on the displaced imaged plane by the specimen under conditions of illumination characterized by the angular aperture, α_c. Thus, electrons leaving any specific point of the specimen will cover in the imaged plane a circular area, "circle of confusion," of radius $\Delta u_o \cdot (\alpha_c + \alpha_s)$ where α_s is half the angular half-width of the scattering introduced by the material of the specimen at the point in question.

$$\alpha_c + \alpha_s \gtrless \alpha_o$$

where α_o is the angular aperture of the objective as defined by a physical aperture. If this radius is equal to the desired resolving power d, Δu_o is the amount that the imaged plane may be displaced from the true object plane in either direction. Then $2\Delta u_o$ is the depth of field, T, of the objective.

$$2\Delta u_o = T = \frac{2d}{\alpha_c + \alpha_s} \tag{17}$$

This equation serves to illustrate once again the supreme importance of obtaining the optimum adjustment of the illuminating system. It also emphasizes another basic phenomenon of electron microscopy, namely, that *the electron optical behaviour for each point of the image is a function of the physical properties of the corresponding point of the object.* For instance Equation 17 shows that in *one image* the depth of field may vary by more than an order of magnitude, if the acceptance angle of the objective is made small by a limiting aperture, or may vary by several orders of magnitude if large aperture operation is used. Figure 10 gives a survey of the depth

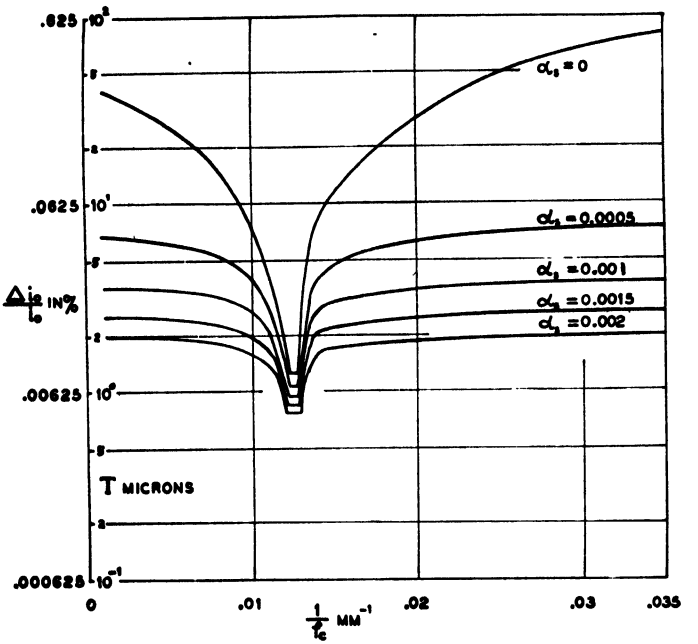

FIGURE 10. The depth of field expressed as a fractional variation of the objective current is plotted as a function of the power of the condenser. The magnitude of the scattering at the specimen is the variable parameter.

of field conditions of a practical objective for which $f_o = 4$ mm, $v_o = 400$ mm, and working under conditions of large aperture operation at an assumed resolving power of 20 Å. Here the depth of field is plotted as a function of the power of the condenser lens $1/f_c$. The depth of field is expressed as an objective current tolerance $\Delta i_o/i_o$.

The fact that the depth of field is at least partly controllable enables the operator to overcome some of the difficulties of focusing the electron microscope at low magnifications. Normally, the magnification used in the electron microscope is an order of magnitude below the useful magnification of the instrument. The reasons for this are numerous. First, the intensity of the final image on the fluorescent screen varies inversely as the square of the magnification, so that low magnifications are desired. Secondly, the exposure time varies directly as the square of the magnification so that low magnifications are indicated if the long-time stability of the power supply is to be within an attainable value. Also, the field of view is inversely proportional to magnification—again indicating the desirability of low magnification.

At magnifications of from 5,000× to 10,000× the details of the image which are separated by the minimum resolvable distance, that is, 20 Å become separated by only

0.01 to 0.02 mm in the image. Fortunately fine grain photographic emulsions can resolve such distances though unfortunately the eye cannot. In fact, the eye can only resolve about 0.2 mm on the fluorescent screen which corresponds to 400 to 200 Å in the specimen. This leads to a fundamental difficulty of operation, which becomes apparent from Equation 17. If we take a practical case where α_o (max) $= 3.12 \times 10^{-3}$ radian and the instrumental magnification is 10,000× the depth of field for visual observation and extremely thin specimens is immediately

$$T = 2.200/(3.12 \times 10^{-3}) \text{ Å} \quad \text{(i.e. } 12.8\mu\text{)}$$

On the other hand, the photographic depth of focus, that is, the depth of focus corresponding to a resolving power of 20 Å is only 1.28 μ. Thus, if the instrument is put in focus in a random fashion one would expect on a statistical basis only one-tenth of the micrographs to have the ultimate resolving power (assuming all other factors are eliminated). The technique of focusing actually used takes care of this difficulty. First, the objective coil currents at which the image seems to just go out of focus in either direction, is determined. Then the value midway between these two extremes is selected for making the exposure. Finally, the power of the condenser lens is adjusted so that α_c is reduced by a factor of ten from α_c(max). This increases the photographic depth of field by a corresponding factor. In this way it is possible to obtain accurately focused images at low practical magnifications. This situation is illustrated in Fig. 11.

If $\alpha_c << \alpha_s$ the technique described above does not lead to consistently satisfactory focusing because α_s is independent of α_c. To overcome this difficulty more recent instruments have light optical stages of magnification which enable the operator to examine the fluorescent image at magnifications as high as 100,000. The use of large aperture optical systems enables the visual intensity of the image to be maintained. This method of focusing has the additional advantage that no change is made in the optics or electrical circuits of the electron microscope in between the focusing and the recording of the image. Unfortunately the mechanical difficulties of mounting large electron microscopes have so far prevented the general use of this method.

A discussion of the practical optics of the electron microscope objective should not be concluded without some mention of the aberrations. Of all the geometrical aberrations only two affect the image in the center. These are the spherical and chromatic aberrations which can be represented in the simplest manner by the expressions:

$$d_{sph} = 0.4C \cdot f_o \cdot (\alpha_c + \alpha_s)^3 \tag{18}$$

$$d_{chr} = K \left(\frac{\Delta V}{V}\right) \cdot f_o \cdot (\alpha_c + \alpha_s) \tag{19}$$

$$\alpha_c + \alpha_s \leq \alpha_o$$

where C is a dimensionless constant characteristic of the objective and K is also a constant. To these aberrations must be added the diffraction defect

$$d_{diff} = \frac{0.61\lambda}{\alpha_c + \alpha_s} \tag{20}$$

where λ is the wavelength of the electrons. It is pointed out that as the spherical aberration is reduced by reducing $\alpha_c + \alpha_s \leqq \alpha_o$ the diffraction defect is increased, so that for a certain value of the objective aperture there is a best resolving power. However, as mentioned earlier the optimum aperture so defined is seldom, if ever, attained in practice. Instead, the specimens are kept thin so that α_s is as small as possible and α_c is kept small by the proper manipulation of the illuminating system as described in the preceding section. The effect of making $\alpha_c + \alpha_s$ much smaller than the optimum value does not seem to have appreciable effect in practice. The theory of such a condition has not been completely worked out. It should be pointed

out, however, that magnetic lenses of the present design have been accurately measured and the aberrations have been calculated. Such calculations show that the resolving power of these lenses should be around 6 Å, leading to a useful magnification as high as 330,000× which has not as yet been achieved.

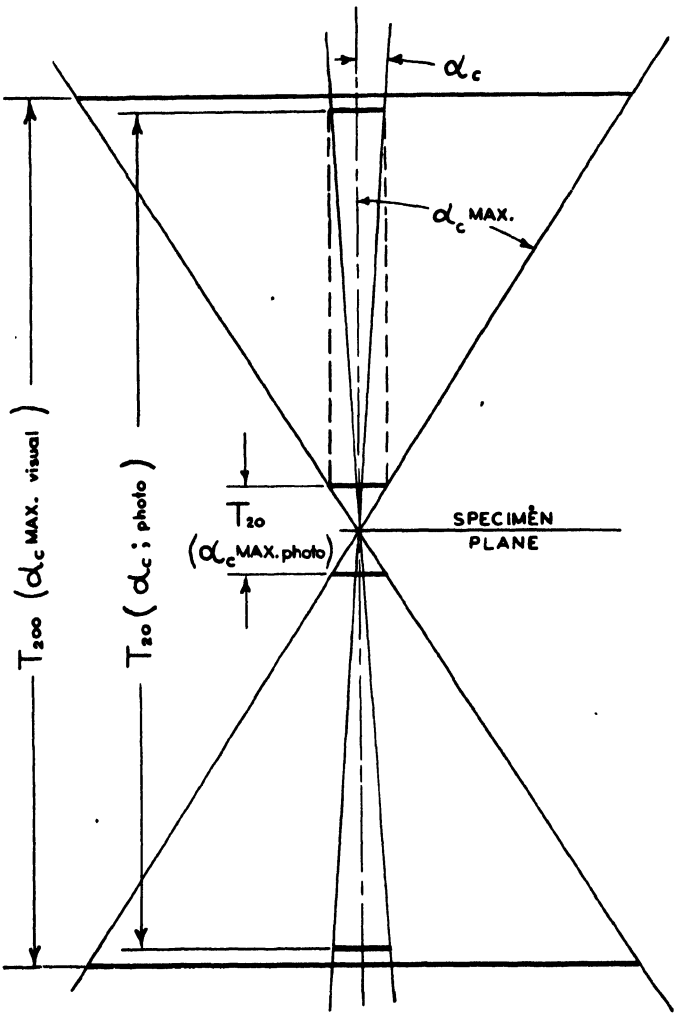

FIGURE 11. A diagram illustrating the difference between visual and photographic depths of field and the method of making them equal by adjusting the angular apertures of the illumination between completion of visual focusing and the making of a photographic record.

Equation 18 indicates that an objective should be operated close to its minimum focal length, that is, at close to the maximum magnification on the curve of an actual polepiece in Fig. 1. However, in practice electron microscope objectives designed for short focal length operation are often operated at focal lengths three to four times normal in order to obtain low magnification images. While such operation achieves the desired results, image quality is sacrificed and alignment difficulties are increased

(by the same factor of three to four). A more satisfactory method of obtaining low magnification images is to remove the polepiece assembly from the objective and use the weak lens formed by the large magnetic gap of the exciting coil. This is possible in most electron microscopes.

In the above, the extreme dependence of the image quality on the nature of the illumination has been pointed out many times. It has always been assumed that the illuminating pencils are in the form of circular cones, that is, α_o is constant and single valued regardless of the direction in which it is measured from the central ray of a given pencil. Defects occurring because α_o exceeds the value indicated by (18) and (20) are expected to appear as a symmetrical diffusion of the image points. In practice, however, the illuminating pencils rarely have a circular cross-section and hence α_o varies accordingly. In extreme cases the illumination may even consist of a number of separate pencils (Fig. 12). Under these conditions it is necessary to keep in

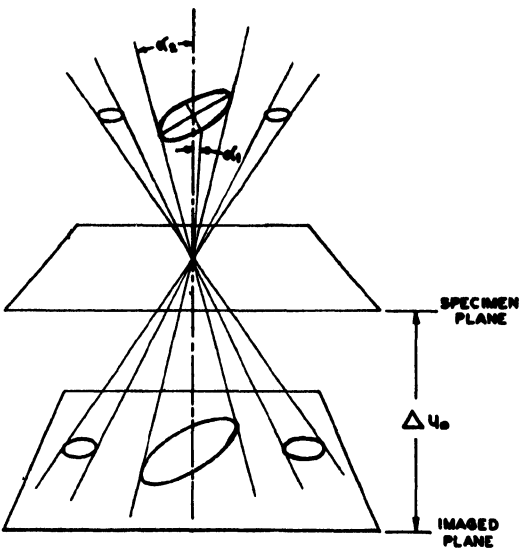

FIGURE 12. A diagram illustrating the production of non-circular and multiple out-of-focus images when the specimen is illuminated by non-circular and multiple pencils.

mind that the aberrations and depth of focus will have different values according to the direction in which the resulting diffusion is measured in the plane of the image. Thus, if the image of the source at v_o (See Fig. 2) is elongated instead of circular because the emitter itself is not circular or because there are varying disturbing electric or magnetic fields, an image of the point in a specimen will appear similarly elongated (Fig. 13). Furthermore, if through improper adjustment or improper design of the illuminating system each point of the specimen is illuminated by a number of pencils, the image consists of two or more well focused but slightly displaced images. (Fig. 14). In Fig. 15a the change of the depth of field due to the existence of the second pencil in the illumination is illustrated. Here T_d represents the depth of field for the normal illumination for a resolving power of d, T'_d represents the depth of field for the second pencil, while T''_d represents the much reduced depth of field for the combined illumination. Thus, if $2\Delta u_o$ lies between T''_d and the lesser of T'_d and T_d two sharply defined but slightly displaced images will be obtained. In Fig. 15b is indicated the effect of spherical aberration on the image when the illumination consists of two discrete pencils. The central pencil forms an image of the speci-

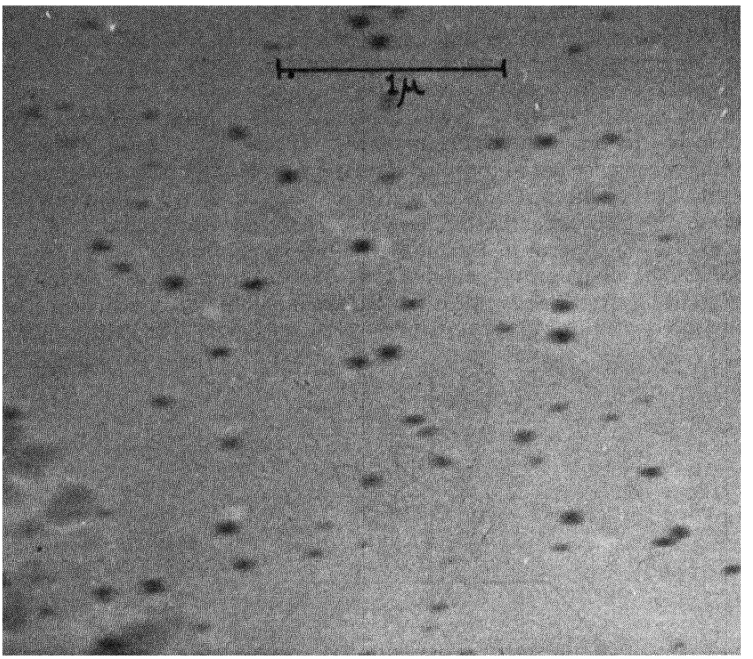

FIGURE 13. Highly magnified image of small crystals of cadmium illustrating the effect of a non-circular illuminating pencil.

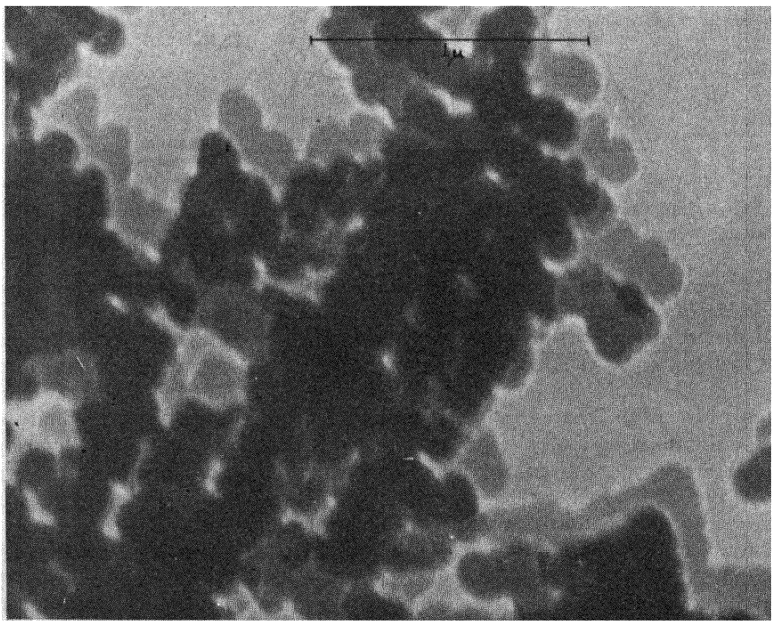

FIGURE 14. A highly magnified, slightly defocused, image of carbon black produced by two discrete pencils of illumination.

men point in the normal way. The extra pencil, however, utilizes a different zone of the objective which, because of the spherical aberration, has a shorter focal length. Thus, a single point in the specimen gives rise to a sharply focused point of the image plus a second point which, because of being formed by an off-axis pencil and imaged by a lens of different focal length, is displaced from the first. Depth of focus considerations show that this second image point is also in focus. The theoretical calculations indicate that such a displacement would be extremely small and would be below the present resolving power of the electron microscope. In practice, however, many cases of multiple images have been encountered where it has been impossible to find an objective focal length for which the images coincided.

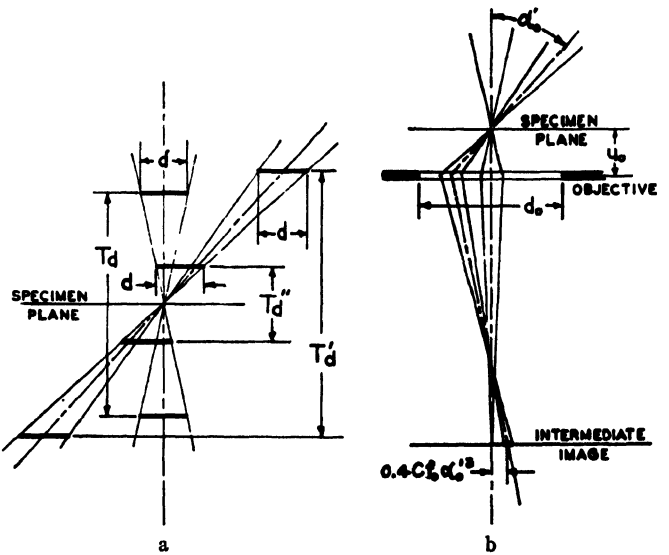

FIGURE 15a. A diagram illustrating the change in depth of field due to the existence of a second pencil in the illumination. This corresponds to the condition causing the effects observed in Figure 14. 15b. A diagram illustrating the effect on the image produced by the spherical aberration of the objective when the specimen is illuminated by two pencils of electrons.

The Projection Lens. It is the function of the projection lens to project on the final fluorescent screen or on a photographic plate a magnified image of the intermediate image formed by the objective. The general character of the lenses employed for this purpose is the same as that of the objective. It follows that the aberrations of this lens are also similar to those of the objective. However, their effect on the image is considerably different. At the objective a region of the object, small compared to the aperture of the lens, is imaged by pencils of relatively large angular aperture, while at the projection lens very narrow pencils image an area of the intermediate image large compared to the lens area utilized by any one pencil. Thus, in the objective the image defects resulting from the lens imperfections are substantially the same for all the object points imaged and equal, in particular, to those for the object point on the axis. The only defects which affect the imaging of this point are, as has already been mentioned, spherical aberration and chromatic aberration. These two produce an unsharpness which is the same throughout the otherwise faithful portion of the intermediate image utilized for the final image.

At the projector, on the other hand, the aperture of the individual pencils is so small (10^{-5} radian) that the central point of the intermediate image is imaged to all

intents and purposes, without aberration. However, since the pencils imaging the marginal portions pass through the outer zones of the lens, they are affected by the lens defects. Whereas the aberrations of the objective determine primarily the sharpness of the image, those of the projector cause deviations from the faithfulness of reproduction; a fact which appears as a pin-cushion distortion of the image and is caused specifically by the spherical aberration of the projector (N.B. These statements are strictly true only for a hypothetical thin lens) the distortion is measured by the ratio of the magnifications at the marginal and central portions of the image. It remains approximately constant (increasing slightly) as the projector magnification is increased, provided that the area of the intermediate image which is reproduced is held constant. However, if the area of the *final* image is kept the same as the projector magnification is increased the visible distortion decreases rapidly. Usually the projection lens is provided with an aperture which limits the field of view to that which can be reproduced with less than a maximum tolerable distortion, usually 10 per cent.

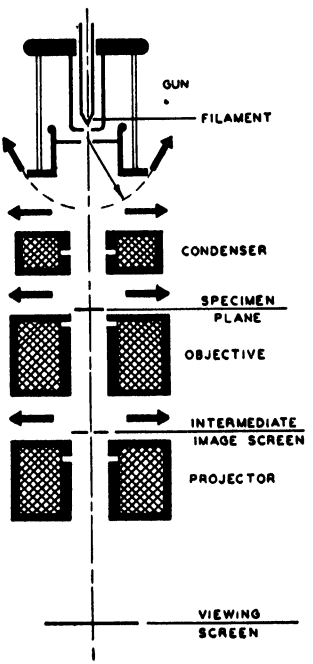

FIGURE 16. A schematic diagram of an electron microscope illustrating the adjustments necessary for complete alignment. Contrary to the practices of light optics the adjustment, as indicated by the heavy black arrow, of any component of the electron microscope, carries everything above that component with it as a unit.

Alignment of a Magnetic Electron Microscope

Next in importance to the actual focusing of an electron microscope is the alignment of the lenses of the instrument. If the specimen is imaged by pencils which are not parallel to the objective axis a number of the third order geometrical aberrations known as field aberrations (for instance astigmatism, and coma) become important. The non-parallelism of the illumination and the objective axis must be kept below 2×10^{-3} radian [14] if diffusion of the image arising because of these aberrations is to be kept below 10 Å. In electron microscopes having large spacing between lenses it is necessary to compensate for inevitable inaccuracies in the construction of the instrument by providing adjustments which permit the axes of all the lenses to be put into coincidence. Fig. 16 is a schematic diagram of a magnetic electron microscope

showing the adjustments which may be provided. The arrangement is such that the electron source and each lens can be translated relative to the section of the instrument immediately below it in a plane perpendicular to the axis of the system. Moreover, the adjustment of any one part carries everything above that part with it as a unit.

It is obvious that since the aberrations of the objective have the greatest effect, the alignment of the illumination to make it parallel to the axis of the objective is the most critical.

The technique of alignment of the objective is identical in principle to that used in light microscopy. It is illustrated in Figs. 17a and 17b. In Fig. 17b the specimen

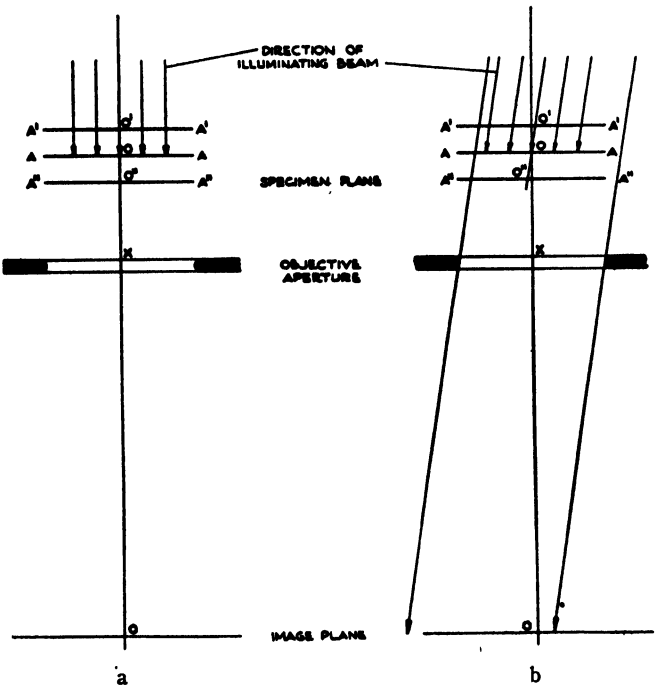

FIGURE 17.

is shown to be illuminated by parallel rays of electrons and to cast a shadow in the direction of the illumination. Thus, as the image plane is raised (e.g. to A′A′) or lowered (e.g. to A″A″) by varying the focal length of the objective, each point of the image will appear to traverse the line which is a projection on the specimen, made parallel to the axis, of the line joining the object point and its shadow in the imaged plane. On the other hand, if the illumination is parallel to the axis of the objective as indicated in Fig. 17a, a change in the power of the objective will cause a diffusion but no displacement of the image points. The method of aligning the instrument now becomes clear. The image of the specimen is focused with α_e reduced as much as possible and the positions on the image screen of a few representative points are noted. The power of the objective is then varied and the translation of the image is observed. With the objective left in the defocused position the condenser lens is translated until the image points assume the same position on the image screen as when the objective was focused. This one operation will align the two most critical elements of any microscope which does not use magnetic lenses. In the latter case,

however, there is a rotation of the image with variations in the power of the objective which, if the instrument is badly misaligned, will produce confusing artificial translations of the image. In fact it can be seen that as the objective power is varied the motion of any image point will be the vector sum of the translation of the image field as indicated above and the motion due to a rotation of the image field about the intersection of the axis of the objective with the image plane. Thus, a deceptive situation arises in which the image point on the axis suffers a translation but at another point in the image field the effects of the translation and rotation instantaneously cancel so that the image appears to rotate about this point. Because of this phenomenon the method of alignment described above does not succeed and it is necessary to use a somewhat different procedure. The pseudo-center of rotation in the image corresponds to a point in the specimen which must be located along a line which passes through the intersection of the axis with the specimen plane, and which is normal to the projection on the specimen plane of the direction of the illuminating rays. Its distance as measured from the axis of the objective is given by the first order equation

$$r_{i(pc)} = \frac{v_o}{u_o} \frac{\Delta u_o}{\Delta \Theta_o} \alpha_o' \tag{21}$$

where

$$\Theta_o = \frac{0.15}{\sqrt{V}} \int_{z_o}^{z_i} H(z)dz \tag{22}$$

α_o' is the angle between the illumination and the axis of the objective and u_o is obtained from the simple lens formula given above. Unfortunately, as far as the normal image is concerned, there is no means of determining where, relative to the pseudo-center, the actual center is located. If, however, the objective lens power is reduced considerably, it is possible to produce an image of the source of illumination on the image screen. Obviously, if the alignment of the illumination relative to the objective were perfect, this image would fall on the center of the image plane. Actually, in the misaligned case it falls at a position which can be easily calculated from the above expression for Θ and the equation $r_{i(o)} = \alpha_o' \gamma_o$. Since $r_{i(pc)} < r_{i(o)}$ in practice, a series of adjustments of the position of the condenser which place the image of the source at the position of the pseudo-center will continually improve the alignment until it is exact.

In actual practice a system of alignment has been devised which leads to these results with the least difficulty or repetition: (1) The electron gun is adjusted until the optimum conditions described in an earlier section are obtained. (2) The power of the condenser lens is increased to the highest value obtainable with the available current. (3) The intermediate image produced by the objective is observed as the objective current is varied from the focal value, down almost to zero. Near the focal value the image will be seen to rotate about the pseudo-center $r_{i(pc)}$ but as the zero value is approached, the image will be condensed into a small bright spot constituting an image of the filament as focused on the intermediate screen by the condenser and objective lenses. This will represent position $r_{(i)_o}$ in the above discussion. (4) The objective current is set so that an image of the source is made to lie in the position of the pseudo-center of rotation. This operation is repeated until, as far as the intermediate image is concerned, the center of rotation appears to remain stationary and coincides with the position of the image of the source. (5) The image is now viewed on the final screen and the objective, with the condenser and the electron gun, is translated until the center of rotation of the final image is near the middle of the projection lens. (6) The power of the objective is reduced from the focal value and the motion of the image points observed in the final image. With the objective left at the power for which the image points are displaced considerably from their focused

positions, the condenser, with the gun, is translated until the image points are returned to original positions. The objective power is returned to its focal value and the operation is repeated until it is possible to observe the same region of the specimen near the middle of the final image screen for the entire range of objective powers from the focused image of the specimen down to a focused image of the source. To a first approximation this places the projector, objective and condenser lenses in alignment. However, because of the high condenser power, the intensity is quite low. (7) To complete the alignment of the filament the intermediate image is observed and the power of the condenser gradually reduced. At some value the illumination will be seen to move off the field of view. This condition is illustrated in Fig. 18. The

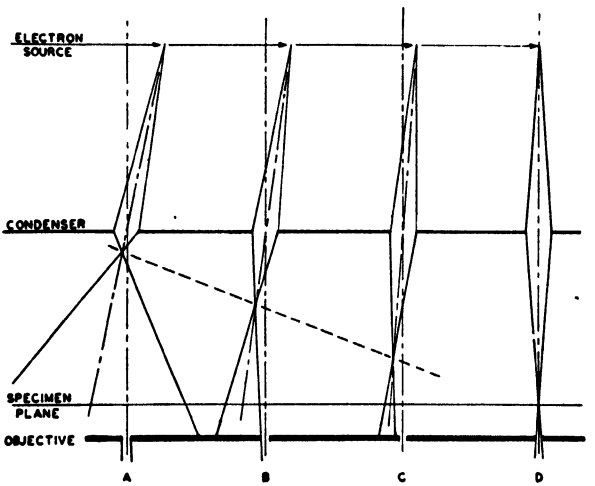

FIGURE 18. A ray diagram illustrating the method of adjusting the transverse position of the electron source.

illumination is returned by appropriate translation of the electron gun. The condenser power is then reduced further until the illumination again moves off, whereupon it is returned by further translation of the electron gun. This procedure is continued until, as observed in the intermediate image, a focused image of the source or the filament is obtained at the plane of the object. This has very nearly placed the electron gun on the axis of the condenser. (8) Since the adjustment described in (7) will have changed the position of the image of the source, as produced at high condenser powers, relative to the condenser and hence, relative to the objective, the operation of aligning the condenser relative to the objective is repeated. (9) After the final adjustment of the condenser relative to the objective, a slight adjustment of the translation of the electron gun is usually necessary to complete the alignment of the system. This alignment will be maintained over long periods of operation except possibly for an occasional slight adjustment of the electron gun which is necessary in order to compensate for movements of the filament tip caused by thermal expansion.

Effects of Contamination

In a well-cleaned instrument the response of the image to the aligning adjustments is very definite and easily identified. If, on the other hand, parts of the instrument are contaminated with dirt which collects charges and hence, disturbs the action of the electron beam, the response is no longer definite but may be quite erratic. Because of this and the fact that contamination can spoil the performance of an electron microscope, a brief description will be given of the effects of various types of contamination in the different sections of the instrument.

Two types of contamination are most noticeable in the electron microscope. The first of these is a coating which appears on any metal surface lying in the direct path of the electron beam. The coating appears to be of a carbonaceous material produced by the interaction of the electron beam with the grease and oil vapors usually present in a demountable system. The second type of contamination is that due to particles of insulating material which may come from a number of sources. They may be introduced with the air when a specimen or photographic plate is changed; they may be left on parts of the instrument, when it is assembled, or they may be introduced on the specimen itself. The first type of contamination is characterized by the slow deterioration which occurs in the performance of the particular unit affected, whereas, the second is characterized by a number of rather obvious affects. In the following the positions in the electron microscope which are sensitive to contamination and the observable effects of such contamination will be discussed in order.

In its course through the electron microscope the electron beam passes first through an apertured diaphragm which is always placed in front of the electron emitter. This particular aperture becomes coated quite rapidly because of the intensity of the electron bombardment, because of the lower electron velocity resulting in higher ionization probabilities and because of the proximity to the high temperature filament. As soon as a sufficient quantity of this contamination has collected a number of spurious secondary sources make their appearance. (See Fig. 8.) In extreme cases the insulating properties of this layer can become so great that an image of the source will present a continually changing picture. Such contamination is normally removed by the use of a fine polishing paper or fine steel wool.

Particles of dust which sometimes adhere to the outside of the cathode assembly may cause unsteadiness of the electron beam and even sudden voltage breakdowns.

It is highly important that any fluorescent screens or other apertures between the electron gun assembly and the condenser lens be absolutely clean. One effect of particles of dirt adhering to the walls of the instrument between the electron gun and the condenser lens is to disturb the symmetry of the action of the condenser lens. This is characterized by the fact that the illumination, as observed on the intermediate image screen, will not spread symmetrically about the image of the source as the condenser current is varied. Particles of dirt on the condenser aperture system will produce similar results. Single large insulating particles in this region of the instrument often cause an oscillatory condition which is characterized by a slow steady drift of the illumination (or change of the intensity) followed by a sudden return. If the disturbance consists of an actual displacement of the illumination relative to the specimen as observed on the intermediate image screen, the particle of dirt is situated between the condenser and the objective lens. If, on the other hand, the oscillation is in the intensity of the beam the dirt is usually above the condenser lens.

The objective lens region is the most sensitive to the effects of contamination. The effects of contamination or particles of dirt in the neighborhood of the specimen will be considered first. An electrical charge on that part of the specimen in the field of view does not in itself affect the image except to add aberrations. However, insulating particles outside the field of view cause difficulty because the conditions of the illumination for observation and for photographic recording are different. In the first case the electron beam is very narrow occupying a region of the object chamber which converges to a minimum of about 25 microns at the specimen. However, when the condenser power is raised in order to obtain a photographic record, the beam is spread so that it may irradiate an area as great as 0.5 mm in diameter. It is obvious that such a change in the area of the specimen illuminated by the electron beam may change the electrical charge condition of the specimen sufficiently to produce large image disturbances. Most common of these is an effect caused by one or more large insulating particles on the specimen or on the specimen holder situated outside the electron beam as adjusted for visual observation. When the beam is

spread for photographic recording, it may extend to the particle and cause it to charge. This causes a slow deflection of the beam in the vicinity of the field of view and hence, a slow drift of the final image. Charged particles on the specimen will also cause asymmetries which prevent the accurate alignment of the objective system. It is very important that a clean and sufficiently thin specimen be used for the aligning adjustment.

Insulating particles in the objective itself can cause serious image disturbances. If the particle is sufficiently conducting it will charge to a constant potential and merely add to the asymmetrical aberrations of the lens. If for some reason the intensity of the illuminating beam changes the potential of the surface of the contamination also changes, causing corresponding shifts in the image. If the dirt is insulating, it may charge until it reaches the breakdown potential whereupon it is discharged. This process is repetitive and causes the intermediate and final image to drift steadily with a periodic sudden return.

If an objective aperture is used it soon becomes contaminated with the coating mentioned above. This material is sufficiently insulating to enable rather high potentials to be built up on its surface. The result is the production of a rather poor electrostatic lens which is superimposed on the magnetic objective. This contamination gradually increases in thickness until the resulting aberrations are no longer tolerable. The only method of correction at the present time is to replace the dirty aperture with a new clean one.

Contaminations or insulating particles in the projection lens produce rather easily observed effects. Large insulating particles at the edge of the limiting aperture of the projection lens produce charge "bubbles" which change the magnification of the image violently in their immediate vicinity. These usually appear as dark circular projections on the image of the edge of the aperture. Sometimes when air is let into the instrument rapidly, pieces of lint collect in the opening of the projection lens. These appear as stationary silhouettes on the image.

Magnification Calibration

Probably the most important auxiliary operation in electron microscopy is the calibration of the magnification of the instrument. The accuracy of calibration, of course, determines the accuracy with which absolute measurements can be made. A number of techniques have been used in the past which have gradually increased the accuracy of the calibration until now, it is considered possible to determine microscopic dimensions with a relative error of less than two per cent.

The first technique of obtaining the magnification of an electron microscope was that used by Borries and Ruska.[17] It involved using a specimen mount with a single measured opening. The diameter of the intermediate image of this opening was measured by means of a scale engraved on the intermediate image screen. By dividing these measurements, the magnification of the first stage was obtained. Then, since the diameter of the opening of the intermediate image screen was known and the diameter of the final image could be measured on the photographic negative, the magnification of the second stage was also known. The product of the magnifications obtained in each stage gave the total magnification of the instrument. This technique was never accurate nor very practical. It led to an error as large as 20 per cent and necessitated the use of a single opening specimen mount. It meant that the diameter of the opening of each specimen holder must be measured and that the projection lens magnification must be kept at a value which permitted the opening in the intermediate image screen to be imaged on the photographic plate.

A more flexible method was introduced in connection with the Toronto electron microscope.[18] In this instrument both the intermediate and final image screens were engraved with circles of known dimensions. The instrument was equipped with a measuring gauge which measured the displacement of the object necessary to move

some point of the image from the center to one of the rings along a radial line. With this instrument it was possible to move the entire upper part of the instrument relative to the projector lens. A second gauge made it possible to measure the displacement of the intermediate image necessary to move a point of the final image from the center to one of the measured circles. From the known diameters of the circles on the image screens and from the measured displacements of the object and intermediate image, it was possible to calculate the magnification of each stage and hence the total magnification of the instrument. While this system placed no restrictions on the nature of the specimen holder or on the projector power it did not give a very high degree of accuracy. In fact, in this case, the error was also of the order of 20 per cent.

With the introduction of the RCA Type B electron microscope in 1940, the power supply was stabilized and the values of voltage and current were so reproducable that it became unnecessary to measure the magnification of each individual micrograph. Instead, a calibration curve which would remain unchanged over a period of several weeks could be drawn up for the instrument. The first technique of calibration used in connection with this instrument was the simple comparison between identical fields of view in the electron and the light microscopes. An object stage micrometer was used to calibrate the optical instrument. At this time the minimum distortion free magnification of this electron microscope was about 4000. This meant that only relatively small fields of view could be compared in the light and electron microscopes, usually of the order of 10 to 15 microns. Since the calibration of a light microscope can only be carried out to within about 1 micron, it leads to an error of something less than 10 per cent. A short time later a new receptacle in the object cartridge was provided which permitted much lower magnifications (1800× without distortion) to be obtained. With this low stage of magnification, it is possible to make direct comparisons between electron and light microscopes, using lengths in the specimen as long as 40 microns. Under these conditions two per cent would be a conservative estimate of the error of the comparison between the light and electron microscopes. Once this comparison is made the electron microscope can be calibrated against itself with extremely high accuracy.

Simultaneously, with the development of the last technique, another method of calibrating the electron microscope to high accuracy was developed by Barnes and Burton.[19] This technique involves the production by a method to be described below of a formvar replica of an optical grating. The grating constant of the replica is obtained by measurements with an ordinary laboratory goniometer. Measurements on the actual replica used are necessary because there appears to be considerable shrinkage during its production. When a low-powered electron micrograph is made of this replica of the distance separating as large a number of lines as possible is measured and the grating constant in the image is obtained. The ratio of the latter to the original grating constant gives the total magnification. This technique also gives the magnification to within about two per cent.

It is pointed out, that the real success of this latter technique also depends on the use of a low stage of magnification, enabling a large number of grating lines to be obtained in one field of view. It is the belief of the authors that in the final analysis the use of the light microscope will be found to be the more convenient one for most laboratories.

Specimen Preparation

Specimens which are to yield satisfactory images in the electron microscope must fulfill a number of conditions. First of all, they must be of sufficiently low mass density to transmit a large fraction of the incident electrons with only minor changes in velocity and direction. For organic matter with a density of approximately unity, the upper limit of thickness at an operating voltage of 60 kV is about 1 micron. For

denser solid matter, the upper limit of thickness is less. Secondly, the specimens must maintain their character in vacuum and under the amount of electron bombardment essential for the formation of the image. By the word *character* is meant the geometrical structure of the specimen. The loss of volatile material, for instance, does not seriously affect the interpretation of the image providing it does not change the shape or size of the specimen structure and providing it is not redeposited in an observable form on some other part of the specimen. These conditions lead to a number of subsidiary conditions which must be considered. For instance, the specimen should always be evenly distributed over the supporting membrane. Otherwise, there will be built up, strong electrical forces, due to the charges accumulated by the specimen, which will tend to rupture the supporting membrane. Also, the dispersion of the specimen must be good. If large aggregates of material are present, they will absorb large amounts of energy from the electron beam reach surprisingly high temperatures and hence, melt the supporting membrane. The specimen should be securely attached to the membrane; otherwise, it may be scattered by electrostatic forces and contaminate the adjacent parts of the objective lens.

Regardless of the nature of the specimen to be examined, it must be mounted on a suitable support. Since the specimen itself cannot exceed a certain maximum mass density, it is obvious that the mass density of the specimen support must be one or two orders of magnitude less if it is not going to affect the image in any way. This support is usually in the form of structureless membrane of light material. However, it requires some means of support itself since it cannot be suspended over indefinitely large areas. In practice, two means of support are used. The first is the metal disk with a single central aperture of suitably small diameter, usually on the order of 75 microns. The second type which is more generally used at present in this country is a wire screen of approximately 200 meshes per inch. The screen may be produced electrolytically or by weaving. It has the advantage that in effect a large number of specimens are provided. If, for some reason or other the supporting membrane across one mesh is ruptured, it is then possible to move to another opening immediately without changing the specimen.

A number of techniques have been developed which provide satisfactory supporting membranes for electron microscope specimens. The oldest and most generally used is as follows: A single drop of a two per cent solution of collodion (cellulose trinitrate) in amyl acetate is dropped on the surface of a clear (preferably distilled) water. This drop immediately spreads over a large area and the solvent evaporates leaving on the surface a circular and extremely thin collodion membrane. A number of specimen screens are then placed on top of the floating film and pressed gently to make sure they adhere firmly. The screens are then fished out by some suitable means. One technique which has been developed in this laboratory is simply to take a standard $3'' \times 1''$ microscope slide and lower it at a slight angle to the membrane on the surface of the water. This motion is continued until the slide pushes down through the membrane and until the screens and the membrane are pushed against the underside of the glass slide. The collodion on the surface of the slide is cut away from the remainder of the film by running a needle or fine glass rod around the edge. The slide is then inverted and drawn out of the water. Since the collodion membrane adhering to the microscope slide holds the wire screens in place, this arrangement is very convenient for preliminary observation of the specimen with a light microscope.

Supporting membranes can also be produced from polyvinyl formal films stripped from the surface of glass slides, by the technique of Schaefer and Harker.[20] In this method a standard $3 \times 1''$ microscope slide is dipped in a solution of polyvinyl formal in ethylene dichloride or dioxane. After the slide is removed, drained and dried the film is marked off in appropriately sized squares by means of a sharp needle or razor blade. The slide is then plunged beneath water surface and allowed to stay there for about a minute. It is then withdrawn slowly allowing the water to drain off the

surface and lowered again at a slow rate. The film floats off on the surface of the water and is mounted on specimen mounting screens in the same manner as a collodion film. Supporting membranes produced in this way have somewhat greater strength and durability than the collodion film described above. However, they require considerably more practice and more time to prepare.

Aluminum oxide films have been introduced as object supports by Hass and Kehler.[21] The technique used in this case is the following: A strip of aluminum foil, one to two centimeters wide and five centimeters long is placed as the anode in a 10% sulphuric acid solution. The cathode is formed by a similarly shaped sheet of platinum placed at a distance of two centimeters from the anode foil. Employing a voltage of 10 volts, yielding an initial current of 0.01 ampere, an invisible aluminum oxide film not yet showing interference colors, is formed in one and one-half minutes. If thinner films are to be obtained, the voltage is reduced. The aluminum strip with the film is then immersed in saturated mercuric chloride solution, which, in a few minutes dissolves in the metallic aluminum. The mercuric chloride, adhering to the film, is removed by subsequent washing in alcoholic iodine-potassium iodide solution. Finally, the film is washed with alcohol and placed on the object support. The film appears transparent by transmission and slightly grayish or yellowish under vertical illumination. Since the film readily swims off the object support it is often advisable to increase its adhesion by placing minute drops of rubber cement on the edge of the object support. Electron diffraction patterns obtained from these films indicate that they are amorphous. Such films are not always entirely free from structure but can stand exceedingly high temperatures in the electron microscope.

A final technique which provides very satisfactory supporting membranes is an adaptation of the polystyrene-silica replica technique of Heidenreich and Peck.[22] In this technique the glass slide is dipped in a solution of polystyrene. After the solvent is allowed to evaporate the plate is placed in an evaporating chamber and a thin film of silica is deposited on its surface. After the surface of the plate is scored to divide the silica film into appropriately sized pieces, the plate is immersed in ethyl bromide to which has been added a small amount of benzene. In a short time, the pieces of silica membrane float off and are fished out on wire screen disks. These are dried on filter paper and then washed in fresh ethyl bromide. Electron diffraction patterns indicate that silica films are vitreous. They will stand quite high temperatures in the electron microscope and have high tensile strength. They are suitable for research work involving large particles and also involving special high temperature investigations. Their usefulness is reduced somewhat by the necessity of possessing an evaporating chamber and by the fact that some materials which are normally prepared by being mixed directly with plastic supporting membranes cannot be as conveniently mounted on silica.

There are a number of ways of mounting electron microscope specimens.

Some specimens do not require any supporting membrane. A number of smokes and dusts are among these. They are simply collected on the wire screen where they adhere by their own cohesive forces.

Similarly, some plastics do not need to be supported. If the wire screen is simply dipped in a solution of the plastic to be studied and the solvent allowed to evaporate, the plastic itself will form a thin membrane across the openings of the wire screen.

Another large group of specimens are mounted from suspensions in media which do not effect the supporting membrane. Thus, most biological materials, such as bacteria and viruses are mounted from distilled water suspensions. A number of chemical particles in the colloidal range can also be mounted directly from water suspension. If the material is soluble in water, other media may be used. Some specimens, usually inorganic particles, can be mounted very conveniently by mixing into the collodion solution before spreading on the surface of the water or into the polyvinyl formal solution before dipping. Fortunately, both collodion in amyl acetate

and polyvinyl formal solutions are excellent dispersing media. On occasion, the presence of the particles changes the physical characteristics of the films in such a way that they are not self-supporting. In these cases a wire screen on which a clear collodion membrane has been already mounted, is used as a support for the specimen.

It is sometimes possible to disperse material in oil which can be spread on the surface of water and picked up on a mounted collodion membrane.

Metallurgy is a field of science which provides one of the major applications of the electron microscope. It has not yet been possible to provide with the electron microscope a direct high resolving power image of the actual surface of a material. To overcome this, however, a number of special techniques have been developed for obtaining exact replicas which are themselves thin enough to be observed in the transmission type electron microscope of the surface to be examined. The use of surface replicas was first suggested by Mahl [23-26] who obtained, in particular, very fine pictures of etched aluminum specimens. The polished and etched aluminum is oxidized anodically in a saturated borax solution with boric acid added. Then, after the surface has been subdivided into several sections with needle scratches, the specimen is immersed in saturated mercuric chloride solution. The mercury liberated at the scratches, where free aluminum is exposed to the solution, lifts up the sections of oxide film. After the remnants of the metal adhering to them have been washed off with dilute hydrochloric acid, these are ready for observation. The contour of the oxide film follows the original etched surface. The film is of uniform thickness—that is, normal to the surface, except insofar as the rate of formation of the oxide depends on the crystallographic orientation of the underlying surface. As a result the crystal surfaces appear darker in proportion as their slopes relative to the plane and the specimen surface are steeper. Mahl has also investigated a considerable number of other methods of forming surface replicas. They include the formation of a thin plastic film on the surface to be studied, its oxidation by heating in the presence of air or oxygen, forming a thin oxide film, the deposition of a foreign oxide film by sputtering in an oxygen atmosphere and the evaporation or electro-plating of a thin metallic film on the surface. In all cases the film is separated by dissolving the base. Rüdiger has successfully employed evaporated aluminum and beryllium films as replicas of etched steel surfaces. Beryllium films may be separated from the steel specimen by immersing the specimen for a few minutes in water slightly acidified with sulphuric acid. With the exception of the plastic film method described below, all these methods are applicable to a restricted range of specimens and result in replicas with a "grain" or characteristic structure which may obscure the finer details of the surface structure to be studied. Among the more general methods of replica preparation, three have proved quite valuable.

The first of these to be developed was the silver-collodion method.[27] In this technique the specimen is polished and etched in the same manner as for metallographic light microscope observations at high magnification. It is placed in a vacuum chamber with one or several tungsten spirals loaded with small pieces of silver mounted above it. When sufficient vacuum is obtained, the filaments are heated and the silver is gradually evaporated. Then the silver is deposited to a thickness which permits it to be pulled off the specimen readily with forceps. This produces a negative silver replica.

A collodion solution is now flowed over the side of the silver film which was in contact with the specimen surface; care being taken that none reaches the opposite side. The concentration of the collodion solution should be such that the first interference colors (yellow and then bluish) are barely visible. After drying, the silver film is immersed in 2 to 3 normal nitric acid with the free silver side up. After a few hours most of the silver should be dissolved. The film may now be washed by replacing the nitric acid with several changes of distilled water. Residues of foreign material may be removed by immersing the film in a solution of iodine in hydroiodic

acid. This produces a positive replica in which ridges on the original specimen are reproduced as similar ridges on the collodion replica. Surface tension causes the free surface of the collodion film to remain approximately flat over any small region of the specimen so that the thickness of the replica becomes a measure of the elevation of the surface structure of the specimen over the average level of the surface. Accordingly, also, with due allowance for the peculiar contrast conditions in the electron microscope, the relative darkness of different parts of the image indicates the relative height of the fine structure of the specimen surface.

A procedure which is much faster than that just described but which requires considerably greater care and dexterity, has been outlined by Schaefer and Harker.[20] It constitutes, in a sense, a refinement of Mahl's plastic film method. A negative polyvinyl formal replica is obtained by direct stripping from the specimen surface. Great care must be taken to have the surface completely cleaned. It may be impossible to remove the film from an etched metal surface if more than five minutes elapse between the drying after the etching of the specimen and the formation of the polyvinyl formal film. Accordingly; directly after the final polishing with magnesium oxide powder and the etching, the surface is dried quickly with a jet of filtered air and lowered face down into a petri dish containing a 0.5% solution of polyvinyl formal in dioxane. The specimen is then swung up into a vertical position above the dish and permitted to dry, the resulting film should have a thickness range of 500 to 750 Å, except at the very bottom where the liquid accumulates. Then the specimen is immersed in water to a depth of about 3 cm and the thick end of the film is carefully teased until it piles up into a small roll. This rolled end of the film is gripped with tweezers and the film is pulled toward the thin end. The separated film, or portion of the film, is swung up so that it reaches the surface in an extended condition where it will shed water and float. The replica is now ready for mounting. Recently a number of new techniques for removing the polyvinyl formal film have been developed.[28] This technique produces a negative replica, ridges on the original surface correspond to valleys in the replica and hence, to bright portions of the electron microscope image; depressions in the specimen appear dark.

A process described by Heidenreich and Peck [22, 28, 32] yields positive replicas on silica with excellent resolution and contrast. (Fig. 19) The specimen is placed in a molding case with enough polystyrene molding powder above it to give a final molding one-half inch thick. The molding is heated to 130° C before applying pressure. Then a pressure of 2,000 to 5,000 lbs per square inch is applied and the temperature is raised to 160° C. The mold is now cooled at constant pressure until the temperature has dropped to well below 80° C. The polystyrene is sawed off the edges of the specimen. If the specimen does not jar loose from the remaining polystyrene molding, the excess of the specimen is sawed off and the remainder dissolved in an appropriate acid. Any mineral acid (other than sulphuric acid) in a concentration less than 1:3, acetic acid, or a caustic may be used without injury to the polystyrene. After careful washing, the polystyrene replica is placed in a vacuum chamber at a pressure lower than 10^{-4} mm Hg. Silica is evaporated onto it from a conically wound tungsten filament made of 0.020″ wire, into which quartz splinters are placed. The amount that must be evaporated depends on the roughness of the surface of the polystyrene block, on its distance from the filament, and on its total area. For a typical specimen of pearlitic steel at a separation (between the apex of a filament and the surface) of 6 cm, the proper amount to be evaporated is about 3 milligrams.

As the silica has a very high mobility on the polystyrene, it will cover all sides of the polystyrene block. Before the block is placed in a solvent (ethyl bromide), the film is removed from the bottom and the sides with fine emery cloth. Then the surface is scratched to separate sections about an eighth of an inch on the side and immersed in the solvent. The remainder of the technique is the same as that described above with regard to the preparation of silica supporting membranes.

Not all the replica procedures are equally applicable to all types of specimens. The sensitivity to heat, pressure, and vacuum, as well as the available equipment, may influence the choice.

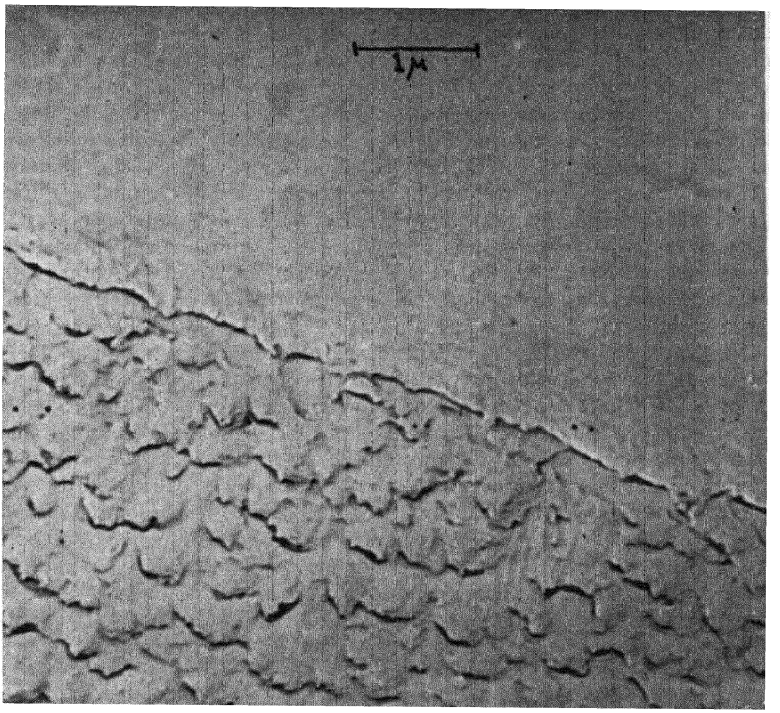

FIGURE 19. Electron microscope of a grain boundary in commercial brass, obtained by the polystyrene silica technique. (Courtesy Dow Chemical Co.)

Little needs to be said with regard to the actual preparation of the specimen material, since in most cases that will constitute a major part of the research problem. However, it is pertinent to point out a few facts which if understood may help the operator to avoid mistakes in interpretation of the images.

It is essential that the purity of the specimen be known. The relative proportion of an impurity will be maintained in the electron microscope specimen. This is also true if the impurity is in solution, though materials which are in solution and which on drying form a continuous overlapping film, ought to be avoided. In the preparation of metallurgical specimens, it is important that the polishing and etching techniques be only those which are used for extremely high powered light microscopy.

Associated Operating Techniques

Most modern electron microscopes are fitted with specimen holders which permit obtaining stereoscopic electron micrographs. Such electron micrographs permit measurements to be made in three dimensions and are very useful for removing ambiguities from the interpretation of the electron micrographs.[29-32] A second auxiliary technique is the use of the electron diffraction camera which may be incorporated with the electron microscope.[33-34] With this instrument it is possible to make electron diffraction patterns of the same specimens as observed in the microscope, thus providing a useful correlation between the physical characteristics depicted in the elec-

tron microscope image and the chemical composition as indicated by the electron diffraction pattern.

Image Interpretation

In the preceding pages some of the operating techniques used in connection with the electron microscope have been described. All these techniques have as their prime aim the achievement of electron micrographs which will provide useful information. Therefore, the most important of all the operating techniques in connection with the electron microscope is the actual derivation of this information from the image.

Resolving Power. The figure of merit most commonly used to evaluate the performance of an electron microscope is the resolving power. Unfortunately, much confusion has arisen with regard to the significance of this quantity. Part of this confusion is due to the fact that, on the one hand, the term "resolving power" is used by the electron microscope designers to indicate the ultimate performance of which a particular instrument is capable and that on the other, it is used rather loosely by the microscope operators to indicate the quality of a given electron micrograph. That the second use of this term has little or no significance is obvious when it is pointed out that, as a result of the dependence of the effective angular aperture of the objective on the physical properties of the specimen point, the resolving power in the electron microscope is a variable quantity which is critically dependent on the property of each specimen point. Thus, in one field of view the resolving power may vary by more than two orders of magnitude, a phenomenon which must always be kept in mind in interpreting an electron microscope image. If the words "resolving power" imply *limiting* resolving power, it may be defined as the least separation between small particles of which the instrument is capable of producing resolved images.

Magnification. While the high resolving power of the electron microscope is responsible for its usefulness, that resolving power is utilized only through the production of magnified images of the specimen. Fig. 20 is a graph showing the rela-

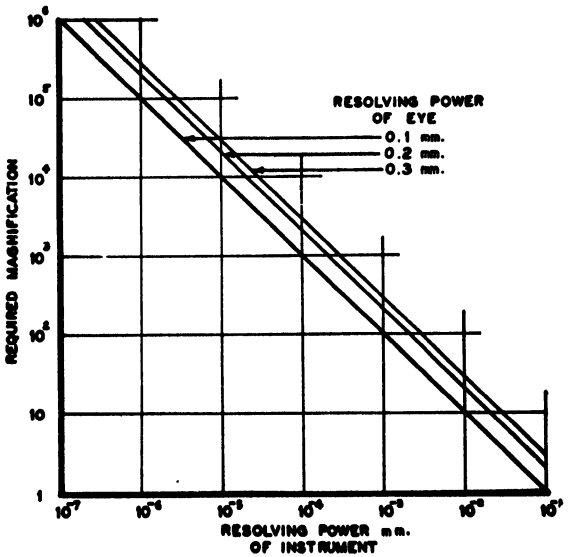

FIGURE 20.

tionship between the resolving power of a microscope and the magnification required for the full utilization of that resolving power. Curves have been drawn for three different values of the resolving power of the human eye. If we follow the custom of

the light microscopist and use 0.2 mm for the resolving power of the human eye, we see from the curves that the total magnification of 100,000× is necessary to demonstrate a magnification of 20 Å. However, electron microscopes should not be compared on the basis of reported total magnification unless those magnifications are known to represent necessary magnifications and if the basis on which they have been computed is also known.*

The actual process by which this total magnification is achieved is of little importance provided, of course, that the *initial* imaging is done electronically and at a magnification which brings the image details within the reach of the subsequent processes. For instance, in theory at least, an electron microscope using a single electron lens at a magnification of only 100 combined with a light microscope working at 1000× would give results identical with those given by an electron microscope working at 100,000× directly. Actually, neither of these systems is very practical. One which is intermediate to them is being used in practice. Since the resolving power of a fine-grained photographic plate is around 25 times better than that of the eye it can record all the details present in the electron microscope image at magnifications as low as 4000. Then enlargement in a conventional enlarger is all that is necessary to make these details visible to the eye. This technique leads to practical values for the field of view and electronic exposure time.

Interpretation of Electron Microscope Images. It is the variations in intensity over the image plane which constitute an image and reveal the *geometrical* structure of the object; that is the sizes of particles and structures, their shapes and their organization in larger structures.

At first sight it would appear that the conditions of formation of an electron microscope image are much simpler than those encountered in light microscopy where the image is a result of a number of complex phenomena. Actually, since the scattering phenomena on which the formation of an electron microscope image depends are accurately understood only for special cases lying at both extremes of those encountered in practice and since the aberrations of the electron lenses (also only inadequately investigated at present) and crystallinity of the specimen introduce serious intensity anomalies, the correlation between the properties of the specimen and the intensity of the image is extremely involved and ambiguous. In the final analysis it appears that the information provided by the electron microscope is identical with some, though not all, of the information provided through our ordinary sense of vision. Thus, in using this new instrument it must always be remembered that it is not possible to make an interpretation which goes beyond the directly measurable factors of size, shape and structure except through the accumulation of additional information either by auxiliary experimentation or by experience.

Applications of the Electron Microscope

Range of Applications. Through the techniques of spectroscopy (over the whole electromagnetic spectrum), and through the study of radioactivity, chemistry, and collision processes our knowledge of the structure of the atom has become quite extensive. The techniques of chemistry and x-ray and electron diffraction have given us much accurate information regarding the first stage of organization of the atoms into molecules and into crystal lattices. When we proceed to the next stage of organization, that is, to the large organic molecules, to the viruses and even to the smaller of the colloidal particles we find that before the development of the electron microscope there was no accurate technique for obtaining information. Now, the electron microscope almost completely fills the gap between the limit of resolving power of the light microscope and the simple molecules. More precisely the electron

* German workers claim their electron microscopes to be capable of useful magnifications of 150,000. However, they use 0.3 mm as the limiting resolving power of the eye. Thus, actually the resolving power of their instruments is still 20 Å.

microscope can be described as being useful for observing structures between 10,000 and 20 Å. (It is to be noted, however, that the lower part of this range which ends at the present lower limit of the magnetic type electron microscope can be covered only inadequately. This is a result of the well-known fact that in microscopy a structure or organism cannot be studied adequately unless it is at least an order of magnitude greater than the limiting resolving power of the instrument.)

In this range of application the electron microscope has one general limitation. As in light microscopy, there is an upper limit which the thickness of the specimen must not exceed if it is to be satisfactory for observation. Due to the complex way in which it depends on the structure and composition of the specimen, on the electron velocity, on the lens aberrations and on the lens aperture, very little quantitative information can be given regarding the exact value of this maximum permissible thickness. It is known, however, that for 60 kilovolt electrons in a magnetic electron microscope, organic specimens of which the thickness does not exceed 5000 Å are quite satisfactory. Lower electron velocity, denser specimen materials and the use of electrostatic lenses, all tend to decrease this maximum permissible thickness.

In actual practice this limitation does not exclude any large group of specimens though it has made the examination of cut sections difficult. Otherwise, the applications of the electron microscope parallel and supplement those of the light microscope.

If the general principles of the electron microscope are understood, the research worker is able to decide for himself regarding its application to a specific problem and a listing of the specific applications of the instrument becomes almost superfluous. However, to the general scientific reader, a discussion of the applications is of interest and has considerable value in providing a better appreciation of the capabilities of the electron microscope.

Applications in Chemistry. The field of chemistry provides some of the most direct applications of the electron microscope. While most of the properties of the chemicals under investigation are determined by other techniques some, such as the particle morphology (if that term may be applied to a chemical) can be determined accurately only by means of the electron microscope. In this particular field, the electron microscope often appears to be responsible for spectacular discoveries, though actually it merely supplies the missing link in the information available regarding a specimen.

The applications of the electron microscope in chemistry can be divided into three rather rough categories. The first includes studies of the structure of materials in which there is a degree of organization, such as in diatoms; (Fig. 21), cellulose and other fibers; (Fig. 22) and even vulcanized rubber. It is in this grouping that the stereoscopic technique is of particular value.

Diatoms

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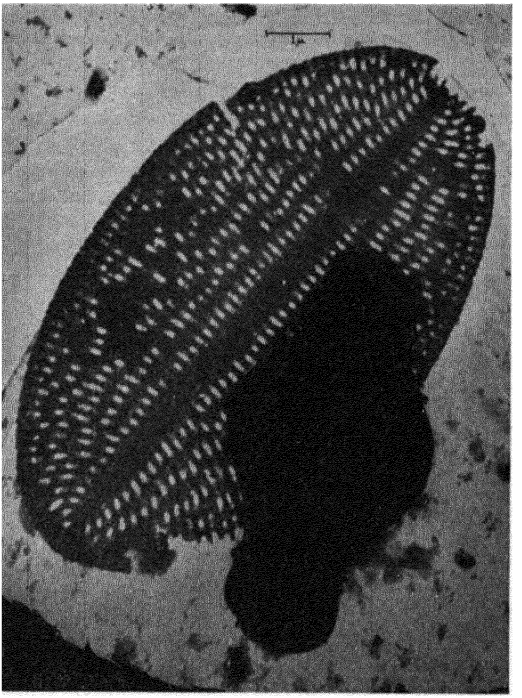

FIGURE 21. Diatom.

FIGURE 22. Cellulose fibers in paper pulp. (Courtesy American Cyanamid Co.)

Into the second category may be put those investigations which involve a study of a process. It is the belief of the author that this will eventually become the most important application of the electron microscope in chemistry. At present, however, it has hardly been more than initiated, though what work has been done looks very promising. For instance, some very interesting preliminary studies have been made on the developing processes in photography and new unsuspected phenomena have come to light. In the study of the setting of cement a considerable amount of work has been done both in Germany and in this country. The action of catalysts has also been under intensive investigation for some time in a number of laboratories in this country but little information has been published.

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Catalysts

Ardenne, M. von, and Beischer, D., *Angew. Chem.*, **53**, 103-107 (1940).

The determination of particle sizes and shapes constitutes the third and at present most important category. One of the first problems of this nature was found in the correlation of the particle size distributions in carbon blacks with their properties as reinforcing agents in rubbers or as pigments in printers inks. Many paint or lacquer pigments are specially adapted for investigation in the electron microscope: titanium dioxide, zinc oxide, iron oxide, azo blue, are only a few. Particles of various types of clay have probably been subjected to more examination by means of the electron microscope than any other type of material. Fig. 23 is a typical electron micrograph of a kaolin. A number of dusts and smokes have been studied in connection with

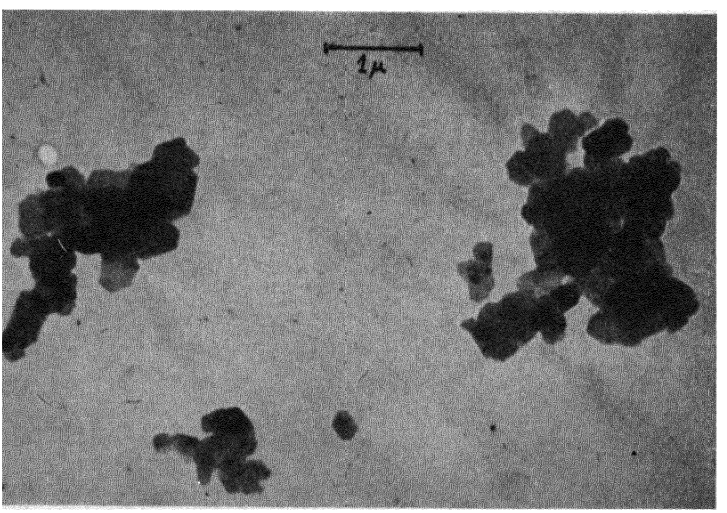

FIGURE 23. Kaolin.

industrial health problems. These also have value as test objects for the electron microscope (Fig. 24). What one might call the "classical" colloids have been investigated. Metallic powders used in the new sintering processes have also been examined. (See Figs. 25, 26.) In fact, any chemical which is produced industrially in the form of a powder may be examined with the electron microscope and, of course, if the properties of that chemical in its final use depend on that particle size, the accurate information available with the electron microscope becomes indispensable.

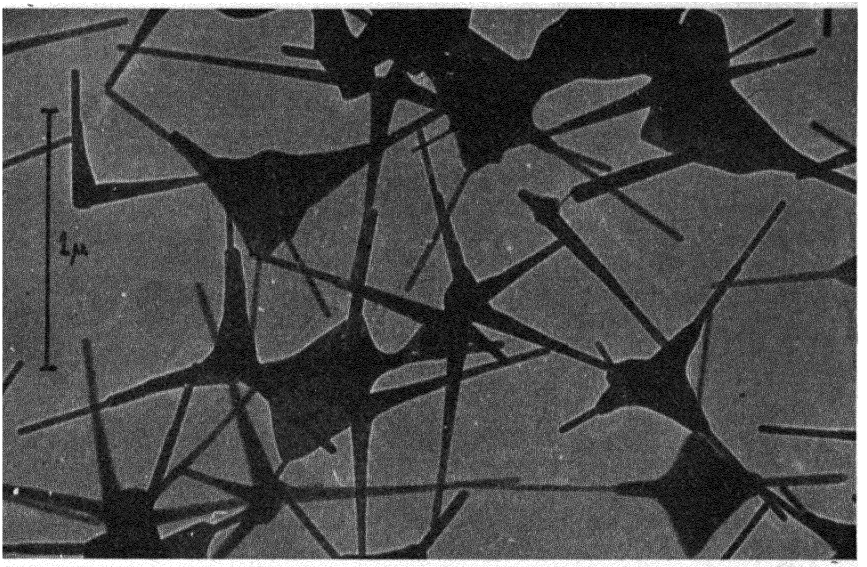

FIGURE 24. Zinc oxide smoke.

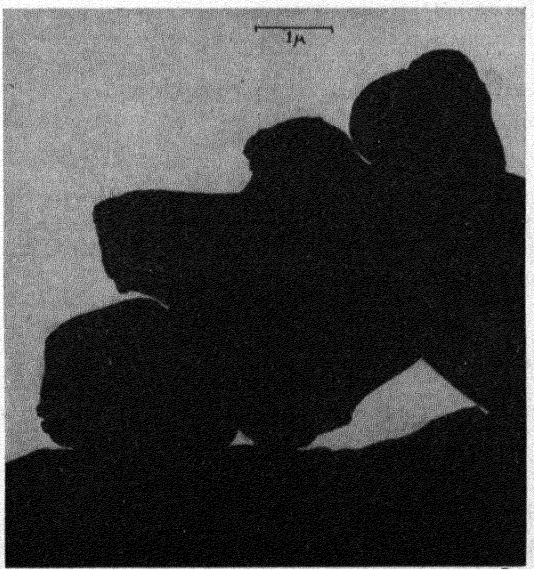

FIGURE 25. Copper powder particles. (Courtesy Hardy Metallurgical Co.)

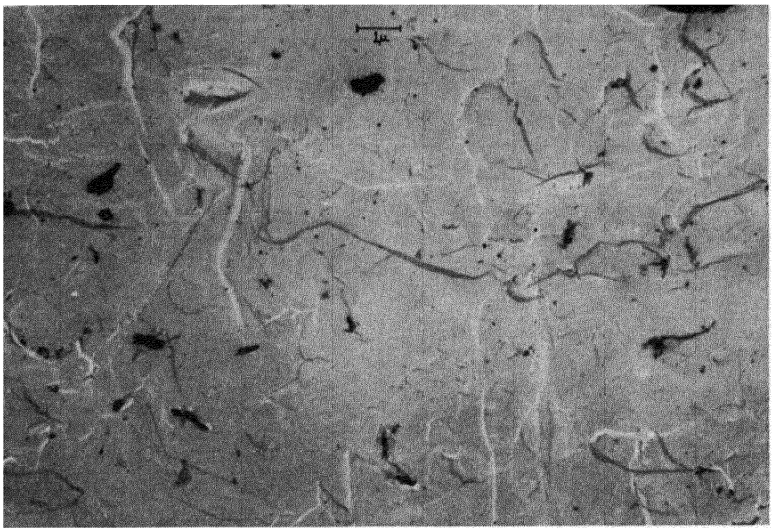

FIGURE 26. Polystyrene silica replica of copper metal produced from the powder shown in Figure 25. (Courtesy Hardy Metallurgical Co.)

Carbon Black

Columbian Carbon Company Research Laboratories, *Columbian Colloidal Carbons*, **2**, 5-53 (1940).
Brown, O. J., Jr., and Smith, W. R., *Ind. Eng. Chem.*, **34**, 352-355 (1942).
Wiegand, W. B., and Ladd, W. A., *Rubber Age*, **50**, 431-436 (1942).
Schoon, Th., and Koch, H. N., *Kautschuk*, **17**, 1-7 (1941).

Pigments

Schmieder, F., *Kolloid Z.*, **95**, 29-33 (1941).
Barnes, R. B., and Burton, C. J., *A. S. T. M. Bull.*, **116**, 34-41 (1942).
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Clays

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Shaw, B. T., and Humbert, R. P., *Proc. Soil Sci. Soc. Am.*, **6**, 146-149 (1941).
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Alexander, L. T., Faust, G. T., Hendricks, S. B., Insley, H., and McMurdie, H. F., *Am. Mineral.*, **28**, 1-18 (1943).
Prebus, A., *Ohio State Univ. Studies, Eng. Expt. Sta. Bull.*, **14**, 3 (1942).

Smokes and Dusts

Friess, H., and Muller, H. O., *Gasmaske*, **11**, 1-9 (1939).
Ardenne, M. von, and Beischer, D., *Z Elektrochem.*, **46**, 270-277 (1940).
Mahl, H., *Z. Tech. Physik*, **21**, 17-18 (1940).
Meldau, R., *V. D. I.*, **84**, 103-106 (1940).
Barnes, R. B., and Burton, C. J., *Ind. Eng. Chem.* (*News Ed.*), **19**, 965-967 (1941).
Kinder, E., *Naturwiss.*, **31**, 149 (1943).

Colloids

Borries, B. von, and Kausche, G. A., *Kolloid Z.*, **90**, 132-141 (1940).
Barnes, R. B., and Burton, C. J., *A. S. T. M. Bull.*, **116**, 34-41 (1942).

A few exploratory studies on structural parts of insects have been made by Anderson and Richards. These probably represent the most successful of the attempts to examine large objects in the electron microscope.

Insects

Anderson, T. F., and Richards, A. G., *J. Applied Phys.*, **13**, 748-758 (1942).
Richards, A. G., Jr., and Anderson, T. F., *J. N. Y. Ento. Soc.*, **50**, 147-167 (1942).
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Anderson, T. F., In Kraemer, E. O., ed. Advances in Colloid Science, Vol. 1, 352-370, Interscience, New York, 1942.
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Applications in Metallurgy

In the above the techniques of applying the electron microscope to metallurgy have been discussed fairly completely. To continue the discussion to the actual applications in metallurgy is not possible at the present time. It is only in the past two years that the techniques of application have been worked out and even in this short time a number of important problems have been started. However, none of these problems has progressed to the point of publication of the results. It is apparent that the electron microscope very successfully extends the range of the light microscope in almost every aspect of metallography. It is also apparent that the difficulties which beset the use of the light microscope for high power metallurgical work are even more important with the electron microscope. For instance, etching techniques which are just good enough for light microscopy will have to be considerably modified and improved if they are to be applied to electron microscopy. New etching techniques or old ones not normally used in light microscopy are being examined. Among these are included, in particular, electrolytic and thermal etching methods.

Applications in Biology

The electron microscope can be used to investigate a very wide variety of subjects in the field of biology. These range from some relatively large suitable organs of insects and animals through the bacteria to the viruses and large molecules. In spite of the fact that the application of the electron microscope in biology is not as direct as in the sciences discussed above and in spite of the preoccupation of the biologists with the pressing problems of war a surprising number of advances have already been made.

In the field of bacteriology, Mudd and a number of co-workers have concentrated on the study of bacterial morphology; a problem for which the electron microscope is ideally suited (Fig. 27). Studies of morphological changes which occur with the life processes in bacteria or in combination with antibodies, organic or inorganic chemicals, and antibacterial agents, are also readily carried out.

Bacteriology

Mudd, S., Polevitzky, K., Anderson, T. F., and Chambers, L. A., *J. Bact.*, **42**, 251-264 (1941).
—, and Lackman, D. B., *J. Bact.*, **41**, 415-420 (1941).
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Morton, H. E., and Anderson, T. F., *Am. J. Syphilis, Gonorrhea and Venereal Diseases*, **26**, 565-573 (1942).
Mudd, S., Polevitzky, K., Anderson, T. F., and Kast, C., *J. Bact.*, **44**, 361-366 (1942).
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Umbreit, W. W., and Anderson, T. F., *J. Bact.*, **44**, 317-320 (1942).
Morton, H. E., and Anderson, T. F., *J. Bact.*, **45**, 143-146 (1943).
Mudd, S., Polevitzky, K., and Anderson, T. F., *J. Bact.*, **46**, 15-24 (1943).
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It is now possible to observe directly many of the filtrable viruses, thus providing an independent check on the information obtained from combination of sedimentation with viscosity and diffusion data and from stream double refraction, ultra filtration, absorption and x-ray studies. A number of viruses have been studied including tobacco mosaic virus and a number of other plant viruses, equine encephalomyelitis, influenza, poliomyelitis, and others (Fig. 28).

Plant Virus

Lauffer, M. H., and Stanley, W. M., In Alexander, J., ed., "Colloid Chemistry," Vol. V, 785-808, Reinhold, New York, (1944).
Kausche, G. A., Pfankuch, E., and Ruska, H., *Naturwissenschaften*, **27**, 292-299 (1939).
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Trurnit, H., and Friedrich-Freksa, H., *Biol. Zentr.*, **60**, 546-556 (1940).
Anderson, T. F., and Stanley, W. M., *J. Biol. Chem.*, **139**, 339-344 (1941).
Stanley, W. M., and Anderson, T. F., *J. Biol. Chem.*, **139**, 325-338 (1941).
Frampton, L. V., *Science*, **95**, 232-233 (1942).

FIGURE 27. Vegetative cell of Azotobacter vinelandii showing a clear representation of the flagella and the almost complete lack of structure in the cell itself.

Equine Encephalomyelitis

Sharp, D. G., Taylor, A. R., Beard, D., and Beard, J. W., *Proc. Soc. Exptl. Biol. Med.*, **51**, 206-207 (1942).
Taylor, A. R, Sharp, D. G., Beard, D., and Beard, J. W., *Proc. Soc. Exptl. Biol. Med.*, **51**, 332-334 (1942).
Sharp, D. G., Taylor, A. R., Beard, D., and Beard, J. W., *Arch. Path.*, **36**, 167-176 (1943).

Influenza

Chambers, L. A., and Henle, W., *J. Exptl. Med.*, **77**, 251-264 (1943).
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Henle, W., and Henle, G., *Science*, **98**, 87-89 (1943).
Taylor, A. R., Sharp, D. G., McLean, I. W., Jr., Beard, D, Beard, J. W., Dingle, J. H., and Feller, A. E., *Science*, **98**, 587-589 (1943).
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Sharp, D. G., Taylor, A. R., McLean, I. W., Jr., Beard, D., Beard, J. W., Feller, A. E., and Dingle, J. H., *J. Immunol.*, **48**, 129-153 (1944).
Lauffer, M. A., and Stanley, W. M., *J. Exptl. Med.*, (In Press) (1941).

Poliomyelitis Virus

Tiselius, A., and Gard, S., *Naturwiss.*, **30**, 728-731 (1942).
Gard, S., *Acta Med. Scand.*, Supplementum, **143** (1943).
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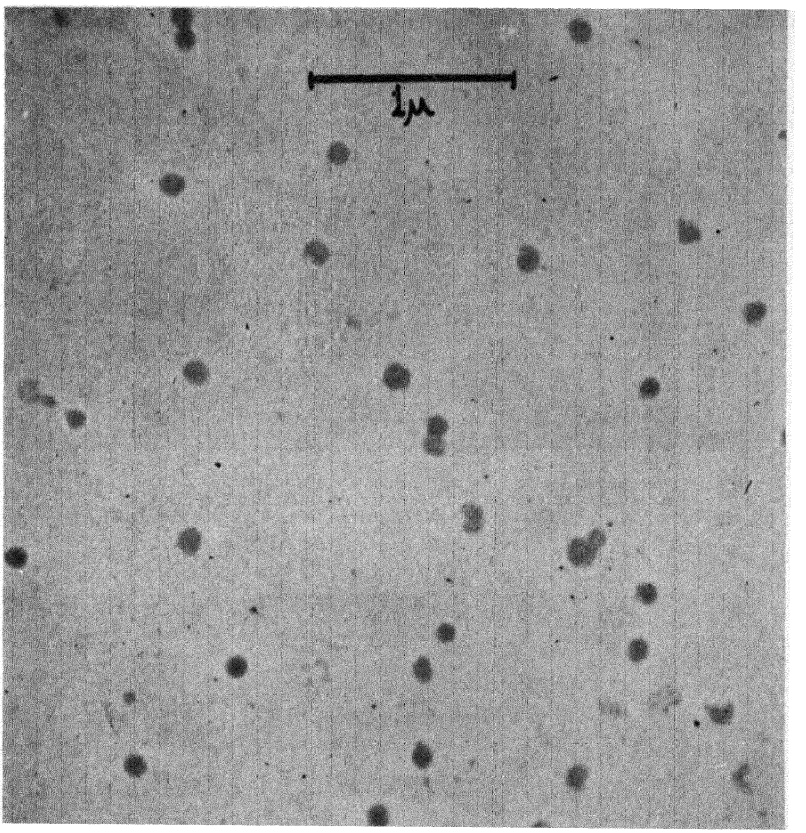
Jungeblut, C. W., and Bourdillon, J., *J. Am. Med. Ass.*, **123**, 399-402 (1943).
Melnick, J. L., *J. Immunol.*, **48**, 25-28 (1944).



Miscellaneous Viruses

Glaser, R. W., and Stanley, W. M., *J. Exptl. Med.*, **77**, 451-466 (1943).
Sharp, D. G., Taylor, A. R., Beard, D., and Beard, J. W., *Proc. Soc. Exptl. Biol. Med.*, **50**, 205-207 (1942).

One of the most interesting of the virus studies is that carried out on bacteriophage. In this work, samples were examined at selected time intervals after the mixing of the bacteria (*E. coli*) and bacteriophage suspensions. Figs. 29 and 30, show part of the resulting sequence.

Bacteriophage

Pfankuch, E., and Kausche, G. A., *Naturwiss.*, **28**, 46 (1940).
Ruska, H., *Naturwiss.*, **28**, 45-46 (1940).
Luria, S. E., and Anderson, T. F., *Proc. Natl. Acad. Sci. U. S.*, **28**, 127-130 (1942).
—, Delbruck, M., and Anderson, T. F., *J. Bact.*, **46**, 57-77 (1943).

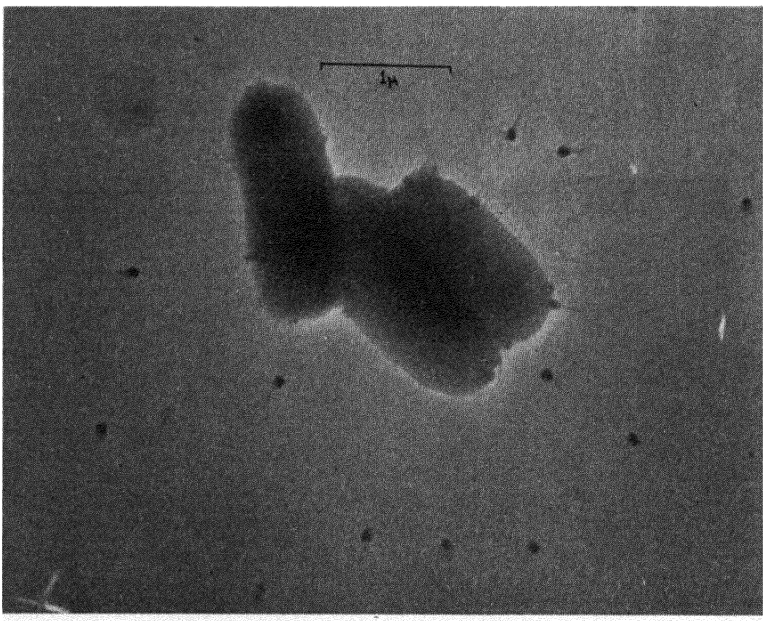


FIGURE 29. E. coli in the presence of bacteriophage particles.

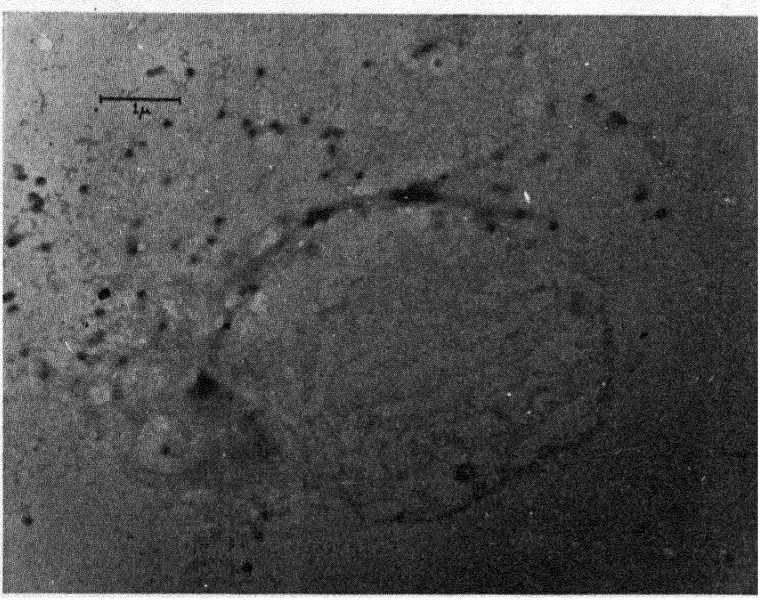


FIGURE 30. Completely lysed E. coli showing a number of the newly produced bacteriophage particles.

Conclusion

In the preceding pages an attempt has been made to present to the technologist some of the fundamental theory underlying the practical operation of an electron microscope. This has been supplemented as far as possible with practical directions for obtaining the best possible electron micrographs.

While the article is primarily about the electron microscope it has been emphasized a number of times that the electron microscope does not usually play the role of apparatus directly connected with a research problem but instead plays an auxiliary role, providing vision in the microscopic range of dimensions and thus providing a control over the actual research.*

* In Ind. Eng. Chem., **17**, 184-7 (March 15, 1945) D. G. Brubaker shows light and electron micrographs of identical fields of various zinc oxides, and comments on them. For electron micrographs of *Mycobacterium tuberculosis*, showing newly demonstrated zoögleal forms, see Eleanor Alexander Jackson in Trans. N. Y. Academy of Sciences, **46**, 127-152 (June 29th, 1945). J. A.

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14. Zworykin, V. K., and others, "Electron Optics and the Electron Microscope," John Wiley (in press).
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Dichroism and Dichroic Polarizers

EDWIN H. LAND AND C. D. WEST
Polaroid Corporation, Cambridge, Mass.

Historical Introduction

The phenomenon of linear dichroism was first observed in the mineral tourmaline by Biot in 1815. Since that time numerous observations, but relatively few quantitative measurements, of linear dichroism have been made on the widest variety of materials; these include, besides natural and artificial crystals, dichroic products obtained by the staining, dyeing or coloring of crystals, fibers, and other biological tissues, films, glass surfaces, and the like. This subject, although faithfully cultivated by a few devotees, never aroused a wide interest in the literature of science and hardly passed beyond a preliminary descriptive stage of development. The data of dichroism remained diffusely scattered through the journals of physics, chemistry, crystallography and mineralogy, biology, and dye and textile technology. This may explain why examples of later rediscoveries of the results of much of the earlier work are fairly numerous in the literature of this subject.

The phenomenon of circular dichroism was first reliably observed in alkaline chromium tartrate solution by another Frenchman, Cotton, in 1895. This property has been carefully measured for a wide variety of optically active molecules in the liquid and vapor states and in solutions; and these measurements have contributed substantially to the development of the theory of optical activity in asymmetric molecules, as related in several books on this subject.

The first satisfactory light polarizer was found in 1828 by W. Nicol, who devised the type of calcite prism which bears his name. The superiority of this type of polarizer needs no other testimony than its leadership of the field for over one hundred years; and it is still the preferred polarizer, when suitably constructed, for giving a completely polarized beam over the spectral range for which calcite transmits the extraordinary ray without absorption, namely about 0.23 — 3.0μ. The limitations of this class of polarizer are equally well recognized and have effectively prevented their application outside the laboratory. These are an angular aperture limited by the optical constants of calcite, and a linear aperture limited by the scarcity of large pieces of calcite of optical quality; great thickness; and occasionally the astigmatism of images transmitted through such prisms.

It was probably recognized quite early that physically the most satisfactory substitute for a calcite polarizer would be some kind of dichroic polarizer. To be specific, tourmaline sections were employed in the simple form of polariscope known as the tourmaline tongs, and also as polarizers for microscopes. The Englishman Herapath in 1852 discovered the intense dichroism of crystals of a sulfate periodide of the cinchona alkaloid quinine. He described in detail his attempts to grow and mount these crystals, which were named herapathite after him, for use as polarizers; and later worked with a similar crystal from cinchonidine alkaloid, a relative of quinine. Later attempts to realize Herapath's conception were described by Zimmern and Coutin in France (1926);[1] and about 1936 A. M. Marks in the United States began commercial production of macrocrystalline cinchonidine herapathite polarizers, while

the Carl Zeiss firm in Germany was doing the same with quinine herapathite polarizers developed by F. Bernauer. In 1935 he [2] had previously outlined general methods for making large area polarizers, but none of these apparently was ever described in any detail. E. H. Land had already been occupied with the same problem for several years, and in February 1932 he had described and demonstrated before the Physical Colloquium of Harvard University a form of dichroic polarizer that was entirely new in that its structure was microcrystalline rather than macrocrystalline. In 1934 Land was in commercial production of this type of polarizer, using quinine herapathite as the crystal component.

The last six years have witnessed a rapid application of dichroic polarizers in a diversity of popular and scientific uses, and an equally rapid development of new types of dichroic polarizers. The most notable of these are not crystalline in the ordinary sense of this term, but would better be described as molecular in structure.

In this brief account we shall treat the general phenomenon of linear dichroism and its measurement, describe the structures of several kinds of useful dichroic polarizers, and point out some of their practical applications.

Dichroism: Definition and Measurement

Absorption. For ordinary homogeneous absorbing media, the absorption of light is conveniently expressed by the optical density of each wave length: $\frac{J}{J_0} = k = 10^{-d}$, or $\log \frac{J_0}{J} = \log \frac{1}{k} = d$. When different thicknesses of the same medium are compared, the law becomes $\log \frac{J_0}{J} = d = Kt$. When the volume concentration of the absorbing agent may be varied as well as the thickness, then in the ideal case the law becomes $\log \frac{J_0}{J} = d = Kt = ect$. It is sometimes more convenient to determine the area concentration c' than the volume concentration c, and in this case by a suitable choice of units $ect = ec'$. The proportionality constants K and e are constants of the absorbing agent, and like d they vary with wave length; when they are employed, the units for c and t must always be stated. We shall take t in cm, c in g per liter, and c' in g per 1000 cm^2; thus our e is a specific extinction coefficient. For ordinary media it is indifferent whether natural, linear, or circular polarized light is used to measure the absorption constants.

Dichroism. It is sometimes overlooked that there exist homogeneous media whose absorption of natural light does not follow the simple thickness law. If we let natural light of intensity J_0 fall on such a medium, and measure successively the emergent intensities J_1 and J_2 after traversing thicknesses t_1 and $t_2 = 2t_1$, we find after making any necessary corrections that $\frac{J_2}{J_0}$ is not equal to $\left[\frac{J_1}{J_0}\right]^2$ as required by $\frac{J}{J_0} = 10^{-Kt}$, but is somewhat greater than $\left[\frac{J_1}{J_0}\right]^2$. If now we analyze the emerging light we find that it has experienced a change in its vibration state; instead of being natural light, it is partially polarized, either circularly or linearly as the case may be. Accordingly, caution must always be exercised in calculating the results of a transmission measurement with natural light to an absorption coefficient if the specimen has this property to an appreciable degree.

Such media are called dichroic, and are characterized by unequal absorptions for two oppositely polarized beams of incident light; in one case the two beams of light are linear-polarized at right angles to each other; in the other case the two beams are circular-polarized in opposite senses. For such media *two* absorption constants are required for a complete description; for example, for linear dichroism $d_\parallel$ and $d_\perp$, or $K_\parallel$ and $K_\perp$ or $e_\parallel$ and $e_\perp$. Then the conventional mathematical expression for dichroism is $\Delta d = d_\parallel - d_\perp$, or ΔK, or Δe.

The constant $d_{\parallel} = \log \frac{1}{k_{\parallel}} = K_{\parallel} t$ of a dichroic specimen denotes the optical density of the specimen for linear-polarized light vibrating parallel to one of the two vibration directions of the specimen, and similarly for $d_{\perp}$. For a linear dichroic specimen $d = \log \frac{1}{k} = Kt$ may be defined and measured in two ways; it is either the optical density for natural or circular-polarized light, or it is the optical density for linear-polarized light vibrating at 45° to the vibration directions of the specimen.

The optical constants, for natural light, of a combination of ideal polarizer plus a dichroic specimen characterized by the constants $d_{\parallel}$, d, and $d_{\perp}$, are found as follows: since the d for an ideal polarizer is $\log 2 = 0.301$, the constants $d_{\parallel}$, d, $d_{\perp}$ are each to be increased by 0.301 to give the constants of the combination; and similarly the k constants are to be multiplied by 0.5 to give the constants of the combination.

Linear dichroism is in fact more complicated than this, for in the most general linear dichroic crystal the absorption constants $K_{\parallel}$ and $K_{\perp}$ vary with the orientation of the crystal section being measured, with respect to the orthogonal principal axes X, Y, Z, of the triaxial absorption ellipsoid. In the dichroic materials treated here, we shall avoid ambiguity by considering only what amounts to crystal sections of fixed orientation, and only that light which traverses such sections at normal incidence.

Detection of Dichroism. While a suitably mounted calcite cleavage rhomb was formerly employed as a dichroscope for detecting linear dichroism, it is now easier to construct an equivalent device by juxtaposing two linear film polarizers (plate P in Fig. 1). If this divided field plate be superposed with a quarter-wave sheet (plate

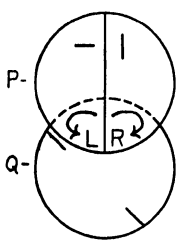

FIGURE 1.

Q), the combination serves as a circular dichroscope when the polarizer layer is held next to the eye, and as a linear dichroscope when it is turned over and the quarter-wave layer is next to the eye of the observer. With dichroscopes of this kind, in fact in the general use of dichroic polarizers, it is a great convenience to have the vibration direction or sense of the transmitted light plainly indicated by a reference mark.

For detecting linear dichroism in extra-visual portions of the spectrum, C. D. West has made use of the interference bands (Müller bands) given by a thin crystal section such as quartz cut parallel to the optic axis. This section is placed in the diagonal position between a known polarizer, such as a Nicol prism, and the unknown specimen, in front of the slit of a prism or grating spectrograph; and varying exposures are made with a light source giving a continuous spectrum. Then the interference bands, which occur at approximately equal intervals on a frequency scale, are registered only in those portions of the spectrum for which the unknown specimen is dichroic.

The Savart plate in conjunction with a Nicol prism is the familiar device for detecting traces of linear polarization in a light source. A convenient and easily made equivalent device results, when a film polarizer whose vibration direction is marked is cemented to a basal section of a strongly birefringent crystal such as calcite. The appearance of isochromatic circles will reveal the presence of polariza-

tion, while the azimuth at which the black isogyres join in the center will indicate the vibration direction of the polarized component.

Measurement of Absorption Constants of Linear Dichroic Media. The absorption constants of a dichroic medium can be measured with any kind of a photometer; but in practice the spectral variation of these constants, as measured with a spectrophotometer, is of primary interest.

It is to be recognized that the measurement of the absorption constants of strongly dichroic samples such as the present polarizing layers is equivalent to the measurement of relatively high and relatively low optical densities; if done with accuracy, these are difficult tasks by any spectrophotometric methods. In contrast to the more usual practice with isotropic liquid solutions, the operator here is generally not free to choose for measurement density ranges over which a given instrument yields results of maximum accuracy.

With a non-polarizing spectrophotometer one measures k, the transmission of a single dichroic layer; k_2, the transmission of two superposed identical layers in the parallel position; and k_x, the transmission of the same two layers crossed. In the measurement of k and k_2, polarization effects in the instrument which would affect the results must be guarded against. The three transmissions should satisfy the relations

$$k_2 \leq k_x,$$
$$2k^2 = k_2 + k_x.$$

The constants k_2 and k_x are related to the transmissions of a single layer for each of two oppositely polarized rays, $k_\parallel$ and $k_\perp$, by the equations (when $k_x = 0$, $k_\perp = 2k = \sqrt{2k_2}$)

$$k_2 = \tfrac{1}{2}(k_\parallel{}^2 + k_\perp{}^2), \qquad k_\perp = \frac{\sqrt{2}}{2}(\sqrt{k_2 + k_x} + \sqrt{k_2 - k_x}),$$

$$k_x = k_\parallel \cdot k_\perp ; \qquad k_\parallel = \frac{\sqrt{2}}{2}(\sqrt{k_2 + k_x} - \sqrt{k_2 - k_x}).$$

Any non-polarizing spectrophotometer may be adapted to measure directly the constants of dichroic layers by inserting a fixed polarizer, preferably a calcite polarizer, in the optical system. By such means one can determine $k_\parallel$ and $k_\perp$ with only a single specimen, which obviously must be rotated through a right angle between the two measurements; k also may be measured in the diagonal position. This method is suggested for the photoelectric spectrophotometers which have in recent years become readily available, and which cover portions of the ultraviolet and infrared spectra as well as the visible.

Polarization spectrophotometers are also available for measurements over the visible spectrum. Such subjective instruments can be employed to measure independently four different constants of a dichroic specimen, namely k, $k_\parallel$, $k_\perp$, and the ratio of the last two or $R = \frac{k_\parallel}{k_\perp}$. For the measurement of the first three of these, the dichroic specimen covers only one window of the photometer, whereas in measuring R the specimen must be large enough to cover both windows. In terms of density the corresponding constants are d, $d_\parallel$, $d_\perp$, and $\Delta d = d_\parallel - d_\perp$. With such an instrument the logical practice is to measure whichever pair of these constants can be obtained with the greater accuracy, for example, Δd and $d_\parallel$, and calculate the other two constants therefrom. Incidentally, these four constants may be readily measured to a fair approximation for a not too strongly absorbing dichroic specimen (*e.g.*, a piece of commercial dyed cellophane) by means of an improvised photometer consisting of the dichroscope plate described above, in combination with an analyser and a divided circle (such as the stage of a polarizing microscope) for reading off the angular settings.

From a measured R the degree of polarization may be calculated as $V = \frac{1-R}{1+R}$, where V is the per cent of linear polarized light, $1 - V$ the per cent of unpolarized light in the total light transmitted.

The k, V and R constants are related to $k_\parallel$ and $k_\perp$ by the equations:

$$k_\parallel = k(1 - V) = \frac{2kR}{1+R}, \qquad k = \tfrac{1}{2}(k_\parallel + k_\perp),$$

$$k_\perp = k(1 + V) = \frac{2k}{1+R}; \qquad V = \frac{k_\perp - k_\parallel}{k_\perp + k_\parallel}.$$

All calculations are simplified by freeing the measured densities ($d_\parallel$, $d_\perp$, d) or transmissions from reflection losses. All the measurements in this paper have been corrected in this manner.

The effect of adding an isotropic absorber to a dichroic absorber is to decrease both the transmission k and the dichroic ratio $d_\parallel/d_\perp > 1$, while the dichroism Δd, the ratio R and the degree of polarization V characteristic of the dichroic absorber are left unchanged.

The average density $\bar{d}$ of a dichroic medium will enter into some of our calculations. It is defined as

$$\begin{aligned} \bar{d} &= \tfrac{1}{3}(d_x + d_y + d_z) \text{ for biaxial media;} \\ &= \tfrac{1}{3}(2d_\perp + d_\parallel) \quad \text{for uniaxial media;} \\ &\sim \tfrac{1}{3}d_\parallel \text{ when } d_\perp \sim 0. \end{aligned}$$

This is distinctly different from the density for natural light of a section of a dichroic medium

$$\begin{aligned} d = -\log k &= -\log \tfrac{1}{2}(k_\parallel + k_\perp) \\ &\sim \log 2 + d_\perp \text{ when } k_\parallel \sim 0. \end{aligned}$$

The spectral curves of $d_\parallel$, $d_\perp$, $\bar{d}$ and d for a strongly dichroic medium are illustrated in Fig. 7; it is seen here how the pronounced absorption band shown by the $d_\parallel$ and $\bar{d}$ curves vanishes completely when the data are calculated to the d curve for this medium. As has already been stated, the constants $d_\parallel$, d, and $d_\perp$ are measures of the intensity of the emergent light when a linear dichroic specimen is traversed by a beam of linear-polarized light vibrating at the respective azimuths 0, 45° and 90° to one of the vibration directions of the specimen. For a better idea of the relations between these three constants the reader is referred to Fig. 12.

Presentation of Results. In comparing a wide variety of dichroic media it is desirable to reduce measured quantities to a uniform system of constants. In the past the practice has been almost unanimous to report values of $d_\parallel$ and $d_\perp$, or absorption constants differing from these by a simple factor. But in describing the current dichroic polarizers one notes a tendency to give other constants, for example k_x and k_y (Strong, 1936) [3] or k and V (Grabau, 1937).[4] This last system is doubtless quite satisfactory from the point of view of the person who expects to use a dichroic preparation as a polarizer; but for the purposes of the present treatment we prefer to retain the older $d_\parallel$, $d_\perp$ system. One advantage here is that not only the dichroism, Δd, but also the dichroic ratio $\frac{d_\parallel}{d_\perp}$ is easily obtained in this system; and this ratio is seen to be, for a given absorbing agent, a constant invariant with respect to changes in concentration and thickness, and thus it serves as a convenient figure of merit, other things being equal. This ratio was early employed in reporting quantitative measurements of dichroism by Pulfrich (1882),[5] and it was more recently resurrected by Preston (1931).[6]

Example of Linear Dichroism. Flow Dichroism of a Hydrosol. Previous measurements of flow dichroism and flow birefringence of colloidal solutions of dyes and

of vanadium pentoxide in water were given in a valuable paper on linear dichroism of Zocher and Jacoby (1927).[7] These measurements give only the difference of the absorption, Δd, but not the value of either $d_{\parallel}$ or $d_{\perp}$ for the systems studied.

West has found that the strong blue color resulting from mixing extremely dilute solutions of α-naphthoflavone and iodine, first observed by Barger and Starling (1915) [8] and lately employed as an iodometric indicator, is characterized by a remarkable flow dichroism and flow birefringence not previously reported. This flow dichroism is positive, which means that the component of the incident light vibrating parallel to the streamlines is the more strongly absorbed; but the flow birefringence is negative (the slow ray is transverse to the streamlines), as would be expected if it were governed by the dichroic absorption band in the far red.

A glass cell was constructed in which the solution could be made to flow with a slow nearly uniform motion about a closed path between stationary walls. Measurements were made of $d_{\parallel}$ and $d_{\perp}$ for the liquid in motion, and of d for the stationary system, by means of a Gaertner polarization spectrophotometer for the visual spectrum.

The accompanying curves (Fig. 2) show the course of the measured d, $d_{\parallel}$, and $d_{\perp}$ curves; and the $\Delta d = d_{\parallel} - d_{\perp}$ and d calc. $= \frac{1}{3}(d_{\parallel} + 2d_{\perp})$ curves calculated therefrom. It is seen that the calculated d points fall on the measured d curve to a good approximation; they would be expected to coincide exactly for a system in uniform uniaxial flow, a condition somewhat difficult to realize experimentally.

Dichroic Polarizers: Structure and Properties

The following list is representative of recent patents disclosing dichroic polarizers or processes of preparing them.*

Linear dichroism is a general property of absorbing anisotropic matter. It is not difficult to state the characteristics of dichroic materials potentially suitable for preparation of dichroic polarizers. Such materials should have:

(1) An absorption band covering the portion of the spectrum it is desired to polarize, ordinarily the visible spectrum 400 — 700 mμ.

(2) An adequately high dichroism throughout this band.

(3) Stability and permanence under the conditions to which it will be exposed in use—or generally, exposure to heat, to visible and ultraviolet radiation, to humidity, and to mechanical stresses.

(4) Freedom from scattering or diffusion of the transmitted component.

Under (2), we might arbitrarily take a dichroic ratio of about 7 as the threshold

* While this paper is intended to represent the state of the art as of January, 1943, this list includes patents up to June, 1944.

E. D. Bailey and M. M. Brubaker. U. S. 2,246,087 (1941).
R. P. Blake. U. S. 2,256,108 (1941).
C. H. Brown. U. S. 2,224,214 (1940); 2,287,598 (1942).
E. Käsemann. U. S. 2, 236,972 (1941).
L. A. Keim. U. S. 2,274,706 (1942); 2,340,476 (1944).
E. H. Land. U. S. 1,918,848 (1933) (Land and Friedman); 1,951,664 (1934); 1,956,867 (1934); 1,989,371 (1935); 2,011,553 (1935); 2,041,138 (1936); 2,078,254 (1937); 2,165,973 (1939); 2,173,304 (1939) (Land and Rogers); 2,178,996 (1939); 2,237,567 (1941); 2,281,100 (1942); 2,289,712 (1942) (Land and West); 2,289,713 (1942); 2,289,714 (1942); 2,298,058 (1942); 2,306,108 (1942) (Land and Rogers); 2,319,816 (1943); 2,328,219 (1943); 2,343,775 (1944); 2,346,766 (1944).
H. Lapp. German 674,840 (1939).
A. M. Marks. U. S. 2,104,949 (1938); 2,167,899 (1939); 2,199,227 (1940); 2,344,514 (1944).
K. Meyer and others. German 675,217 (1939); 681,237 (1939); 681,347 (1940).
L. Pollack. U. S. 2,286,569 (1942); 2,346,784 (1944).
H. G. Rogers. U. S. 2,255,940 (1941); 2,284,590 (1942).
O. Vierling and P. G. Gänswein. U. S. 2,344,117 (1944).
G. Wilmanns and W. Schneider. U. S. 2,176,516 (1939).
H. Zocher. U. S. 1,873,951 (1932).

of usefulness. A polarizer with $k_{\parallel} = 0.01$, $d_{\parallel} = 2.0$; $k_{\perp} = 0.50$, $d_{\perp} = 0.30$; and $k = 0.25$, $d = 0.61$, $V = 96.1$ per cent, would approximate this figure. It is of interest that colored tourmalines so far reported have a dichroic ratio of this order of magnitude, irrespective of their color. An ideal polarizer would have, for comparison, $k_{\parallel} = 0$, $d_{\parallel} = \infty$; $k_{\perp} = 1.00$, $d_{\perp} = 0$; $k = 0.50$, $d = 0.30$, $V = 100$ per cent, giving an infinite dichroic ratio.

Linear dichroic polarizers are conveniently treated in three classes according to structure: macrocrystalline, microcrystalline, and those associated with oriented linear high polymers. In the following, dichroic specimens of these classes will be illustrated by $d_{\parallel}$, $d_{\perp}$ curves, all taken in these laboratories by means of the Gaertner spectrophotometer (Martens type) previously mentioned, and all corrected for reflection losses (Figs. 2-18); these are chosen to show the nature of the absorption bands

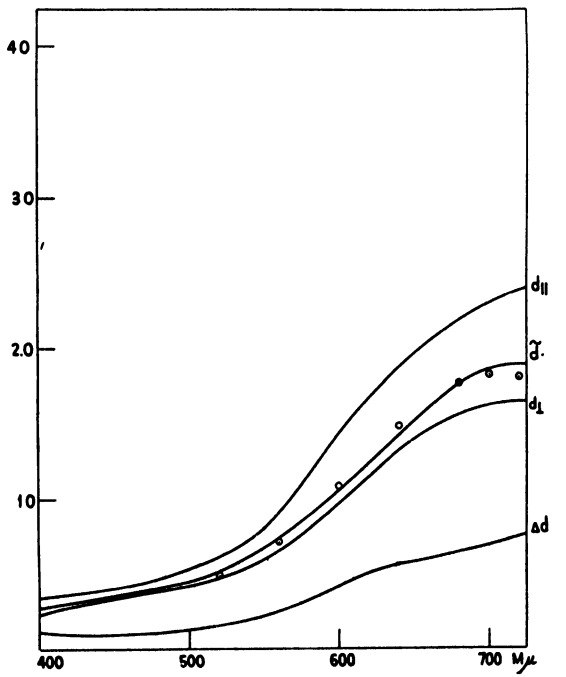

FIGURE 2. Flow dichroism of α-naphthoflavone product with iodine. The curve of average density $\bar{d}$ is for the fluid at rest, the circles are values of $\bar{d}$ calculated from $d_{\parallel}$ and $d_{\perp}$ for the fluid in motion. Cell thickness 2 cm.

in question rather than to be representative of the commercial polarizers which are or may be prepared from these materials.

In considering these curves it is to be kept in mind that optical densities greater than 3 are in general subject to increasingly large errors of measurement as the density increases above 3.

We wish to mention, among other members of the research laboratory of Polaroid Corporation, especially W. F. Amon, Jr., who prepared many photometric samples, and A. S. Makas, who took many spectrophotometric curves, which were the necessary preliminary to the discussion of the following section.

Macrocrystalline Polarizers. These are prepared by cutting, or by growing, sections of dichroic crystals of suitable orientation and thickness to give useful po-

larizers. When the section is thin or mechanically weak, it is cemented between transparent protecting covers such as glass plates.

Tourmaline Polarizers. This relatively abundant silicate mineral crystallizes in the trigonal system, and when colored always shows stronger absorption of the ordinary ray (negative dichroism). As with all uniaxial crystals, the maximum dichroism is exhibited by sections parallel to the optic axis, whereas sections perpendicular to the axis are isotropic. In the past the absorption constants $K_{\parallel}$ and $K_{\perp}$ have been repeatedly measured through the visible spectrum for specimens of various colors, and while they are found to vary quite widely, the dichroic ratio is substantially constant. This suggests that the absorbing agent is of the same nature in all tourmalines, but is present in varying concentrations. No explanation of the dichroism has yet been undertaken; it is recognized only that colored tourmalines generally contain cations of the transition metals, for example manganese in rose tourmaline and iron in the brown or black varieties. The dichroism of a black tourmaline is shown in the accompanying density curves (Fig. 3).

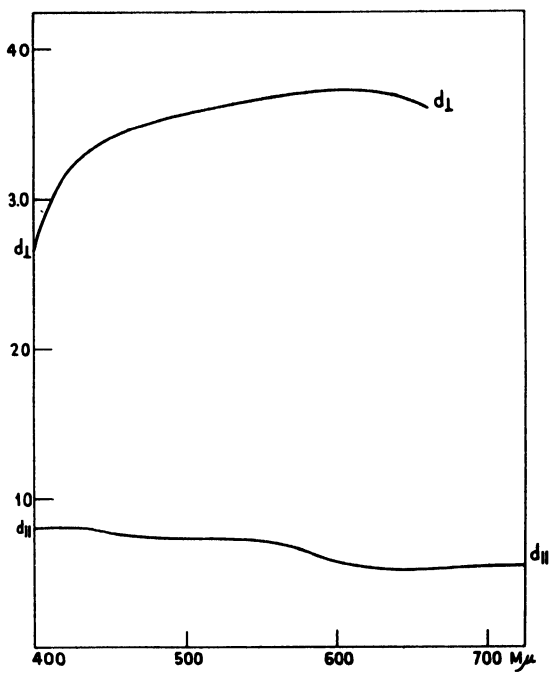

FIGURE 3. Dichroism of black tourmaline, section about 0.2 mm thick, cut 24° from parallelism with the optic axis, for light traveling perpendicular to the optic axis.

A mineral which, when colored, has a very strong uniaxial positive dichroism colorless-deep blue, but whose absorption constants have not been measured, is the rare silicate, benitoite, $BaTiSi_3O_9$ or $BaO{\cdot}TiO_2{\cdot}3\ SiO_2$. It is interesting to speculate whether the absorption here might be due to the presence of another transition metal, trivalent titanium, which is known in water solutions to have a narrow absorption band with a peak at 744 mμ.

Quinine Herapathite Polarizers. This quinine sulfate tri-iodide crystallizes in thin pinacoidal plates belonging to the orthorhombic system, which absorb one vibration in their plane and transmit the other two vibrations (positive dichroism). Its

formula, according to Jörgensen (1876),[9] is $4C_{20}H_{24}N_2O_2 \cdot 3H_2SO_4 \cdot 2HI \cdot 2I_2 \cdot xH_2O$, and it has been observed in these laboratories to begin to melt at about 165°. The crystallography of this material has been described by West (1937).[10] The absorption constants $K_{\parallel}$ and $K_{\perp}$ of this crystal are not yet accurately known, since $d_{\parallel}$ and $d_{\perp}$ have not been measured for specimens of known thickness; however, a thickness of about 0.0002 inch (5 microns) is probably enough to give a good polarizer. Plates that are too thin have red extinction, while those that are too thick have red-brown transmission when viewed against a white light source. The absorption curves for this crystal are illustrated by the data for a Zeiss Herotar filter (Fig. 4).

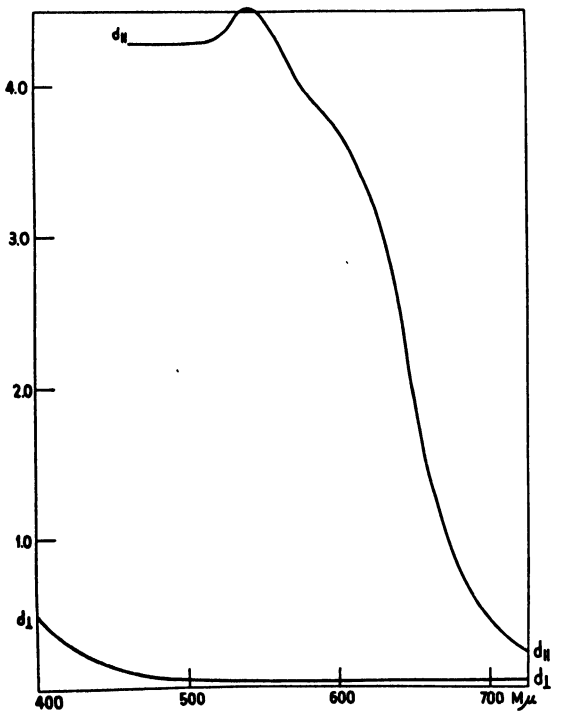

FIGURE 4. Dichroism of a Zeiss Herotar filter (quinine herapathite).

Cinchonidine Herapathite Polarizers. The crystal habit and optical properties of cinchonidine herapathite are similar to but not identical with those of quinine herapathite; it grows in orthorhombic pinacoidal plates, which begin to melt at about 154°. The formula given by Jorgensen (1876),[11] $12C_{20}H_{24}N_2O \cdot 9H_2SO_4 \cdot 8HI \cdot 12I_2 \cdot 8H_2O$, requires revision, since the formula now accepted for cinchonidine is $C_{19}H_{22}N_2O$. This crystal is superior to herapathite in that its positive dichroic absorption band persists into the near infrared, while that of herapathite cuts off in the visible far red; but as in the preceding example the absorption constants have not yet been published for this crystal. Presumably they will be of the same order as the constants of herapathite. Measurements on a Marks polarizing plate may be taken as representative of the dichroism of this crystal (Fig. 5).

Microcrystalline Polarizers. Polarizers of this type, invented by Land, are made by first preparing a suspension of dichroic crystal needles in a viscous medium, and then subjecting the suspension to a uniform flow process which will yield a sheet containing the crystal needles all oriented parallel to a common direction, namely the

direction of the streamlines in the flow process. After the flow process the sheet is hardened, as by the escape of the volatile solvent used in preparing the viscous medium. Practically the process differs from the example of flow dichroism described in a previous section in respect to the higher concentrations, viscosities, and velocity gradients employed. Suitable crystal needles may have one of two main kinds of dichroism: they may absorb light vibrating parallel to the needle length, and transmit the two light vibrations perpendicular to this direction (positive dichroism), or they may transmit the parallel vibrations and absorb the two perpendicular vibrations (negative dichroism); a third possibility would be offered by a crystal needle which transmitted the parallel vibration and absorbed only one of the two perpendicular vibrations. In practice, only crystal needles of the first class, those characterized by positive dichroism, have so far been employed. If one starts with a strongly dichroic crystal species, the quality of the resulting polarizer depends chiefly on the perfection of the orientation attained, and this is conditioned by two factors: first, all the crystals in the suspension should have the correct shape and should fall in a certain size range; second, the flow conditions should be correctly chosen to set them all in parallelism. There are further obvious precautions to be observed in making these polarizers: the viscous medium should not have an appreciable solvent power for the crystal; temperatures must be avoided which melt, decompose or dissolve the crystals; and mechanical stresses must be avoided which break the crystals.

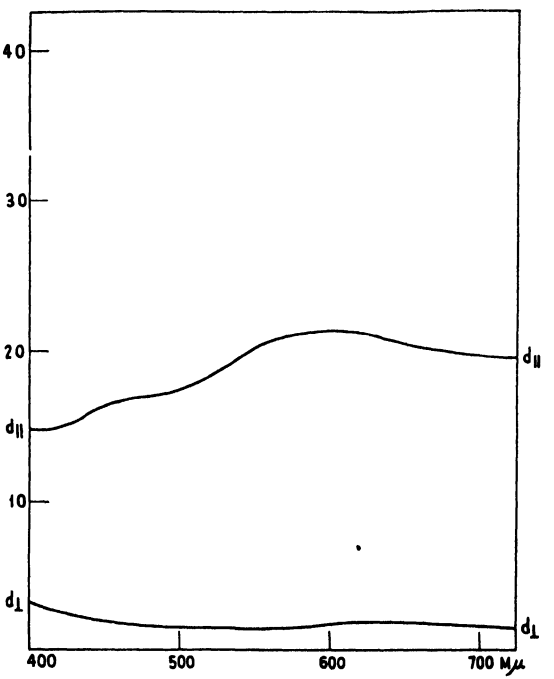

FIGURE 5. Dichroism of a Marks Polarizing Plate (cinchonidine herapathite).

West has observed that a section of Polaroid J-sheet cut across the needle axes is found to be not isotropic but weakly dichroic, which indicates a departure of its optical properties from strict uniaxiality. If we denote the film normal by X, the direction of the needle axes in the plane of the film by Z, and the transverse direction in the plane of the film by Y, then the absorptions are in the order $Z \gg Y > X$. Con-

sistent with this is the observation that when a film is immersed in mineral oil and tilted about Y, two positions (corresponding to the optic axes of a biaxial dichroic crystal) are found where the dichroism vanishes. The angle between these two positions measured in the XZ plane over X might be termed the "monochroic angle." The simplest interpretation is that the long axes of the needles have a spatial distribution such that they are more nearly parallel to the plane of the film (YZ plane) than they are to the XZ plane.

Dichroic polarizers of this class are often characterized by a slight scattering of the transmitted light; this scattered light is far from having a uniform distribution, rather it reaches a maximum in what we have just called the XY plane. This subject was studied by Farwell (1938).[12] While this sometimes undesirable property would be minimized by having the refractive index of the medium as close as possible to the refractive index of the crystals, practically it is found easier to control it by keeping the largest crystals below a limiting size. It would be even more effectively eliminated, as Land has suggested, by using negative dichroic crystals if such were available.

The conclusion from experience so far is that microcrystalline polarizers are technically easier to produce than macrocrystalline polarizers, over any useful range of areas.

Useful dichroic polarizers have been made by this process from both quinine and cinchonidine herapathites. The preparation of quinine herapathite suspensions for this purpose was described in the Land patents and in a recent paper by Godina and Faerman (1941).[13] The commercial polarizer known as Polaroid J-sheet is of this type and consists of oriented quinine herapathite needles in a cellulose acetate film. It is of interest that overheating under suitable conditions will shift the dichroic absorption band of this film towards the blue. The effect of this shift is to change the extinction color of crossed films from purple to red, when viewed against a white light source. Absorption curves for a dichroic film made by the Polaroid J-sheet process before and after such heating are shown in the accompanying figure (Fig. 6).

Data are also given for a dichroic film prepared from microcrystalline cinchonidine herapathite (Fig. 7). A general similarity of Figs. 7 and 5 and likewise of Figs. 6 and 4, is to be observed.

A third microcrystalline dichroic polarizer was developed by Polaroid Corporation in 1942 from an acid periodide of 3, 4, 5, 6 dibenzacridin. The somewhat lower dichroism of this polarizer (see Fig. 8) as compared to the two preceding ones, is to some extent offset by the higher melting point of this crystal, which is in the neighborhood of 200°. The colored sorption compound of dibenzacridin with iodine was described in a paper by Kermack, Slater and Spragg (1930).[14]

Dichroic Polarizers Associated with Oriented Linear High Polymers. Linear high polymeric materials initially in an isotropic state are quite generally capable of being put into a uniformly oriented state by subjection to a relatively large uniform tensile strain or deformation under suitable conditions. The deformation is generally at least partly recoverable, likewise under suitable conditions. The process of orienting a linear high polymer may be formulated as a rather complex case of combined elastic and viscous deformation, the resistance to which is quite large; much larger, apparently than the viscous resistance encountered in the manufacture of the microcrystalline polarizing films treated in the preceding section.

Evidences of the oriented state of a linear high polymer are the anisotropy of mechanical properties (increase of modulus and tensile strength in the direction of the original tension); the anisotropy of optical properties (birefringence which cannot be explained in terms of internal stresses, uniaxial about the direction of the original tension); and frequently but not always the property of giving an x-ray fiber diffraction pattern, when the primary beam travels perpendicular to the direction of the original tension. Some natural fibers such as ramie (cellulose) and silk

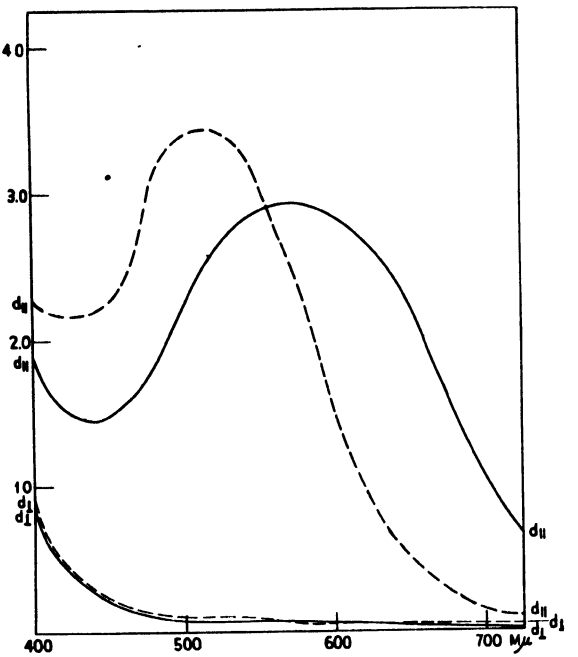

FIGURE 6. Dichroism of a quinine herapathite microcrystalline polarizer before (full lines) and after (broken lines) heat treatment.

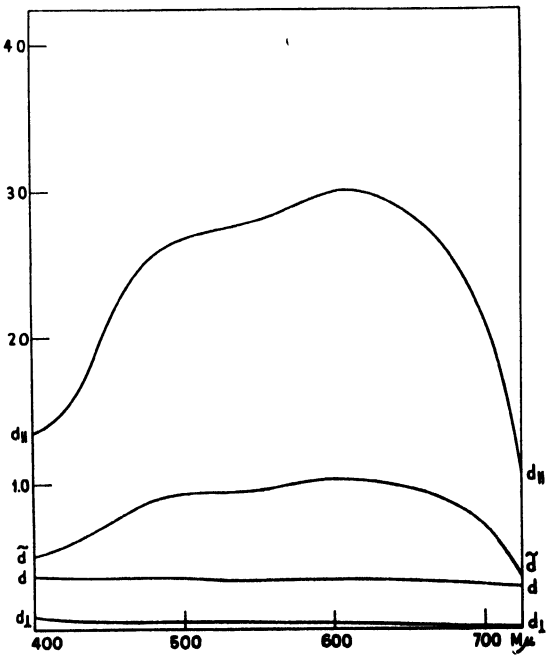

FIGURE 7. Dichroism of a cinchonidine herapathite microcrystalline polarizer. Curves of average density $\tilde{d}$ and density for natural light d are also shown.

represent quite perfectly oriented states of linear high polymers, but these are not very suitable for preparing dichroic polarizers.

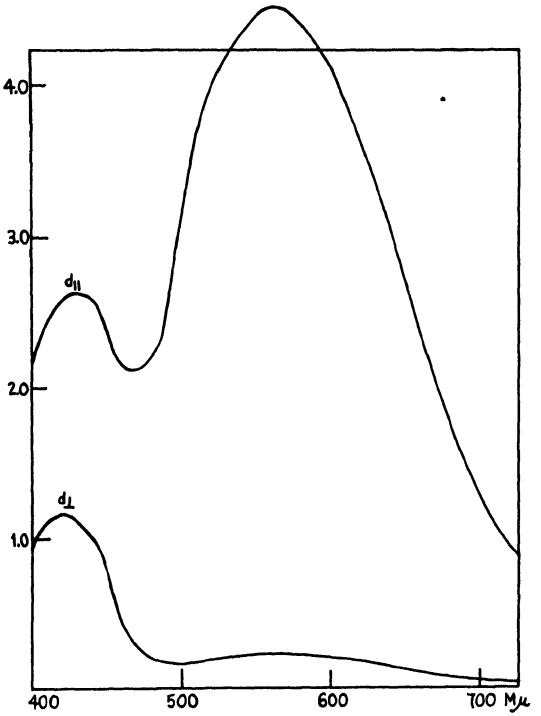

FIGURE 8. Dichroism of a dibenzacridine periodide polarizer.

A polymer which Land has found to be well suited for preparing the present class of dichroic polarizers is the synthetic product polyvinyl alcohol $(-CH_2-CHOH-)_x$, manufactured commercially by hydrolysis of polyvinyl acetate $(-CH_2-CH(OOCCH_3)-)_x$. This polymer, which has an extensibility of the same order as that of rubber, is formed into sheets which are oriented by uniform tensile deformations. The fully oriented sheet has a definitely fibrous structure and is characterized by high tensile strength in the fiber direction, of the order of 10^5 psi; by uniaxial positive birefringence ($\varepsilon = 1.560$, $\omega = 1.526$, $\varepsilon - \omega = 0.034$ are representative saturation values); and by a sharp x-ray fiber diffraction pattern. The atomic structure of the oriented polyvinyl alcohol fiber as worked out by x-ray methods by Mooney (1941)[15] has a plane zigzag of carbon atoms (*trans, trans, . . .*) with hydroxyls attached to alternate carbons (1, 3 diol groups) and all lying on the same side of the plane of the carbon chain. As is true of cellulose films, the transparency of polyvinyl alcohol films extends over considerable ranges into the ultraviolet and infrared. The weak ultraviolet absorption band reported for polyvinyl alcohol at 280 mμ by Marvel and Denoon (1938)[16] does not exist, according to our measurements.

As with the microcrystalline polarizers, all the useful dichroic polarizers so far made from oriented high polymers are characterized by positive dichroism.

Dye Polarizers. Preston (1933)[17] found that dichroic products resulted from the application of direct dyes to films or fibers of oriented cellulose, and published quantitative data on the dichroism; he also referred to earlier observations of this effect.

Other dichroic polarizers can also be made from oriented polyvinyl alcohol films, and these are found to have useful dichroic ratios.

An outstanding characteristic of such preparations is that the light absorption by each dye molecule (more strictly, ion) does not change very much, whether it is measured in solution, in the unoriented film, or in the oriented film. This observation suggests that the dye goes onto the oriented film in single molecules, and that the dichroism of the film generally may be taken as a direct measure of the dichroism of the individual dye molecules. In making this comparison, one measures the e of the solution in the customary manner for comparison with the average extinction coefficient $\tilde{e}$ of the dichroic film, as we have already done in the example of flow dichroism. This line of investigation is a relatively easy one, first because it is possible to cast the dye directly into the polyvinyl alcohol film by the aid of mutual solvents; secondly, because it is possible to calculate the e's of the dye in the film from the measured d's through the area concentration of the dye, taken as the product of the weight per cent of the dye in the film times the area density of the film: c' = (g dye per g of dyed film) × (g dyed film per 1000 cm^2); then $\tilde{e} = \tilde{d}/c' = \frac{1}{3c'}(2d_\perp + d_\parallel)$. In this way the labor of a chemical analysis becomes unnecessary.

Another indication that dichroic direct dyes on oriented high polymers are present as single ions, and not as polymeric forms, is afforded by the observation that x-ray diffraction photographs of such preparations show only amorphous scattering even when the dye is present in high concentrations. Our unpublished data confirm Valko (1941)[18] on this point.

Figs. 9 and 10 illustrate the constancy of the absorption by the Congo Red anion; curves are also given for dichroic preparations of both the red and the blue (acid) forms of this dye.

The curves for Congo Red are representative of the generality of direct dyes: the absorption bands of single dyes are too narrow to cover the entire visible spectrum satisfactorily at once. For this purpose one may combine two or more dyes in separate parallel films, or in the same oriented film (Fig. 11). Also it is seen that

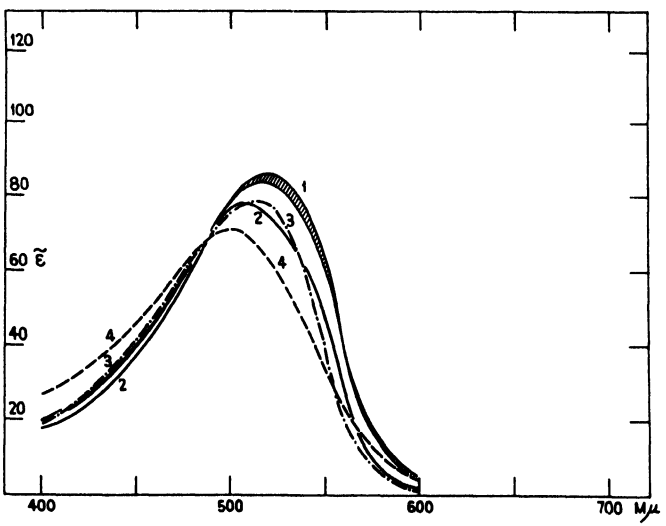

FIGURE 9. Absorption curves of Congo Red in varying environments. (1) Two dichroic preparations on polyvinyl alcohol, $c' = 0.00566$ and 0.01187 respectively. (2) Isotropic preparation on unoriented polyvinyl alcohol, $c' = 0.01155$. (3) Methyl "Cellosolve" solution. (4) Water solution. For (3) and (4), $c = 0.0174$, thickness = 1 cm.

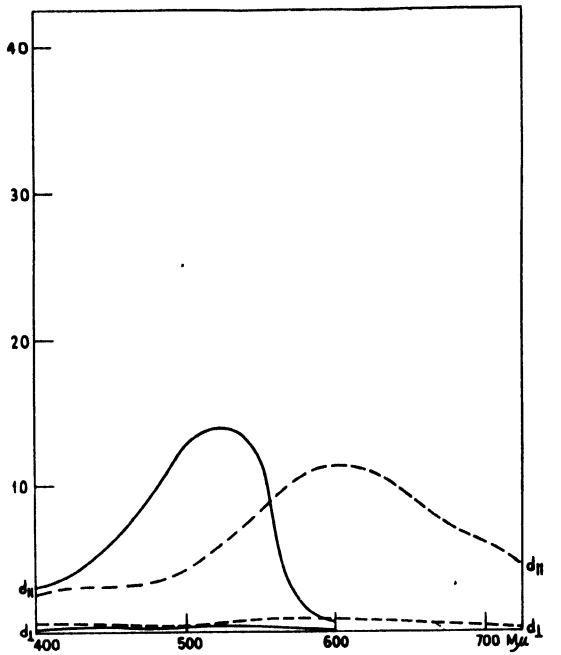

FIGURE 10. Dichroism of Congo Red on oriented polyvinyl alcohol, red (full lines) and blue (dotted lines) forms.

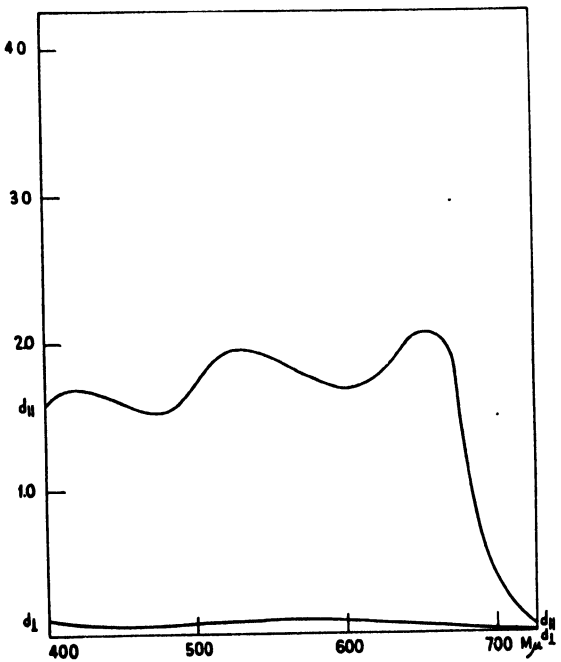

FIGURE 11. Dichroism of a mixture of dyes on oriented polyvinyl alcohol: yellow (Color Index No. 622), red (C. I. 278), and blue (C. I. 518).

quite striking effects are observed when two dichroic films, made with dyes whose absorption bands do not overlap, are crossed and examined with a dichroscope. Absorption curves of such a combination are shown in Fig. 12. When the two dyes in

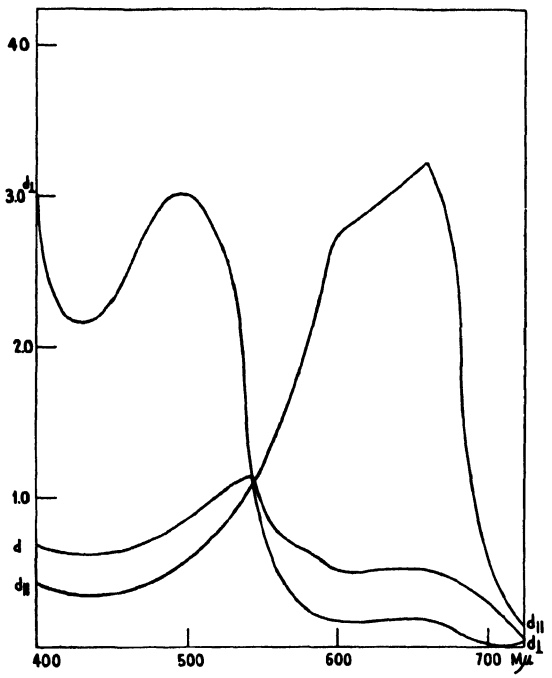

FIGURE 12. Dichroism of crossed dyed films of polyvinyl alcohol, orange (C. I. 374) and blue (C. I. 518).

a crossed combination of this kind are complementary, such combinations when taken in pairs have the interesting property of extinguishing white light when rotated to the crossed position.

It should not be inferred from the foregoing that only direct dyes give useful dichroism on oriented polyvinyl alcohol. The basic dye methylene blue, in which the dye ion is a cation, is an example of a dye with a dichroic ratio of about ten on the oriented polymer.

For dyes having disc-shaped molecules one would expect to find a maximum dichroic ratio not greater than 2, namely $\frac{d_\parallel}{d_\perp} = \frac{e_z}{\frac{1}{2}(e_x + e_y)}$, which equals 2 when $e_z \sim 0$ (z denotes the normal to the molecule plane, x a direction in the molecule plane). This is confirmed by observations of such dye cations and anions as crystal violet, aurin, and picric acid on oriented polyvinyl alcohol.

From the complete absence of dichroism of other dyes on oriented polyvinyl alcohol, one concludes that their structures are substantially spherically symmetrical. An example is the coördination compound of trivalent iron, Naphthol Green B.

From evidence of this sort one is justified in drawing conclusions concerning proposed structural formulas for dye molecules. The stilbene dye Color Index 620 has a dichroic ratio of about 15; therefore, the ring structure assigned to it seems highly improbable. Similarly, the observation that aniline black applied to oriented polyvinyl alcohol in a variety of ways always exhibits negligible dichroism apparently

precludes the beautifully linear structures ascribed to this molecule in its various stages of oxidation.

The present method also has some value in helping to identify the several absorption maxima of a dye molecule with geometrical directions or axes in the molecule. Our experience has been that when a given molecule has positive dichroism for its strongest absorption maximum in the visible, then a second maximum will generally exhibit dichroism of the same sign. For example, when polyvinyl alcohol sheet containing ¼ per cent by weight of the much studied basic dye 1, 1'-diethyl-2, 2'-cyanine chloride is stretched and its dichroism is measured, twin maxima having the same dichroism (dichroic ratio about 5) and the same sign are found at 527 and 495 mμ; from which we conclude that both these maxima are identified with electronic transitions along the long direction of the planar molecule. Such a conclusion is at variance with the views of Scheibe, and of Lewis and Calvin, who ascribe the 495 maximum to an electronic transition transverse to the long direction of the molecule and in its plane.

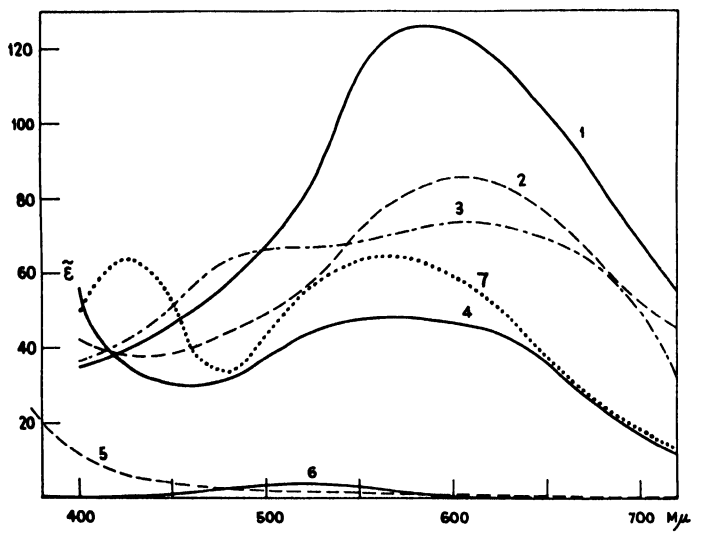

FIGURE 13. Absorption curves of iodine in varying environments. (1) Starch-iodine (2.54 mg I, 50 mg starch per 100 cc water; $c' = 0.0254$). (2) Iodine in preparation of Fig. 14, $c' = 0.012$ by titration. (3) Iodine in preparation of Fig. 7, $c' = 0.014$ calc. (4) Iodine in preparation of Fig. 6, $c' = 0.02115$ calc. (5) Iodine in aqueous KI, after Brode, *J. Am. Chem. Soc.*, **48**, 1877 (1926). (6) Iodine in hexane, after Groh, *Z. physik. Chem.*, **149**, 153 (1930). (7) Iodine in preparation of Fig. 8, $c' = 0.02625$ calc.

Iodine Polarizers. The ability of iodine to give dichroic dark colors on oriented cellulose has been known for some time. That a water solution of polyvinyl alcohol gives a blue coloration with iodine, when the concentrations are relatively high as compared for example with the starch-iodine system, was shown by Staudinger (1927)[19] and by Gallay (1936).[20] Land has prepared films of extraordinarily high dichroism from iodine and the oriented polymers of vinyl alcohol and vinyl butyral; and this reaction seems to be a fairly general property of oriented polyvinyl oxy-compounds, represented by the formula $(-CH_2-CHOR-)_n$, where OR is taken to indicate hydroxyl, acetal, ketal, ether or ester groups, etc., or mixed polymers thereof.

These colored products differ distinctly from the foregoing products made with dye molecules. For all simple iodine solutions, whether brown or violet, are charac-

terized by relatively weak absorption in the visible spectrum, and especially in the red, whereas iodine in association with water solutions of suitable polymeric materials gives very intense absorption bands in the visible, as for example the well-known blue color with starch solution or the red color with dextrine solution. The state of the iodine in these water solutions is evidently similar to the state of the iodine in the dichroic preparations from oriented films of cellulose or polyvinyl alcohol, but must be radically different from the state of the iodine in the brown or violet solutions in simple solvents, as shown by an examination of the quantitative absorption curves (Fig. 13).

A vast amount of work has been done and published in the past with the object of elucidating the structure of this strongly absorbing state of iodine, which is called forth by the presence of suitable high polymers and water; but even the recent activity in this field has not given the final word.

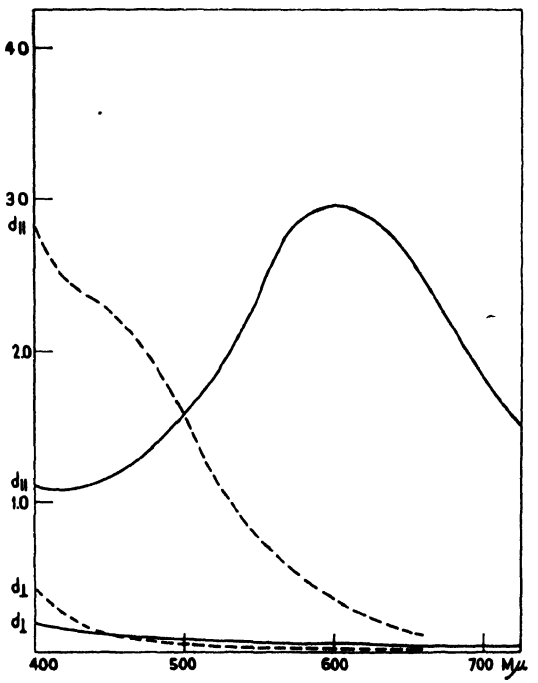

FIGURE 14. Dichroism of iodine on oriented polyvinyl alcohol, blue (full lines) and brown (broken lines) forms.

West has obtained definite evidence, not yet published, from the x-ray diffraction study of dichroic films of iodine on oriented polyvinyl alcohol that the iodine is present in a *polymeric* form, namely as independent long strings of iodine atoms all lying parallel to the fiber axis, with a periodicity in this direction of about 3.10Å. A slightly smaller interatomic distance is known for the tri-iodide ion in crystals.

The commercial polarizer known as Polaroid H-sheet is of this type.

When oriented polyvinyl alcohol film is stained with iodine in the absence of water, a dichroic brown product results. An x-ray photograph of one such preparation indicates the presence of polymeric iodine here also.

Absorption curves of brown and blue dichroic preparations of iodine on oriented polyvinyl alcohol are shown in Fig. 14.

Polyvinylene Polarizers. Land and Rogers found that when an oriented transparent film of polyvinyl alcohol is heated in the presence of an active dehydration catalyst such as HCl, the film darkens slightly and acquires a strong positive dirchroism. It is also observed that the darkened film, which has undergone only a slight decrease in weight of the order of 1 per cent in the process, can still be strongly swelled but no longer dissolved in hot water.

The chemistry of this change in light absorption obviously involves a partial dehydration of the transparent polyol $(-CH_2-CHOH-)_x$ to form an unsaturated compound or polyene $(-CH=CH-)_x$. The polyene must be pictured as a conjugated polyene, with the conjugation extending through long chains, in order to provide an acceptable explanation for the absorption of visible light. To account for the insolubility of the product, it seems quite probable that some dehydration takes place between chains; this would have the effect both of interrupting the conjugation and of forming a three-dimensional structure from the original linear polymer.

$$\left.\begin{array}{l}-CH_2-CHOH-CH_2-CHOH-CH_2-CHOH-\\ -CHOH-CH_2-CHOH-CH_2-CHOH-CH_2-\end{array}\right\} \xrightarrow{-H_2O} \left\{\begin{array}{l}-CH=CH-CH-CH=CH-CH-\\ \qquad\qquad\quad |\qquad\qquad\ |\\ -CH=CH-CH-CH=CH-CH-\end{array}\right.$$

There might also be some oxygen bridge formation by elimination of water from hydroxyl pairs in adjacent chains.

$$\left.\begin{array}{l}-CHOH-CH_2-CHOH-CH_2-\\ \\ -CHOH-CH_2-CHOH-CH_2-\end{array}\right\} \xrightarrow{-H_2O} \left\{\begin{array}{l}-CH-CH_2-CH=CH-\\ \quad |\\ \quad O\\ \quad |\\ -CH-CH_2-CH=CH-\end{array}\right.$$

As required by this conjugated polyene structure, which was first proposed by West, the product is found to be bleached by common oxidizing agents with relative ease, but it is very stable indeed when oxidizing agents are excluded.

A quantitative determination of the number of double bonds in a photometered specimen of this polarizer would allow a comparison with the known absorption of light by the low molecular polyenes, a subject extensively studied by Kuhn and his associates (1935,[21] 1938[22]). Qualitatively the foregoing picture is consistent with both Kuhn's experimental work and Mulliken's theoretical treatment of this subject. We quote from a summary by the latter (1939):[23] "The longest wave length electronic transition of appreciable intensity in absorption (in a conjugated polyene $CH_3(=CH-CH=)_nCH_3$) is then $N \rightarrow V_1$. This shifts to longer wave lengths with increasing n. The calculations showed that if the polyene chain has the most elongated possible form (*trans, trans, trans,* . . .), the $N \rightarrow V_1$ transition should be far stronger than all the other $N \rightarrow V$ transitions together, and its strength should increase with the length of the chain. This calculated result is paralleled by experimental data on the polyenes, especially the carotinoids. The calculations showed that for less elongated (more *cis*-like) molecules, the intensity of $N \rightarrow V_1$ should be reduced in favor of $N \rightarrow V_2$, $N \rightarrow V_3$, and so on. A further point of interest was that the $N \rightarrow V_1$ transition in molecules of the most elongated form should be polarized approximately along the long axis of the molecules."

When oriented polyvinyl alcohol films are heated in the absence of active dehydration catalysts, dichroic yellow, orange or brown products result; the structure of these products has not been more closely investigated. The absorption curves for such a preparation are also shown in Fig. 15.

To give a better picture of the spatial relationships involved in the foregoing linear polymer polarizers, the approximate atomic dimensions of polyvinyl alcohol, of the Congo Red molecule and the iodine and polyvinylene polymers, are shown in the accompanying figures (Fig. 16).

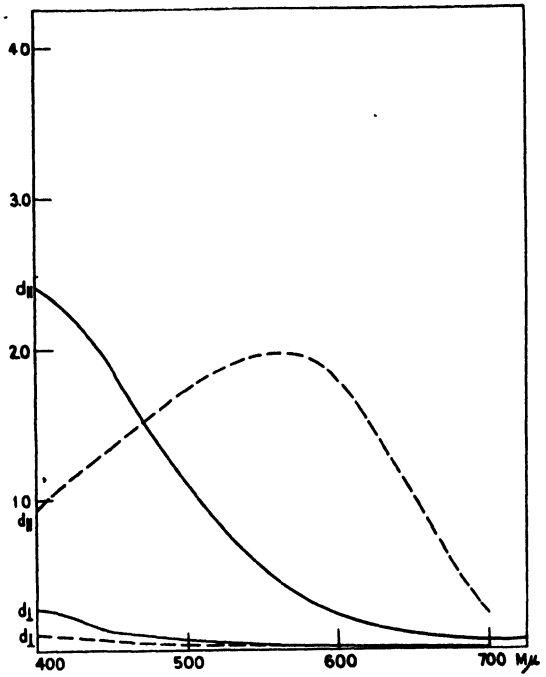

FIGURE 15. Dichroism of oriented polyvinylene (dotted lines) and of yellow product from polyvinyl alcohol (full lines).

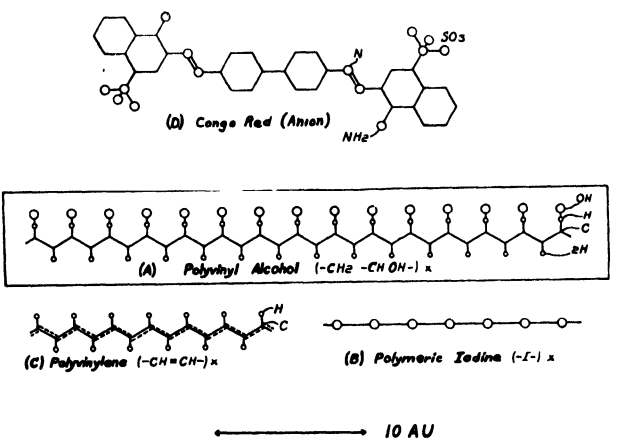

FIGURE 16. Schematic drawings, approximately to scale, of polyvinyl alcohol, Congo Red, polyiodine and polyvinylene molecules.

Metallic Polarizers. When metallic salts are incorporated in oriented linear high polymers and are subsequently reduced to the metals, the product is often characterized by a strong dichroism. The preparation and the structure investigation of such products has been described at some length by Frey-Wyssling (1937),[24] although the writers are not aware that quantitative measurements of dichroism have

yet been published. For example, Frey-Wyssling finds for dichroic preparations made by depositing gold or mercury on oriented cellulose, that the gold is microcrystalline with its well known cubic structure and the mercury is liquid; the metallic particles are extremely small, widely separated rods oriented parallel to the cellulose fibers. Particle dimensions of the order of 10mμ diameter, 100mμ in length, are mentioned by Frey-Wyssling. Thus these particles are plainly much larger than the dichroic molecules treated earlier in this section. Furthermore, in contrast to all the polarizers so far treated, the oriented absorbing particles here are not of themselves dichroic, since every cubic crystal or liquid particle is of necessity an optically isotropic system.

An earlier review of this subject was given by Berkman, Boehm and Zocher (1926) [25]; these writers show how some of the optical properties of dichroic metal preparations may be predicted from O. Wiener's theory, but point out the failure, important from practical considerations, of this theory to relate the optical properties of a given preparation to the dimensions of the metallic particles. Figs. 17, 18, and 19

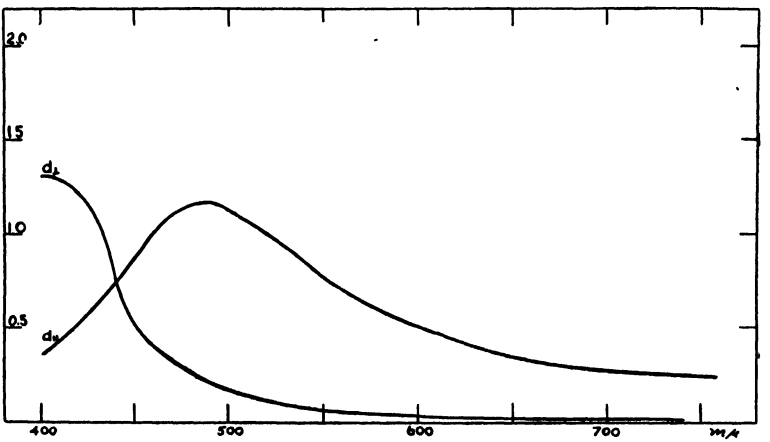

FIGURE 17. Dichroism of silver on oriented polyvinyl alcohol.

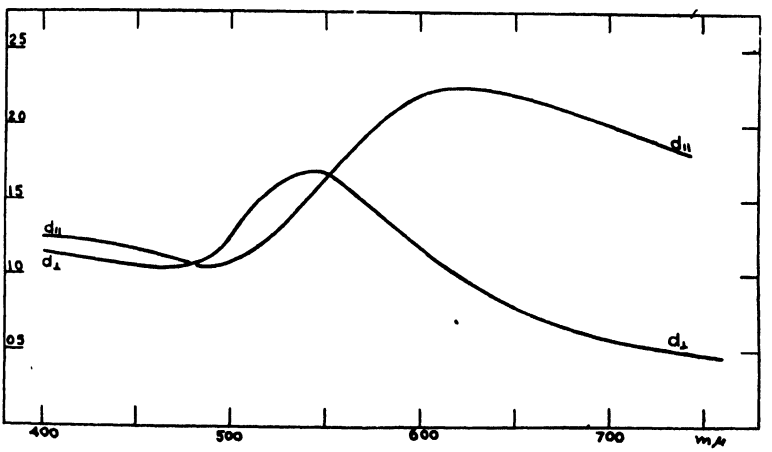

FIGURE 18. Dichroism of gold on oriented polyvinyl alcohol.

give data for dichroic preparations made from silver, mercury and gold on oriented polyvinyl alcohol. It is of interest that for the gold preparation, which has a red-green dichroism, the curves show a suggestive resemblance to some of Lange's (1928) [26] absorption curves for gold hydrosols of measured particle diameters; and namely the $d_{\parallel}$ curve resembles in shape Lange's curve for the 56mμ hydrosol, while the $d_{\perp}$ curve is close tó that of the 7mμ hydrosol, even if their relative heights are out of order. It is seen that these dimensions are of the same order as those obtained by Frey-Wyssling by entirely different methods.

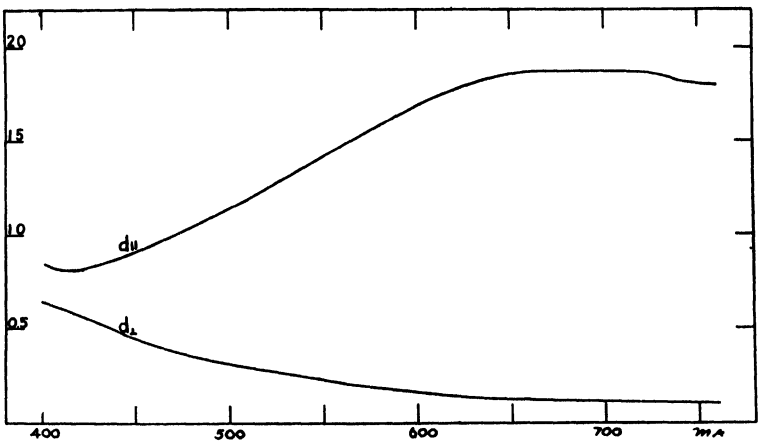

FIGURE 19. Dichroism of mercury on oriented polyvinyl alcohol.

Circular Polarizers. It appears doubtful that useful polarizers will ever be made from homogeneous circular dichroic materials, because the dichroism here is so far of such a low order of magnitude. The circular polarizers widely used in polariscopes designed for photoelastic investigations are customarily made by combining linear dichroic polarizers with quarter-wave birefringent films. However, if anyone ever discovers a useful circular dichroic polarizing material, this could obviously be combined with a quarter-wave film to make a useful linear polarizer also.

Summary. The useful artificial dichroic polarizers treated here, setting an arbitrary threshold of usefulness at a dichroic ratio of about 7:1, all have linear positive dichroism, and are made either by growing dichroic macrocrystals (herapathite), or by orienting dichroic microparticles. These particles may be dichroic microcrystalline needles (herapathite), dichroic simple molecules (dyes), or dichroic polymeric molecules (iodine, polyvinylene). The preferred methods of orienting the absorbing microparticles all involve some kind of a flow process in a viscous fluid medium.

SOME PRACTICAL APPLICATIONS OF DICHROIC POLARIZERS

Introduction

Since the applications of dichroic polarizers have in recent years been repeatedly written up in readily available sources, as shown by the following list of general papers, a brief recapitulation will suffice here.

W. E. Forsythe and E. Q. Adams, "Polarized Light." *Gen. Elec. Rev.*, **42**, 346-52 (1939).
H. Freundlich, "Polaroid Films." *Chemistry & Industry*, **56**, 698-9 (1937).
M. Grabau, "Polarized Light Enters the World of Everyday Life." *J. Applied Phys.*, **9**, 215-25 (1938).
—, "Introduction to Polarized Light and Its Applications." 46 p., Cambridge, Mass., Polaroid Corporation, 1940.

M. Haase, "New Po.....on Filters Using Dichroic Crystals." *Z. tech. Physik,* **18,** 69-72 (1937).
H. A. Levey, "New Polarizing Media and Their Applications." *Ind. Eng. Chem., News Ed.,* **17,** 527-8 (1939).
E. Nähring, "Polarization Filters," *Phot. Ind.,* **38,** 599-601; 629-30 (1940).
A. Pollard, "Polarization of Light and Some Technical Applications." *Nature,* **138,** 311-14 (1936).
S. Rösch, "Some Properties and Applications of Dichroic Polarizers." *Z. Instrumentenk.,* **58,** 181-92 (1938).
L. W. Taylor, "Physics, the Pioneer Science." Chapter 38, pp. 549-75, Polarized Light. Boston, Houghton Mifflin Co., 1941.

For our purposes we may consider applications of dichroic polarizers for the man in the street or in the home, and applications for the man in the laboratory or in the lecture hall. In the former class, the numerous uses of dichroic polarizers are characterized throughout by novelty, even though some of the underlying ideas were proposed before the advent of practical dichroic polarizers, and by a practically exclusive concern with visual processes, either directly or at second hand through photography. In the latter class of applications, dichroic polarizers have widely replaced calcite polarizers for many laboratory uses. In some of the more expensive precision polarizing instruments, the instrument maker has been understandably slow in making the change. The period of active exploration in both classes of applications is by no means closed. Military applications, a third class which has now outstripped the other two, are not treated here.

Dichroic Polarizers in Applied Science

As Aids in the Visual Process. The widest application of dichroic polarizers so far has been in aiding the visual process. This end is achieved by cutting out, by means of one or more polarizers between the eye and the light source, some of the visual radiation, so that one may see more clearly or more comfortably with what radiation is left. This field of applied physical optics is primarily subject to physiological, and to some extent to psychological considerations.

There are three general ways of using polarizers to aid vision:

(1) A single polarizer is used over the eye, to cut out undesired light partially polarized by natural reflection and scattering.

(2) A single polarizer is used over the source for the same purpose as (1).

(3) The polarizers are used in pairs to cut out undesired light, and either superposed in space, or else separated in space, so that one of the pair goes with the eye, the other with the source.

Sun Glasses. By observation as with a dichroscope it is quickly found, first, that when sunlight is reflected or scattered from flat surfaces, it thereby generally becomes partially polarized with the vibrations normal to the plane of incidence predominating; secondly, that this component of the light is a hindrance rather than an aid in perceiving detail in or possibly under the flat surface. The degree of polarization varies widely with the angle of incidence, reaching a maximum for angles intermediate between normal and grazing incidence, and with the nature of the flat surface.

The function of the sun glasses is to absorb the component of the light vibrating normal to the plane of incidence, and to transmit only the component vibrating in the plane of incidence. Since flat surfaces are more often horizontal, for example the surface of a body of water, the pavement of a road, etc., polarizing sun glasses commonly have a fixed orientation so as to transmit only vertical vibrations.

It is of interest that when the sun is in the zenith on a clear day the skylight just above the horizon is partially polarized by scattering with the horizontal vibrations predominating, so that polarizing sun glasses "selectively absorb," so to speak, this horizon light as well as the ground light.

Reading Lamps. The light scattered or reflected from printed pages, by which we read, is also found to be partially polarized, and here too perception of detail under the optimum conditions is greatly aided when only vibrations in the plane of incidence are admitted to the eye. As would be expected, some improvement may be noted when one reads with sun glasses under high levels of illumination. It is generally more efficient and more convenient to employ a polarized source of light, that is, a lamp provided with a polarizer and designed so that its radiation is incident on the printed page at an angle to give a maximum effect. The improvement is especially noticeable with material printed on glossy paper.

Variable Density Filters. Under some conditions it is desired to attain a wider range of illumination control than is possible by absorbing a single component of the light. There is then the possibility of using dichroic polarizers in pairs, and either superposed, or separated in space.

Large polarizers have been used superposed in pairs to provide variable daylight illumination through windows, smaller polarizers similarly in variable-density sun glasses. The illumination in both cases is varied by rotating one polarizer of a pair with respect to the other.

When the problem arises of completely eliminating the mirror reflection from any flat surface, regardless of the angle of incidence of the light and the nature of the mirror, the solution is found in polarizing the light source in or normal to the plane of incidence, and in viewing the reflected ray with an analyser crossed with the polarizer. Then the flat surface can be seen only by that light, if any, which is depolarized as by scattering or by defects in the mirror. By suitable rotations of one polarizer with respect to the other more or less of the mirror component of the reflected light may be transmitted to the eye.

Automobile Headlights. Here the polarizers are to be used in crossed pairs to eliminate dazzle, with the components of the crossed pairs necessarily separated in space. The polarizers have a fixed orientation so that the analyzer in front of a driver's eyes is always automatically parallel to the polarizers over the headlights on his car and on other cars driving in his direction, while it is always crossed with the polarizers over the headlights of all approaching cars. This is effected by orienting the vibration directions of all polarizers at a uniform angle of 45° from the horizontal, always measured in the same sense.

Of all the applications of dichroic polarizers this probably has been the one most thoroughly discussed in the patent and technical literature.[27-34]

From the manufacturing point of view, the polarized headlight that fills the rather exacting requirements of this application is best made by starting with a headlamp of the sealed beam type and applying to the outer surface of its lens a thin layer containing dichroic polyvinylene.

Photographic Images. Many of the principles which apply in improving visual images through the use of polarizing filters can be utilized equally well in photography. Here, however, the situation is somewhat simpler in that ordinary cameras have only one objective, and filter holders which can be set at any desired azimuth are readily available for most cameras. In using a polarizing filter one must take into consideration the curve of its transmission for natural light as a function of wave length, since the sensitivity curve of the photographic layer may be quite different from the sensitivity curve of the eye.

There is already a considerable literature on the photographic uses of polarizing filters. Filters over the objective are employed to cut out vibrations perpendicular to the plane of incidence when there is undesired illumination from reflecting surfaces,—horizontal mirrors such as bodies of water, vertical mirrors such as window panes, etc. Such filters too are advantageously employed to darken a background that is illuminated by light partially linear-polarized by scattering, such as the sky-

light 90° from the sun on a clear day; their use in underwater photography has been proposed on the same principle.

In photography too there is the already mentioned possibility of using polarizers in pairs—together as with both components over the objective or over the source, or more commonly separated as with one polarizer over the source and one over the objective, to vary the illumination over wider ranges than is possible with a single rotatable polarizer. Polarizers have been used in pairs over the objectives of motion picture cameras for taking fades and lap dissolves.

As Aids in Viewing Stereoscopic Pairs of Images. Polarizing devices have already been widely used for viewing stereoscopic pairs of images, either directly or after projection. Three different systems may be cited here to illustrate some of the possibilities.

In all these systems, the observer employs polarizing spectacles to admit the one image of the stereo pair to the eye to which it belongs.

Projection of juxtaposed stereo images through twin projectors.[35, 36] This system is the exact analog of the anaglyph system, except that polarizing filters are employed in place of complementary (*e.g.*, red and green) color filters.

Projection or viewing of vectograph stereo images.[37, 38] In this strikingly novel application, due to Land and Mahler, each image of the stereo pair is formed directly as a positive image in a polarizing layer; for the high lights, $d_{\parallel} = d_{\perp} = 0$, while for the shadows $d_{\perp} = 0$, $d_{\parallel} > 0$. For viewing or projection, the two images are superposed with their axes crossed; thus only a single ordinary projector is required in contrast to current practice for the preceding case. The vectograph may also be viewed directly, and either as a diapositive, or by backing with a suitable nondepolarizing diffusing layer. An aluminum lacquer has been used for this purpose as well as for preparing projection screens for reflecting polarized images without depolarization.

In addition to their uses in stereoscopic viewing or projection, vectographic images have other novel applications.

A third system,[39] also due to Land, has been used for stereoscopic viewing of the large diapositives encountered in x-ray radiographic work.

Display Devices. The full range of interference colors obtainable with doubly refracting materials of the normal dispersion of birefringence, when viewed between polarizers against a standard white light source, has been analytically determined, tabulated and plotted in a valuable paper by Buchwald (1940).[40] This writer starts with the I.C.I. (International Commission on Illumination) data, using the illuminant B and gypsum as bases for calculation, and ends up with the first five orders of interference colors (gypsum thicknesses 0-0.30 mm) tabulated according to the color triangle coördinates x, y, and the dominant wave length λ and saturation σ derivable therefrom. The color curves for the first three orders of such a gypsum wedge between crossed and parallel polarizers respectively are shown as spirals around the white point in Figs. 20 and 21; the colors of the fourth and fifth orders between crossed polarizers are shown in Fig. 22; and the brightness, Hx, for the first five orders between crossed polarizers is shown in Fig. 23 (the brightness for parallel polarizers is $H\parallel = 100 - Hx$). These data for $(x, y, H)_{\perp}$ and $(x, y, H)\parallel$ could advantageously be presented in three-dimensional figures. Fig. 24 shows the transition of the color in a 0.10-mm section of gypsum to its complementary as the analyzer is rotated from the crossed position ($\beta = 90°$) to the parallel position ($\beta = 0°$).

Buchwald's results would be of scientific interest only, were it not for the fact that some common transparent sheet materials such as cellophane are characterized by birefringence and normal dispersion thereof. This means that any point on Buchwald's color curves can be reproduced by selecting a suitable piece of birefringent film and viewing it between dichroic polarizers. Still other colors are

obtainable by preparing transparent films having abnormal dispersion of birefringence.

An application of such polarization colors, either alone or in combination with ordinary isotropic colors or the dichroic colors described earlier, has been made in various display devices. Common to many of these is the play of colors resulting from continuous rotation of one or more members of the optical system, ordinarily one of the polarizers.

Dichroic Polarizers in Scientific Research

The papers of the following two lists have in common that they all include some mention of dichroic polarizers. Somewhat in the manner of *Science Abstracts*, the

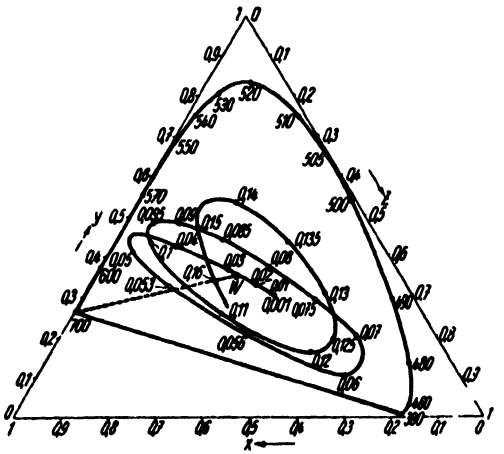

FIGURE 20. Metric of normal linear-birefringent interference colors, reproduced from E. Buchwald. Gypsum sections 0 to 0.30 mm thick, I.C.I. illuminant B. Crossed polarizers, orders I-III.

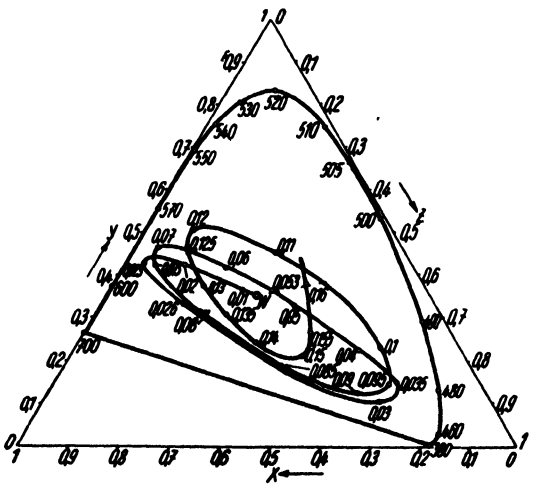

FIGURE 21. Same as Figure 20, with parallel polarizers, orders I-III.

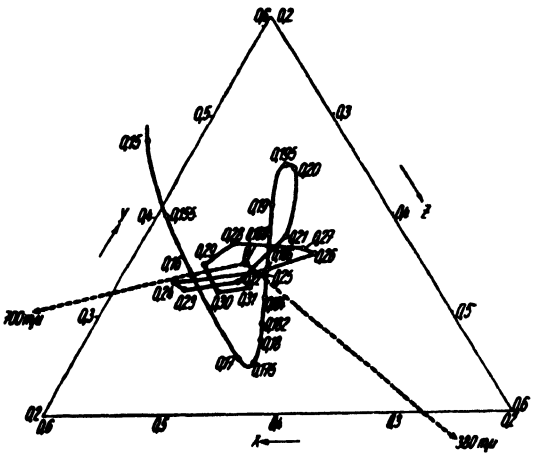

FIGURE 22. Same as Figure 20, with crossed polarizers, orders IV and V.

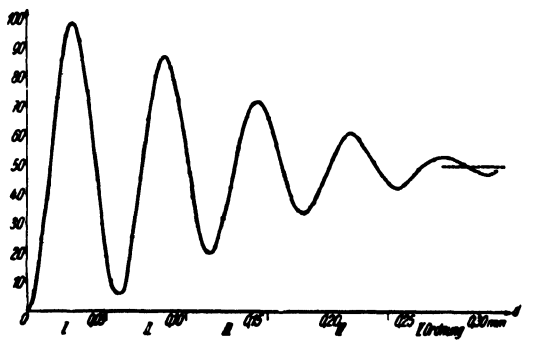

FIGURE 23. Same as Figure 20, with crossed polarizers, brightness for orders I-V.

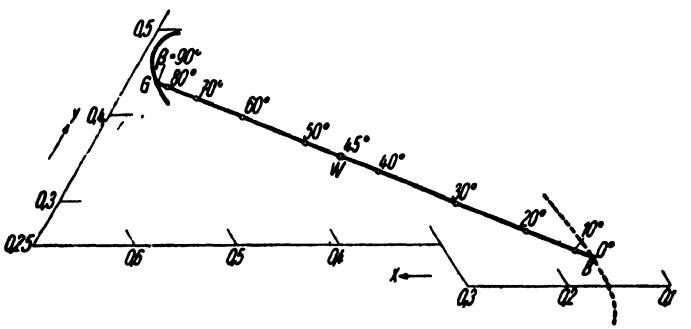

FIGURE 24. Same as Figure 20. Transition of interference color of 0.10 mm section to its complementary as analyzer is rotated from crossed ($\beta = 90$) to parallel position ($\beta = 0$).

first is by subjects and the second deals with apparatus and instruments. While these lists are not offered as exhaustive, it is hoped that they will be fairly representative of the uses to which dichroic polarizers have been put in the laboratory up to January 1943.

For colloid chemists, there are several fields of direct interest in which polarization effects are observed and measured:

(1) The study of the size and shape of colloid particles from the state of polarization of the light scattered thereby. S. Bhagavantam (1940) has treated this subject in his book "Scattering of Light and the Raman Effect."

(2) The study of certain fluid systems by the optical anisotropy of flow. This term is used broadly to include both birefringence and dichroism, and to include matter in states of both actual flow and "frozen" flow. A valuable review of streaming birefringence has been written by J. T. Edsall (1942), as cited below.

(3) The study of very thin films by methods involving the reflection of polarized light.

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Colloid Chemistry of Clay Minerals and Clay Films

E. A. HAUSER * AND D. S. LE BEAU †

Introduction

Clays are of far greater importance to mankind than is generally realized. As an essential part of soils they are of outstanding importance in agriculture.[72] For the same reason they are, although indirectly, important in many kinds of construction work, for example, in highways, earthen dams, artificial reservoirs, and even buildings, because these projects are either actually built with clays or are erected on soils containing clays, or they are even built through clay-containing ground as in tunnel constructions.[125] Besides these fields of basic importance, different types of clays are used in increasing amounts in such varied industries [15] as the ceramic,[81, 97] rubber, paper, oil,[9] chemical, pharmaceutical, and cosmetic industries as well as in metal foundry work and even in medicine. The geologist, as well as the archaeologist and palaeontologist, is interested in clays because their occurrence gives evidence of the geological age of such regions.‡ This in turn permits us to estimate when certain extinct animals or plants, perfect impressions of which are frequently found, existed in these regions.

It is therefore not astonishing that scientists connected with the above-mentioned fields have long been extremely interested in clays.

Although a vast amount of information on clays has been accumulated, it must be said that real progress has been made only during the last 15 to 20 years, when for the first time it was possible with the aid of new research tools and the formulation of new concepts [27, 37, 74, 102, 103] to embark on a really fundamental study of clays. This gigantic work has resulted in a far better and a far more complete understanding of the occurrence, composition, and properties of clays. Extensive studies of x-ray diffraction patterns have not only revealed that even the finest fractions of clays are crystalline in structure and not, as previously assumed,[7, 70, 98, 119] an amorphous § mixture of different metal oxides and hydroxides, but they have also demonstrated that all clays are composed of comparatively few and simple building units. The difference in the properties of various clays is now believed to depend on the spatial arrangement of these units in the crystal lattice.

Since this contribution is devoted exclusively to a discussion of the colloid chemistry of clay minerals, the authors will limit their discussion to the most recent structural concepts and attempt an explanation of the variability in properties of clays on this basis. Excellent surveys of the older concepts, definitions, and terminology were recently presented by Grim [27] and Hofmann.[61]

The Clay Minerals

For a long time clays were considered to be composed of amorphous matter,[7, 107, 111, 119] and all attempts to interpret their properties had to be based on the

* Associate Professor, Department of Chemical Engineering, Mass. Institute of Technology, Cambridge, Mass.

† Research Associate, Department of Chemical Engineering, Mass. Institute of Technology, Cambridge, Mass.

‡ See paper by C. A. Reeds in Vol. V of this series. J. A.

§ In earlier literature the word "amorphous" generally indicated our inability to discover the arrangement of structural units at submicroscopic levels. J. A.

findings of strictly chemical methods of investigation. When Hadding [35] in 1923 and Rinne [106] in 1924 proved by x-ray diffraction analysis that clays were composed almost entirely of crystalline matter,* a radical change in the deductions based on previous work became essential. This discovery coupled with refined and precise optical studies [28, 87, 108] permitted a more specific identification of the various components of clay materials, thus offering a firm basis for the most recent developments and establishing the presence of a group of minerals generally known today as the clay mineral group.

A careful comparison between chemical analytical data, thermal analysis and x-ray diffraction patterns of a number of members of this group reveals that different chemical analyses do not necessarily result in differences in the x-ray diffraction pattern. It has also been found that several members of the clay mineral group give different x-ray diffraction patterns but agree in their chemical analysis (Table 1).

GROUP	MINERAL	CHEMICAL COMPOSITION	TYPE OF CRYSTAL LATTICE
KAOLIN	KAOLINITE DICKITE NACRITE HALLOYSITE	$Al_4(Si_4O_{10})(OH)_8$	KAOLINITE (DICKITE) x) (NACRITE) x) KAOLINITE
	HYDROHALLOYSITE	$Al_4(Si_4O_{10})(OH)_{16}$	HYDROHALLOYSITE
MONTMORILLONITE	PYROPHILLITE	$Al_4(Si_8O_{20})(OH)_4$	MONTMORILLONITE
	TALC	$Mg_6(Si_8O_{20})(OH)_4$	
	MONTMORILLONITE	$Al_4[Mg](Si_8O_{20})(OH)_4 \cdot x H_2O$ xx)	
	NONTRONITE	$Fe_4^{+++}[Mg](Si_8O_{20})(OH)_4 \cdot x H_2O$ xx)	
	BEIDELLITE	$Al_4[Mg](Si_8[Al]O_{20})(OH)_4 \cdot x H_2O$ xx)	
	SAPONITE	$Mg_6(Si_8[Mg]O_{20})(OH)_4 \cdot x H_2O$ xx)	
HYDROMICA	ILLITE	$Ky \cdot Al_4[Fe_2^{++}Mg](Si_{8-y}[Al_y])O_{20}(OH)_4$ xxx)	MONTMORILLONITE
MICA	MUSCOVITE	$K_2Al_4(Al_2Si_6O_{20})(OH)_4$	MICA

TABLE NO. 1.

x It is questionable if minute differences in the x-ray diffraction pattern of kaolinite, dickite, and nacrite justify a separate classification for the structure of the latter two minerals.

xx Symbols in brackets indicate that they may substitute for the symbol written to the left of the bracket.

xxx Only when $y = 2$ and no substitution for the aluminum in the gibbsite layer exists, is this formula transformed into that of muscovite.

The modern concept of clay mineral structure [102, 103] has enabled us to explain the cause for these discrepancies as follows: In the latter case a difference in the lattice arrangement must be made responsible, whereas in the former case an exchange of elements without a change of the lattice structure must have taken place.

A comparison of analytical results with the varied properties of the clay minerals, furthermore, stresses this concept, adding to it the assumption that the various clay minerals must be built up of at least similar, if not identical, and simple building units. Thus, the differences in properties can be explained by changes in the spatial arrangement of these units. A detailed knowledge of the composition and structural configuration of these building units, therefore, is essential for an understanding of the structural and varied properties of the clay minerals. The detailed knowledge of the building units of the silicates and their reactivity is unquestionably responsible for the recent developments of polymerizable organic silica derivatives which form the basis for a variety of so-called "silicon" plastics.†

* It must be remembered that crystals may be of colloidal dimensions, as Scherrer found with particles of colloidal gold too small to be seen in the ultramicroscope. J. A.

† See paper in this volume by E. G. Rochow and F. J. Norton. J. A.

The Building Units

A silicon atom binding four oxygen atoms forms a *tetrahedron* (Fig. 1a); the radii and distances between the silicon and oxygens are such that the four oxygens touch each other and form a cavity just large enough to include the silicon.

The second building unit consists of aluminum combining with six oxygens; the oxygens again completely enclose the aluminum atom. (Fig. 1b) The latter can also be exchanged for magnesium, but the magnesium, being a larger atom, does not fit exactly into the cavity and causes a slight strain in the structure. These two combinations are known as *aluminum-oxygen- or magnesium-oxygen-octahedron* respectively.

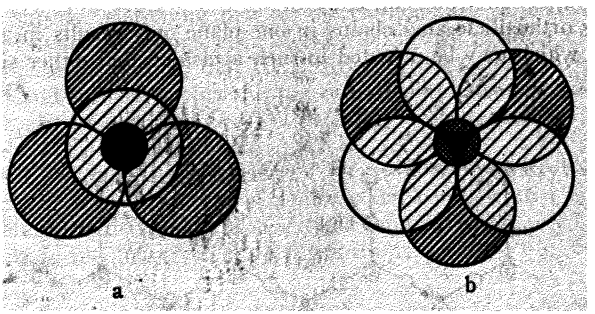

FIGURE. 1. a. Silicon-oxygen tetrahedron (schematic) representing a top view of the model. The oxygen atom on top has been drawn as a transparent sphere to show the location of the silicon atom in the cavity formed by the four oxygens.[37] b. Aluminum- (magnesium) oxygen octahedron (schematic); the oxygen atoms constituting the upper layer have been drawn transparent to show the location of the aluminum or magnesium atom in the cavity formed between the two oxygen (hydroxyl) layers.[37]

These building units are held together by chemical valencies, or in other words, by the sharing of electrons (covalent bond). Since each silicon atom can share four of its outer electrons, whereas each oxygen atom needs two electrons for saturation, a silicon-oxygen-tetrahedron as described above is unsaturated, lacking four electrons. If, however, the oxygens are replaced by hydroxyl groups the system is saturated, the missing electron having been supplied by the hydrogen of the hydroxyl group. This compound is generally known as hydrated silica or *orthosilicic acid* (H_4SiO_4). If several orthosilicic acid molecules combine, or we might say condense, with loss of water, two silicon atoms will share one oxygen, thereby forming chain-like structures (Fig. 2). The hydrogens in the remaining hydroxyl groups can be replaced by sodium, which has the same electron surplus as hydrogen. Such fibrillar arrangements of sodium silicate, if dispersed in water, represent the structure of water-glass. The hydration of the sodium ion and the chainlike structure offer an

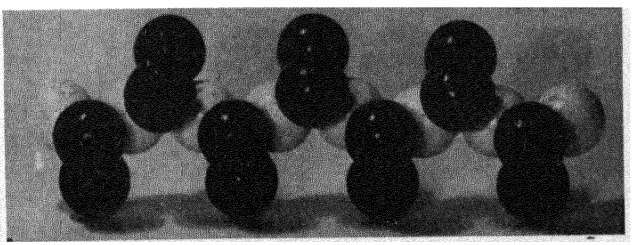

FIGURE 2. Model of a silicic acid chain, (theoretical) top view, white balls represent oxygen atoms, black ones hydroxyl groups.[37]

explanation for the great solubility of water-glass and its high viscosity in solution. If all the hydrogens are not replaced by sodium, or if we consider simple orthosilicic acid chains, it is possible that upon partial evaporation of water, condensation of chains to a network structure takes place, and the visible result will be a gel. Upon complete evaporation of the entrained water, these chains are bound to become entangled and so allow film formation to take place just as is the case with high molecular organic compounds.

The formation of a *well-oriented* tridimensional structure of silicon-oxygen tetrahedra will result in either quartz, tridymite, or cristobalite, depending on the particular orientation taking place, which in turn depends on external conditions, such as temperature, environment, etc.

Condensing orthosilicic acid chains in one plane only results in a *silicon-oxygen sheet* (Fig. 3) which may be oriented in such a fashion that either six silicon atoms

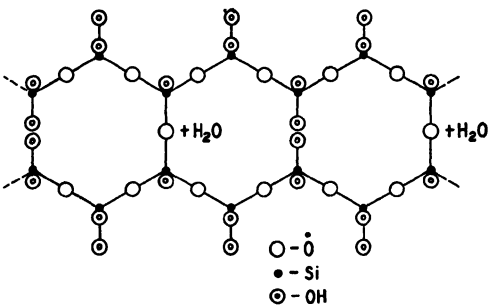

FIGURE 3. Formation of the network structure of a symmetric silicon-oxygen tetrahedra sheet by condensation (schematic).[87]

form a symmetrical hexagonal ring by sharing oxygens between them, or the ring formed by the silicon-oxygen tetrahedra is unsymmetrical in both number and configuration. In the first case we obtain a typical crystalline structure; in the second we obtain what is known as a *silica glass* (Fig. 4).

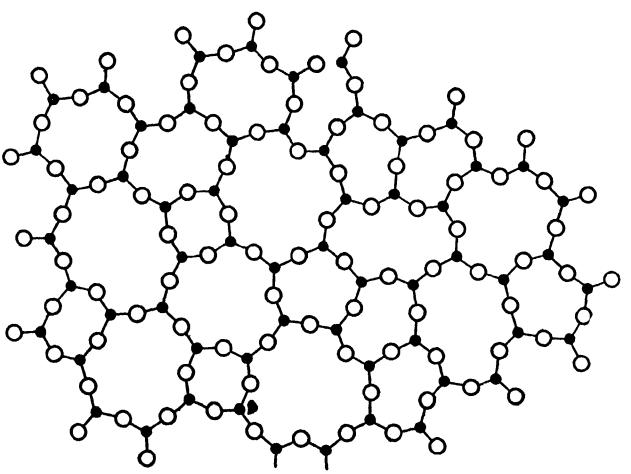

FIGURE 4. Structure of an unsymmetrical silicon-oxygen sheet; silica glass (schematic)—after W. H. Zachariasen (*J. Am. Chem. Soc.*, 54, 3841 (1932)). Only one plane is shown.

Starting with orthosilicic acid we will find that in forming a silica sheet, every oxygen atom located in one plane is shared by two silicon atoms, except the oxygens located at the edges of the sheet, which remain unsaturated; the oxygens in the vertex position of the tetrahedra have a hydrogen attached. This structure is then saturated and known as a hydrated silica sheet. However, if we join *non*-hydrated silicon tetrahedra to form such a sheet we find that all oxygen atoms are saturated except those in vertex, edge, and corner position. Consequently any unsaturation occurring due to edge or corner positions of atoms will be negligible compared to the surface unsaturation of such a structure.

The second building unit—the aluminum or magnesium octahedron—is capable of forming similar sheets. Assuming that all the oxygens are saturated by hydrogen, then two layers of hydroxyl groups, each in close hexagonal packing, can be cemented together by magnesium atoms, so that six hydroxyl groups share three magnesiums. Except for edges and corners, such a sheet is saturated and neutral. Several of these composite layers can be held together by secondary forces, such as van der Waals forces.

It is interesting to note that by cementing two of the hydroxyl sheets together with magnesium, the high symmetry of a hexagonal configuration is disturbed and reduced to a monoclinic one since the hydroxyl sheets are staggered. The mineral built up according to the above structure is known as *brucite* (Fig. 5a).

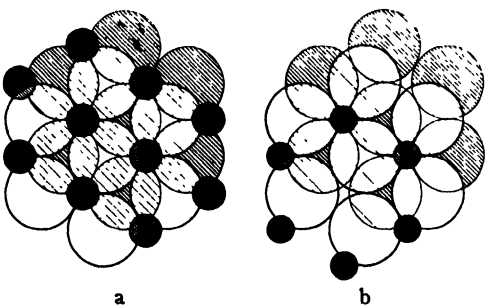

FIGURE 5. a. Brucite, $Mg(OH)_2$ (schematic); the hydroxyl groups constituting the upper layer have been drawn transparent so that the location of the magnesium atoms sandwiched between the two staggered layers may be seen clearly.[87] b. Gibbsite, $Al(OH)_3$ (schematic); the hydroxyl groups in the top layer have been drawn transparent to show the location of the aluminum atoms sandwiched between the two staggered layers. (Compare the positions of the aluminum atoms with those of the magnesium atoms in brucite.)[87]

If aluminum replaces the magnesium in the octahedra sheets, changes have to be made in order to retain a neutral sheet. Aluminum can share three electrons, magnesium only two. Consequently, one-third of the places formerly occupied by magnesium must remain vacant. Therefore, the aluminum-octahedra sheets will not be so densely packed as the magnesium-octahedra sheets. This mineral is known as *gibbsite* (Fig. 5b).

Just as silicon-oxygen tetrahedra sheets are built up from single silicon-oxygen tetrahedra, gibbsite from aluminum-oxygen octahedra, and brucite from magnesium-oxygen octahedra sheets, the minerals of the kaolinite, montmorillonite, and illite group are built up by joining gibbsite or brucite sheets to silicon-oxygen tetrahedra sheets.

Kaolinite, if quantitively analyzed will result in the same chemical composition as *dickite* and *nacrite,* but x-ray patterns show some slight differences. Analyzing the structure of kaolinite we find that a silicon-tetrahedron sheet is topped with a slightly

distorted gibbsite sheet, both being joined by condensation and splitting off of water between adjoining hydroxyl groups in vertex position.[82] (Fig. 6) Thus, one oxygen

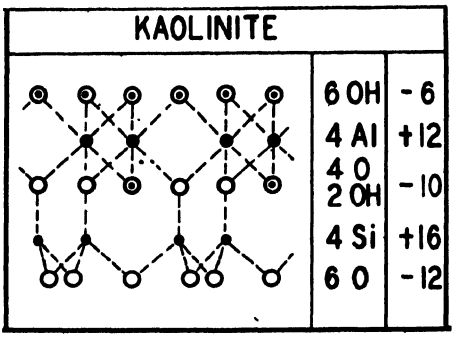

FIGURE 6. The schematic drawings in the first column represent the composition of the unit cell of the crystal lattice. All atoms are projected in one plane. The second column gives the number and type of atom or group in every lattice plane. The third column reveals the amount of necessary or available electrons in every sheet. If the (+) and (−) in this column compensate each other the crystal is electrically neutral. If they do not, the lattice carries either a positive or a negative charge. The plus and minus charges being listed for every layer, it is easy to determine which part of the lattice is not balanced.[37]

remains and is shared by the two layers, forming a primary valence bond between them. Naturally only opposing hydroxyl groups will condense. The gibbsite layer contains more hydroxyls than the silica tetrahedra sheet. The non-opposing hydroxyls are so located that they are placed inside the hexagonal rings formed by the silicon-oxygen tetrahedra vertices, and having no possibilities for condensation they remain there. The unit parcels of the two layers are perfectly balanced in regard to their electron distribution and therefore are electrically neutral. Several such parcels may be held together by the rather strong secondary forces acting between the hydroxyls of the gibbsite layer and the basal oxygens of the silica tetrahedra layer of the next unit. The possibility of a hydrogen bond ($:\ddot{O}:H:\ddot{O}:$) tying two units together may also be taken into consideration. This might account for the fact that it is difficult to obtain very small particles from kaolinite by cleavage.

The minute differences in the structure of dickite and nacrite as revealed by x-ray diffraction and optical methods[33, 34, 58] may be explained by a displacement of the lattice layers toward each other and by differences in the distance separating them.

Anauxite, another member of this group, exhibits a somewhat higher molecular ratio of silica to alumina. The most recent suggestion offered is the assumption that some of the aluminum positions in the gibbsite layer are vacant, the lattice charges being balanced by appropriate changes in the arrangement of the oxygen and hydroxyl groups.[54]

Halloysite, another clay mineral in the kaolinite group, might be defined as "incompletely formed kaolinite." It possesses exactly the same layer structure as kaolinite, but condensation has not yet taken place between the gibbsite and the silica tetrahedra layer. We find the interesting case of a mineral whose unit cell is held together by secondary forces only. Halloysite is rather unstable, as can be expected from its structure: above 40° C condensation takes place whereby ten hydroxyl groups split off four molecules of water, leaving the remaining vertex oxygens to link the two layer sheets by primary valence forces.[92] (Fig. 7) A lattice practically identical with that of kaolinite results. This might also explain why deposits of halloysite are comparatively rare.

It must be admitted, however, that some sound arguments can be voiced against this concept. For example, the energy required for the interaction of the hydroxyl groups should call for a higher temperature; besides that, the intensities of certain x-ray deflections do not agree with those to be expected as a result of the above assumption.[52] A number of new suggestions for the structure of the halloysite unit have been made;[17, 29, 59, 118] so far, however, none can be considered as altogether satisfactory. For the time being it seems most probable that halloysite is not an absolutely uniform product but that it consists of a mixture of units of perfect and of random orientation.

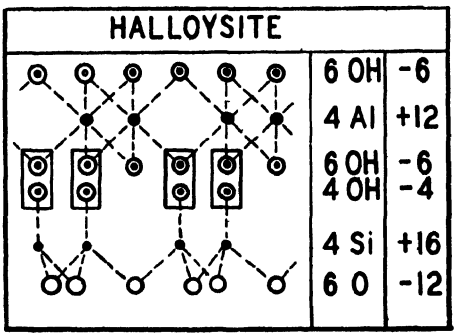

FIGURE 7. Same as for Figure 6.[87]

The next group of clays generally known as the *montmorillonite* group is of special interest to this country, which possesses the largest deposits in the world.

The structure of ideal montmorillonite is somewhat more complex than that of kaolinite, although the building units are the same. The unit cell consists of three layers: a gibbsite sheet enclosed between two silica sheets with their vertices pointing toward each other (Fig. 8).[60, 65, 80] As in the kaolinites, these layers are glued to-

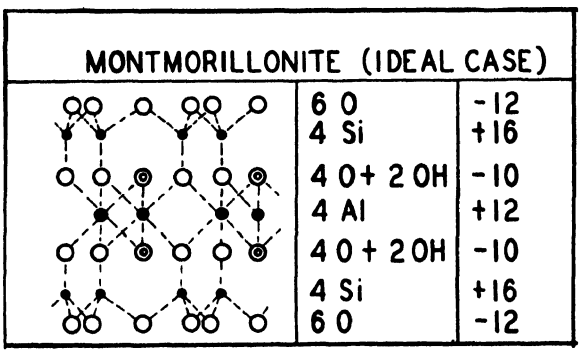

FIGURE 8. Same as for Figure 6.[87]

gether by primary valence forces, due to sharing of oxygen atoms in vertex position. Again those hydroxyl groups of the gibbsite layer which could not find opposing hydroxyls from the top and bottom silica sheets remain located in the hexagons formed by the oxygens in the vertex position of the silica sheets. Weak secondary forces (O—O or OH—OH bonds) act between two such composite parcels. Montmorillonite parcels conforming to the theoretical structure are neutral from the point of view of electron distribution except for unsaturated edge and corner positions.

The clay mineral *pyrophyllite* provides such an ideal case, with the following exceptions: the difficulty of obtaining small particles of pyrophyllite by simple dispersion in water and the fact that the *c*-axis dimension of the unit does not vary with varying percentages of moisture present in the clay. These facts may be explained

by a shift in adjacent layers, setting up residual attraction forces between units, or simply by molecular cohesion forces between units acting at close range. The idea of close stacking of units finds support in the difference in height of the unit cell of pyrophyllite and montmorillonite along the *c*-axis in the dry condition (9.2 and 9.6 Å. respectively). This decrease may be explained by the absence of adsorbed cations between adjacent surfaces of two units.[64] Another possible explanation might be that one of the silica sheets per unit has alternate tetrahedrons inverted, and a corresponding substitution of OH for the oxygen position thus retaining the electrical balance. This concept, which is very similar to some recent suggestions made for the structure of halloysite and montmorillonite,[17] would permit the setting up of strong OH—O bond forces between adjacent units, identical with those previously discussed in kaolinite. According to Hendricks [56] the most significant features of pyrophyllite are its limited base-exchange capacity, slight amount of isomorphous replacement and its possibly large crystal size. It is probably the large crystal size that limits isomorphous replacement, thus minimizing the possibility of base exchange. Hendricks assumes that these properties result from the mineral being formed by hydrothermal processes, often without a liquid phase being present.

Even though the ideal structure would account for easy cleavage between units and a change of the dimensions of the *c*-axis by water entering between the units, it nevertheless is incapable of explaining other important properties of montmorillonite such as base exchange, orientation in an electric field, etc. A number of suggestions have been made,[11, 17, 23, 65, 66, 76] none of which, however, seem to be entirely satisfactory. The reason for this failure seemed to be the belief that the aluminum-silicon ratio is constant for clays exhibiting identical x-ray diffraction patterns. We find, however, that montmorillonite found in nature very rarely conforms to the ideal composition. The chemical analyst formerly believed in a fixed ratio between aluminum and silicon according to which he appraised the kind of clay with which he was dealing. Today it is known that the ratio of aluminum to silicon is apt to change. In addition, one is able to find, in the course of an analysis, magnesium and iron which cannot simply be classified as impurities. *Nontronite,* for example, is a mineral which, according to x-ray diffraction patterns, has the same structure as montmorillonite, but aluminum has been partially or completely replaced by trivalent iron. However, the electronic balance of the sheets will be destroyed if replacement by metal atoms of a different valency occurs. It is assumed that the mineral *beidellite* distinguishes itself from pure montmorillonite by partial replacement with aluminum of the silicon in the top and bottom layer.[62, 84, 94] Aluminum, having only three electrons to share in comparison with the four electrons of silicon, will therefore cause a patchwork of negative charges on the surface of the layer sheet, calling for saturation by adsorption of cations from the environment. In the case of beidellite the absence of potassium as an exchangeable cation is noteworthy (see illites, p. 199). According to Ross and Kerr [110] beidellite differs from montmorillonite in that it has a molecular silica-to-alumina ratio of 3:1 instead of 4:1. Grim,[27] in contrast thereto, offers some indications that beidellite is nothing but a mixture of montmorillonite and limonite.

Magnesium likewise is able to substitute for aluminum in the gibbsite layer. If such substitution occurs only in places originally occupied by aluminum, the center of the crystal lattice will acquire a negative charge. This is the structure of the clay mineral *saponite* which also has the tendency to bind loosely cations on the surface of the units. A complete replacement of a gibbsite by a brucite layer results in the structure of the clay mineral *talc.*

We shall see later that surface or center substitution has a very marked effect on the properties of the mineral.

It has been the custom for some time to coin for any mineral not exactly conforming to the chemical formula of montmorillonite, a new and often rather compli-

cated name, proclaiming it a new discovery. This is not only confusing but also utterly wrong, particularly if such minerals still retain an x-ray pattern fully conforming to montmorillonite. Names like waxite, hectorite, eyrite MS, etc., belong in this group. They are montmorillonites in which a high degree of aluminum substitution by magnesium has taken place.

Besides sodium, lithium is frequently present in these montmorillonites as a counter ion.

The last group of clays of general importance consists of the *illites*, their basic structure being very similar to montmorillonite. Illite consists of three layer sheets, one of them a gibbsite sheet, sandwiched between two silicon sheets, sharing the vertex oxygens with them. However, a considerable amount of silicon (about 15 per cent) is replaced by aluminum, thus upsetting the electronic neutrality of the crystal. This results in a negatively charged surface similar to that previously reported for beidellite. This negative charge on the surface is the cause of fairly strong attraction forces for positive charges. If potassium ions are available to balance this charge, they virtually act as a bridge between two units.[31] The reason potassium is chosen in preference to any of the other alkali or earth alkali elements so abundant in soils and rock, seems to lie in its size. Of all the common elements the potassium ion is the only one whose effective diameter is larger than the diameter of the open hexagonal rings formed by the silica sheet. The potassium connecting two neighboring unit crystal parcels will also prevent swelling or prying apart of such parcels by the entry of water as happens in center-substituted montmorillonites (Fig. 9).

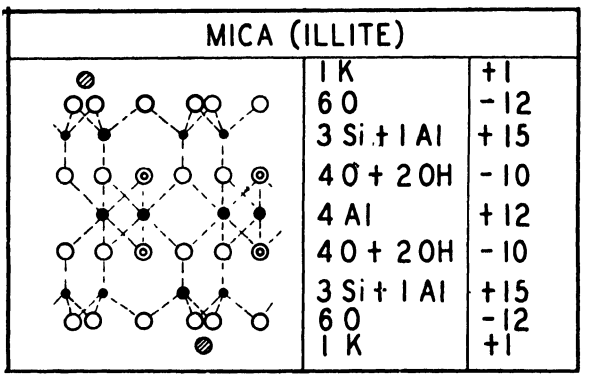

FIGURE 9. Same as for Figure 6.[37]

A number of other substitutions may take place, such as the replacement of aluminum by iron or magnesium in the gibbsite layer, or the addition of magnesium in the brucite position. The results of such substitutions have been discussed previously.

Replacement of 25 per cent of the silicon in the top and bottom layer of the unit parcel by aluminum, *without* either magnesium or iron being present, results in the structure of *muscovite* (*mica*).

Up to recently it was assumed that *attapulgite*, another clay mineral, had a structure closely related to that of mica.[77] The present concept, however, attributes a fibrous structure for this mineral.[10] Its building unit is supposed to consist of a brucite sheet sandwiched between two silicon-oxygen-tetrahedra sheets. The layer lattice extends indefinitely in one direction only, so that ribbons are formed. Electron microscope photographs of attapulgite taken by C. E. Marshall, R. P. Humbert, B. T. Shaw, and O. G. Caldwell substantiate the presence of fibrous particles.* The

* See the chapter on "The Electron Microscope" by Albert F. Prebus in Alexander's "Colloid Chemistry," Vol. V, p. 152.

long axis of these ribbons is parallel to the *c*-axis. In addition, the ribbons are joined by oxygen bonds of the silicon sheets (Fig. 10). Its ideal composition would be

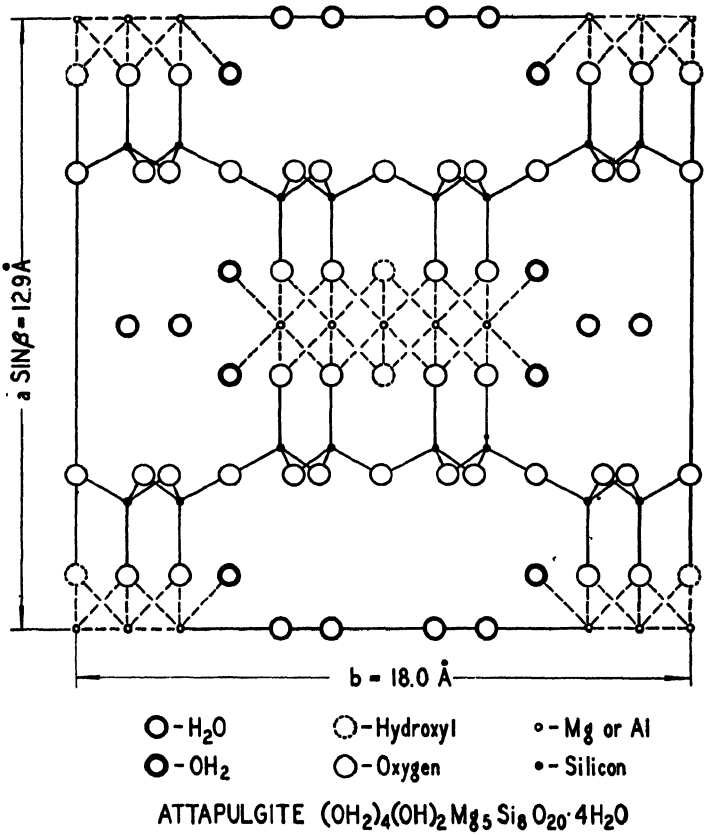

FIGURE 10. A schematic drawing of the mineral Attapulgite. All atoms are projected in one plane.[8]

$(OH_2)_4(OH)_2Mg_5Si_8O_{20}\cdot 4H_2O$. Replacement of magnesium or silicon by aluminum may occur to a small extent.

A number of clay minerals are frequently referred to in the literature as *chlorites*. Although they are of varying composition the chlorites which so far have been investigated seem to have identical structures, with alternating mica and brucite sheets.[90] An ideal formula for these minerals would be $Al_2Mg_5Si_3O_{10}(OH)_8$.

For completeness reference should be made to *allophane*,[109] which today includes all non-crystalline amorphous materials found associated with certain clays.

As has been shown the structure of clays is really not too complicated if it is considered from the point of view of its building units. These ultimate building units, the silica tetrahedra and alumina or magnesia octahedra, repeat themselves not only throughout one of the minerals, but throughout the whole group.

Base Exchange

It is now evident that the varied properties exhibited by different members of the clay mineral group can not simply be attributed to differences in chemical composition or to the basic principle of their structure, but that they can be accounted for

only by a complete understanding of their structure and its bearing on the ionic arrangement of the medium in which they are suspended. To offer a specific example let us compare a kaolinite and a bentonite * particle. The former must be considered as neutral.[55] The only possibility of the development of net electric charges lies in fractures along the *c*-axis, *i.e.*, at edges or corners of the individual sheets.[19] Such areas are by necessity small in comparison to the surface areas of the sheets. Particles of montmorillonite are mostly negatively charged because of lattice substitutions usually existing.[62, 84, 94] These charges located in the sheet surfaces overshadow any charge due to edge or corner unsaturation.[58]

The most striking colloidal phenomenon exhibited by clays is a direct consequence of the charge carried by the solid particle or nucleus. First reported by Thompson [121] in his studies of soils, it is known as base exchange reaction. Systematic work was first undertaken by Way [123] in the middle of the last century. Leading chemists of those times viewed his results with considerable scepticism, but their importance was later fully recognized and has resulted in a vast amount of work directed toward a better understanding of this phenomenon.

The ability of clay minerals to adsorb cations is the result of their unbalanced lattices. The magnitude of this adsorptive power, therefore, depends on the structural arrangements of the different clay minerals and is expressed in milliequivalents of base (cation) per 100 grams of clay. These cations are electrostatically attracted and held to the negatively charged clay particle. When dispersed in water these cations will, depending on their valency and hydration, dissociate from the nucleus to a more or less pronounced degree. We therefore can compare such a clay particle in suspension with an electrolyte composed of a complex colloidal anion and a number of simple cations.

By the same reasoning clay minerals must also be capable of adsorbing anions, where net positive charges are set up in the clay crystal, or where the hydrogen of an OH group can be exchanged for a more powerful anion, like PO_4.[118] Owing to the lattice structure of the clay minerals, the latter condition is relegated to a secondary position and therefore very little work has been done in regard to anion adsorption and exchange.

The adsorbed cations can be exchanged for others. The water softening properties of certain natural and artificial hydrous alumino-silicates are based on just this phenomenon. Schematically we can represent the reaction as follows:

$$\boxed{\text{Clay}}\begin{matrix}-\,Na^+\\-\,Na^+\end{matrix} + Ca^{++}Cl^-_2 \longrightarrow \boxed{\text{Clay}}\begin{matrix}-\\-\end{matrix}\,Ca^{++} + 2Na^+Cl^-$$

Increasing valency and decreasing hydration [124] facilitate exchange. A reversal can be accomplished by mass action, *i.e.*, by high concentrations of the exchanging cation, if the latter is of lower hydration and valency than the adsorbed one.

As a first approximation the Hofmeister or lyotropic series for cations holds. Besides valency and hydration, the size of the ions seems to have an important bearing on its replaceability. Thus ions which are at least as large as the diameter of the hexagonal net of oxygens in the silica sheet, *i.e.*, 2.64 Å. are difficult to replace.[37, 43, 99]

Since the potassium ion has an effective diameter of 2.66 Å., its importance as a bridging cation in the illites and in mica becomes evident.

Recent work suggests that ion exchangeability of different clays cannot be accounted for by a general concept as outlined,[6, 118] but that it follows an exchange series specific for every clay mineral. The differences found may be explained by

* Bentonite designates a rock formation, mainly composed of members of the montmorillonite group of clay minerals.

considering the size of the cation in relation to the lattice configuration causing ion adsorption.

Base exchange is not limited to inorganic cations. It has been demonstrated that organic cations can be introduced.[24, 86, 51, 83, 104] They are firmly held between the unit cells, destroying the expansion of the lattice, *i.e.*, rendering the clay non-swelling.

Methods to determine the base exchange capacity are numerous, but so far none has yielded a result of high accuracy [19, 49, 63, 95, 107] owing to a number of factors adversely affecting the analytical process.[12, 18, 82] The determination of the specific exchangeable cations is even less accurate [19, 25, 63] unless a perfectly clean clay is used.[68]

Generally accepted values for the base exchange capacity for some of the more common clays are given in the following table.

Mineral	Base Exchange Capacity (meq/100 gr of clay)
Montmorillonite	60-100
Attapulgite	25- 30
Illite	20- 40
Kaolinite	3- 15

Effect of Particle Size

It is evident that base exchange capacity will vary with particle size, if changes in the latter result in different degrees of electrical unsaturation of the colloidal particle. The fact that the units of montmorillonites are loosely held together by weak O—O bonds, permitting very easy cleavage by water entering between them, would indicate that base exchange is independent of actual particle size, since all exchangeable positions are always readily accessible. This assumption, derived here by purely theoretical reasoning and based on the present concept of the structure of montmorillonite, has been experimentally verified.[41] With kaolinite, illites, or mica this should not be the case. Here the units are held together either by strong OH—O bonds or by cation bridges (potassium),[26] thus preventing the entry of water between them. Cleavage is not so easy along the surface planes. Besides, in kaolinite these planes do not carry the appreciable net charge essential for ion adsorption. However, if we increase the number of unsaturated edges or corners by mechanical comminution and if we could leach out the potassium bridges in illites or micas, then the base exchange capacity should increase with decreasing particle size. This too has been experimentally proved.[71, 116]

Particle Size Determination

The determination of actual particle size and particle size distribution offers considerable difficulties. The main reason is again to be found in the structural characteristics of the clay minerals and the different forces and ionic arrangements associated therewith. We know that particles of clay minerals when suspended in water disintegrate into smaller units. But the degree of such comminution will vary considerably from clay to clay. Montmorillonite with a high base exchange capacity, having adsorbed sodium ions, will disperse readily in water into very small particles, whereas some illites will and others will not disperse. The comminution of kaolinite by simple agitation in pure water does not lead to an appreciable reduction in particle size. In an alkaline medium, however, reduction in particle size can be more readily accomplished. On the other hand, montmorillonites with calcium or hydrogen ions will be less amenable to peptization than a sodium clay.

To understand fully these differences, a discussion of the fundamental electrokinetic phenomena here involved is essential. But as far as the methods for particle size and particle size distribution are concerned, it must be admitted that they only permit determination of the degree of disaggregation and rarely of the actual particle size.* [47, 48, 50] Furthermore they all are based on the determination of an apparent

* See paper in Vol. V of this series on the electron microscope by A. F. Prebus. J. A.

spherical diameter, with the exception of direct visual observation by the use of the electron microscope. Electron microscopy has demonstrated that the clay particles are plates.[67, 114, 115] Therefore the apparent spherical diameter is only an approximation for lack of a more accurate determination.

For particles with an equivalent spherical diameter over 1μ, hydrometer methods [13] have been quite satisfactory. For finer particles substitution of gravity by centrifugal force has given good results.[96] At present the Sharples supercentrifuge will give the most accurate results and is the only one which permits fractionation of larger quantities.[48]

The Concept of the Double Layer, Stability of Clay Sols, Their Gelation and Coagulation

Because of the effect which electrolytes exert on clay sols, colloidal clays must be classified as electrocratic * sols. Their stability or instability is largely governed by electrokinetic phenomena, resulting from the presence or absence of charges on the surface of the clay particle, and the type, concentration, and arrangement of ions present in the dispersion medium.

To be more specific, the stability or instability of colloidal clay sols depends on the condition of the diffuse electric double layer (Goüy-Freundlich) surrounding the particles or in other words on their ζ-potential. Differences in the lattice structure of various clay minerals will result in diffuse double layers being formed by different mechanisms. For example the electric double layer of a sodium montmorillonite exhibiting high base exchange capacity will consist of the negatively charged surface of the crystallite as the inner rigid layer, the adsorbed hydrated sodium ions representing the counter ions in the diffuse outer layer. In the case of kaolinite or other clay minerals which have a balanced lattice structure, the individual particle carries no net charge and therefore no ions are adsorbed onto the particle. Because such particles if placed in pure water are incapable of building up a diffuse electric double layer, they form suspensions of very low stability. However if these particles are suspended in an alkaline medium, negative OH ions are preferentially adsorbed on the unsaturated metal ions in the corner or edge positions of the lattice, causing the particles to acquire a net negative charge.[69] The cations of the electrolyte (alkaline medium) function as the counter ions. That such unsaturated metal ions in corner or edge positions are available for adsorption has been indirectly demonstrated by color reactions occurring when clays and organic amino compounds are mixed together.[8, 46, 57, 75, 100]

Another possibility is the adsorption of OH ions from the alkaline medium onto the oxygens of the silica layer by dipolar bonds.

The ζ-potential of a given colloidal particle in a given dispersion medium depends on the electric charge and fictional thickness of the double layer. Assuming the charge to be constant, increased thickness of the double layer will result in an increase of the ζ-potential. Since the thickness is a function of ion hydration and ionic distribution (stand-off distance of the ions, which in turn depends to some extent on their valency), it is evident that a clay colloid carrying monovalent, highly hydrated cations will result in a sol of maximum stability.

The fact that the adsorbed counter ions are electrostatically bonded to the clay particle prevents their complete dissociation from the latter. Thus, they surround the clay particle at a certain distance and may be considered as forming an imaginary membrane. If pure water is used as a dispersion medium, osmotic imbibition of water through this hypothetical membrane occurs and the clay swells to its maximum (Fig. 11).[91] If an electrolyte is either present in or added to the dispersion medium, the ion concentration inside the membrane and outside of it will follow the Donnan

* The term "electrocratic" is applied to colloid sols, like those of gold, which owe their stability to electric charges. J. A.

equilibrium. This in turn will result in a decrease of the net excess of ions inside the membrane, causing water to flow away from the particle, and thus reduce the swelling of the clay. A further increase of electrolyte will concentrate the counter ions close to the surface of the particle. This, in conjunction with the above-mentioned dehydration, results in a decrease of the thickness of the double layer and in a decrease of the ζ-potential. The system becomes increasingly unstable. As a result of these considerations it becomes evident that cations of higher valency or of lesser hydration will replace or exchange such cations as sodium.

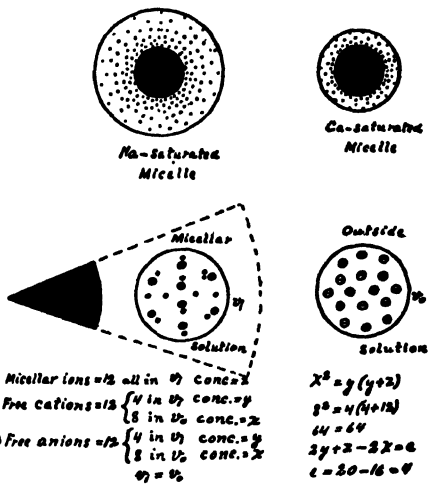

FIGURE 11. Schematic drawing of the imaginary membrane (formed by the counter ions) around the clay particle. The Donnan equilibrium can be applied to the system (Mattson).[91]

Frequently the concept of ion hydration has been used not only to explain the water hulls (lyospheres) surrounding the individual particles but also to account for the entire water film which separates the clay particles. These "films" are of considerable thickness. However, such a concept necessitates the assumption of extremely thick lyospheres, for which ionic hydration alone cannot account.

Systematic studies of extremely dilute suspensions of clays and other colloids have demonstrated that these systems can be transformed into rigid gels, even if the distances separating the particles are greater than could be explained by assuming that their lyospheres touch one another.[44, 49] Such a concept would necessitate the further assumption that all the water in the gel is immobilized. This is contrary to experimental observations.

A simple explanation for these facts without the necessity of questionable assumptions, can be offered by a recently suggested general theory of gelation and coagulation.[40] The following quotation from the original publication will serve best to explain this new concept:

"We know that the electrical forces associated with a given colloidal particle in electrolytic media arise from two sources. One set of forces arises from the ions predominantly of one sign, which are rigidly adsorbed on the surface of the particle, and the other set arises from the ions of opposite sign, which gather about the particle in an effort to neutralize this charge. Since the particle possesses a net charge, we may assume that the total number of ions that gather about the particle in accord with the Goüy concept, are not sufficient to neutralize the charge on the particle. Some of these ions of opposite sign may be floating about in random motion in the disper-

sion medium so that the dispersion medium has a charge opposite to that on the particles. A picture showing the relative magnitude of the electrical forces associated with a given colloidal particle and demonstrating how this effect can occur, may be obtained from Fig. 12. Line A represents the rate of decline of the electrical forces

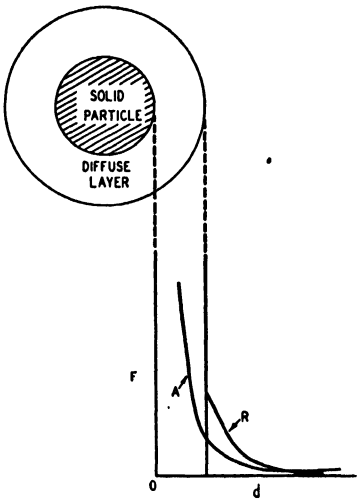

FIGURE 12. A simplified picture of the nature of the forces associated with the charge of a colloidal particle, the diffuse layer, and any given charge possessing the same sign as the particle, as a function of the distance separating them.[40]

as one travels outward from the surface of the particle; this is due solely to the ions that give the basic charge to the particle. This is essentially a plot of K/d^2 where d is the distance out from the surface of the particle. Line R represents the rate of decline of the electrical forces associated with the diffuse double layer of net opposite sign and is also a plot of the function of k/d^2, where k is smaller in value than the K in the former expression, and the vertical axis represents the center from which all the ions of the diffuse layer may be considered to be acting. This idea of a center of action is essentially the same as that assumed in the Helmholtz equation for the zeta potential.

"Thus, since the ions in the different layers are opposite in sign, we may consider curve A as representing the attraction forces associated with the particle, and curve R as representing the repulsion forces associated with the particle toward ions of opposing sign in the dispersion medium. To be concrete we shall let curve A represent the effect of negative adsorbed ions and curve R that of positive ions.

"We may observe from the diagram that up to the point of intersection the repulsion forces due to the diffuse layer predominate except at small distances out from the surface of the particle. Thus, an ion of the same sign as those in the diffuse layer cannot approach the vicinity of the particle beyond that point, since the effect of Brownian motion is relatively small. When we travel out beyond that point, attraction forces, although relatively weak, are found to exist. It is a likely assumption that the kinetic energy of the individual ions is sufficient to prevent them from being restrained at this point, and hence they are moving about in random motion in the dispersion medium. However, although the forces associated between the individual ions in the dispersion medium and the ions of opposite charge on the inner layer of the colloidal particle are relatively small, considerable forces may be set up between the ions on the inner layer and the ions in the dispersion medium taken as a whole. In other words, the dispersion medium may act as an oppositely charged electrical field, which effects the condensation and the orientation of the particles.

"Since the dispersion medium may be considered as possessing an excess of ions

of the same charge, due to the adsorption effects of the colloidal particles, these may interact and form groups of ions which have a greater charge associated with them. Thus these groups may act as nuclei about which the colloidal particles may condense, owing to forces of an electrical nature. On the basis of this idea, if orientation and condensation do take place, this will occur up to the point where the attraction forces between the basic charge on the particles and the ions in the dispersion medium are balanced by the forces of repulsion between the ions in the diffuse layer and the ions in the dispersion medium. Thus a rigid gel may form, which may be made fluid by redistributing the ions in the system (by shaking—thixotropic gel). It is difficult to form an integrated picture of the whole process, because as orientation and condensation take place the diffuse layer surrounding the particles is probably compressed; this results in a further neutralization of the basic charge on the particles which, in turn, changes the nature of the forces surrounding them. However, it is seen that the particles of a colloidal suspension may orient under suitable conditions into fixed positions, where their behavior is controlled predominantly by electrical forces. This orientation may then result in the condensation of the particles about the ions in the dispersion medium, so that finally coagulation is achieved. As the picture of this process depends upon the adsorption characteristics of the particles and the ions and upon the charge on the ions, we shall attempt to show how it changes with variations in these factors.

"It is known from experiment that to obtain the maximum gelation effects in an electrocratic colloidal system, monovalent ions that possess a sign opposite to the charge on the sol are most suitable. Furthermore, the effectiveness in this respect seems to follow the Hofmeister series. In other words, for a negative bentonite sol, the effectiveness of the ions inducing gelation follows the series lithium, sodium, potassium, hydrogen, etc., and it is important to note that the effectiveness of the adsorption of the ion in the diffuse layer increases as we travel from lithium to hydrogen. This would appear to show that the less strongly the ion carrying a sign opposite to that of the sol particle is adsorbed in the diffuse layer, the more powerful it is in forming gels and causing coagulation. This is in accord with the idea discussed above, for the less adsorbed the ion is, the greater tendency it has to move about in the dispersion medium and create stronger forces to exist between the sol and the dispersion medium. On the other hand, we should expect that polyvalent ions would behave altogether differently from monovalent ions. First, they would be more strongly adsorbed in the diffuse layer because of the greater electrostatic attraction and, secondly, there would be greater forces of repulsion between the ions of like sign in the dispersion medium, thus reducing any tendency of interaction of the ions to form ionic groups and making the system more diffuse. For this reason, the mechanism of coagulation should be considered as somewhat different in the case of the polyvalent ions from the case when monovalent ions are employed. Since in the case of coagulation by polyvalent ions the forces, as pointed out above, between the particles of the sol and the dispersion medium are relatively small, coagulation must be due mainly to the neutralization of the charges on the particles. This allows the particles to be impelled together by their kinetic energy, so that they may be held together by molecular forces acting at short distances of separation. This is borne out by considerable experimental data, which show that an appreciable charge exists on the particles of certain sols when coagulated by monovalent ions and practically no charge exists on the sols when they are coagulated by polyvalent ions.

"Thus the electrocratic behavior of a sol depends in general upon the individual adsorption characteristics of the ions in the systems and the adsorption behavior of the colloidal substance present."

With this theoretical background it is possible to discuss adequately some of the most important applications of the clay minerals and to explain some of nature's most puzzling phenomena.

Properties and Applications [14]

Aside from the importance of base exchange in agriculture,[71, 72] the most important properties of clay minerals in the presence of water are unquestionably plasticity, bonding strength, compactability, and gelation, including thixotropy as well as viscosity. Particle size, shape, and surface configuration are also important for certain applications, for example, in the paper and rubber industries.

Plasticity is one of the most important factors of the clay minerals in *ceramics.* In a plastic system, for example a kaolin slip, truly viscous flow is achieved only after some force inherent in the system has been overcome. The work which has to be expended to accomplish this is generally described as the yield value of the system. In accordance with the concepts discussed above, plasticity in the present case can be considered as the outwardly noticeable resultant of attractive and repulsive forces acting throughout the system between the clay particles and the ions of the dispersion medium. If the system under consideration consists of pure kaolinite and pure water, the only forces of consequence are the molecular attraction forces between the uncharged particles (van der Waals forces). At an economically interesting concentration of clay, such a slip would be of such high plasticity that it could not be worked satisfactorily. If, however, an alkaline medium (NaOH) is used instead of pure water preferential adsorption of the OH ions takes place in the surface of the particles, setting up repulsive forces between the particles. This in turn decreases the amount of force needed to shear the system, which is synonymous with a reduction of the yield value. The slip is now in a deflocculated condition; and although its concentration has not been changed, its fluidity has been increased to such a degree that it now may be too thin for satisfactory workability. However, reverting to the previously developed concepts, such excessive fluidity might be reduced by the use of electrolytes having cations of a higher valency until a system of desirable workability is obtained.[45, 69]

In the case of montmorillonites with high base exchange capacity, plasticity for a given concentration of the slip will depend largely on the type and concentration of cations present in the system. The lattice-substituted particle already carries a substantial negative charge, so that any possible increase in charge due to anion adsorption would be insignificant. It is evident that a sodium montmorillonite will be the least plastic of the commonly known montmorillonites; calcium and barium bentonites will exhibit noticeable plasticity, hydrogen clay being the most plastic.

Thus recent theoretical developments in the colloid chemistry of clay minerals are of greater and greater assistance in the successful application of these minerals.

The *soil engineer,* as well as the soil chemist, is making increasing use of these modern concepts and is finding satisfactory explanations for empirically established facts. For example the beneficial effect of "soil sweetening" by the addition of lime can now be explained as the result of changes in the clay colloid due to the exchange reaction. The prevention of water seepage by proper conditioning of the clay used in the construction of dams, ponds, or lagoons are other typical examples. One of the most striking examples occurred during the construction of a sweet-water lagoon on San Francisco's Treasure Island. When the lagoon had been completed—using locally available clay as construction material—and filled with sweet water, the seepage proved to be economically unprofitable. Of all the suggestions offered the simplest and cheapest by far was highly successful. The sweet water was temporarily replaced by sea water. After the latter had remained in the lagoon for several days, it was pumped out and once more sweet water was introduced. The seepage had been stopped.[125] Base exchange of course was responsible for this result.

In recent years the bottoms of fish hatchery ponds and the like have frequently been sealed by racking bentonites of high base exchange capacity into the ground. When water is flowed into the pond the bentonitic clay swells and prevents seepage.[4]

Even cracks in concrete dams have been successfully closed by introducing bentonites.[3, 79]

Bentonite suspensions exhibit thixotropic properties whenever their concentration and ionic distribution are properly adjusted.[22, 42, 49] Such suspensions are used in the drilling of oil wells, where they are generally known as "drilling muds." [21, 117] * One of the greatest problems with which the mud engineer is faced is the maintenance of this thixotropic effect in soils where an excessive ion concentration is suddenly introduced during the drilling operation. This frequently occurs whenever a formation rich in soluble salts is struck. Only a thorough knowledge of the phenomena involved will enable the engineer either to adjust his clay suspension properly or to select a clay which as a result of its ionic arrangement, will be specifically suited for such conditions.†

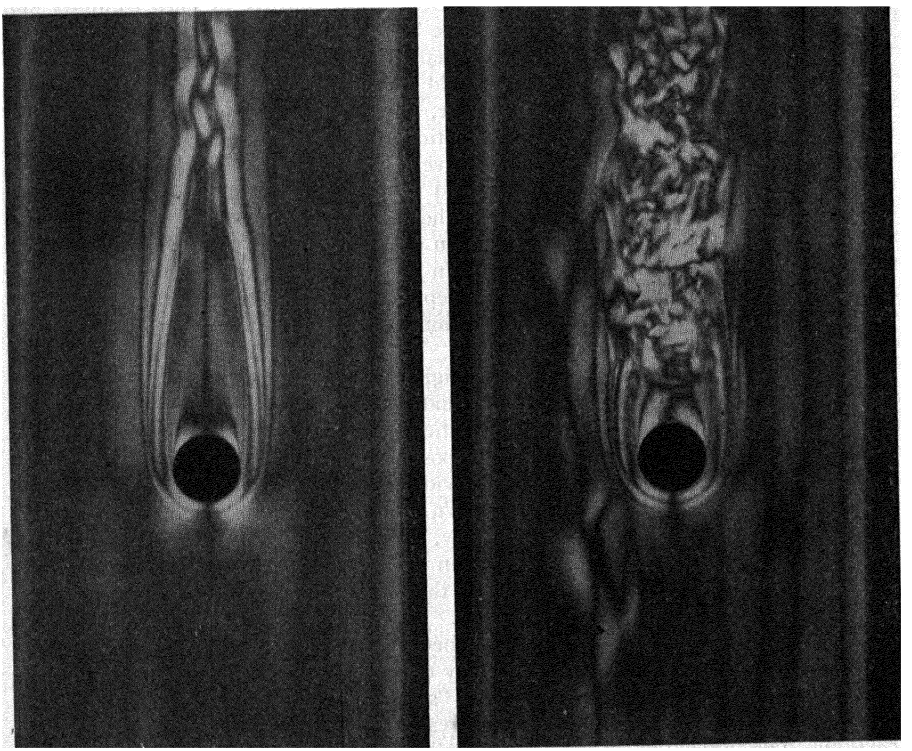

FIGURE 13. a, b. Two different rates of shear patterns of flow past a cylindrical model as shown by the streaming double refraction of a dilute bentonite suspension.[88, 89]

The *metal industry* frequently uses plastic clays as the bonding agent in foundry cores. An ideal bonding material is one which will give a strong bond with a minimum of material. Bentonites of medium base exchange capacity, *e.g.*, fairly plastic montmorillonites, have proved very satisfactory for this purpose.

The fact that clay minerals having high base exchange capacity and carrying highly hydrated counter ions result in suspensions of high viscosity at low concentrations is the reason for their frequent use in holding other materials in *suspension.*

* See paper on drilling muds by D. H. Larsen in this volume. J. A.
† See paper in this volume by H. Winterkorn. J. A.

They are applied for this purpose in the preparation of various medical prescriptions[2] and as retarders in the setting of *Portland cement* (*bleeding*).

High swelling bentonites are also used as carriers in *insecticide sprays*,[1] *in the clarification of turbid water and wines*,[5] *as solid emulsifiers, etc.*

Some of the most recent applications of colloidal clays are based on the pronounced *double refraction* exhibited by bentonite sols. This double refraction can be produced either by causing the sol to flow or by applying an electric field to the system. In the former case the flow tends to orient the particle, the degree of double refraction being a function of the rate of flow. This method has proved very successful in the study of flow of liquids and is particularly adapted for studies in hydrodynamics and aerodynamics.[88, 39, 78] (Fig. 13a, b) The latter development makes use of the large electro-optical effect of bentonite sols and permits the study and measure of non-homogeneous electric fields by an optical method analogous to photoelasticity.[93] (Fig. 14)

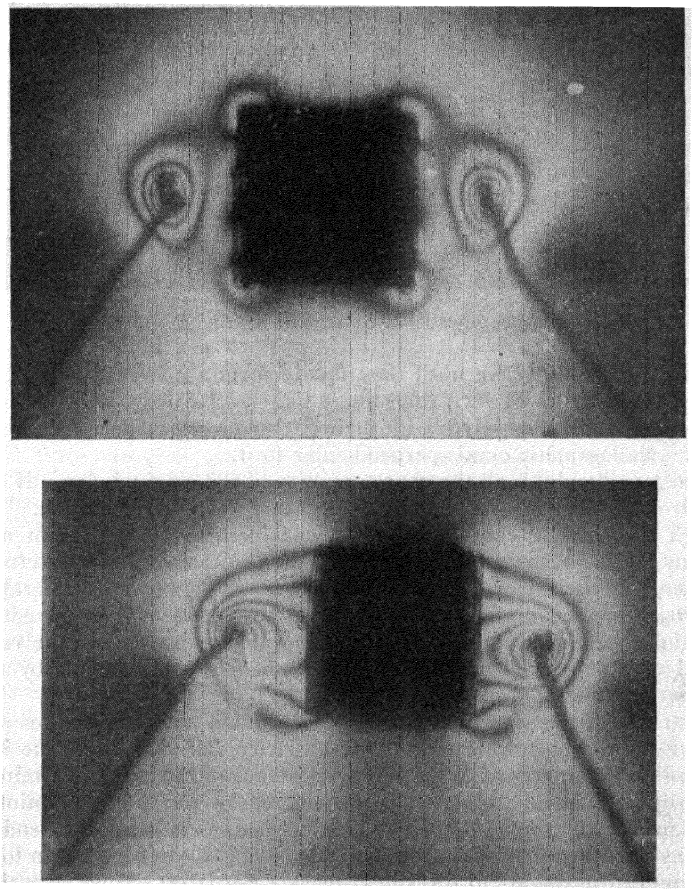

FIGURE 14. The distortion of an electric field applied between two parallel wires (150 volts, 10,000 cycle A.C.) in a bentonite suspension and as obtained by interposing a quadratic block. *Top*: The quadratic block is a dielectric (bakelite). *Bottom*: The quadratic block is a conductor (nickel). The observations were made through circular polarizers. (Courtesy Prof. H. Mueller, Mass. Institute of Technology, Cambridge, Mass.)

Inorganic, Non-metallic Films

One of the latest developments in the application of clay minerals is the production of coherent, self-supporting films.[36, 41, 120, 122] It has been found that bentonite hydrosols or gels can be transformed into coherent, self-supporting films by careful evaporation. These films have been termed "Alsifilm" (*Al*uminum-*Si*licate *film*s).

A study of the formation of these films carried out with a microscope fitted with an opaque illuminator, revealed that the individual particles of the clay colloid align themselves during evaporation to threadlike aggregates (Fig. 15). These aggre-

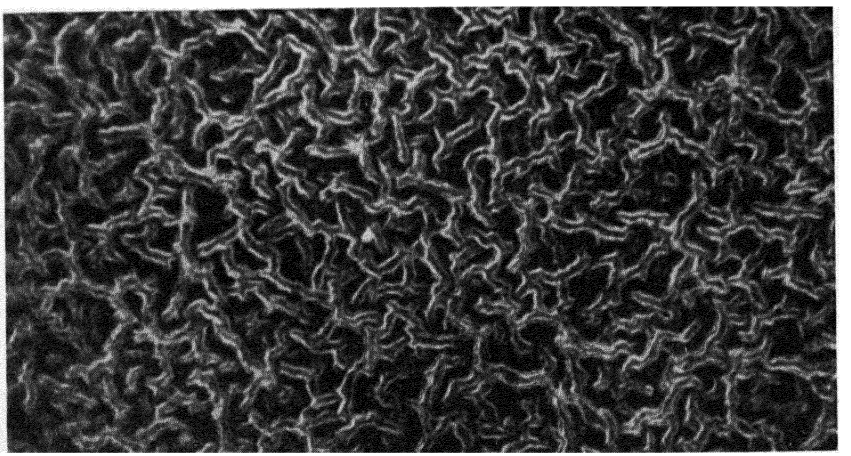

FIGURE 15. Microphotograph of desiccated bentonite. (Alsi film) [41, 43]

gates intersect and interweave until they finally form a coherent fabric-like microstructure. X-ray studies of such films show that the particles which are of a plate shape have all oriented themselves with their flat surfaces parallel to the support, *i.e.*, with their crystallographic *c*-axis perpendicular to it.

Such sheets still exhibit all the characteristics of the original clay. If brought in contact with water they will swell and finally revert to the sol condition.

Although these crude clay films are of considerable interest from a scientific point of view and have successfully been used as membranes in the determination of ion activities,[85, 86] their lack of water resistance limits, to a considerable extent, their industrial applicability, as electric insulators or as wrapping materials etc. However, since these films proved to be as amenable to base exchange reactions as the original clay, it seemed possible to render them water resistant by the use of electrolytes containing appropriate cations.

A comparison of the structure of lattice-substituted montmorillonites with illites and muscovite mica not only reveals their similarity, but also shows the importance of the potassium ion in regard to the water resistance of the two latter minerals. As has been previously pointed out there is good reason for the assumption that the ease or difficulty with which an adsorbed cation can be exchanged depends not only on its valency and degree of hydration, but also on its size in correlation to the opening of the oxygen hexagons in the silica sheets (Fig. 16). Thus potassium which snugly fits into this opening is difficult to replace. It also acts as a bridge between two crystal units thereby holding them tightly together. Base exchange of "Alsifilm" with potassium salts proved this point; a water insoluble clay film was obtained. However other ions of similar dimensions, for example, lead, rubidium, ammonium, cesium, and organic ammonium complexes give the same results.[36, 43]

Although none of the films so treated is water-soluble and all can be desiccated until no moisture is retained in them, they differ somewhat in their ability to reabsorb moisture if immersed in water or if they are subjected to a highly humid atmosphere. The more hydrophobic the exchanged cation as well as the anion of the electrolytes are, the less the moisture pickup will be. If metallic salts of fatty acids are used as electrolytes, it has been found that the moisture pickup decreases with increasing chain length of the acid radical. The explanation for this phenomenon may lie in the difficulty of completely removing the bulky anions from the clay structure after the exchange has taken place.

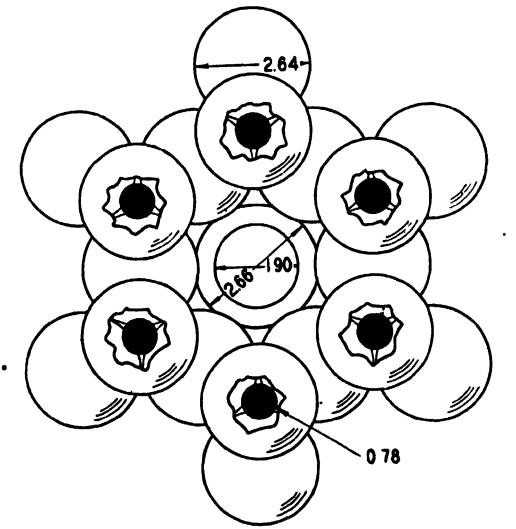

FIGURE 16. Hexagonal arrangement of silicon-oxygen tetrahedra in a silica sheet (top view, schematic); the top oxygens have been cut open to show the location of the silicon atoms.[74] Two concentric circles have been drawn into the center shape. The larger one corresponds in diameter to a potassium atom, the smaller one to a sodium atom. The actual dimensions in Å. are as indicated for the different atoms.[87]

Another point of interest is the fact that even films treated with lead salts are excellent electric insulators, closely approaching the best types of mica in their quality. This may be taken as further confirmation that the lead ions introduced are completely isolated from one another by the oxygen hexagons which surround them. Furthermore they are so strongly held in the structure that even prolonged leaching of the films in boiling water will not remove them.

The production of water-resisting "Alsifilm," now also known as "Diaplex," * as a film material of high electrical and thermal insulating properties, may well be taken as a good illustration for the application of the latest concepts in structural research in the development of an entirely new product. However the idea on which this development is based is naturally not limited to the formation of films and similar structures, but can find its application also in the field of plastics in general.

Although prevailing regulations do not permit a more detailed discussion of the various possibilities at this time, it nevertheless can be stated, that the combination of clay minerals with certain organic compounds has built an interesting bridge between the two kingdoms of matter. It may well lead to a new and fascinating field for scientific research and industrial applications.

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Catalysis and Its Industrial Applications

P. H. EMMETT *

Department of Chemical Engineering, Johns Hopkins University

Contact catalysis has long been recognized as one of the important subdivisions of colloid chemistry and as such merits a periodic review of progress that is being made in understanding its theoretical aspects and in applying it more effectively to industrial problems. The vastness of the literature that has accumulated and the rapid expansion of industrial applications in recent years makes it impossible, of course, to deal critically in one short chapter with the many ramifications of the subject that the expert might want discussed. Furthermore, many readers will be more interested in a summary of the present general points of view held by those working in the field of catalysis than in a detailed technical discussion of theoretical and mechanistic studies of specific catalysts.

In the present chapter an attempt will be made to keep in mind both groups of readers by considering (1) the present picture of contact catalysis generally held by those working in the field; (2) the new tools and approaches that have recently been made available to those studying catalyst reaction mechanisms; and (3) some of the newer work that has been published relative to the functioning of catalysts in various industrial processes. This third item has of necessity been drastically curtailed and is very incomplete. For a more detailed and comprehensive description and discussion of the subject the reader is referred to the numerous books [1] that have been published and to the many fine articles in recent journals.

Present Concept of Contact Catalysis †

Mechanism. For many years the question has been argued as to whether a solid catalyst surface functions by a mechanism of intermediate compound formation or by the mere adsorption of the reactants on the catalyst surface with an enhancement of reaction rate resulting from the longer time of contact of the adsorbed molecules with one another. It seems that an answer to this query can be succinctly given by saying that there are well established instances to prove that catalytic reactions may operate by either of these mechanisms as well as by mechanisms that may be regarded as intermediate between these two.

The intermediate compound formation theory includes those instances in which the catalyst reacts with one constituent by a recognized chemical reaction and then is restored to its original chemical form by reaction with the other constituent. For example, Fe_3O_4 seems capable of being alternately reduced by CO to Fe and reoxidized to Fe_3O_4 by water vapor in catalyzing the reaction

$$CO + H_2O = CO_2 + H_2 \qquad (1)$$

* Present address Mellon Institute of Industrial Research, Pittsburgh, Pa.

† See paper on Contact Catalysis by Hugh S. Taylor, in Vol. II of this series; and paper on Catalysis As a Biological Factor by J. Alexander, in Vol. V. See also two papers on the adsorption of hydrogen by tungsten by W. G. Frankenburg, J. Am. Chem. Soc. 66, 1827-47 (1944). J. A.

The catalytic combination of hydrogen and oxygen over copper-copper oxide mixtures is another reaction that appears to fall in this category in certain temperature ranges.[2] Similarly, the functioning of numerous polymerization catalysts, such as sulfuric acid and phosphoric acid, involves intermediate formation of esters between the acid and the olefin followed by interaction of two such intermediates or by one intermediate reacting with an additional olefin molecule.[1e] Many other instances might be cited.

At the other extreme one finds those catalytic reactions that appear to take place as a result of purely physical adsorption. Before describing these, however, it may be well to call attention to the existence of two types of adsorption ordinarily encountered in gas-solid systems.

A gas at temperatures sufficiently close to its boiling point can always be physically adsorbed upon the surface of any solid. The gas molecules are presumably held to the surface by van der Waals forces, usually equilibrate rapidly with the surface, and involve energies of adsorption that are ordinarily only 50 to 100 per cent greater than the heat of liquefaction. A second type of adsorption generally known as "activated" adsorption [3] is chemical in nature. It occurs between gases and solid surfaces as a result of chemical interaction between the two. Frequently this type of adsorption is slow and extremely sensitive to temperature changes. It appears to involve an energy of activation and has therefore been termed activated adsorption. Usually activated adsorption attains an appreciable rate only at temperatures at which van der Waals adsorption has decreased to nearly zero. Sometimes it occurs at such low temperatures that the energy of activation must necessarily be very low, even though the adsorption clearly involves chemical binding. These rapid low temperature cases of chemical adsorption have occasionally been separately designated as "chemisorption." [4]

The examples of catalysis occurring as a result of purely physical adsorption are not numerous. It was rightly concluded many years ago that in general the mere increase in the density of a gas resulting from its physical adsorption on a surface does not lead to its reacting. One example, in which physical rather than activated adsorption plays a major role, might not be called a chemical reaction by some, for it is the low-temperature catalytic interconversion of para-hydrogen and ortho-hydrogen that occurs over paramagnetic or ferromagnetic substances. The interconversion in liquid hydrogen without a catalyst is extremely slow, whereas it occurs in a few seconds contact at −195° C with charcoal,[41] iron,[4b] and number of paramagnetic oxides.[4a] The recently reported [100] catalysis of the reaction

$$H_2 + D_2 = 2HD \qquad (2)$$

by tungsten at 77° K through van der Waals adsorption, if correct, furnishes an even better example, since it actually involves an interchange of atoms between molecules.

By far the larger number of catalytic reactions probably take place through a mechanism that may be considered either as intermediate formation of "surface compounds" or as activated adsorption, or chemisorption, of the reactants on the surface of catalysts. As an illustration, one may point out that the synthesis of ammonia over iron catalysts is now generally believed to take place through the activated adsorption of nitrogen on the surface of the iron,[5] followed by reduction of this "surface nitride" with hydrogen to form ammonia. Nitrogen at the temperature of ammonia synthesis, 450° C, will not form a separate solid phase of nitride with pure iron until the pressure is increased to about 5000 atmospheres.[6] Clearly, however, as nitrogen molecules strike the surface of iron they, as individuals, would tend to behave as though they were forming the nitride Fe_4N, in which the nitrogen atoms are 3.6 Å apart instead of about 1.10 Å for normal nitrogen molecules. Such nitrogen molecules that have momentarily reacted with the outermost surface iron atoms may be regarded as illustrative of either "activated adsorption" or of intermediate "surface

compounds."[7] Briefly then, this type of mechanism involves the chemical interaction of reactants with the surface atoms of the catalyst sufficient either to rupture or to activate the original reactants and permit the formation of the reaction products.

Promoter Action. Certain substances added to catalysts will, though inactive themselves, enormously increase catalyst activity. These are known as promoters. As an example of promoter action may be cited the addition of about one per cent aluminum oxide and one per cent potassium oxide to iron oxide to form, on reduction, active catalysts for the synthesis of ammonia. If the added inert material is present in large excess it is generally considered merely as a catalyst support. Many catalysts are made by supporting the active constituents on pumice, kieselguhr, or some other suitable inert material having a large surface area. If the added material is present in fairly large quantities and has activity by itself, it is generally regarded as forming a mixed catalyst. The present brief discussion will be limited to the explanation usually given for true promoter action.

Promoters may function by either a physical or a chemical mechanism. In certain instances they apparently accumulate on the surface of the catalyst and by hindering surface mobility of the catalyst atoms prevent crystal growth and thus preserve a large surface area of the catalytic material. An excellent example of this kind of promoter action is aluminum oxide in iron catalysts for the synthesis of ammonia.[8] A pure iron catalyst at 450° C will sinter rapidly and lose its catalytic activity. For example, a freshly reduced 50-gram sample of pure iron catalyst may have a surface sufficiently large to hold by physical adsorption 20 cc of nitrogen as a monolayer. A few hours' operation at 450 to 500° C will cause the surface to decrease until only 4 or 5 cc of gas would be required for a monolayer. By contrast, if the iron contains a few per cent of aluminum oxide in the original sample of Fe_3O_4, the reduced iron catalyst will require about 100 to 120 cc of nitrogen for a monolayer, and will not lose an appreciable amount of its surface when operated in the range 450 to 500° C for many hours. At least one function of the aluminum oxide is apparently the preventing of crystal growth in the reduced iron.

Chemical promoter action may be made to include all other known examples, if we class as chemical in nature all instances in which the catalytic activity per unit area of catalyst is definitely increased by the presence of the promoter. Space does not permit a detailed discussion of the many examples of such promoter action. In general they are not any too well understood even at the present time. For example, potassium oxide added as a second promoter to an iron catalyst containing aluminum oxide results in a still further improvement of the iron catalyst for NH_3 synthesis, though the mechanism by which the alkali molecules accomplish this is still obscure.[56] In general the chemical promoter action may result from either the activation by the promoter of one of the reactants or the removal by the promoter of one or both of the products of reaction by formation of suitable complexes. For example, the promoter action of ThO_2, Al_2O_3, etc., on Ni catalysts for the reaction

$$CO + 3H_2 = CH_4 + H_2O \qquad (3)$$

was postulated by Medsforth[9] to occur through the dehydrating action of the oxide on some intermediate (possibly CH_3OH) formed on the nickel as a step in the catalysis, the resulting $Ni—CH_2$ complex being hydrogenated rapidly to CH_4.

Poisons. Catalyst poisons are usually assumed to affect solid catalysts by covering up the parts of the catalyst that are active. Such poisoning may be either temporary or permanent. If the poison is readily removed by one of the reactants as soon as the source of poison is cut off, it is classed as the temporary variety. Oxygen-containing compounds, such as CO, CO_2, and water vapor, are temporary poisons for ammonia synthesis over iron catalysts.[10] As soon as the poison is eliminated from the hydrogen-nitrogen mixture, the trace of oxygen poison on the surface of the catalyst

is quickly removed by the hydrogen, and the catalyst resumes its original activity. On the other hand, the permanent poisons are very tenacious and are removed slowly, if at all, by the reactants. Sulfur poisoning of metallic nickel catalysts is of this kind. The activity decreases steadily as the poisoned gas passes over the catalyst and at low temperatures does not increase again when the poison is removed. Intermediate in behavior is PH_3 as a poison for Pt gauze catalysts used in ammonia oxidation. Even one part of PH_3 in 100,000,000 parts of an air-ammonia mixture is capable of reducing the activity of the catalyst several per cent. From slight poisoning with PH_3, however, the catalyst seems able to recover; whereas from charges as high as 22 parts per hundred million the recovery is extremely slow and the activity of the catalyst appears to be permanently decreased.[11]

Catalyst poisons might also be classed as complete or preferential. There are apparently well substantiated cases in which poisons in small amounts may decrease or eliminate the activity of a catalyst for one reaction without stopping it for another. Thus, Myddleton [12] points out that cobalt-thoria catalysts in the Fischer synthesis may be preferentially poisoned by sulfur compounds so as to produce large concentrations of olefins in the reaction products. In other words, sulfur compounds can poison the catalyst toward the hydrogenation of ethylene without poisoning it for the CO—H_2 reaction. Such poisoning action is clearly of great importance in attempting to obtain preferential action of catalysts toward certain desired reactions.*

The Catalyst Surface. The activity of solid catalysts will depend upon the total extent of surface and upon the activity per unit surface. Originally large catalyst surfaces were obtained by finely dividing the catalyst material. In recent years it is being increasingly recognized [13] that part of the "inner" surface of porous catalysts is also accessible to the reactants and that accordingly catalysts can be made active and still be present in rather large, conveniently usable particles, provided the big lumps or particles are sufficiently porous and the pores are of a sufficient size to permit ready ingress of reactants and egress of products.

The activity per unit surface appears to depend in most cases upon the surface concentration of regions generally designated as "active points." Taylor's original suggestion of active points [14] on catalyst surfaces was well fortified by a large amount of experimental data tending to show that the catalyst surface was not homogeneous. For example, he pointed out that according to experiments by Pease and Stewart,[15] the covering of only a per cent or so of the surface of copper with carbon monoxide was able to decrease by 90 per cent the activity for hydrogenating ethylene. A more recent, excellent illustration of active points has been given by Burstein,[45] who discovered that covering 0.1 per cent of the surface of charcoal with chemisorbed hydrogen at 500° C completely eliminated its activity at −185° for the hydrogen-deuterium exchange. The general heterogeneous nature of the solid catalyst surface implied by this postulate is still commonly accepted, although there do appear to be certain examples of catalysts whose surfaces are rather uniform in activity.[16]

The exact nature of the "active points" is a matter of conjecture. They have been considered as amorphous patches on the catalyst surface, as corners and edges of catalyst crystals, as peaks or "trees" built out on the surface as a result of the method of preparation or activation of the catalysts,[14] and finally as preferred planes on the crystalline catalysts. The latter view arises from the very interesting and significant experiments of Beeck [18] in which he has established that thin films of Ni, Fe, and similar metals, deposited under such conditions as to cause the plane of least dense packing to be parallel to the surface of the glass support, are about 5 times as active per unit surface as those in which the crystal orientation is random. Regardless of the exact nature of the active points, there seems to be no question but that a given element or compound may vary greatly in its catalytic activity per unit area depending on the method by which it is prepared. Until a better interpretation is sug-

* This has been termed "beneficial poisoning." J. A.

gested, such catalysts may conveniently be considered as varying in activity because of a variation in the number of active centers per unit catalyst area.

It is well known that catalysts are very specific in their actions, frequently catalyzing one reaction without affecting others. This specificity is not especially surprising since specific chemical forces and interactions between the catalyst and the reactants are usually involved. It should, however, be pointed out that the geometric configuration of the catalyst surface also may be capable of effecting marked specificity. The above-cited illustration of the dependence of the activity of metal films for the hydrogenation of ethylene upon the closeness of packing of the atoms in the exposed crystal faces is one example of this.[18] Another illustration that has received a great deal of attention in the literature is the claim by Balandin [19] that only those metals capable of exposing surfaces with definite geometric relationships can hydrogenate benzene to cyclohexane. Specifically, he found that all the known metal hydrogenating catalysts for benzene that were active in the low-temperature region had planes of hexagonal symmetry (111 planes of the face-centered cubes, for example) and had atoms falling within a narrow size range. He concluded that none of the known body-centered metal catalysts should be active for benzene hydrogenation even though they might be excellent hydrogenating catalysts for the double bonds of non-aromatic compounds. In agreement with his views, it is true that every catalyst thus far shown to be active for benzene hydrogenation at low temperatures (less than 200° C), has a face-centered structure, detectable by x-ray analysis.[20] Iron catalysts, for example, that are capable of hydrogenating ethylene to ethane at −100° C [21] will not hydrogenate benzene to cyclohexane below 200° C.[22] However, his postulate must apparently be considered as a necessary but not a sufficient condition for aromatic hydrogenation activity, since Cu with a face-centered crystal structure and an atomic spacing of the right dimensions is inactive, if pure, toward the hydrogenation of benzene.[22, 23, 23a] Regardless of the ultimate verdict relative to Balandin's postulate, there seems to be little doubt that the surface configuration of a catalyst will sometimes be the principal factor responsible for its specificity.

Selection of Catalysts. The selection of catalysts is still an art; the time has not yet come when it is possible to predict in advance with any degree of certainty the exact type of catalyst that will be most effective for a hitherto untried reaction. Accordingly, a résumé of the principal catalysts used for industrial reactions should serve a useful purpose. A very comprehensive recent classification of catalysts appears in the book of Berkman, Morrell and Egloff; [1a] for the present chapter, a very brief summary of the principal types of catalysts is given in Table 1.

New Working Tools for Studying Catalytic Mechanisms

The last ten or fifteen years have witnessed the introduction and utilization of a number of new working tools with the help of which a better insight into the fundamentals of catalysis is being gained.

Ortho-para Hydrogen Conversion. The discovery of the catalytic interconversion of ortho- to para-hydrogen by Bonhoeffer and Harteck [41] introduced a new method of studying catalytic hydrogenation, for it appeared likely that both the ortho-para interconversion and hydrogenation involved a dissociative adsorption of hydrogen on the catalyst surface. Unfortunately it soon developed that another mechanism [42, 43] of catalytic interconversion existed that depended on a magnetic perturbation of physically adsorbed and undissociated hydrogen molecules. With this discovery the correlation between the activity of the hydrogenating catalysts and their ability to effect the ortho-para conversion became less certain. Nevertheless when due cognizance of the magnetic conversion is taken the ortho-para hydrogen conversion is still proving useful for mechanism studies.

Isotopes. The discovery of heavy hydrogen permitted even greater progress to be made toward elucidating hydrogenation reactions. The hydrogen-deuterium ex-

Table 1

Reaction Type	Catalysts	Examples
Hydrogenation and dehydrogenation	*Metals:* Ni, Co, Fe, Cu, Pt, Rh, Ir, and Os are strong low temperature hydrogenating catalysts.	Ammonia Synthesis (commercial): Iron catalysts promoted with a few per cent of a difficulty reducible oxide such as Al_2O_3 in combination with an alkali such as K_2O.[38]
	Pure Cu and Fe will not hydrogenate the benzene nucleus.[29]	Higher hydrocarbon synthesis from CO—H_2 mixtures (commercial): Promoted and supported cobalt catalysts.
	Pt and Cu will not hydrogenate CO to CH_4 at an appreciable rate.	Olefin hydrogenation (commercial): Promoted and supported nickel catalysts.
		Unsaturated organic acids and esters (commercial): Nickel salts are used in hydrogenating vegetable oils to edible fats.
		Hydrogenation of the benzene nucleus: Metal catalysts other than Fe and Cu are used—Ni being one of the principal catalysts.
	Metal oxides: ZnO, Cr_2O_3, Al_2O_3, Mo_2O_3 and similar oxides are mild hydrogenating catalysts, usually requiring higher temperatures than metals.	Methanol synthesis (commercial): ZnO, Cr_2O_3, Cu or combinations of these. Cu by itself is a poor catalyst for the reaction $CO + H_2 = HCHO$,[27, 27a] a step in CH_3OH synthesis, but is effective in combination with ZnO.
	These oxides have little or no activity for the hydrogenation of the benzene nucleus [24, 24a] or the carbon-carbon double bond [25]	Higher alcohols from CO—H_2 mixtures (commercial). A methanol catalyst plus a strong alkali,[28, 29, 70, 71] ZnO—K_2CO_3 for example.
	Metal sulfides: MoS_2, SnS_2, etc. are hydrogenating catalysts used for hydrogenations in which sulfurous gases are present.	Crude oil to gasoline with sulfur removal (commercial): Sulfides of molybdenum, tungsten and tin are used as catalysts.
		Coal hydrogenation to gasoline and lubricating oil (commercial in Europe): WS_2, MoS_2, SnS.
Oxidation	*Metal oxides and metals:* Any metal oxide capable of being reduced at the temperature of the catalysis to a lower oxide or to metal and of being reoxidized by the oxidizing gas rapidly at the same temperature should be capable of functioning as an oxidation catalyst [33]: Fe_2O_3, CoO, Co_2O_3, NiO, CuO, MnO_2, V_2O_5, Mo_2O_5, WO_3, Ag_2O are in this class.	Ammonia oxidation to NO (commercial): Pt or Pt alloy gauzes[34] (usually multiple gauzes) at 800-850° C and times of contact the order of 10^{-3} seconds are used. Cobalt oxides, promoted usually with Bi_2O_3 are also employed.
		Ammonia oxidation to N_2O: MnO_2 is active [34] in the range 100-300° C and can be made to produce almost quantitative conversion of NH_3 to N_2O
	Pt and its alloys, and probably some other oxidation catalysts function through adsorptive mechanisms without forming known intermediate oxides.	Oxidation of sulfur dioxide to sulfur trioxide (commercial): Pt supported on SiO_2 [34a] or on $MgSO_4$, and V_2O_5 or some of its salts are commercial catalysts. Fe_2O_3 was formerly used.
		Carbon monoxide oxidation (commercial): Hopcalite (CuO—MnO_2—Ag_2O mixtures) used for low temperature oxidation of carbon monoxide in air and also for its preferential combustion from hydrogen-carbon monoxide mixtures.[35, 35a] Oxides or chromates of Co, Cu, and Ni are also low temperature catalysts; [36] chromates of Zn and Fe [36a] are active for oxidizing CO in automobile exhausts.
		Partial oxidation of naphthalene to phthalic anhydride (commercial): V_2O_5 or its salts are the principal catalysts.[37] Oxides and salts of Mo and W are also used.
		Partial oxidation of toluene to benzoic acid and benzaldehyde (commercial): Same as for naphthalene oxidation.
		Partial oxidation of ethylene to ethylene oxide (commercial): Supported silver catalysts are employed.
		$CO + H_2O = CO_2 + H_2$ (commercial). Promoted Fe_3O_4 catalysts [39] chiefly used; Co and Co—Cu catalysts are more active at lower temperatures [39a] than Fe_3O_4 on sulfur-free gas.
Hydration and dehydration	*Oxides, salts and acids:* Al_2O_3, tungstic acid, phospho-tungstates and ThO_2 are active in catalytic hydration and dehydrations. Presumably the easy formation of complex hydrates is an essential for such catalysts.[38, 38a]	Olefins + H_2O = alcohol. Al_2O_3, tungstic acid, and phospho-tungstate.
		Alcohols + NH_3 = H_2O + Amines (commercial). Supported P_2O_5 or phosphoric acid catalysts are used; Al_2O_3 is also active.
	H_2SO_4, H_3PO_4 are active liquid catalysts.	

Table 1—*Continued*

Reaction Type	Catalysts	Examples
Polymerization, alkylation and isomerization [1a, 1c 1d 1e 1g]	*Halides and acids:* All three of these processes occur principally over certain metallic halides such as $AlCl_3$ and $AlBr_3$. H_2SO_4 and H_3PO_4 are active—especially for polymerization and alkylation. Nearly every group of the periodic table is represented in the list of catalysts claimed to be active for these reactions.	Butane + isobutene = iso-octane (commercial). H_2SO_4 as catalyst. Butene-1 + isobutane → trimethylpentane (commercial). H_2SO_4 as catalyst. Butane → isobutane. Dry $AlCl_3$ + HCl as catalyst.
Cyclization [1a, 1d, 1e, 1g]	*Metallic oxides:* The conversion of straight chain hydrocarbons into aromatics with simultaneous dehydrogenation can be accomplished by such oxide catalysts as Cr_2O_3, Al_2O_3, and Mo_2O_3.	*n*-Heptane = toluene + $4H_2$ (commercial). Cr_2O_3 is used as catalyst.[93]
Hydrocarbon cracking [1a]	Al_2O_3—SiO_2 mixed catalysts are the ones commonly used commercially for converting higher hydrocarbons into lower by high temperature cracking.	
Halogenation and dehalogenation	*Halides* of numerous metals are active. *Strong adsorbents* such as *charcoal* are also used.	C_2H_4 + HCl = C_2H_5Cl (commercial) $AlCl_3$ is used as a catalyst. C_2H_6 + 6 Cl_2 = C_2Cl_6 + 6 HCl (commercial). Active carbon is used as a catalyst. $CH{\equiv}CCH{=}CH_2$ + HCl → $ClCH_2{-}CH{=}C{=}CH_2$. Metal halides are used as catalysts.

change reaction (2) has generally been interpreted [44] as going by way of a dissociative adsorption of hydrogen and deuterium on the catalyst surface and has therefore been construed as a positive indication of the occurrence of the type of hydrogen adsorption apparently involved in catalytic hydrogenation. The question has been raised as to the possibility of the H_2—D_2 exchange proceeding by interaction between physically adsorbed hydrogen and deuterium molecules. Burstein [45] postulated such a mechanism to explain the very rapid formation of HD at −195° C on a sugar charcoal degassed at 900° C. In spite of a very few examples of this kind in which physical rather than chemical adsorption may be involved in the D_2—H_2 exchange, the general utility of this reaction in helping to unravel the detailed mechanism by which hydrogen is able to interact with other molecules is not seriously to be questioned.

The use of isotopes in mechanism studies is, of course, not restricted to deuterium. Isotopes of nitrogen, oxygen, carbon and other elements have also been employed. Some of them are detected by the differences in mass, others by their radioactive character. The exchange of $N^{14}N^{14}$ and $N^{15}N^{15}$ over iron catalysts [61] at 450-500° C to be discussed below will serve as an example of the way in which various isotopes other than deuterium can throw light on catalytic reactions. It seems certain that only a beginning has been made in the use of miscellaneous isotopes in elucidating catalytic mechanisms.*

The use of non-radioactive isotopes in the study of catalysis has become widely applicable by the introduction of mass spectrographs capable of showing the relative abundance of molecules of various masses without simultaneously causing additional intermolecular exchange of atoms. Thus, for example, mixtures of CH_4, CH_3D, $C_2H_3D_3$, CHD_3, and CD_4 can be analyzed without any alteration in their relative amounts being incurred during the analysis. The mass spectrograph also will be valuable for identifying the very first products formed in catalytic surface reactions. The Geiger counter serves a similar purpose in determinations of radioactive isotopes of hydrogen, phosphorus, chlorine, and other elements.

* A complete table of isotopes and their properties, prepared by Robley D. Evans, is given in Vol. V of this series. J. A.

Molecular Beams and Metal Films. Two valuable research approaches have been suggested by the work of Beeck on molecular beam experiments,[46] in dehydrogenation reactions, and on his formation of oriented metallic films [18] by controlled condensation of metal vapors. His original results indicated that some polar molecule such as H_2O or H_2S [46] must be present on the metal surface before dehydrogenation would occur. They also showed single-step dehydrogenation in which ethylene formed by the dehydrogenation of ethane would evaporate without further decomposition, even though at the same temperature a stream of ethylene molecules striking the surface could be dehydrogenated to acetylene. It is hoped that this valuable work will be resumed when conditions permit, because it holds such promise in studying catalytic mechanisms.

The detailed studies that Beeck [18] has made of catalytic hydrogenation over metal films are likely to be among the most illuminating of all recent experimental work on catalytic mechanisms. They seem to establish definitely not only the preferential activity of the most loosely packed crystal faces of a given metal for ethylene hydrogenation, but also the marked preferential activity of certain metals because of their optimum atomic spacing rather than because of their known chemical properties.

Electron Microscope. Another recent development that is being heralded as useful for studying catalysts is the electron microscope.[47] Without a doubt certain information will be gathered with this new and important instrument of research that will throw additional light on the structure of catalysts, especially on the question of their particle sizes and pore diameter.*

Surface Area Measurements. It has long been recognized that catalyst surfaces should be as large as possible to assure high activity per unit weight of catalysts. Only recently, however, has a method been worked out for measuring the total surface area of porous or finely divided catalysts that promises to enable one to speak of activity per square centimeter of catalyst surface instead of activity per gram of catalyst.[48] Suitable low-pressure modifications [101] of the method appear to make it useful in studying samples having as little as 100 sq cm surface area. It should, of course, be clearly understood that large surface areas do not in themselves necessarily mean high catalytic activity. Nevertheless, if one alters the promoter content or method of preparation of a catalyst he will be able to ascertain whether the changed activities are indicative of an alteration in the extent of surface or in activity per unit area.

The existence of a method for measuring surface area raises the question as to the extent to which the "inner" surface of a porous catalyst is active.[13] Several examples so far exist in which the activity of particles of a porous catalyst appears to be a function of the total inner and outer surface and not of the outer or geometric area alone. For example, the precipitated cobalt catalysts tested by Juliard [49] for the synthesis of hydrocarbons from water gas underwent no change in activity per gram when the mesh size of the porous catalyst particles was varied 14 fold from 0.05 to 0.7 mm. There seem to be size limits within which particles can vary without becoming large enough to contain an inner core that does not contribute appreciably to the reaction. Surface area measurements should prove very useful in this aspect of the study of solid catalysts.[48]

Progress in the Study of a Few Industrial Catalytic Processes

In this section a brief discussion will be given of some of the newer mechanism studies that have been made on catalysts used in industrial processes. Space and time limitations do not permit this discussion to be exhaustive or to include much factual matter relating to the operation or industrial importance of the various processes. Only the mechanism of ammonia catalysts is dealt with in fair detail. It is hoped,

* See paper in this volume on the electron microscope; also paper by Albert F. Prebus in Vol. V of this series. J. A.

however, that even this brief discussion will give some idea of the present state of our knowledge of the way in which certain industrial catalysts function, and will indicate lines of approach that promise to be especially fruitful in catalytic studies now being prosecuted.

Ammonia Synthesis. Probably no catalytic reaction has received more intense study than the synthesis of ammonia. Accordingly, it merits special attention in any detailed consideration of the recent contributions to a better understanding of catalytic reactions of industrial prominence. Before 1930 it had become well established that the best synthetic-ammonia catalyst was one composed of iron to which had been added a few per cent of suitable promoters.[26] A particularly effective combination of the latter consisted of 1 or 2 per cent of some non-reducible oxide, such as Al_2O_3, and about an equal amount of one of the alkali oxides such as K_2O. Such catalysts are made by fusing a fairly pure natural or artificial magnetite and stirring into the molten mass the desired amounts of promoter.[50] The cooled mass when crushed and reduced in hydrogen yields the standard catalyst.

Early mechanism studies revealed a number of points of interest in regard to these catalysts.[11] They were all poisoned somewhat by traces of oxygen-containing compounds as well as by sulfur compounds, phosphine, HCl, and miscellaneous other common poisons. The catalysts containing both aluminum oxide and potassium oxide were much more active at high pressures on a pure 3:1 hydrogen-nitrogen mixture than were those containing only aluminum oxide (13-14 per cent ammonia in exit gas at 5,000 space velocity, 450° C and 100 atm compared to about 9 per cent ammonia). Incidentally, it is of interest that K_2O itself is a catalyst poison rather than a promoter. In other words, the combination of an alkali and aluminum oxide will produce a much better catalyst than will either promoter alone. The aluminum oxide catalyst is more resistant to poisoning by water vapor than is the doubly promoted catalyst, though with the usual commercial concentrations of water vapor (less than 0.01 per cent) the doubly promoted catalyst is much the more active.

A phase-rule study of the iron-nitrogen system[6] revealed that in the range of temperatures of interest to commercial synthesis (450 to 600° C) the formation of a series of nitrides will occur as ammonia is gradually increased in a hydrogen-ammonia mixture. For example, at 450° C practically no nitrogen is taken up by an iron sample exposed to an ammonia-hydrogen mixture until the gaseous mixture contains about 30 per cent ammonia. The iron is then gradually converted to a nitride approximating closely the formula Fe_4N. With further ammonia increases no additional nitrogen is picked up until the gas contains about 70 per cent ammonia,[52] at which point the Fe_4N is converted at 450° to a nitride approaching Fe_3N in composition, but tending to nitrogen contents lower than that of Fe_3N as the temperature is raised toward 600° C.[51] When the ammonia is increased still further, the nitrogen content increases gradually, a series of solid solutions being formed covering the range Fe_3N to Fe_2N. The latter compound is formed when substantially pure ammonia is passed over the iron.

By combining the equilibrium constants for the reactions

$$8Fe + 2NH_3 = 2Fe_4N + 3H_2 \tag{4}$$

and

$$N_2 + 3H_2 = 2NH_3 \tag{5}$$

one is able to calculate that the dissociation pressure of Fe_4N according to the reaction

$$2Fe_4N = N_2 + 8Fe \tag{6}$$

is about 5000 atmospheres at 450° C. This is an instance in which it is possible to determine in a glass apparatus the dissociation pressure of a reaction, even though it amounts to several thousand atmospheres. Such a determination is possible only

because the decomposition of the nitride is very slow at 450° compared to the rate at which the equilibrium in reaction (4) is established.

The high dissociation pressure of Fe_4N makes it at once apparent that the formation of a separate Fe_4N phase cannot be an intermediate step in the synthesis of ammonia. As will be shown in detail below, only surface nitrides or nitrogen atoms held to the iron surface by activated adsorption are involved as intermediates in the actual catalytic NH_3 synthesis.

An attempt to determine the nature of the promoter action for iron catalysts made it imperative that some method be found for measuring the surface area of the reduced catalyst, since otherwise it was impossible to differentiate between promoters that increased the activity of the iron per unit surface area and those that merely maintained a high surface area by preventing sintering. Such a method was finally developed. It involved making low-temperature adsorption isotherms on the reduced catalysts close to the boiling point of the gas used.[48] A number of the by-products of this study that threw light on some aspects of ammonia catalysis will now be discussed.

In making adsorption isotherm measurements with different gases on the iron catalysts it was discovered that the total adsorption of carbon monoxide was excessively high.[4] A group of such isotherms is reproduced in Figure 1. Further study showed that if the catalyst on which CO had been adsorbed at −183° was evacuated at −78° and then used for another adsorption isotherm measurement at −183°, an adsorption curve was obtained (curve 1B, Figure 1) that agreed with

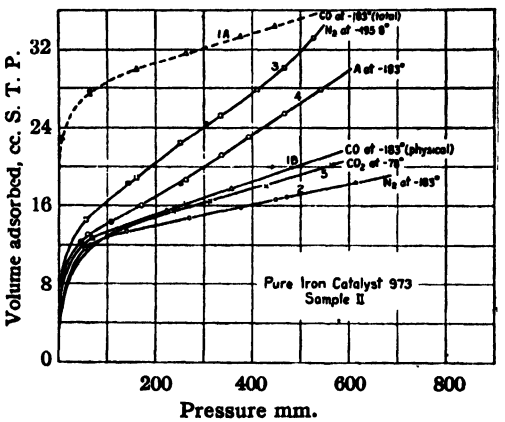


FIGURE 1. Low temperature adsorption isotherms for pure iron synthetic ammonia catalyst 973.[4]

those for nitrogen and argon. It then became clear that the difference between curves 1A and 1B represented a chemisorption of CO on the iron catalyst. Similar experiments showed that carbon dioxide was chemisorbed at −78° C by catalysts containing alkali and that the volume of this chemisorption added to the volume of carbon monoxide chemisorbed by the same catalyst at −183° was approximately equal to the amount of nitrogen required to form a complete physically adsorbed monolayer over the entire catalyst. In other words, the conclusion was reached[53, 56] that the carbon monoxide was chemisorbed on the iron surface and the carbon dioxide on the alkali promoter. A combination of these two measurements therefore permitted for the first time an estimate to be made of the fraction of the iron surface covered with alkali and the fraction covered with iron atoms. Isotherms for CO and CO_2 adsorption are shown in Figures 2 and 3. Apparently the 1.59 per cent K_2O and 1.3 per cent Al_2O_3 in catalyst 931 accumulate on the surface sufficiently during reduction to cover about 60 per cent of the catalyst surface. This enables one to understand how such a small percentage of promoter can have such a marked effect on the activity of the

iron catalyst. (Pure iron catalysts will yield at 450° C about 3 to 4 per cent NH_3, 5000 space velocity and 100 atmospheres' pressure, compared to 13 to 14 per cent for good doubly promoted catalysts.)

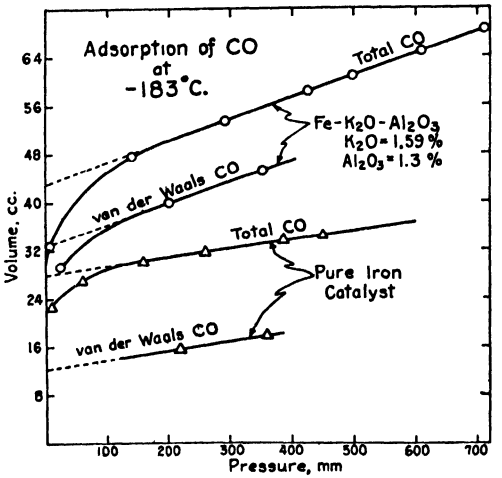


FIGURE 2. Adsorption of carbon monoxide at −183° C on pure iron catalyst 973 and promoted iron catalyst 931.[58]

The distribution of promoters deduced from these adsorption experiments has been amply verified by the measurements of Beebe and Stevens [54] on samples of the same iron catalysts. The heat of adsorption of an amount of carbon monoxide required to cover about 40 per cent of the surface is in the range 8,000 to 35,000 calories per mol, indicating the existence of a chemical binding. The heat of the physical adsorption of CO was found to be about 4,000 calories per mol. Similarly the heat of adsorption of enough carbon dioxide to cover about 60 per cent of the surface is

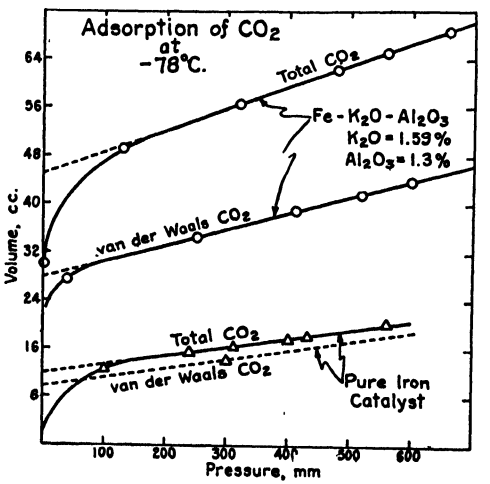


FIGURE 3. Adsorption of carbon dioxide at −78° C on pure iron catalyst 973 and promoted iron catalyst 931.[58]

in the range 18,000 to 32,000 calories per mol and clearly corresponds to a chemical type of binding between the carbon dioxide and the promoter constituents of the doubly promoted catalysts.

It is interesting to note that catalysts 973 (pure iron), 931 (doubly promoted) and 954 (promoted with 10.3 per cent Al_2O_3) require per 50 grams of catalyst—about 5,

40, and 120 cc of nitrogen, respectively, for a monolayer. Thus the doubly promoted catalyst that is much the best of the three for ammonia synthesis at high pressure has a surface area only about one-third as great as that of the singly promoted catalyst. In other words, the alkali added as a promoter in catalyst 931 has increased the activity per unit iron surface many fold over that yielded by the pure iron or the singly promoted catalyst.

At this stage of the work it became desirable to know more about the specific sorptive capacity of the various iron catalysts for hydrogen, nitrogen, oxygen, CO, and O_2, and the influence of these various adsorptions on each other. It was already known [5] that activated adsorption of nitrogen occurs on the iron at temperatures ranging upward from 200° C, the energy of activation involved in the adsorption process being about 15,000 calories per mol of nitrogen, and the heat of adsorption being about 35,000 calories. Hydrogen [55] was found to undergo two types of activated adsorption (Figure 4). At about −100° C a low-temperature type of activated

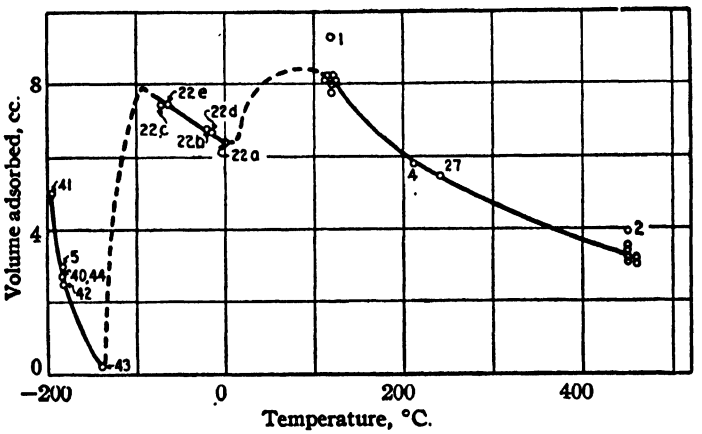


FIGURE 4. Adsorption isobar (760 mm) of hydrogen on doubly promoted iron synthetic ammonia catalyst 931.[58]

adsorption began to attain a considerable rate; over the range −78° to 0° C it could be followed at equilibrium and was shown to decrease steadily as the temperature increased, the pressure being kept always at 1 atmosphere. At 100° C a higher-temperature type of hydrogen adsorption became fairly rapid and then decreased in quantity at equilibrium as the temperature increased. The low temperature-activated adsorption had an energy of activation of about 10,000 calories per mol and appeared to correspond in rate to the number of hydrogen molecules striking the catalyst surface with the necessary energy of activation. The low temperature-activated adsorption was called type A; the higher-temperature variety, type B.

The specific natures of these two types of hydrogen adsorption have not as yet been completely ascertained. The catalytic interconversion of para-ortho hydrogen at −190°, however, helped to establish definitely the existence of two types of activated adsorption of hydrogen [4b]; it was found to be poisoned eight times as much per unit volume of adsorbed gas by type B adsorption as by type A (Figure 5). This, together with the adsorption isobar shown in Figure 4, established definitely the existence of two types of hydrogen adsorption on iron.

Oxygen had been found [4] to be picked up by the iron catalysts at −195° C as an oxide layer as much as ten molecules thick. The heat of this oxygen sorption was shown by Beebe and Stevens [54] to correspond closely to that evolved in the formation of the various iron oxides.

A detailed study of the influence of these various chemisorptions on each other has also been made.[56] Some idea of the breadth of the work can be gathered from the following list of effects studied: the influence of the chemisorption of carbon monoxide and carbon dioxide on type A hydrogen adsorption; the influence of the chemisorption of carbon monoxide and carbon dioxide on type A hydrogen adsorption; the influence of the chemisorption of oxygen and nitrogen on type A hydrogen; the effect of the chemisorption of nitrogen on type B hydrogen adsorption; the effect of type A and type B hydrogen adsorption on the chemisorption of carbon monoxide; the effect of the chemisorption of nitrogen on that of carbon monoxide; the effect of the chemisorption of oxygen on that of carbon monoxide; the effect of nitrogen, oxygen, and type A and type B hydrogen adsorption on the chemisorption of carbon dioxide; the effect of carbon monoxide chemisorptions on oxygen chemisorption; the effect of carbon dioxide chemisorption on carbon monoxide chemisorption; and the effect of carbon monoxide chemisorption on carbon dioxide chemisorption.

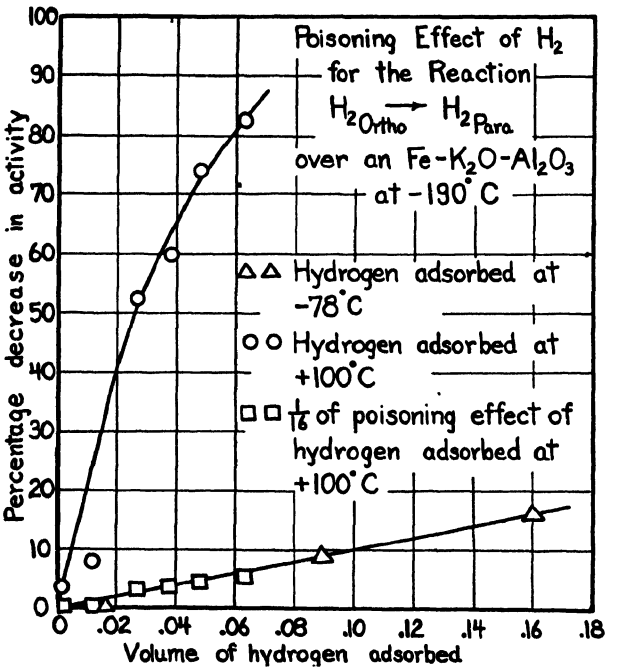


FIGURE 5. Poisoning effect of activated adsorption of hydrogen on the ortho-para conversion rate at —190° on iron synthetic ammonia catalyst 931. Curve 1 is for type B activated adsorption of H_2 (put on at 100° C); curve 2, for type A (put on at —78° C).

In the course of this work the following conclusions were reached:

(1) Nitrogen and hydrogen both appear to be adsorbed on the iron surface as atoms. One of the chief bits of evidence for this was the fact that neither chemisorption had much of an inhibiting effect on the chemisorption of CO.

(2) Carbon monoxide and carbon dioxide are both adsorbed as molecules, the former being held by the iron atoms and the latter by the promoter molecules containing alkali.

(3) The aluminum oxide-promoted catalysts, but not the doubly promoted catalysts, apparently permitted the formation of considerable adsorbed NH_3. Thus on the doubly promoted catalyst nitrogen chemisorption decreased type B hydrogen

adsorption roughly atom per atom. On the other hand, on the singly promoted catalyst, nitrogen chemisorption not only failed to decrease the adsorption of hydrogen but actually increased it. For example, a catalyst capable of holding 37.2 cc of type B adsorption at 100° C was able to hold 44.8 cc *after* 14.5 cc of nitrogen had first been chemisorbed. This surprising result suggests the probable formation of NH_2 groups on this catalyst, and marks aluminum oxide as more than an inert insulating material tending to prevent sintering of the catalyst surface.

(4) The promoter on the surface of the iron catalysts is molecularly distributed and not present in large patches or islands. This was made evident by the extent to which chemisorption of carbon dioxide on the alkali promoter apparently influences adjacent iron atoms sufficiently to inhibit markedly the adsorption of CO; conversely, the chemisorption of CO on the iron part of the surface was able to prevent about one-half the usual carbon dioxide adsorption.

A series of kinetic measurements [57] on the decomposition of ammonia over iron catalysts confirmed the suspicion that aluminum oxide promoters have some specific effect on the iron catalyst other than maintaining small crystals and hence large surface areas. The difference between the doubly promoted and singly promoted catalyst is well illustrated by a plot of the reciprocal of the absolute temperature against their respective activities for decomposing ammonia, as shown in Figures 6 and 7. The

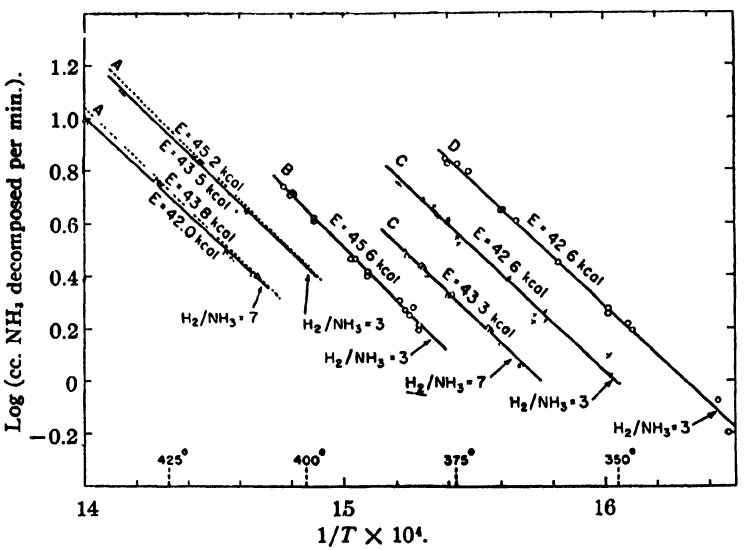


FIGURE 6. Temperature dependence of rate of ammonia decomposition over samples A (0.8 cc), B (1.5 cc), C (5.0 cc), and D (12.5 cc) of iron synthetic ammonia catalyst 931.[57]

doubly promoted catalyst yielded the usual type of straight line, and indicated an energy of activation for ammonia decomposition of about 43,000 calories. The curve for the singly promoted catalyst, on the other hand, is very unusual in appearance. There is a temperature range between about 420 and 450° C (the exact temperature range depended on the composition of the ammonia hydrogen mixture used) in which the rate of decomposition did not increase with temperature. At both lower and higher temperatures the rate of ammonia decomposition increases with temperature, though not as rapidly as with the doubly promoted catalyst.

The reaction kinetics of the decomposition over the two catalysts also showed marked contrast in this temperature range. On the doubly promoted catalyst the rate

of decomposition [57] of ammonia was proportional to $\frac{P_{NH_3}^{0.6}}{P_{H_2}^{0.9}}$. On the other hand, the kinetics of decomposition at about 420° C on catalyst 954 (10.3 per cent Al_2O_3 as promoter) showed the rate proportional to $(P_{H_2})^{1.2}/(P_{NH_3})^{0.8}$. These "reverse kinetics" were totally unexpected and point to a complexity of decomposition not hitherto envisaged. They certainly indicate an effect of Al_2O_3 that is specific and entirely separate from the prevention of sintering. The interpretation of the decomposition results over the aluminum oxide-promoted catalyst is not as yet certain. There are strong indications, however, that decomposition at temperatures below 400° C on this catalyst proceeds by a different mechanism than that outlined below for doubly promoted catalysts.

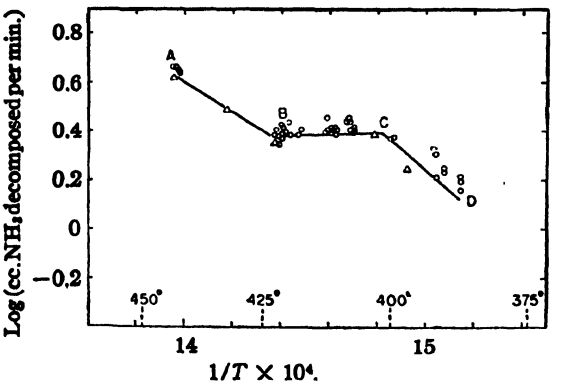


FIGURE 7. Temperature dependence of rate of ammonia decomposition over a sample of iron synthetic ammonia catalyst 954 (10.2 per cent Al_2O_3 promoter).[57]

The marked difference in the kinetics of ammonia decomposition over singly and doubly promoted iron catalysts suggested the possibility of trying to convert a singly promoted catalyst to one having the properties of a doubly promoted catalyst by adding alkali *after* the reduction of the singly promoted catalyst. The results of a few such attempts are shown in Figure 8. The catalyst was converted to one having the properties of double rather than a single promotion. From this it seems likely that an improved ammonia catalyst might be made by adding sufficient alkali to a prepared singly promoted catalyst to give it the general properties of double promotion and yet retain a much larger surface than is ordinarily present in the latter.

Love and Brunauer [60a] actually succeeded in converting a singly promoted iron catalyst into a more active doubly promoted one by soaking the unreduced singly promoted catalyst 191 (0.42 per cent Al_2O_3 as promoter) in solutions containing suitable concentrations of K_2O. The results can be illustrated by Figure 9. Catalyst 191-B contained 0.18 per cent K_2O; catalyst 191-D, 0.44 per cent. Catalyst 191-B is more active throughout the entire temperature range covered than singly promoted catalyst 191.

The authors also point out that in Figure 9 the curve for catalyst 441 (0.84 per cent Al_2O_3 and 0.35 per cent K_2O) is between that for catalyst 191-B and catalyst 191-D.

Catalyst 191 (0.42 per cent Al_2O_3) has the same peculiar kinetics and temperature coefficient found for singly promoted catalyst 954 (10.5 per cent Al_2O_3). On the other hand, it may be noted that according to the results of Love and Brunauer [60a] the rate of NH_3 decomposition on doubly promoted catalyst 441 is inversely proportional to $P_{H_2}^{0.15}$. Such a slight dependence of rate on the partial pressure of hydrogen

is in marked contrast to the behavior of doubly promoted catalyst 931, and seems to indicate a lack of uniformity in the kinetics over various doubly promoted catalysts.

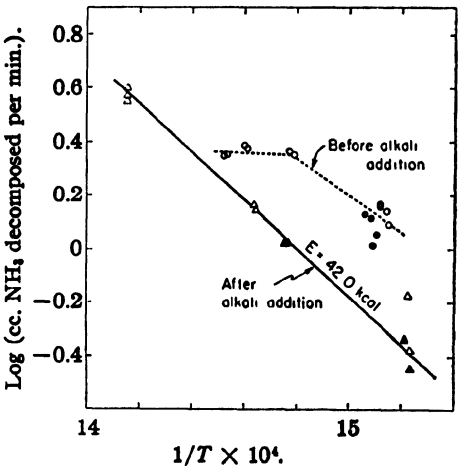


FIGURE 8. Effect of addition of K_2O to a reduced sample of iron synthetic ammonia catalyst 954 (10.2 per cent Al_2O_3) upon the temperature dependence of the rate of ammonia decomposition over the catalyst.[57]

About two years ago Temkin and Pyzhev [58] published one of the most significant papers ever written relative to the mechanism of catalytic ammonia synthesis. Winter [59] had carried out measurements of ammonia decomposition in a flow system and had concluded that the rate of decomposition was proportional to $(P_{NH_3})/(P_{H_2})^{3/2}$. This he had interpreted in terms of a series of equations that left as the slow step the desorption of nitrogen atoms from the surface of the iron catalyst. Temkin and Pyzhev pointed out that such a mechanism was impossible, since the heat of binding of the nitrogen atoms to iron was of the order of 90,000 calories per mol of nitrogen atoms. To clarify the situation they suggested that nitrogen escapes from the surface as molecules and not as atoms, but that the rate depends very strongly on the fraction of the surface covered. They proposed the use of several equations for expressing the adsorption equilibrium between gaseous nitrogen and iron and for representing the rate of adsorption and desorption of nitrogen, as follows:

$$(7)\ \theta = 1/f \ln a_o p \qquad (8)\ v = k_a P e^{-\alpha\theta} \qquad (9)\ w = k_d e^{g\theta}$$

where θ is the fraction of surface covered; p the equilibrium pressure of nitrogen; v the rate of adsorption; P the instantaneous nitrogen pressure; w the rate of desorption; and f, a_o, k_d and g are constants. Using these three equations, Temkin and Pyzhev proposed an explanation for the kinetics of ammonia decomposition that agreed with the kinetic results obtained by Winter, and at the same time gave an approximately correct value for the energy of activation.

In applying these equations to the kinetics of ammonia decomposition the authors make the assumption that the adsorption of nitrogen on iron in the presence of an ammonia-hydrogen mixture will be the same as it would be at equilibrium with the partial pressure of nitrogen equivalent to the existing partial pressure of ammonia and hydrogen in the gas mixture. Thus since the equilibrium constant for ammonia synthesis is $K = (NH_3)^2/(H_2)^3\,(N_2)$, the partial pressure of nitrogen can be represented as being equal to $(NH_3)^2/K(H_2)^3$. Accordingly, in equation (7) Temkin and Pyzhev replace the pressure p by the equivalent pressure of ammonia and hydrogen to yield:

$$\theta = 1/f \ln a_o \frac{(NH_3)^2}{K(H_2)^3} \qquad (10)$$

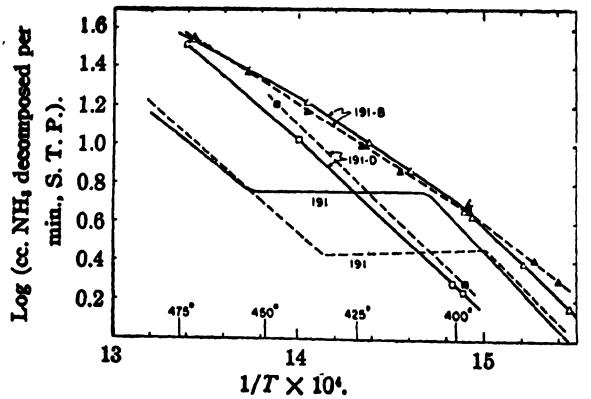


FIGURE 9. Temperature dependence of the rate of ammonia decomposition over catalyst 191, (0.42 per cent Al_2O_3); 191-B (.42 per cent Al_2O_3, 0.09 per cent K_2O); and 191-D (.42 per cent Al_2O_3, .44 per cent K_2O). Open symbols for flow of 315 cc H_2 and 45 cc ammonia per minute; closed symbols for flow of 225 cc H_2, 98 cc N_2, and 45 cc ammonia per minute.[60]

If the slow step in the decomposition is then the escape of nitrogen molecules from the surface of the catalyst, the rate of decomposition becomes:

$$w = k_d\theta^{h/f} \ln a_0 \frac{(NH_3)^2}{K(H_2)^3} = k\left[\frac{(NH_3)^2}{(H_2)^3}\right]^{h/f} \tag{11}$$

This equation is identical with that obtained by Winter, provided we assume that h/f is equal to 1/2. With this assumption the temperature coefficient of the decomposition can be shown to calculate out as about 46,000 calories, using the values for the energy of activation (15,000) and the heat of adsorption of nitrogen on iron (35,000 cals.) obtained by Emmett and Brunauer.[5] The details of the basis for believing that h/f could reasonably be taken as 1/2 were not given by Temkin, though the existence of an analysis leading to such a value was clearly implied.

It is evident at once from equation (11) that, to obtain the kinetic expression found by Love and Emmett for the decomposition over a doubly promoted catalyst, it would be necessary to assume that h/f equals 1/3. This may also be viewed in another way. If the slow step is assumed to be the escape of nitrogen molecules from the surface, one might expect it to be proportional to (N) (N), where (N) represents the surface concentration of nitrogen atoms. But, according to the nitrogen adsorption results on iron,[5] the amount of adsorbed nitrogen (and hence the number of adsorbed atoms) is proportional to $(P_{N_2})^{1/6}$. Hence the rate of decomposition would be equal to:

$$k(N)(N) = k(N_2)^{1/6}(N_2)^{1/6} = k(N_2)^{1/3} = k\frac{(NH_3)^{0.67}}{(H_2)^{1.0}} \tag{12}$$

This equation is in agreement with the experimental results actually found.[57]

In a recent paper Brunauer, Love and Keenan [60] avoided making empirical assumptions as to the value of h/f in equation (11) by calculating the correct constant from the experimental data for the rate of adsorption of nitrogen on the iron catalyst. Their fundamental equation for the rate at which nitrogen was taken up by the catalyst expresses in reality the difference between the rate of adsorption and desorption of nitrogen according to the equation

$$dv/dt = k_a p v_m e^{-\gamma v/v_m RT} - k_d v_m e^{\beta v/v_m RT} \tag{13}$$

where $k_a v_m$, γ/v_m, $k_d v_m$, and β/v_m are constants that are evaluated from a single adsorption isotherm. The numerical values turn out to be 0.02, 2100, 0.000957, and

800 respectively for the nitrogen isotherm at 397° C on catalyst 931. At equilibrium $dv/dt = 0$ and from the above equation

$$\ln p = \ln \frac{k_d}{k_a} + \frac{\beta + \gamma}{v_m RT} v \tag{14}$$

With this equation it then becomes possible to calculate the adsorption isotherm for nitrogen on this catalyst. The calculated and observed values for the nitrogen adsorption as a function of pressure are shown in Table 2. The agreement is astounding. This calculation is the first of its kind in the literature and adds greatly to the significance of rate- and isotherm-activated adsorption data for catalytic systems.

Table 2 [60]. Adsorption Isotherm of Nitrogen on Catalyst 931 at 396° C

p(mm	v_{obs} (cc at S.T.P.)	v_{calc} (cc at S.T.P.)
25	2.83	2.88
53	3.22	3.22
150	3.69	3.70
397	4.14	4.15
768	4.55	4.45

The exponent h/f for equation (11) was shown to be $\beta/\beta + \gamma$. From the above numerical values of the constants, therefore, the exponent for equation (11) becomes 0.276 and the rate of ammonia decomposition is proportional to $\frac{(NH_3)^{0.55}}{(H_2)^{0.88}}$, which agrees nicely with the experimental results.[57] In other words, with the help of Temkin's interpretation of the mechanism of ammonia decomposition over promoted iron catalysts, Brunauer, Love and Keenan have been able to calculate the correct kinetics of the decomposition from a single rate of adsorption equation for nitrogen on iron—an accomplishment that is both brilliant and significant.

Isotopic exchange has been used by Joris and Taylor [61] in a recent study of the adsorption of nitrogen on iron synthetic-ammonia catalysts. They measured the rate of the reaction

$$N^{14}N^{14} + N^{15}N^{15} = 2N^{14}N^{15} \tag{15}$$

over promoted iron catalysts in the temperature range 450 to 500° C, and obtained the surprising result that the exchange is very much slower than the rate of nitrogen desorption from the iron. The explanation of their results is not yet certain. It is difficult to see how nitrogen desorption can occur so much more readily than the exchange if the adsorbed nitrogen is, as we believe, present on the surface as adsorbed atoms.

A possible explanation can be deduced from a picture of the iron catalyst surface by Kobosev.[62] By some experimental and theoretical work on the decomposition of ammonia over an iron catalyst supported on charcoal, Kobosev was led to the conclusion that the active atoms on the surface of promoted catalysts are predominantly in groups of three; each group of three atoms is supposed to be separated from the others by promoter molecules. If this picture is correct it is easy to understand how molecules of nitrogen adsorbed on a group of three iron atoms might well dissociate into atoms, react with hydrogen to form ammonia and yet not react with the nitrogen in another island of iron atoms because of the difficulty of nitrogen diffusing over or around the promoter molecules.

One further utility of Temkin's approach to the kinetics of ammonia synthesis and decomposition should be pointed out. By making the assumption that the slow step in the synthesis is the rate at which nitrogen is adsorbed on a surface already partially covered with nitrogen and that the slow step in decomposition is the rate at which nitrogen molecules are desorbed from a surface already partially covered with nitrogen, Temkin set up and integrated an equation for the rate of ammonia synthesis at

high pressure from a hydrogen-nitrogen mixture. Space does not permit a detailed discussion of his calculation. It will suffice to point out that his conclusions are in agreement with the experimental data of Larson and Tour [63] for ammonia synthesis as shown in Table 3. Furthermore, from these synthesis data and Temkin's equation it is possible to calculate a value for the temperature coefficient of the decomposition of ammonia. This turns out to be 42,000 calories, in good agreement with values actually observed for the decomposition.

Table 3. Kinetics of Ammonia Synthesis [58]
Data from Larson and Tour [63] at 420° C

Pressure (atm)	Space Velocity at Exit, (V_2)	Volume % Ammonia 100%	Rate Constant (k)
10	0	2.98	—
10	5,000	2.65	1.1×10^4
10	10,000	2.15	1.1
10	20,000	1.71	1.1
10	40,000	1.35	1.1
31.6	0	8.48	—
31.6	5,000	6.65	1.0
31.6	10,000	5.46	1.1
31.6	20,000	4.24	1.2
31.6	40,000	2.88	1.0

From all the above work the picture of the mechanism of ammonia synthesis over a standard doubly promoted iron catalyst becomes much clearer. The slow step in the synthesis is apparently the rate at which nitrogen can be picked up by a surface which is already partly covered with adsorbed nitrogen to an extent that depends upon the partial pressure of ammonia and hydrogen present. This picture is consistent with the finding of Taylor,[64] who showed that D_2 will interchange rapidly with ammonia to form deuterated ammonia and that, accordingly, the reduction of the chemisorbed nitrogen or the successive addition of hydrogen atoms to NH or NH_2 groups is not the slow step in the synthesis.

For singly promoted catalysts, confusion still reigns. The Temkin approach definitely will not explain the results illustrated by Figure 7.

In conclusion, attention should perhaps be called to the amazing results that are claimed for the synthesis of ammonia at super-pressures ranging from 2,000 to 4,000 atmospheres.[65] It is useless to speculate extensively in regard to the super-pressure work until more experimental data are obtained. At present it appears necessary to conclude that, assuming the present data are correct, the mechanism and nature of super-pressure synthesis is quite different from that obtained for the lower-pressure synthesis over iron catalysts. Indeed, for the super-pressure range the claim is made that catalysts are unnecessary, and that synthesis will occur readily on the walls of the high-pressure vessel or on the refractory of the heater.

Hydrogenation of Organic Compounds. At the present time a chapter is being unfolded in the study of metallic hydrogenating catalysts that promises a deeper insight into the mechanism of catalysis than has ever before been revealed. The initial impetus in the study [66, 67, 68] was given by the discovery of the catalytic ortho-para-hydrogen conversion and the hydrogen-deuterium exchange reaction. The climax is apparently being attained through the painstaking experiments of Beeck and his co-workers on the hydrogenation of ethylene over thin but highly active oriented metallic films. Much of the work has not yet been published and hence cannot now be discussed in detail. In informal discussions, however, the authors have expressed the opinion that ethylene appears to hydrogenate effectively only when it impinges on correctly spaced absorbed hydrogen atoms. If the ethylene strikes the bare surface it undergoes a destructive adsorption that gradually poisons the metal surface. The atoms in the 110 faces of face-centered cubic metals and in

the 111 faces of body-centered metals appear to be especially active. The maximum activity seems to be obtained with rhodium; the length of its unit cell, 3.79 Å, represents about the optimum spacing for hydrogen atoms that are to react with impinging ethylene molecules.

Iron synthetic-ammonia catalysts conform in most respects to the concepts formulated by Beeck for the mechanism of ethylene hydrogenation. They are very active at low temperature for the hydrogenation of olefins, ethylene hydrogenating at −100° C and other olefins [69] at somewhat higher temperatures. It appears that activated adsorption of the olefin is not necessary for this hydrogenation, only the hydrogen having to be activated by adsorption. It is interesting to note that the promoter constituents that enhance the activity of the iron catalysts for ammonia synthesis exert a definite inhibitory action on the rate of olefin hydrogenation. Presumably the promoter molecules cut down enormously the number of pairs of iron atoms available for olefin hydrogenation.

The mechanism of the *synthesis of methanol* was extensively studied a few years ago when high-pressure synthesis was first introduced commercially. It was established that mixtures of ZnO and Cr_2O_3 decompose methanol readily to CO and H_2 and also are excellent for synthesizing methanol.[29] As a matter of fact, the influence of the $ZnO:Cr_2O_3$ ratio on the activity toward synthesis is practically identical with the influence on decomposition. The synthesis seems to proceed with intermediate formation of formaldehyde.

Pure copper is not very effective [27] for the synthesis of methanol, though it will readily decompose it into methyl formate with the formation of only a few per cent CO. It appears that for some unexplained reason copper is a poor catalyst for the synthesis and decomposition of formaldehyde and therefore is rather ineffective in methanol synthesis. This is consistent with the excellence of copper as a partial oxidation (or dehydrogenating) catalyst for the conversion of methanol into formaldehyde. The x-ray studies of Frolich and his co-workers make it appear that methanol catalysts furnish an additional illustration of the importance of surface geometry on the activity of catalysts. The change of space-lattice dimensions of both Cu-ZnO and $ZnO-Cr_2O_3$ crystals bears a remarkably close resemblance to the change of activity for methanol synthesis or decomposition.

The synthesis of higher alcohols from water gas requires, according to Natta [28] the presence of a strong alkali in addition to an active methanol catalyst. Natta goes so far as to say that if a strong alkali is not present, methanol catalysts will produce no higher alcohols regardless of the time of contact, temperature, and pressure of operation. Strong evidence for his claim is contained in two of his experimental observations. In the first place, any strong alkali, such as potassium hydroxide, initially present in a methanol catalyst like ZnO will in the course of operations as a higher-alcohol catalyst be converted quantitatively into organic acid salts. Secondly, the reduction of these organic salts by hydrogen at the temperature and pressure used for higher-alcohol synthesis actually produces yields of products that are similar in amounts in the presence or absence of ZnO. He postulates that the series of reactions involved in higher-alcohol synthesis is as follows:

$$CO + 2H_2 = CH_3OH \quad (16)$$
$$CH_3OH + KOH = CH_3OK + H_2O \quad (17)$$
$$CH_3OK + CO = CH_3COOK \quad (18)$$
$$CH_3COOK + 2H_2 = C_2H_5OH + KOH, \text{ etc.} \quad (19)$$

A different mechanism for the higher alcohol synthesis has been proposed by Frolich [70] who postulated that the chief reaction involved is a dehydration between two methyl alcohol molecules according to the reaction

$$2CH_3OH = C_2H_5OH + H_2O \quad (20)$$

He cited a number of high-pressure experiments to support his thesis. At the present time it does not seem possible to conclude with certainty which of the two mechanisms is the more nearly correct. Perhaps both of them with their numerous detailed side reactions may play a part in actual higher-alcohol synthesis.

Fischer and Tropsch [72] pointed out in 1925 that when hydrogen mixtures are passed at suitable controlled temperatures over promoted cobalt catalysts, liquid hydrocarbons are formed that can be used as motor fuel. This higher-hydrocarbon synthesis is already highly important in continental Europe and in England, though it has not as yet attempted to compete in America with the plentiful supply of petroleum.* It has been said, however, that the details of operation of such a plant from waste gas of the oil fields in this country have all been worked out. The actual cost of the raw materials of a properly located plant is supposed to be only about ½ cent per gallon of synthetic fuel.

The mechanism of the synthesis of higher hydrocarbons has been the subject of a great deal of experimental work that is too voluminous to review in detail. The experimental facts relating to the reaction have been well summarized, however, in detail recently by Craxford [80] as follows:

"1. At the temperature of the Fischer synthesis, carbon monoxide reacts slowly with the Fischer catalyst to give cobalt carbide, as

$$2Co + 2CO = 2Co_2C + CO_2$$

but this reaction is always slower than the reduction of the carbide by hydrogen at the same temperature.

"2. At this temperature the catalyst reacts with carbon monoxide and hydrogen to give carbide as,

$$2Co + CO + H_2 = Co_2C + H_2O$$

and this reaction is faster than the reduction of the carbide by hydrogen under the synthesis conditions.

"3. Reduction of cobalt carbide may lead to methane or to higher hydrocarbons, according to the conditions, and the experiments have shown that when oils are being produced by the Fischer synthesis, the ortho-para hydrogen conversion is inhibited, showing that very little chemisorbed hydrogen occurs on the catalyst surface.

"4. Under all the varied conditions for which methane is the product of the synthesis instead of oil, the ortho-para hydrogen conversion occurs freely, showing that chemisorbed hydrogen is then present.

"5. The water-gas shift reaction runs parallel to the ortho-para hydrogen conversion; it occurs when methane is being formed, but is inhibited during oil formation by the Fischer synthesis.

"6. The hydrogenation-cracking of paraffin hydrocarbons on the Fischer catalyst is similarly inhibited during the Fischer synthesis, and also by the presence of carbide on the catalyst surface, but otherwise it occurs freely at similar temperatures.

"7. If ethylene is added to the reacting gases during the Fischer synthesis it becomes incorporated in the products, but it leads simultaneously to the formation of organic substances containing oxygen, such as alcohols, acids, etc."

His theoretical deductions and explanations of these facts he sums up in the following way.

"1. The first step in the Fischer synthesis is the alternate formation and reduction of cobalt carbide to give CH_2 groups, the carbide being formed by the reaction

$$2Co + CO + H_2 = Co_2C + H_2O$$

"2. In the presence of chemisorbed hydrogen, these methylene groups are further hydrogenated to methane.

"3. When the conditions are such that the formation of carbide is more rapid

than its reduction, there will be very little chemisorbed hydrogen on the surface, and the CH_2 groups will link up to give long chains.

"4. The products actually obtained are broken off the long chains on the surface by attaching of chemisorbed hydrogen.

"5. When carbon monoxide is adsorbed in the outer adsorption layers and not in direct contact with the catalyst surface its reduction leads to compounds containing oxygen, rather than hydrocarbons."

Oxidation. Catalytic oxidations may for convenience be divided into various classifications: (1) complete oxidations, (2) partial oxidations, and (3) selective oxidations. The first of these is illustrated by the oxidation of SO_2 to SO_3; the second, by the oxidation of naphthalene to phthalic anhydride; and the third, by the preferential oxidation of CO from a hydrogen-CO mixture.

The two most important industrial examples of complete catalytic oxidation are the oxidation of ammonia to nitric oxide and that of sulfur dioxide to sulfur trioxide.

The most widely used complete oxidation catalyst is probably platinum. For ammonia oxidation it is usually in the form of a gauze; for SO_2 oxidation it is supported on silica gel, $MgSO_4$, or other materials.

The mechanism of the oxidation of ammonia has been extensively studied for many years, but is even now none too well understood. Some of the best early work was that of Andrussow.[78] He showed conclusively that under a wide variety of operating conditions no ammonia gas could be found at the exit of the converter. This led him to believe that NH_3 passing the gauze catalyst was being destroyed by a subsequent reaction with NO. He demonstrated the utility of multiple gauzes as a means of effecting more complete oxidation of NH_3 to the desired product NO.

Andrussow postulated the following series of reactions:

$$NH_3 + O_2 = NH_3{\cdot}O_2 \quad (21)$$

$$NH_3O_2 = HNO + H_2O \quad (22)$$

$$2HNO + O = NO + H_2O \quad (23)$$

$$HNO + NH_3 = N_2 + H_2O + H_2 \quad (24)$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O \quad (25)$$

As confirmatory evidence of the existence of HNO as intermediate, he points out that he has been able at low temperature to obtain as much as 10 per cent conversion to N_2O over a platinum catalyst, this gas being the anhydride of HNO. Later work at low pressure by Bodenstein[75] has indicated the formation of hydroxylamine as one of the intermediates. The matter cannot be definitely settled at present.

Cobalt oxide catalysts promoted with bismuth oxide are also used commercially for the oxidation of ammonia. It is probable that they function through an alternate oxidation and reduction mechanism, though little work on them has been published.

Von Nagel[34] showed that over MnO_2 catalysts it is possible to exidize ammonia almost quantitatively to N_2O instead of to NO. The optimum temperature for N_2O is about 100° C, the time of contact being of the order of a second.

The catalytic oxidation of SO_2 to SO_3 has been carried out for many years over iron oxide, V_2O_5, or Pt catalysts. The greater activity of the last two has led to their almost exclusive use for commercial oxidation.

Sulfur dioxide oxidation over V_2O_5 furnishes an excellent example of a theory of catalytic oxidation proposed by Pourbaix.[83] He advances the hypothesis that all catalytic oxidations with free oxygen in which the mechanism is an alternating reduction and oxidation process must make use of a catalyst whose oxide is reducible to the next lower oxide or metal by the substance being oxidized at the temperature of the catalysis. In quantitative terms, his theory means that for the catalytic oxidation of CO, for example, the free energy change of the reaction

$$MO + \tfrac{1}{2}CO = \tfrac{1}{2}CO_2 + M \quad (26)$$

must be zero or negative if the metal oxide, MO, is to act effectively as a catalyst through an alternating reduction and oxidation mechanism. The free energy change of the reaction $SO_2 + V_2O_5 = V_2O_4 + SO_3$ is negative to the extent of −8,330 calories,[76, 77] according to data in the literature. Accordingly, V_2O_5 can function as a catalyst for this reaction through an alternating reduction and oxidation process, whereas an oxide holding its oxygen more tightly would not be able to do so. This theory, of course, does not preclude the possibility of adsorption catalysis on systems not capable of undergoing alternating reduction and oxidation, or of some other type of compound formation as an intermediate step in the reaction.

The partial oxidation of organic compounds takes place over a group of catalysts which would normally be termed weak oxidation catalysts and which, in accordance with the Pourbaix hypothesis, are oxides capable of reduction to lower oxides or metal by rather weak reducing agents. The three principal components of partial oxidation catalysts are V_2O_5[37], WO_3, and Mo_2O_5[78].

Very little research has been done on the theory of partial oxidation. Numerous industrial examples are now known, including the catalytic oxidation of napththalene to phthalic anhydride. It seems possible that all these reactions proceed through an alternate reduction of the oxide and the reoxidation with free oxygen, but the detailed mechanism cannot as yet be stated with certainty.

Carbon monoxide oxidation first gained prominence in World War I in connection with the development of a suitable gas mask canister for protection in atmospheres containing toxic concentrations of CO. It was found [79] that "Hopcalite," said to be a mixture of CuO, MnO_2, and a few other oxides, was a very effective catalyst for removing CO in concentrations ranging up to 0.5 per cent in air. Later the preferential removal of CO from a mixture of CO-H_2 was accomplished by adding suitable amounts of water vapor and oxygen.[35, 35a] It was apparently possible to poison the CuO catalyst for the oxidation of hydrogen without destroying its activity toward CO. Very recently considerable work has been done on higher-temperature catalysts such as might be suitable for the removal of CO from automobile exhaust gases.[36a] The chromates of zinc and iron have for this purpose been found to be particularly effective. Alternating reduction and oxidation is a possible mechanism for some of these instances, though catalysis by activated adsorption is more likely to be the explanation of the removal of CO that occurs at room temperature.

A final example of partial oxidation that may gain prominence in the future is that of the oxidation of hydrocarbons to organic acids. The ease of oxidation increases with the length of the hydrocarbon chain. Only minor yields of formaldehyde have been reported in the literature from the oxidation of methane over solid catalysts,[88] whereas liquid-phase oxidation of long straight-chain hydrocarbons with free oxygen over vanadium oxide or other catalysts seems to be a practical process for obtaining fatty acids.[88a, 1d]

Petroleum Catalysis. Few industries have found as much use for catalytic processes in recent years as the petroleum industry. The various types of catalysts used may be divided into the following general classes: hydrogenation and dehydrogenation, polymerization, alkylation, isomerization, cracking, and cyclization.

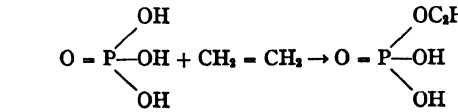
In a discussion limited to new interpretations and theories of industrial processes, little need be said about catalytic hydrogenation and dehydrogenation in the petroleum industry other than has already been included in Table 1 or discussed above. For detailed papers on mechanism studies, reference should be made to the excellent collection of papers in a recent symposium on hydrocarbon chemistry.[84]

Polymerization [1c] has taken its place as one of the outstanding modern industrial developments important to the petroleum, rubber, resin, and plastic fields. The industrial development has, however, far outstripped fundamental work on the theory of polymerization. Accordingly, in discussing catalytic polymerization one can do

little more than list a few general types of catalysts and illustrate some of the ways in which the reactions may be taking place.

Polymerization catalysts for the most part fall into one of the following groups: alkaline compounds, acids, salts, elements, metallic oxides and miscellaneous materials, such as glass, porcelain, pumice, and tetraethyl lead. Phosphoric acid, sulfuric acid, boron trifluoride, $AlCl_3$, and various phosphates comprise the more important industrial catalysts.

Perhaps one of the most widely quoted mechanisms of polymerization is the intermediate compound theory. This can be illustrated by the following equations by which Ipatieff [1e] has represented the polymerization of ethylene over phosphoric acid catalysts:



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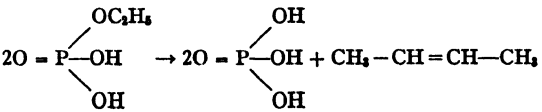


(28)

His formulation is similar to the very old theory of Berthelot [1a] and of Butlerow,[1a] except that the latter authors postulated as the second step the reaction of the acid ester with another olefin molecule rather than the interaction of two acid ester molecules.

This interpretation has been somewhat modified by a recent mechanism study by A. Farkas and L. Farkas [85] in which acid catalysts containing deuterium were employed. Their conclusions agree with the deuterium exchange data, and also with the generalized working rules of Wachter [85a] by which the probable products of polymerization can be predicted. Two other proposed mechanisms are the free radical theory and Whitmore's hydrogen-ion theory.[86a] Final choice among these various theories cannot as yet be made. Indeed it seems rather probable that no one theory will explain all polymerization reactions.

One of the newer intriguing catalytic reactions in the petroleum field today is that of the conversion of normal hydrocarbons to aromatics by the process known as cyclization.[40, 86, 87, 88, 89, 90, 91 92, 93] It has been found that over suitable catalysts (see Table 1) the reaction.

$$C_7H_{16} = C_7H_8 + 4H_2 \qquad (29)$$

n-hexane toluene

will proceed at a sufficient rate to enable it to be the basis for an industrial process. Much of the toluene used in munitions manufacturing in the present war will be made in this way. Final conclusions as to the detailed mechanism of the process cannot yet be drawn. Tentative mechanisms have been discussed by Pitkethly and Steiner,[106] and by Hoog, Verheus, and Zuiderweg.[107]

Alkylation is usually defined as the addition of an olefin to a saturated paraffin or to an aromatic, such as benzene. It is accomplished at room temperature in the presence of some of the same general catalysts that are used for polymerization. In a recent article, Caesar and Francis [94] described the very interesting results obtained on alkylating various paraffins with ethylene, propylene, or butylene. Of special interest is the relationship they found between the thermodynamics of formation of the various possible isomers and the actual relative ratios obtained. For example, in forming the heptanes by alkylating isobutane with propylene, eight different

isomers are theoretically possible. The free energy of formation of these is shown in Table 4, as calculated by Francis on the basis of the data of Rossini.[102] Investigation of the products of alkylation showed that they contain only two of the isomers in appreciable quantities. It is interesting to note that these two are present in approximately the amounts that one would expect, thermodynamically, on the basis of complete isomerization equilibrium between the two isomers. Yet, under the conditions of the run, the rate of isomerization of the two isomers is quite low. There appears to be no *a priori* reason why the isomers should form in the relative amounts calculated for equilibrium. Nevertheless, such was found to be the case for the isomeric pentanes, hexanes, heptanes, and octanes studied.

Table 4.[94] Thermodynamic Equilibria of Isomeric Paraffin Hydrocarbons at 25° C

	$\Delta F(n=0)$	Per Cent	Per Cent in Alkylate	
			Calc	Found
n-Butane	0	32	32	20[100a]
Isobutane	−442	68	68	80[100a]
n-Pentane	0	4	13	10[100a]
Isopentane	−1097	25	87	90[100a]
Neopentane	−1720	71	0	0
n-Hexane	0	4	0	0
2-Methylpentane	−558	11	26	10-25
3-Methylpentane	−558	11	0	0
2,2-Dimethylbutane	−1341	42	0	0
2,3-Dimethylbutane	−1165	32	74	75-90
n-Heptane	0	0.7	0	0
One branch (3)	−1035	4	0	0
2,2- and 3,3-dimethylpentanes	−1817	14.5	0	0
2,3-Dimethylpentane	−1543	9	50	50 ± 5
2,4-Dimethylpentane	−1543	9	50	50 ± 5
Triptane	−2426	40	0	0
n-Octane	0	0.3	0	0
One branch (4)	−577	0.8	0	0
Gem groups (3)	−1361	2.9	0	0
2,3- and 3,4-dimethylhexanes	−1185	2.1	0	0
2-Methyl-3-ethylpentane	−1185	2.1	4.7	0-10
2,4-Dimethylhexane	−1185	2.1	4.7	10-15
2,5-Dimethylhexane	−1185	2.1	4.7	
Isooctane	−2654	25	56	50-60
2,2,3-Trimethylpentane	−1968	8	0	0
2,3,3-Trimethylpentane	−1968	8	17	25-30
2,3,4-Trimethylpentane	−1793	6	13	
Hexamethylethane	−2752	30	0	0

Caesar and Francis have advanced the following empirical rules for predictinig the manner in which the olefin attaches itself to an isoparaffin and for predicting, accordingly, the exact isomers that will be formed. "Influenced in some manner by the catalyst the olefin is able to wedge itself in between a methyl group and the rest of the isoparaffin so that the methyl group adds to one side of the double bond and the rest of the isoparaffin to the other. The methyl group farthest from the tertiary carbon is the one split off when isopentane is the isoparaffin." This simple rule seems to give remarkably good agreement with most of the experimental results so far obtained, though the authors intimate that steric factors have to be considered in some cases.

Isomerization is a process in which normal paraffins are converted into isoparaffins, or one isoparaffin changes into another. It is obviously of huge potential interest

to the petroleum industry, since branched-chain hydrocarbons have been found to possess higher anti-knock values than straight-chain hydrocarbons. Isomerization is in general much slower than alkylation, though it will occur over the same general type of catalyst. In the presence [95] of $AlCl_3$ and dry HCl, 13 per cent of a charge of normal butane was converted to isobutane in 4 hours at 195° and 35 atmospheres' pressure; 10 per cent of the original butane was left unchanged, the remainder being cracked. Alkylation over this same catalyst can be carried out much more rapidly than isomerization.

Catalytic cracking of hydrocarbons is among the most important but perhaps least understood reaction of petroleum catalysis. A number of different processes are in commercial use, all of them employing an alumina-silica catalyst. Activated adsorption of the hydrocarbon on the surface of the catalyst cannot be detected by the usual technique at the temperature at which cracking takes place, although there are some indications that deuterated hydrocarbons will exchange their D atoms with H in non-deuterated hydrocarbons over cracking catalysts at temperatures well below those at which cracking occurs. It seems likely that cracking is preceded by a dehydrogenation reaction in which certain of the hydrogen atoms of the hydrocarbon split out under the influences of the Al_2O_3-SiO_2 catalyst surface.

Catalytic Hydration and Dehydration. The hydration of olefins to alcohols is a reaction of potential industrial value upon which a great deal of experimental work has been reported. Dodge and Sanders [38] have carried out a detailed search for catalysts for ethylene hydration and have concluded that suitably prepared alumina, ammonium phosphotungstate, tungstic acid, or combinations of these, furnish the most promising catalysts for the dehydration of C_2H_5OH. They point out, however, that "there is no very active catalyst yet developed for the vapor-phase hydration of ethylene." Appleby, Glass and Horsley [90] have produced considerable ethanol in a small pilot plant, using a cadmium phosphate catalyst. The reverse process of dehydrating alcohols over Al_2O_3 to form the olefin is standard commercial practice in those instances in which large supplies of pure olefin are desired for synthesizing various organic compounds.

The hydration of C_2H_2 to acetaldehyde, acetic acid, and acetone are well known commercial processes that need not be described here.

A number of dehydration reactions that split out water from an alcohol and ammonia to form amines have now been put on a commercial basis. For example, methanol and ammonia react to form mono-, di-, and trimethylamines over a variety of dehydrating catalysts. P_2O_5 supported on pumice has been found especially active.

The catalytic dehydration and dehydrogenation of isoamyl alcohol, and the catalytic elimination of carbon monoxide from valeraldehyde have been compared by Balandin and Rubinstein [98] using a series of 1:1 $Ni:Al_2O_3$ catalysts. Energies of activation, Q, ranged from 8850 to 22,400 for the dehydrogenation; 17,950 to 45,100 for the dehydration; and 14,500 to 33,100 calories per mol for the aldehyde decomposition. The ratios of the Q values for any two of the three processes were the same, within experimental error, over all the catalysts. Thus the ratio $Q_{\text{dehydrogenation}} : Q_{\text{dehydration}}$ was 0.51 on all catalysts; $Q_{\text{dehydrogenation}} : Q_{\text{aldehyde decomp'n}}$ was 0.69 and $Q_{\text{dehydration}} : Q_{\text{aldehyde decomp'n}}$ was 1.26. From these data the authors conclude that all three processes must be occurring at the juncture of the two phases Al_2O_3 and Ni.

Storch has published some instructive calculations and correlations relative to the rate of dehydration of alcohols over bauxite.[103] If one represents the rate of a zero order catalytic reaction by the equation $k = Ae^{-E/RT}$ it is possible to obtain information as to the rate of energy transfer from the catalyst surface to adsorbed molecules in certain special cases. A should equal SZ, where S is the number of active centers on a gram of the catalyst and Z is the frequency of energy exchange between the adsorbed molecules and the catalyst. In some kinetic experiments by Dohse [104] it was

possible to conclude that S was 2×10^{19} centers per gram of bauxite. From the observed rate of reaction k and energy of activation E, it was then possible to calculate values for A, and hence for Z, for each alcohol studied. The results are summarized in Table 5. All the alcohols yielded values of A that were the same within a factor of five, and values for Z, ranging from 4×10^{10} to 2×10^{10} per second. This is smaller by a factor of a thousand than the vibration frequency of the atoms in the solid catalyst, and is approximately constant for primary, secondary, and tertiary alcohols.

Table 5. Dehydration of Alcohols on Bauxite [103, 104]

Alcohol	E (kcal)	$\log_{10}A$ (molecules per sec per g catalyst)
Propyl	28.5	29.2
Butyl	28.0	29.0
s-Butyl	24.0	28.9
i-Propyl	26.8	29.6
i-Butyl	20.0	29.1

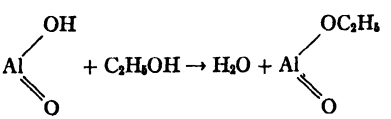
Numerous important dehydration reactions have been disclosed in the patent literature. An excellent summary of these presented in Chapter XVII of reference (1d) includes the dehydration of 1,3-butylene glycol to butadiene, abietyl alcohol or oleyl alcohol to diolefins, and castor oil to octadecanediol-1, 12.

As a general mechanism of all these reactions the formation of intermediate complexes, as originally suggested by Sabatier and Senderens a number of years ago, will probably suffice. Thus, for example, dehydration might proceed through the reaction

$$Al_2O_3 + 2C_2H_5OH = Al_2O_2(OC_2H_5)_2 + H_2O \tag{30}$$

$$Al_2O_2(OC_2H_5)_2 = Al_2O_3 + 2C_2H_4 + H_2O \tag{31}$$

Ipatieff [1a] prefers to believe that the hydrate of alumina is the catalyst, the intermediate reactions being



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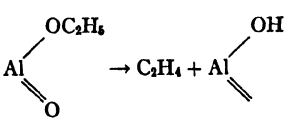
and



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It seems possible that isotope exchange experiments may eventually establish definitely the mechanism of these hydration-dehydration catalytic reactions in much the same way that the brilliant experiments of Polanyi and Szabo [99] using O^{16} and O^{18} isotopes have thrown light on the hydrolysis of esters in acid and alkaline solutions.

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The Commercial Surface Active Agents

LAWRENCE H. FLETT

National Aniline Division, Allied Chemical and Dye Corporation

Commercial Development of Synthetic Detergents

Surface-active agents such as soap and egg albumen have been used since antiquity. Today a large number of new synthetic chemicals are finding wide use as surface-active agents in the home for washing and baking and in industry for preparing emulsions, softening leather, processing paper, manufacturing roads from portland cement, dyeing textiles, manufacturing lace, cleaning metals, processing chemicals, and a multitude of other purposes. The uses to which the older types of surface-active agents could be put were limited by their lack of stability to acid, lime salts and other water conditions, by their tendency to decomposition or putrefaction, and by their relatively poor surface activity.

Starting about a century ago when industrial chemistry was coming into full swing, chemists set about the task of producing better surface-active agents. Through more involved chemical process, surface-active agents were sought which would have a more general utility. Foremost among the new products at that time were the sulfated oils known as "soluble" or "sulfonated" oils, which became economically important in the dyeing, textile finishing and leather industries. These "soluble oils" were obtained by treating vegetable or animal oils with sulfuric acid. The sodium salts were reasonably stable; they dispersed in water, generally to give clear solutions; they were not completely precipitated by lime salts in hard water; and they had some limited stability in acid solution before the sulfate group split off.

More recently, but prior to World War I, the synthetic tanning agents were recognized as having some cleaning properties.

In World War I the alkylated naphthalene sulfonates were developed in Germany to relieve the acute shortage of soap. The commercial product had alkyl groups having three to four carbon atoms. These propyl and butyl naphthalene sulfonates were sold under the name of "Nekals." They were poor soap substitutes from the standpoint of washing, but they found interesting uses which led to their further development. They fell short of the high dispersing or washing action which was later to lead to the general industrial and domestic application of the synthetic detergents. None of the early surface-active agents, except soap, had sufficient dispersing action to make them valuable washing agents. The lack of washing power was not important in all cases, since a large proportion of these agents were used where washing was not a factor. However, those which did not have washing action generally lacked effectiveness; either the benefit they gave was not worth the trouble of using them, or such large amounts were required that the cost was prohibitive.

In the period from 1925 to 1935 came the industrial development of a new group of surface-active agents which will be referred to here as the synthetic detergents. Their commercial use expanded so rapidly that there can be no doubt but that they filled a real need not met by earlier surface-active agents. A sulfated lauryl alcohol prepared by H. Th. Boehme A.G. from alcohols produced by the Deutsche Hydriewerke, and sold under the trade name "Gardinol" was the first commercially important synthetic detergent to be introduced into this country. The lauryl alcohol was

prepared by the hydrogenation of esters made with the fatty acids from coconut oil, so it was in fact a mixture of straight-chain primary alcohols with 6, 8, 10, 12, 14, 16 and 18 carbon atoms. "Gardinol" was first introduced to the American market by National Aniline Division, Allied Chemical & Dye Corporation. It was a clean, white, fresh-smelling detergent which dissolved quickly, even in hard water. "Gardinol" broke up in acid solution to give the original alcohol and sulfuric acid, but it could be successfully used in acid if the period of exposure was not too great. It was a truly great advance over the "soluble oils" because it would wash. "Gardinol" found ready acceptance, particularly in the textile industry.

At about the same time as "Gardinol" became commercially important, the German I.G. introduced the "Igepons" which were amides and esters of fatty acids, having a sodium sulfonate group which was not attached to the fatty acid residue. The "Igepons" represented a further improvement in the development of surface-active agents from the unchanged fatty acids of vegetable and animal oils. This development of useful detergents and surface-active agents from natural fatty acids had been going on since prehistoric times. First, there was soap, made by saponifying vegetable and animal oils. This was of little use in hard water and was effective only in alkaline solution. About a century ago the commercialization of the sulfated vegetable oils began. When the oils were sulfated, before neutralizing with caustic soda they lost their washing action, but they became effective agents for use in hard water. Finally in the "Igepons," the fatty acids of the oils were converted to esters and amides and solublized with a sulfonic acid group. The "Igepons" were good detergents and were relatively stable, unless acids or alkalies were present under conditions which would break up the amide or ester linkage.

The enthusiasm for synthetic detergents which led National Aniline Division, Allied Chemical & Dye Corporation to introduce "Gardinol" also led them to carry out research on the development of a synthetic detergent which would be stable in any ordinary processing solution regardless of whether it was acid, neutral, or alkaline. The products of this development made and sold by this company under the trade name "Nacconol" are chemically stable alkyl aryl sulfonates.* The preparation of a stable detergent was the goal toward which the surface-active agent industry had been progressing for a century. These products were also unique because they represented the first effective synthetic detergents prepared from petroleum hydrocarbons.

The commercial improvement of the synthetic surface-active agents to produce synthetic detergents, *i.e.*, products with washing action, brought about an immediate expansion in their use. There is hardly an important industry today which does not employ them. The new field which had been created and the broadening demand for the new synthetic detergents led to the immediate commercial development of hundreds of new surface-active agents.

There is one outstanding difference between these and the earlier surface-active agents which led to the rapid expansion of their commercial production. The synthetic detergents are remarkably efficient in relatively dilute solutions. In many cases care must be exercised not to use them in excessive proportions. The most serious and common mistake in applying synthetic detergents is to start experimental tests with too high a concentration, under the mistaken idea that if the material is going to do any good it will be evident when an excessive amount is used. This is not the case, and in many cases the synthetic detergents show anomalous behavior at high and low concentrations.

The Composition of Commercial Surface-Active Agents

Although many types of water-dispersible organic chemicals show surface-active properties, all the commercial synthetic surface-active agents have been built up on

* *Chem. Eng. News*, 20, 844 (1942).

a basis of (1) an aliphatic hydrocarbon group commonly known as the hydrophobic group, and (2) a solublizing group commonly called the hydrophilic group.

The Aliphatic Carbon Chain

It is not necessary that a surface-active agent contain aliphatic carbon chains, but probably all dispersible products with aliphatic chains have surface active-properties. Furthermore, surface-active agents with saturated or nearly saturated aliphatic chains are generally colorless or faintly colored, which is very important from the standpoint of commercial utility. Another factor which tended to confine the development of surface-active agents to products with aliphatic groups was the relatively low cost of the raw materials used to introduce the aliphatic group, *e.g.* petroleum hydrocarbons, mineral oil, alcohols, animal oils, and vegetable oils.

Derivation of the Aliphatic Group

The many hundreds of surface-active agents which have been offered commercially derive their aliphatic carbon chains from the widest variety of commercial products. A great number have been derived from fatty oils and fatty acids which, in many cases, are used directly, and in other cases are modified by conversion to the alcohols, amides or amines. Generally the vegetable oils are used. Castor oil, oleic acid and fatty acids from coconut oil have found a very general use.

Petroleum has been an important source of raw material since National Aniline's early development of synthetic detergents of the alkyl aryl sulfonate type. The long hydrocarbon chains in petroleum have been modified so that solublizing groups could be introduced. Many years before the development of these detergents, surface-active agents were made by directly sulfonating the aromatic constituents of the petroleum; but they did not develop commercially because they had little or no washing action. They were generally dark in color and had poor surface-active action. More recent products of this type are greatly improved in color and effectiveness. Synthetic detergents are now prepared by direct sulfonation of the aliphatic hydrocarbons in petroleum.

The gases from petroleum refining and acetylene from carbide manufacture have served as building stones for aliphatic alcohols, amines and chlorides, many of which have served to produce surface-active agents. For example, there might be mentioned the isopropylated and butylated naphthalene sulfonates referred to above, the 2-ethyl hexyl ester of sodium sulfosuccinate, which is a powerful wetting agent sold under the trade name "Aerosol" by the American Cyanamid Company, and the powerful wetting agents of the Carbide and Carbon Chemicals Corporation under the trade name "Tergitols." Generally speaking, such built products have branched aliphatic chains which give agents with powerful wetting action, but without any appreciable detergent action.

Length of the Aliphatic Group

Products with aliphatic groups containing even one or two aliphatic carbon atoms, such as xylene sulfonate, have been found to have usable surface-active properties. Even naphthalene sulfonate has these. Such products are not very effective and have found little use, except those with methylene groups separating a chain of radicals derived from sulfonated naphthalene.

The length and nature of the aliphatic group has an important bearing on the properties of the surface-active agent. In order to predict how a surface-active agent will perform, probably the best guide is to make a comparison between the properties of the surface-active agent and those of the corresponding soap, that is, the soap made from a fatty acid with an aliphatic carbon chain of the same length. This comparison is listed below with respect to surface-active agents prepared by

sulfating normal primary alcohols derived from fatty acids and soaps prepared by saponifying the corresponding fatty acids:

SOAPS		SODIUM ALKYL SULFONATES
Sodium Formate		Sodium Methyl Sulfate
Sodium Acetate	Dispersing Agents when Used in Concentrated Solutions	Sodium Ethyl Sulfate
Sodium Propionate		Sodium Propyl Sulfate
Sodium Butyrate		Sodium Butyl Sulfate
Sodium Valerate		Sodium Amyl Sulfate
Sodium Caproate	Solublizing Agents	Sodium Hexyl Sulfate
Sodium Caprylate		Sodium Capryl Sulfate
Sodium Caprate	Wetting and Foaming Agents	Sodium Decyl Sulfate
Sodium Laurate		Sodium Lauryl Sulfate
Sodium Myristate	Washing Agents	Sodium Myristyl Sulfate
Sodium Palmitate		Sodium Cetyl Sulfate
Sodium Stearate		Sodium Stearyl Sulfate

The effect of the carbon atoms in the aliphatic group must be defined in terms of unbroken carbon chains. A large number of the commercially important surface-active agents have more than one aliphatic group. For example, diisopropyl naphthalene sulfonate is important commercially under a number of trade names, whereas the monopropyl naphthalene sulfonate has probably disappeared from the market. The dioctyl sulfosuccinate is another example of an important commercial product with two alkyl groups. Generally speaking, when the alkyl group is short, it is very beneficial to have more than one. If there is more than one group having 12 to 18 carbon atoms, the product generally loses its effectiveness as a detergent in aqueous solutions.

The Solublizing Group

The part of the molecule which contributes the water solubility or water dispersibility is often referred to as the hydrophilic group. There are many different types of solublizing groups in commercial detergents, just as there are many different types of aliphatic hydrocarbon groups. In the commercial production of surface-active agents, the sulfate and sulfonate groups have become overwhelmingly important as the solublizing groups. It is probable that over 95 per cent of the production of surface-active agents is made up of products which have either a sulfonate or a sulfate group.

The sulfonate group may be obtained by direct sulfonation or by reaction with a sulfite. The sulfate group may be obtained by the esterification of alcohols by means of sulfuric acid or chlorosulfonic acid, or by the addition of sulfuric acid to olefins.

The sulfonates, sulfates and similar compounds are known as anionic detergents. In dilute solutions they may form true solutions and ionize. Their surface activity depends on their action as colloids. In the presence of salt or in stronger solutions, colloidal ions are formed which generally carry the charge of the part of the molecule which is responsible for the surface action.

Surface-active agents with the alkyl group in the cation are also well known, and there are many commercial cationic detergents. At the present time they are probably next in commercial importance to the anionic detergents. Their dispersion in water to give colloids, which are generally positively charged, depends on the solublizing action of an ammonium or amino group.

There are three principal types of surface-active agents. In addition to the anionic and cationic surface active agents just mentioned, there are the non-ionic detergents. Unlike the anionic and cationic detergents, the non-ionic detergents do not form salts, and their dispersed colloidal particles generally do not carry electric charges. An example of such compounds would be a compound solublized by a series of ether or alcohol groups. For instance, the hydroxy polyethylene ether of alkyl phenol is a commercial example of a non-ionic surface-active agent.

The solublizing group plays a very important part in the action of the surface-active agent because it generally controls the charge on the colloidal ion. The anionic detergents are generally better washing agents in acid than in alkaline solutions, whereas the cationic detergents are generally better washing agents in alkaline than in acid solutions. The non-ionic detergents are particularly valuable as emulsifying agents, where the electric charges on the colloidal ions of the anionic and cationic surface-active agents often serve to break emulsions.

It was mentioned above that substantially all the more recently developed surface-active agents are derivatives of sulfuric acid. There are many other types of anionic surface-active agents. Soap, which is the sodium salt of a fatty acid, is an anionic detergent. In the recent developments in this field phosphates, thiosulfates and phosphonates have been used as solublizing groups.

Very often more than one group plays an important part in the solublizing action. Thus the surface-active agents may be both sulfonates and carboxylates. The sulfonates may contain alcohol, ether, phenolic, amide or other solublizing groups. Many of the commercially important surface-active agents have more than one solublizing group, although generally speaking, the solublizing action is limited to one group.

Impurities

The final factor which should be mentioned as influencing the properties of commercial surface-active agents is the presence of impurities. This will vary depending on the sources of raw material and upon the chemical processes used. Inorganic salts, sodium sulfate and organic impurities play an important part in the activity of the surface-active agent, particularly where wetting and washing operations are involved. Generally speaking, impurities are beneficial if present in small amounts, and are damaging if present in large amounts. The important organic impurities are water-insoluble materials. Easily dispersible alcohols are often desirable additions to surface active agents. Care should be taken to make certain that the surface-active agent is never so overloaded with impurities that the surface activity is entirely used up in dispersing the added impurities.

The Future of the Commercial Surface-Active Agents *

In the field of surface-active agents the synthetic detergents are second only to soap from the standpoint of commercial importance. There is no doubt that as the price of the synthetic detergents has dropped the commercial utilization has increased at a remarkable rate. This increase in production may be continued in the future. These synthetic detergents are new tools for the colloid chemist and may be considered a permanent and important part of the American chemical industry.

* A list of these and their manufacturers appeared in *Ind. Eng. Chem.*, 35, 126 (1943).

Industrial Adhesives *

ALFRED E. GUTMAN

Naval Ordnance Laboratory, Washington, D. C.

All the readers of this volume have had occasion, at one time or another, to use some form of adhesive. As chemists, they have recognized the essentially colloidal nature of the product and the fact that its functioning depended on basic physical chemical principles. A fact not often realized, however, is the magnitude of the production involved; one authority [35] estimates about $100,000,000 worth, or at least 500,000,000 pounds, during 1943. Thus a worthwhile market exists for the products of the chemical industry. The bases most generally utilized have been organic materials of natural origin, such as starch, animal glue, and casein, though synthetic resins are finding increasing employment in a number of important applications. Most of the recent patents on resins, plasticizers, and related materials propose their usage in the preparation of adhesives, but practical industrial adhesives are specialized materials carefully prepared to fit particular applications.

A major stimulus to the development of industrial adhesives has been the growth and extension of the practise of automatic packaging. Whereas adhesives were formerly employed mainly in the preparation of high-strength bonds between surfaces, the largest proportion of present-day tonnage is consumed in the fabrication and closure of containers and boxes, wrappers and labels, and combination laminated sheetings. Specific adhesion to a variety of materials is still a major problem, since packaging materials in active use include paper and cardboard in dozens of varieties, glass, wood, metal foils and cans, and plastics.

The mechanisms used for applying glue vary greatly with the type of materials being adhered and the objective to be accomplished. A detailed description of this machinery would be out of place in this paper, but some consideration must be given to the conditions involved in typical applications insofar as they affect the design of the adhesive to be used.

The simplest type of applicator, such as is often found on plywood gluers and laminating machines, is a roller which picks up glue (on its lower half) from a reservoir, and then applies this film, suitably regulated in thickness by a doctor blade, to the moving sheet of material. This applicator permits a rather wide latitude in the choice of an adhesive, but a fluid, non-tacky product will be chosen in typical laminating work to permit the sheets to pass over the rollers at high speed. The proportion of solids to solvent in the adhesive is adjusted to the capacity of the drying equipment, and to limit the warping or other effects produced by the solvent.

More complex adhesive applicators may employ a multiplicity of rollers in contact with one another to convey the glue some distance from the reservoir, the thickness of the applied film being determined by the pressure between the rolls. In one machine widely used for labelling bottles a transfer roller remains in contact with the glue roller for a fraction of a second and then moves across to deposit its accumulation of adhesive on two flat blades. These blades in turn contact the label, remove it from its pile by the suction of the wet glue film, and apply the label to a bottle as the blades

* See also paper on Cohesion and Adhesion in Vol. III of this series, pp. 9-26, by J. W. McBain and J. Alexander.

spread and permit the bottle to pass between them on a moving belt. Such a complex adhesive transfer operation demands a product which will not "string" or "cotton" as it is passed from one surface to the next—an objectionable feature of many concentrated colloidal dispersions. Obviously, too, the adhesive must be extremely sticky, or tacky, if it is to pull the label from the label pad and grip the bottle firmly on being applied. The drying rate must be slow enough to prevent accumulation of the glue on the transfer surfaces, and yet the glue must "set" fast enough to counteract the tendency of a paper label to wrinkle and curl away from the wet side.

Other factors remote from the choice of a joining material of suitable strength and working properties enter into the formulation of an industrial adhesive. The wetting attendant upon the application of any aqueous solution to paper or chipboard tends to cause curling and warpage as drying proceeds. To prevent this, so-called "plasticizers" are incorporated in the glue, usually humectant (humidifying) agents such as glycerol, ethylene glycol, sorbitol, glucose, or some hygroscopic salt. These tend to make the film more flexible, and, in the case of glucose or highly soluble salts, raise the concentration of solids in the adhesive so that dimensional changes during drying are minimized.

Perfect stability over a period of months is not easy to achieve in a colloidal system based on materials of natural origin, but this problem must be conquered if an industrial adhesive is to be usable. In carbohydrate and protein products stability research involves the study of chemical preservatives to inhibit fermentation, bacterial action, and mold growth. In addition, most starch conversion products tend to revert, a process characterized by an increase in viscosity and a tendency toward pastiness of the colloidal suspension. Careful adjustment of the conversion process, often coupled with some amount of rapid aging, as by low temperatures, is called for in this case. The fluid synthetic resins, marketed for adhesive usage as partially polymerized or condensed systems with separate catalyst solutions, are subject to the same stability limitations. These must be surmounted for any degree of commercial utility. The emulsion adhesives discussed below are especially susceptible and have received considerable study in this regard.

The raw materials used in the preparation of industrial adhesives cover the entire range of the chemical industry, and in the succeeding pages an attempt will be made to outline the methods of fabrication and the fields of use for the more important types.

Carbohydrate Adhesives

The simplest adhesive in common use is the well known flour paste. If wheat or rye flour * is cooked at 170-180° F. with about five parts of water, a soft, grainy paste will result. A few per cent of caustic alkali will increase the degree of dispersion and make a smoother product; inorganic salts such as alum [1] improve the working properties, build up the solids, and bleach the paste; and preservatives such as phenol, formaldehyde, or beta naphthol control spoilage and mold growth. Such pastes find wide usage in hand fabrication of a variety of paper products both because of their low cost, and also because the gluten-starch combination is considered by some to have superior adhesive strength. Where low solids, slow drying, and lack of tack are tolerable, flour pastes may be used in simple machines, although they do not flow readily to the glue roll, and tend to splatter in operations involving the use of stencil gluers.

The low content of solids in flour pastes makes shipment over long distances uneconomical, but by drying the pastes over drum-dryers, or by quick-cooking the flour-water dispersion on hot rolls, so-called "paste-powders" are obtained which swell in cold water. On agitating these with seven or eight parts of water for a few hours a good grade of flour paste results.

* Winter wheat flour of suitable grade is generally used. J. A.

By far the largest proportion of the adhesives used in automatic packaging is based on the refined starches derived from corn, tapioca, potatoes, or the sago palm. All these starches swell when cooked in water to give clear solutions that thicken on cooling, and become pasty in time. However, they differ widely in viscosity, rate of reversion, and cohesiveness or gumminess of the concentrated solution. Such characteristics carry over into the "converted" or hydrolyzed starch products when made into adhesives, giving the chemist considerable latitude in his choice of raw material for accomplishing a given result. Tapioca is the preferred base for most products to be operated in machines. It gives tackier, more stable concentrated solutions, but many smooth, pasty products can readily be made from corn or other starches.*

Plain starch pastes are occasionally used, but the bulk of industrial work requires some chemical modification of the raw starch. The mildest action involves the treatment of a dilute starch suspension with hypochlorite or dilute acids[2, 3, 4, 5] at a temperature well below the swelling point of the starch, filtering, and drying. Such "thin-boiling" or "fluidity" starches give solutions which are less viscous than raw starch, and are assumed to be the products of the depolymerization of the starch molecule. Occasionally "thin-boiling" starches are used as the starting point in the preparation of a dextrin or an adhesive, but their main application is in sizing yarn, textiles, or paper.

More drastic treatment of starch is necessary to develop its maximum adhesive strength, and to make possible higher dry content of the finished product. It is possible to hydrolyze starch merely by heating a suspension above its gelatinization temperature for some time, or by heating under pressure, and such treatment may be employed where only mild degradation of the starch is desired.

Treatment at elevated temperature with a few per cent of hydrochloric acid[6] produces a thick, fluid, white, fairly tacky adhesive suitable for use in mechanical gluing equipment. In practice, difficulty is sometimes encountered in neutralizing concentrated starch suspensions evenly, and so the conversion process may be carried out in dilute solution, which is later evaporated. The resulting paste makes a good base for a board-lining or laminating glue, as well as for the manufacture of paper bags and boxes, since it spreads easily, dries quite rapidly, and has good adhesive strength. When modified by the addition of a little alkali and some borax, such a product may be applied to the automatic sealing of corrugated boxes. The alkali aids in penetrating the layer of rosin size on these kraft papers, and the buffer action of borax stabilizes the paste while causing the glue film to "set" rapidly.

Borax is peculiar in its effect on starch and dextrin, and is a valuable aid to the chemist in this field. It not only causes a sharp rise in the viscosity of a starch solution, but seems to act over a critical range of viscosity so that a small loss of water at some stage causes a disproportionately large rise in the viscosity of the paste. For example, case-sealing glue is applied at such a dilution that the adhesive can be spread easily without the gelling that characterizes concentrated borated starch products. The flaps of the case are then folded over, and the whole put under compression for half a minute or so, usually under a moving belt. During this short period only a small amount of moisture soaks into the cardboard. Nevertheless, the viscosity of the adhesive rises to a point where, although far from dry, it has sufficient cohesive strength to hold the flaps of the case in place when pressure ceases. An interesting illustration of this mechanism is disclosed in a recent patent.[37] It is suggested that a borax solution be applied to one of the surfaces to be adhered and the concentrated starch solution to the other. Since the starch solution immediately gels, rapid adhesion may be obtained.

* Starch from so-called "waxy" corn or sorghum is said to resemble tapioca, and may soon be obtainable commercially. See H. H. Schopmayer, G. E. Felton and C. L. Ford, *Ind. Eng. Chem.*, **35**, 1168 (1943). J. A.

Hydrolysis in alkaline solution by means of an oxidizing agent such as hydrogen peroxide or sodium peroxide[7, 36] produces a paste lower in dry content than that obtained in acid treatment. Such pastes have a slightly gummy, sticky texture desirable in a number of fields, as in gluing the overlap of can labels where the machine design calls for a paste, but more than average tack is required to hold the label in place.

The action of malt diastase in degrading starch is well known, and has for many years been a useful tool of the adhesive manufacturer. Most starch treatments avoid the development of excessive amounts of dextrose, because of its hygroscopic nature. Enzyme conversions, on the other hand, result in a high percentage of maltose, a less hygroscopic sugar; and since the presence of sugar is advantageous for some purposes, this forms a convenient and cheap method of preparation. Since sugar solutions can be made up to very high concentrations with comparatively little rise in viscosity, it is obvious that a starch product rich in sugars may be readily obtained at a rather high dry content. Incomplete malt conversions are pasty, slow drying, and tacky. If the malt conversion is carried to its practical limit, a dark brown, fluid, easily workable product results, similar in appearance and stickiness to a dark tapioca dextrin solution, but much higher in sugars. This causes the adhesive film to be hygroscopic, but is an aid in limiting wrinkling of labels or warping of paper boxes.

The effect of caustic alkali on starch solutions is probably similar chemically to acid hydrolysis, although there is some evidence which suggests that there may be an alkali-starch compound analogous to alkali-cellulose. However, the character of the finished product is radically different from that of acid-treated material. Alkaline conversion develops a translucent, cohesive, stringy product as opposed to the opaque, sluggish or pasty, acid types. The dried film, too, reflects this difference. Films of causticized starch are quite tough and continuous, whereas acid conversions dry to a crystalline, brittle film. As a result, joint strengths are far higher with the former and adhesion to smooth, impermeable surfaces is much improved.

Many tons of alkali-converted tapioca are used annually in the manufacture of plywood. The starch product is so much cheaper than animal glue, and so much easier to use than hot-pressed albuminous or synthetic-resin adhesives, that it commands a wide market, despite lower tensile strength and relatively poor water resistance. The tapioca is generally given a mild treatment with caustic soda, occasionally cold, though more frequently hot; but many patents[8-12] have been issued on improvements in the processes for this specialized field. Among the recommended agents are formaldehyde for water resistance,[14] potassium dichromate and calcium dioxide as an oxidizing conversion that is claimed to proceed more smoothly and give a degree of water resistance to the product; and pretreatment with mineral acids to give higher solid content and a swifter reaction.

Until recently the caustic treatment of starches was carried no further than the mildly gelatinous, fluid products used in the plywood industry. More drastic treatment gives a heavy product resembling concentrated rubber solutions in cohesiveness, practically impossible to spread except at extreme dilutions, and difficult to dilute because the gelled mass does not readily accept water. This unusual combination of properties has since been recognized as peculiarly suited to labelling soft-drink bottles, since the film is extremely adhesive, and once dried is appreciably water-resistant. Even after being thoroughly moistened, the cohesive, gummy film still maintains sufficient continuity and toughness to keep a label in place. Large quantities of alkali-treated starches are now used in bottle labelling. Preferably based on one of the more cohesive raw starches such as tapioca or sago, up to ten per cent of caustic soda may be used, together with high temperatures and vigorous agitation to convert the starch to a highly concentrated, gelatinous, semi-transparent, usually dark-colored mass. Despite their unwieldy texture such products operate satisfactorily in ma-

chines, since they break down to a more fluid condition under the action of the glue roller. In this state they are "short" or non-fibering, and extremely tacky.

Interesting and useful products are obtained by treating starch with certain neutral salts; but a much larger proportion of active agent is required than with acid or alkali. Thus, on treating starch in aqueous dispersion with calcium chloride at temperatures below the swelling point,[24] preferably with equal weights, there is obtained a smooth, easily spread paste, which makes a flat-lying glued sheet of hygroscopic nature.

The manufacture of dextrins has been fully described in this series by another author.* As he points out, it is to the high-solids dextrin solutions that the adhesive manufacturer turns for products that are particularly fast-setting and tacky. Solutions of white dextrins are similar in properties to the acid-converted starches described above. British gums are stable and tacky, but higher in viscosity than yellow dextrins and hence slower drying.

For the utmost in speed in mechanical packaging operations, in fact whenever the requirements call for two paper or cardboard surfaces to be brought into momentary contact and yet give an immediate bond with sufficient strength to resist strong tension, the practical answer is the use of a concentrated solution of dextrin. Such difficult conditions are the rule rather than the exception in modern fabrication jobs. Carton-sealing adhesives hold after only a few seconds of compression. Special dextrin "gums" are applied to the surface of tin cans a fraction of a second before the can rolls over the label stack, and yet the adhesive unfailingly picks up the label at the rate of six or eight hundred cans per minute.

Some applications of dextrin adhesives rest on their ready solubility. Great quantities are used in postage-stamp gumming, and in the manufacture of gummed labels, while special grades are designed expressly for use in the manufacture of envelopes.[88] Here, in addition to the adhesion problems imposed by the frequent use of hard-surfaced bond papers, and the color and taste of the flap glue or "front seal," rigid specifications are necessitated by the use of high-speed envelope-making machines.

Compared with the starches converted in solution, dextrin adhesives are expensive. The remarkable thickening effect of borax is therefore particularly valuable, and it is widely used to obtain speed and tack with appreciably lower solids content.

In work such as case sealing, where the presence of caustic soda in the dextrin solution is helpful in penetrating hard sizes and improving adhesion, borax seems to permit larger amounts of alkali to be added before adversely affecting the stability of the dextrin solution. On the other hand, when a light-colored gum is desired, phosphoric or hydrochloric acid may be added in small proportions to improve adhesion.

Many other additives are employed in the formulation of most starch adhesives to fit them to individual applications. For example, to preserve starch products against mold growth and decomposition phenol, beta naphthol, formaldehyde, or sodium orthophenyl phenate may be used. Viscous adhesive solutions entrap objectionable quantities of air during use on machines, so that the use of anti-foam compounds is imperative. Vegetable oils, higher alcohols, and many synthetic products are in use.

The tendency of the glue film to contract on drying, coupled with the wrinkling of paper products after moistening, is a major problem in adhesive formulation. In combatting these effects glycerin, glycols, or hexahydric alcohols keep the film flexible through their lubricating action and the retention of a certain proportion of equilibrium moisture in the film. Glucose is a cheaper and poorer plasticizer, but can be used in much higher proportion without such deleterious effect on tack. Inorganic

* Vol. IV, pp. 187-92, by V. G. Bloede. Individual dextrins differ enormously in working properties. J. A.

salts are also employed as a cheap way of raising the solids content to limit penetration, and, in the case of the hygroscopic salts, as a method of holding some moisture in the film. Urea is useful in dextrin adhesives marketed in the dry form.

All these agents must be used with discretion. Excessive amounts will cause remoistening in high humidity with consequent staining through of papers, rusting of metals, or sticking of open gummed faces. Drying rates are retarded excessively by large percentages of plasticizers. One novel approach appears in a recently patented [18] envelope gum, in which water-soluble ethers are employed as non-hygroscopic plasticizers.

In view of the present interest in synthetic resins it is natural that a variety of starch-resin combinations should be proposed. The water-soluble resins are of particular interest as modifiers of starch products,[16, 39] and interesting possibilities are suggested by the condensation of urea and formaldehyde in the presence of starch.[40]

A promising field of practically untouched possibilities lies in the esterification of starch. All the modifications described above were obtained from some type and particular degree of hydrolysis. An even greater variety is obtainable from esterification reactions now being described in the literature.[41, 42, 43] Starch acetates, which have received most interest to date, will find numerous adhesive applications if a low enough cost can be achieved. One reference [44] points out that dibasic acid esters, and the benzoate of starch, dissolved in organic solvents, show noteworthy adhesion to steel, wood, glass, and paper.*

As a result of the extremely brittle, crystalloidal nature of dried starch and dextrin films, their adhesion to impervious or heavily sized surfaces leaves much to be desired. To soften the film and obtain a less brittle bond, moderate proportions of glycerin are sometimes added; animal glue and latex are frequently recommended in the patent literature for the same purpose. However, the latter detract too much from the working properties of dextrin to be practical, except in rare instances.

The application of decorative varnish and lacquer coatings to packaging materials, as well as the extensive use of waxed papers, poses many a knotty problem for the adhesives chemist. The incorporation of up to 20 per cent of some suitable organic solvent in the adhesive frequently serves to penetrate the resinous coating and permits the adhesive to anchor to the base. Water-soluble solvents are readily incorporated, but they lose most of their activity by excessive dilution. On the other hand, water-immiscible solvents are tolerated only in small amounts before separation occurs, but in equal amount give more effective penetration. Alcohol, carbon tetrachloride, and benzene are the most frequently used; alcohol occasionally serves to improve the dispersion of hydrocarbon blends.

Protein Adhesives

The carbohydrate adhesives just described are used in great quantities for automatic packaging and the fabrication of paper products. Where higher joint strength is required, as in the woodworking trades, various protein adhesives are more suitable.

The commonest of these are the animal glues, known as bone or hide glue depending on the origin of the raw materials, and classified into many grades according to the viscosity and the gel strength of the glue at a given concentration. Users soak animal glue in cold water for a few hours and then heat to 140-160° F for complete dispersion. The hot solution may be employed for jointing wood, the manufacture of plywood, sandpaper, and a variety of products. Frequently tanning agents such as formaldehyde, hexamethylenetetramine, alum, or chromates are added to improve the water resistance and strength of the final bond.

Quite a bit of animal glue goes into the manufacture of gummed tape, particularly heavy kraft paper shipping tape. Animal glue is a better remoistening glue than

* Regarding the action of formic acid on starch, see paper by J. Alexander, *J. Soc. Chem. Ind.*, 55, 206-9 (1936).

dextrin because it develops a higher degree of stickiness or tack on moistening. In addition, animal glue will not wash off as readily if moistened with an excess of water. For this reason it is generally used to gum decalcomania transfers [25] and lithographed sheets which are later to be mounted with the printed side against glass. Dextrin films can not be made to adhere smoothly to such varnished sheets, but animal glues suitably plasticized and containing a moderate proportion of varnish solvent are most effective.

Animal glue has an amazing tolerance for glycerin, and will carry up to an equal amount without losing its ability to form a tough film, and without the development of objectionable hygroscopicity. Known as "flexible glues," such blends are of great value in bookbinding, since they remain flexible for many years. A glue containing over 60 per cent of glycerin, glycol, or sorbitol is considered permanently flexible, and a wide range of products based on various grades of glue to obtain different rates of set are marketed in the form of flexible, cast slabs.

Similar glues are sold for covering fine paper boxes, since the plasticized animal glues do not cause warping. Here the cheaper sugars are generally used in place of glycerin, together with glues of lower gel strength.

A few animal-glue products are also marketed in liquid form, some liquefying or peptizing salt being added to break down the colloidal gel structure. Many electrolytes are known to have this effect, but sodium naphthalene sulfonate [15] has been recommended as being odorless, neutral, and non-hygroscopic. Twenty-five per cent of the salt on the weight of glue is suggested, but this varies with the gel strength of the glue used. Occasionally acetic acid, zinc chloride, calcium chloride, or various other chlorides or nitrates may be preferred. In the case of the lithograph glues mentioned above, a considerable amount of alcohol is also added, and this seems to have some liquefying effect on the glue, at least insofar as retarding gelling at low temperatures is concerned.

Animal-glue adhesives are ruled out for use in most high-speed gluing machines because of their tendency to fiber and "cotton" between transfer surfaces. To improve these machining characteristics, pasty starches are sometimes added to the liquefied animal glue. Such blends, with benzene * or carbon tetrachloride added, are commonly used as seam and bottom sealers in the automatic fabrication of waxed paper bags. Waterproof sandpaper is made with plastics.

Modified starches are mixed with partially liquefied animal glues to prepare adhesives with a high degree of resistance to degluing in cold water. Such "ice-proof" glues are extensively used in labelling soft-drink bottles, since by only partially liquefying the glue, advantage is taken of its ability to gel in ice water and yet soften rapidly in hot water. A product of this type [45] comprises equal quantities of glue and starch together with about 60 per cent of the dry weight of the glue of ammonium thiocyanate. The liquefying action of the salt permits the adhesive to be run in standard labelling machinery. When a bottle carrying such a glued label is immersed in a water cooler the soluble salt rapidly dissolves out, leaving the film with sufficient gel strength to retain its adhesion. This bottle is later returned to the bottling plant for cleansing, and here the "ice-proof" gel is rapidly melted away under the action of hot water.

Closely related to the animal glues, but lacking their gelling property, are the fish glues. Such products may develop high joint strengths in wood fabrication, and are widely sold in small package form as a convenient, strong, liquid glue. Their powerful odor and high cost have militated against more widespread use.

Blood and egg abumins are of primary interest as adhesives which become insoluble on heating. Their chief application has been in the manufacture of plywood, where until the advent of modern synthetic-resin adhesives they gave the most durable

* Benzene may give rise to acute or chronic poisoning and its effect may be cumulative. See U. S. Public Health Reports, July, 1926 (Reprint No. 1096).

and water-resistant bonds. Blood albumin is soaked in cold water for a few hours, then blended with ammonia and a tanning agent such as lime or paraformaldehyde [46] to form a mixture stable for half a day or so. The glued sheets are pressed at a temperature of 180-250° F for about three minutes, depending on the thickness of the panel.

Egg albumin is a pure food product peculiarly well suited to affixing cork to the inside of bottle caps. Albumin solution is dropped on the inner surface of the cap, the cork liner is inserted, a plunger pressed down, and the cap passes over a flame. A permanent, moisture-resistant bond is thus formed at high speed.

Milk casein has been discussed elsewhere in this series.* As mentioned there, casein glues are usually made with soda ash, borax, ammonia, trisodium phosphate or similar alkaline materials. With hydrated lime, an insoluble calcium caseinate is formed, and the reaction is widely applied with minor modifications to produce strong, waterproof wood joints.

Dry powders containing casein, an alkaline agent, lime, and a preservative are marketed as marine glues in which the type and amount of alkali used fix the rate of insolubilization. Paraformaldehyde or hexamethylenetetramine develop water resistance in casein which is especially suited to the manufacture of plywood.

Liquid casein solutions, stable over extended periods, are not easy to prepare. Protection against bacterial decomposition is important, and considerable amounts of preservative must be used. Such solutions must be well buffered, and if strong alkalies are used in peptizing the casein, partial neutralization will aid in maintaining a stable solution. For use on automatic machines, casein dispersions must be made up to at least a 25 per cent dry solids content to have a useful degree of tack. By heating to 160° F with 10 per cent of caustic soda or 20 per cent of trisodium phosphate, fluid viscous solutions may be obtained with up to 40 per cent of solid content. These products have a limited industrial usage.

Urea and sulfonated oils are also recommended in the literature as fluidifying agents for casein, and borax is suggested as an aid in buffering strongly alkaline dispersions.

Concentrated solutions of casein serve as bases to be modified by blending with latex,[47] lacquers, or plasticized natural resins. The casein film has intrinsically good adhesive powers, and is an excellent dispersing medium, tolerating a wide variety of substances that are incompatible with starches.

In recent years the production and use of the protein from soy-beans has been widely extended. Two forms find application in adhesives [48, 49]: an unrefined flour analyzing 50-60 per cent in protein, and a purified 95 per cent protein grade. The former is in the price range of cereal flours or starch, and gives opaque, pasty dispersions. It finds its major use at the present time in plywood manufacture. Prepared with lime and silicate of soda, soy flours develop a bond comparable in cost to the starch glues, but superior to starch in weather resistance. Purified soy protein is competitive in price with milk casein, and solutions of the two are similar in most respects. Soy protein solutions are a little darker in color and gel more, but a greater tolerance for formaldehyde gives them a much longer working life. Further development and familiarization of the adhesive user with this protein will undoubtedly result in its wider application.

Natural Gums and Resins

Gum arabic is the most useful water-soluble natural resin. Despite its higher cost, gum arabic is preferred for office mucilage and the gumming of some cigarette papers because of the light color of its solutions. In certain envelope seals where the product is to be used in the tropics, even the smallest amount of sugar in dextrin is conducive to "blocking," and gum-arabic adhesives are therefore specified. Highly con-

* Vol. IV, pp. 399-414, by F. L. Browne; see also paper by Dunham in this volume.

centrated gum-arabic products have a bit more tack and dry a trifle faster than the best comparable dextrins, and hence are used in a few very difficult packaging operations.

Gum tragacanth, gum karaya, and the alginates are at the opposite pole, since a few per cent dissolved in water gives a solution of appreciable viscosity. Their use in adhesives is limited to serving occasionally as thickeners for other materials, such as latex.

The solvent-soluble natural gums are applicable to a variety of specialized work. The cheapest and most abundant is rosin, which has the additional advantage of being readily saponified by alkaline media. The resulting solutions dry quickly to a sticky film, but their adhesive strength is low, and generally some film-forming material must be added. If, for example, rosin is plasticized and then dispersed in an alkaline casein solution, the product has excellent wetting powers for greasy tin plate, and is widely used as a tin labelling paste. Tons of rosin are also used in the thermoplastic adhesives discussed below.

Shellac is a better film-forming material than rosin, as well as being much more stable. Its alcoholic solution is quite frequently employed for odd cementing purposes, usually because it is a convenient, thin, quick-drying fluid.

Manila and damar gums, while occasionally recommended in the patent literature, are mainly of importance in commercial adhesives as resinous components of cellulose-base lacquers. They lend adhesiveness and raise the dissolved solids content of such products.

Rubber Adhesives

Solutions of rubber in hydrocarbon solvents have some of the properties of a perfect adhesive, so far as bonding ability is concerned. Their "specific" adhesion is of the highest order for literally dozens of difficult surfaces; and when properly formulated their "mechanical" adhesion [22] is excellent. Their tensile strength is not exceptional, but elasticity and shock resistance compensate for this. The drawbacks to their wider application lie in the low solids obtainable at any viscosity, and the unwieldy cohesive and stringy character of the products.

The fabrication of rubber cements is a specialized art carried out by rubber manufacturers and allied trades, since masticating rolls are required to "break down" the rubber prior to solution. The highest practical solids content is about ten per cent, but loading materials such as carbon black, zinc oxide, and kaolin amounting to half the weight of the rubber are sometimes added to build up and extend the rubber. Natural resins of the cumar or ester gum type are useful too in promoting adhesiveness; rosin gives the film a sticky character.

The main tonnage of such cements goes into shoe manufacturing, where it serves to stick leather and rubber soles and linings in place. The automobile industry uses rubber cement in bonding felt and cloth to metal, and for cementing rubber gaskets and stripping, since these cements are the only adhesives having any affinity for rubber surfaces.

Of greater utility to the adhesives manufacturer is latex, the stabilized aqueous dispersion of rubber. As it comes from the tree, the natural product contains about 30 per cent of solids, but by creaming, evaporation, or centrifuging it is brought to a concentration of 60-75 per cent. It is in the concentrated form that latex enters adhesive formulations. Such dispersions are heavy creams, spreading easily, setting rapidly through destabilization and coagulation of the natural emulsion, but lacking in tack. To stabilize the emulsion and lend it some degree of tack, a concentrated casein dispersion may be added. The film deposited by the raw emulsion is fairly adhesive and extremely elastic, but with up to equal parts of casein it becomes far more adhesive and less elastic. For labelling and sealing many impervious materials and coatings, the surface type of adhesion afforded by such latex-casein glues is in-

valuable. Together with a small proportion of aqueous plasticizer, or resinous dispersion [28] they make first-class adhesives for laminating metallic foil to paper or transparent sheeting.

Colloidal bentonite is a good stabilizer and toughener for latex, making a soft paste that has been patented [26] and widely marketed for hand-labelling tins.

Dextrins are too acid to be blended with latex, but neutral oxidized starches or slightly alkaline causticized starches are frequently used as cheap fillers and extenders. Quite a bit of the "suction" or "specific" adhesion of the latex is lost this way, but, more accurately, these starch combinations employ the latex to soften the starch film and improve its water resistance and adhesion. The shoe industry uses such products extensively in fabricating cloth and felt uppers and linings.

A compromise product of some utility involves the addition of an appreciable percentage of a rubber solvent, such as toluene, to an aqueous latex. The solvent emulsified in the latex softens and swells the rubber globules; on drying, a more rubbery film is deposited than in the case of pure latex. The process is not easily carried out, since the solvent tends to destabilize the dispersion; hence it is rarely applied to latex containing over 40 per cent of rubber.

An interesting property of latex is the way the dry, non-sticky film instantly adheres to a similar coating. Patented self-seal envelopes and laundry bands are made on this principle.[21]

Synthetic-Resin Adhesives

Solutions of nitrocellulose and synthetic resins have appealed to the adhesives chemist since the time of their introduction. The strong adhesion of properly formulated lacquer films to metals, wood, ceramic ware and cloth, as well as their flexibility and adjustable drying rate are all factors of interest. However, such lacquers are relatively high-priced, and somewhat troublesome to handle because of their inflammable nature and the necessity for special solvent thinners. As a result, until very recently they were used only in specialized cases of waterproof adhesion, the bonding of unusual materials, or as packaged "household" cements.

The advent of transparent sheeting as a wrapping material has created a demand for lacquer adhesives, since many potential applications depend for their success on the development of suitable glues. Ordinary regenerated cellulose is readily cemented by dextrin or starch glues, but the moisture-proof grades and cellulose acetate are susceptible to attack only by organic solvents.

Properly formulated nitrocellulose solutions [54] adhere satisfactorily to synthetic sheetings and coatings, but many different cements are required to meet various mechanical and physical specifications. For example, bag making requires a thin, fast-drying seam glue and a heavy, tacky bottom glue; on the other hand, laminating adhesives must be quite fluid, and capable of being run in large glue troughs for hours at a time. "Scotch tape" adhesive is tacky at room temperature.

In general, basic lacquer technology, as developed in the coating field, applies to the preparation of adhesives. As a rule though, the products are more highly plasticized to give softer films. Higher resin proportions are employed [57] in cements to impart adhesiveness and to increase the solids content. Odor is an added problem where food products are packaged; this rules out many useful solvents. Drying rates as high as possible are usually desired in automatic sealing, but if carried too far, excessive thickening in the glue pot will result. Tackiness or immediate sticking power is desirable but rarely obtainable, despite the use of fillers and high resin content. Color, too, is extremely important where transparent sheetings are being joined, further limiting the raw material choice to those resins giving no more than a deep amber coloration.

Plywood manufacture has developed a demand for many tons of synthetic resins annually. Bonds made with such resinous adhesives are unique in being absolutely

waterproof, mold and fungus resistant, and having high strength. Phenol-formaldehyde resins first became practical for this purpose with Weber and Hengstebeck's invention in 1920 of resin-impregnated tissue paper which could be interleaved with the wood plies, and developed its bond strength under heat and pressure. Introduced into this country in 1929, the process has been widely adopted, and has stimulated the development of a broad line of phenol-formaldehyde adhesives.*

The sheet type phenolic is still considered the most convenient and effective, but less costly urea-formaldehyde products are used with only slightly inferior results. For lower cost, use is made of cold-press liquid adhesives, with the resin solution furnished separate from the resin-setting catalyst, to be mixed just prior to application. Both phenolic and urea-formaldehyde solutions are available for this class of work.

Polymerized vinyl esters, notably the acetate and chloride or copolymers of the two, are remarkable for their toughness, elasticity, transparency, and lack of color, thus perfectly suiting them for wide usage in the manufacture of safety glass [17] as well as for a variety of miscellaneous gluing operations.† Because of their thermoplastic nature, cements can be prepared which dry hard and nontacky but readily bond to a variety of surfaces [18] on the application of a temperature of about 300-400° F. Photographic mounting tissues and thermal sealing labels are made in this way. Some difficult fabrication problems can be solved by precoating one surface with a solution of vinyl or similar resin, drying, and then later sealing simply by the application of heat. Solvent odors are eliminated; and since the seal is obtained almost instantaneously, high production rates can be obtained. Two impervious surfaces can be joined by this method, since no point of escape for solvents is required. Such applications are described in greater detail below.

Vinyl derivatives unique for their water solubility are the polyvinyl alcohols. Their ability to form flexible, non-hygroscopic films makes them valuable as modifiers for starch products,[27] thickeners for latex, or dispersing agents for lacquer adhesives.[19] Some grades which can be remoistened have been proposed as non-curling, colorless, envelope seal gums.

The good adhesive strength of ethylcellulose may be further improved by blending with plasticizers and ester gum or any of the hard resins, to give useful, general purpose adhesives. With thermoplastic resins it forms heat-sensitive coatings similar to those from the vinyls, but generally with a lower temperature of activation. In such formulations the superior compatibility of ethylcellulose with a wide variety of materials is advantageous.

Chlorinated rubber retains most of the superior adhesion of raw rubber, but with greatly improved solubility characteristics. Properly plasticized, and occasionally with other resins added for increased solid content, such solutions will adhere to virtually any surface imaginable. Unfortunately, the high viscosity grades, which are best for adhesive purposes, fiber and string excessively due to the cohesive nature of the base, which limits machine usage.[28]

Thermoplastic Adhesives

Thermoplastic adhesives, used in the molten condition at an elevated temperature, have long been recognized for their excellent adhesion to impervious surfaces. Sealing wax, a combination of shellac, rosin, and a filler, was frequently used for adhesive purposes, and many similar combinations of natural resins plasticized with vegetable oils have been described.

A simple thermoplastic glue, used in sizeable quantities in the automatic labelling of cans, is the "pickup" gum which is applied to the can to grip a label as the can

* See paper by C. Henning in this volume. J. A.

† Fine or colloidal dispersions of polyvinyl acetate are now commercially available as adhesives. When dry they yield strong films, especially when used with plasticisers. J. A.

rolls over the label stack. Only temporary stickiness sufficient to pick up the label is required, since the label is pasted to itself after wrapping around the can. Rosin plasticized with mineral oils or waxes is frequently used, being applied from an electrically heated glue pot at about 250° F.

Where a lacquer type of bond is desired, but solvent odors are ruled out, or where immediate tackiness is necessary, thermoplastic cements are likely to be used. If two impenetrable surfaces must be stuck together, leaving no outlet for solvent vapors, a thermoplastic adhesive is almost the only practical solution.

Rosin, ester gum, and the coumarone resins are the cheapest thermoplastic bases, but when plasticized to a degree where they become sticky and adhesive, they give low bond strength with excessive cold flow. It is thus desirable to add some strong film-forming material to such combinations, and the synthetics are generally employed for this purpose. Just a few per cent of ethyl cellulose,[55] for example, will toughen the bond and greatly reduce tendencies toward cold flow.

Asphalts are occasionally used for adhesive purposes, although their dark color naturally limits their utility. Duplex wrapping materials wherein two layers of kraft paper or cardboard are joined by a layer of asphalt are widely used to make a highly moisture-proof sheet. However, asphalt has the drawback of being sensitive to temperature fluctuations, tending to give brittle sheets in cold weather and staining through occasionally in hot weather. Improvement has been effected in recent years, but its use is still limited for the most part to the low-cost field.

Many difficult adhesion problems are solved by the polyvinyl acetate and chloride thermoplastic or "hot melt" compositions. Rather high temperatures are required to render this resin sufficiently fluid for smooth machine application. On the other hand, this very property is a distinct advantage in limiting cold flow—the tendency of thermoplastic products to yield slowly to continued stress at normal or slightly elevated temperatures. One interesting application of the vinyls is in the fabrication of paper milk containers.[31] Although a water-resistant bond is desired, the joint must be able to resist extreme tensile stress immediately after sealing. Of course no solvent odor can be tolerated in the container. A heat-sensitive coating is therefore applied to one of the faces, and they are rapidly sealed under pressure as the glue freezes.

The water-white, thermoplastic methacrylate resins may also be used[29, 56] in the manufacture of milk containers, bottle tops, laminated sheets, and in packaging. Common blending agents are the damar and coumarone resins and ester gum; these, with the *n*-butyl and isobutyl polymers, give adhesives which are more fluid and of lower melting point than vinyl resin compositions.

A thermoplastic packaging adhesive unique in its employment of water-soluble ingredients is a patented[30] blend of acetamide and dextrin in approximately equal parts. To this may be added other water-soluble colloids and water-insoluble gums, to produce adhesives for special package-sealing work.

Emulsion Adhesives

It has been recognized in the adhesives industry, as in the paint field, that it is uneconomical to produce resinous films entirely with the aid of expensive solvents which serve no purpose other than as temporary carriers. Other incentives for the use of resinous materials in aqueous dispersions originate in the need for improved operation on machines.

The obvious solution has been to emulsify lacquer adhesives in water, preferably using an adhesive material as a carrier and protective colloid.[33, 34] Many rules have been given concerning the proper methods of preparing stable oil-in-water emulsions, but these usually refer to emulsions low in solids such as are used in cosmetics, polishes, and food products. The adhesive chemist generally employs as an aqueous base the high solids, stable, casein solutions mentioned above, for best working prop-

erties on machines. A homogeneous dispersion of lacquer in the continuous phase is more readily obtained with these viscous solutions, often without the use of colloid mills or other special equipment. As a matter of fact, too fine-grained an emulsion is often so creamy and pasty as to be just as lacking in tackiness as the original lacquer. If an alkali-soluble resin like rosin or ester gum is incorporated in a lacquer, it will partially saponify in the alkaline phase, thereby aiding the emulsification process. Most standard directions warn against the use of more than minor percentages of water-soluble solvent, if the emulsion is to be stable; but an adhesive emulsion will frequently have more tack and better working properties if high proportions of active water-soluble solvents are employed to combine the two phases to some extent. The result will be to reduce somewhat the normally creamy, pasty body of the dispersion.

Many resin manufacturers are now developing stable, aqueous dispersions of their products. In some cases, like the polyvinyl acetate emulsions, these have been polymerized in the aqueous solution. Plasticizers can be stirred into such emulsions to give highly adhesive films, while solvents, usually water-insoluble types, may be added to aid wetting, penetration, and anchorage to many surfaces.

Aqueous dispersions of polyterpene resins from coal-tar bases, and some alkyd resin dispersions which are also being produced, have no great tensile or adhesive strength in themselves, but they blend well with latex or other film-forming bases to give useful products.

Urea-formaldehyde resins in aqueous dispersions have been applied especially to plywood manufacture,[51, 52] some with a heat-activated catalyst for hot-press work, others with separate catalyst solutions for cold-press work.[20] Interesting dry grades, useful as marine glues, have been prepared by spray-drying solutions of the water-soluble urea-formaldehyde resin and adding the catalyst in dry form.[50] These powders dissolve rapidly in cold water, but dry to give an insoluble bond.

Some of the disadvantages of bitumens for thermoplastic work have been overcome by dispersing asphalt in an emulsified form. Since in this manner most of the bond strength is retained while staining is reduced, these emulsions promise to extend the usefulness of asphalt adhesives.

Inorganic Adhesives

All the adhesives discussed above are organic products. Inorganic materials are almost invariably crystalloidal in nature, and hence have but little tendency to form strong films. A few inorganic salts develop a glassy character on drying, and will adhere to porous surfaces.

Certain grades of silicate of soda * are extensively used for adhesive purposes; the types usually employed in adhesives lying in the range between 2:1 and 3.5:1 silica to sodium oxide ratio. The higher-ratio grade is quite thin, and sets almost instantaneously when spread on a porous surface, due to the formation of a silica gel on the loss of only a very small amount of water. The low-ratio type is a much thicker, viscous product, which has more tackiness and a slower drying rate. It therefore finds more widespread use. Many tons of high-ratio silicate are used annually in the fabrication of corrugated board. Its phenomenally fast setting rate permits high production speeds; it is low in cost; and its films are brittle and stiff, lending desirable rigidity to the finished board.

In mechanically sealing cases and cartons, silicate products are often used, the lower-ratio grades being the choice for this service because of their stickiness and range of action. A number of special applications take advantage of the non-inflammable and moisture-resistant character of silicates, either alone or blended with starch or casein adhesives.

* See paper on sodium silicate solutions by Wm. Stericker in Vol. III of this series, pp. 289-96.

A much larger amount of lime will dissolve in a concentrated sugar solution than in plain water. A complex forms which dries to a smooth, glassy, tough film, much less hygroscopic than sugar alone. Attempts to use the mixture as an adhesive have not been particularly successful, but a material of this type is occasionally employed as a modifier for starches or animal glues.

The sulfite waste liquors from wood-pulp manufacture carry a high percentage of organic and inorganic solids which dry to a flexible, adhesive film. This so-called "lignin liquor" is low in cost; one commercial article in which it is used is linoleum cement, used to hold floor coverings in place. The concentrated, viscous solutions are quite sticky and tacky, but as the color is a dark brown, the film hygroscopic, and the odor rather strong, they are suited for a limited class of service. The very abundance and low cost of sulfite liquor has offered a continual challenge to the adhesives chemist, and a good deal of work has been published on possible methods of utilizing this waste in adhesives.[58]

Summary and Conclusions

Reference to the chemical literature will disclose literally hundreds of suggested adhesive formulations, many of which have not been mentioned in this paper. In addition, many new materials commercialized by the chemical industry have possible application to adhesive manufacture. This paper has endeavored to acquaint the chemist with the outlines of modern adhesives technology as an aid in the evaluation, formulation, and application of these important colloidal products.

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Industrial Applications of Soybean Lecithin

JOSEPH STANLEY

American Lecithin Company, Inc., Elmhurst, Long Island, N. Y.

The phosphatides of the soybean are of technical interest,[55] and their commercial production on a large scale has inspired much research on their application in industry.[43] In the course of producing soybean oil by extraction or expression, the phosphatides find their way into the oil.[3] The phosphatides are then separated by hydration, centrifuging, and drying *in vacuo*. So produced, they represent the soybean phosphatides or "lecithin" of commerce, and are invariably associated with 35-40 per cent of adsorbed soybean oil.[30] By convention it has become customary to call this commercial product "soybean lecithin," or simply "lecithin."

Commercial soybean lecithin is a light-brown, waxy material of bland taste and neutral odor. It is substantially anhydrous and imputrescible, and may therefore be stored for years without decomposition. It can be bleached with hydrogen peroxide to a light-yellow product.[40] Soybean lecithin is soluble in aliphatic and aromatic hydrocarbons, but only partly soluble in alcohols and esters. Acetone will dissolve out the adsorbed soybean oil, and this solvent furnishes a convenient means of preparing oil-free phosphatides. Soybean lecithin imbibes varying percentages of all solvents, including acetone and ethyl alcohol, to form thin imbibitions. It readily hydrates and emulsifies in water, particularly at a pH above 8, forming emulsions indefinitely dilutable with water.

Soybean lecithin is freely soluble in mineral oil, but insoluble in cold vegetable or animal oils. However, it will dissolve in warm vegetable or animal oils, and will stay in solution if a considerable percentage of fatty acids is present. Soybean lecithin is saponified and hydrolyzed by heating with aqueous alkali or acid.

As the phosphatides are insoluble in acetone and the soybean oil is soluble, the oil is sometimes removed by taking advantage of this difference in solubility. In this case the oil-free phosphatides are sold as such, or the oil is replaced by some other oil, such as mineral oil or cocoa butter. As a rule, however, commercial lecithin contains about 65 per cent of acetone-insoluble or phosphatides, and a carrier of about 35 per cent of acetone-soluble or oil; the moisture and benzene-insoluble substances are insignificant. The total phosphorus is about 2.2 per cent, and the total nitrogen 0.9 per cent.

Unlike animal lecithin,[17, 26] soybean lecithin contains a considerable amount of adsorbed carbohydrate[35] material, as well as phytosterols.[56] However, it contains no sphingomyelin.[48] It was formerly thought that soybean phosphatides contained only soybean oil, lecithin, and cephalin.[17, 50] The soybean oil could be quantitatively extracted with acetone, leaving a residue of phosphatides.[28] The latter were then extracted with ethyl alcohol, and it was supposed that the alcohol-soluble part was lecithin, and the alcohol-insoluble part cephalin. Since the discovery of serine and inositol in soybean lecithin, some revision has taken place in its nomenclature.[12] It is now believed that the phosphatides are composed of phosphatidyl choline, phosphatidyl ethanolamine, and phosphatidyl serine,[14] which may be regarded chemically as the phosphatidic acid[8] ethers of the respective nitrogen compounds.[1, 25, 18] In

addition to these there is present an inositol complex of obscure structure, but supposedly esterified with tartaric acid, galactose, phosphoric acid, and a fatty acid, called lipositol.[52]

It is thus seen that the phosphatides of the soybean are natural interface and wetting agents.[44] The molecules of its various constituents contain lipophilic fatty acid groups on one end, and hydrophilic phosphoric acid ethers at the other end. Their chemical structure makes their solubility and emulsifying properties clear. As wetting agents they have an affinity for spreading in monomolecular layers on interfaces, markedly affecting surface and interfacial tensions. In addition to these properties, the phosphoric acid and amino compound combination give them antioxidant properties.[11, 18]

Lecithin is a natural wetting agent and interface modifier. As such its application in food products is of great interest. In fact most natural foods contain lipid material of one sort or another in which phosphatides are always found. This includes the lipids of flour, cereals, skim milk, and their numerous combinations used as food. These prepared foods are random systems of hydrophilic and lipophilic matter, often in the finely comminuted or colloidal state. Most frequently one encounters a glyceride intermixed with protein or carbohydrate matter in varying degrees of dispersion, with or without water.[5] In such foods lecithin displays its colloidal properties at the interfaces of heterogeneity.

Having reviewed the physical and chemical properties of soybean lecithin, we are now in a position to clarify its technical applications. As an emulsifying agent it finds much use in pharmacy, confectionery, and baking. It may be used to make emulsions of cod-liver oil, castor oil and the like. In confectionery it is now standard practice to add 1 per cent of soybean lecithin to the oil used in making the confection.[21] In this case it functions as a high-temperature emulsifying agent when the oil is boiled with sugar solutions. It promotes better intermixture of the constituents and avoids greasiness and graininess on storage. Small percentages of lecithin are used in bread dough and cake batters. The shortening effect is improved, which makes possible the saving of considerable shortening. Cakes containing soybean lecithin[57] have a more uniform structure and are tenderer. In the case of yeast-raised doughs more absorption is possible; the structure and crumb are much improved, and the finished product does not dry out or stale so rapidly.[22]

Soybean lecithin is a natural and wholesome edible wetting agent. As such it is employed in chocolate and the like where a finely comminuted solid is dispersed in a fat.[46] Chocolate is made by grinding sugar with or without milk powder in chocolate liquor and cocoa butter.[45] The manufacture of chocolate was a long and wasteful process before the introduction of soybean lecithin. The use of about 0.3 per cent of lecithin makes possible large savings in cocoa butter. It appears that the lecithin spreads on the particles in a monomolecular layer, producing instant wetting by the fat.[47] This effect results in liquefaction of the chocolate with consequent great reduction in viscosity. There are other technical advantages. For example, the chocolate is more resistant to the thickening effects of moisture, more resistant to "blooming," and sets with a brighter gloss. These beneficient results accrue because of the stabilized wetted condition of the dispersed phase.

Another important application of soybean lecithin is in margarine.[9] This product is made by emulsifying cultured milk with a fat. In order to simulate butter more closely, an emulsifying agent of definite characteristics must be used. When fractional percentages of lecithin are used in margarine a better intermixture of the various glycerides is obtained upon solidification; at the same time better sorption of the water is secured, thus effectively preventing "bleeding," or the extrusion of droplets of water on storage. When lecithin-containing margarine is used in frying, it boils quietly with a fine foam and without spattering, leaving behind a brown, movable sediment which does not stick to the bottom of the pan.

Soybean lecithin functions beneficently in almost any fat-containing food. In ice-cream,[7, 10] for example, the inclusion of 0.5 per cent lecithin gives a velvety smooth product effectively protected from sandiness on storage, even in the presence of excessively high percentages of serum solids. The use of soybean lecithin in macaroni products has been studied extensively.[20, 59] The gluten hydrogel formed on cooking macaroni needs the naturally present or added lecithin for its proper structure.[18] Lecithin is adsorbed at the gluten interfaces, stabilizing the cooked macaroni to the extent of preventing syneresis.[80] The use of 1 per cent soybean lecithin makes it possible to make macaroni from soft wheat flour of a quality comparable to that made from hard wheat flour.

Soybean lecithin is used as an antioxidant for oils and fats. As little as 0.05 per cent can be used to counteract rancidity and hydrolysis in lard, oleo oil, and shortening.[4] This use is well established and has been studied in detail. It is interesting to note that combinations of lecithin with other antioxidants produce an effect far beyond their additive result. For example combinations of lecithin with ascorbic acid, alpha-tocopherol, hydroquinone, or nordihydroguaretic acid produce a much greater antioxidant effect than any of them alone. This unusual behavior is known as the synergistic effect of a combination of antioxidants.

Other industries as well utilize soybean lecithin to advantage. It usually functions as an emulsifying, penetrating, detersive, wetting, or antioxidant agent. Used medically it acts as a source of cholesterol-free choline and inositol; in cosmetics and soaps it acts as an emollient agent and a repressor of alkalinity.

The use of soybean lecithin in the paint, lacquer, and printing-ink trades is well known. It functions primarily as a wetting and dispersing agent. Even water paints are improved by lecithin because it stabilizes the emulsion, and gives body to flat wall paints. About 1 per cent of soybean lecithin is used on the pigment basis. It first of all assists in the grinding of poorly wetting pigments. It permits increased pigment concentration without stiffening the mass, thereby increasing grinding output. Other specific advantages may also result; for example, soybean lecithin counteracts sagging in architectural enamels, acts as an anti-flooding agent with chrome green, chrome yellow, ferrites, and carbon black; and with toluidine toner its dispersing action makes possible an increase in color strength.

Soybean lecithin is of service in the textile industries.[29] Small amounts dissolved in the oils and fats used not only stabilize them against rancidity, but impart an unusual softening and lubricating power. Thus the addition of soybean lecithin to textile and rayon oils increases the penetrating and spreading properties of these oils on the fibers, giving a thin and uniform film.[81] The presence of the lecithin also helps in the removal of the oil from the goods by scouring in preparation for dyeing and printing. To achieve these results as little as 1 per cent of soybean lecithin in the oil is sufficient. Aqueous emulsions of lecithin containing small amounts of benzyl alcohol have also been used effectively.[6] For use in textiles and rayon the bleached product is preferred. Its emulsion in water is light yellow, but it imparts no color to the goods. The emulsion is indefinitely dilutable and is stable in neutral and alkaline media, but it cannot be used in acid media, or with excessively hard water. Lecithin used in wet doubling solutions, gives a certain loading of the yarn and a soft lustrous product. After mercerization the yarn is more lustrous, and in dyeing the lecithin has a leveling effect.[27]

In some cases emulsions of soybean lecithin replace egg-yolk, as in tanning.[86] As a rule egg-yolk is of variable composition and expensive. For this purpose a 10 per cent emulsion works well, and is thus used advantageously in the fat-liquoring of leather. An emulsion of soybean lecithin and neat's foot oil in slightly alkaline water and containing soap solution and sulfonated castor oil is used in the greasing of leather. In its greasing action the lecithin penetrates deep into the pores of the leather and develops a high degree of suppleness.

In cosmetic and pharmaceutical products soybean lecithin finds interesting and extensive applications.[2] Small amounts improve the keeping qualities, emulsifiability, and penetration of petroleum jelly, medicinal mineral oil, benzoinated lard, paraffin, and beeswax. Cosmetic creams, hair-tonics, and medicinal salves are improved by lecithin because of its colloidal, antioxidant, and penetrative effects. The skin appears to tolerate, adsorb, and respond to lecithin. Experiments show that the incorporation of 2 per cent of soybean lecithin in soap imparts emollient properties. It appears that washing the skin with lecithin-soap causes some of the lecithin to be selectively adsorbed by the skin, which counteracts the harshness of hydrolytic alkali. The skin is left soft and smooth as if after the application of a delightful emollient salve. For this purpose it finds use in all soaps: liquid, cake, flakes, and powder. Another use in this connection is the application of soybean lecithin in brushless shaving cream. In this type of product it acts as a wetting as well as a softening and emollient agent. As such it acts to soften the beard and keep the lather moist, allowing the razor to cut better, leaving the skin soft and smooth. It has even been found that the razor remains sharp longer. In using it in soaps, shaving creams, and the like the lecithin should be added immediately after saponification. For the same reason soybean lecithin finds application in many types of cosmetic preparations, such as skin creams, tissue creams, shampoos, lipsticks, and brilliantines. In the presence of much water without alcohol it is advisable to use some preservative in cosmetic preparations, such as hexamethylenetetramine or the methyl ester of parabenzoic acid.

The phosphatides of natural rubber were investigated some years ago.[51] The isolated phosphatides of *Hevea* latex, in common with other vegetable phosphatides, contain a carbohydrate and in this particular case considerable phosphatidic acid. The isolated *Hevea* phosphatides were used experimentally in the curing of rubber and materially increased the acceleration. For this and other reasons soybean lecithin finds some application in rubber manufacture, and a number of patents have been allowed in this connection.[34, 37]

The petroleum industry uses soybean lecithin to good advantage as an additive and antioxidant in lubricants, gasoline,[42] and cutting oils. For example 0.5 per cent of soybean lecithin has been found effectively to extend the life of lubricating oil. In crank-case lubricating oil it acts as a detergent, and counteracts varnish and sludge formation, as well as increase in viscosity and acid in the lubricant during use. It is also very effective in counteracting corrosion of bearings, especially those of the Cu—Pb or Cd—Ag type.[33] Soybean lecithin is particularly effective in solvent-refined lubricating oils. It appears that solvent-refining removes the natural antioxidants in the oil, and for this reason an additive, such as soybean lecithin, is desirable in this type of lubricant. Some types of gasoline, such as those derived from high-sulfur crudes, or those containing tetraethyl lead or a metallic carbonyl as an antidetonant, tend to cloud on exposure to light.[32] A loss in octane rating results, and the fuel becomes corrosive. Small amounts of soybean lecithin added to the gasoline stabilize it against such decomposition. About 10 lbs of soybean lecithin per 1000 bbls of gasoline is used to inhibit cloud formation, decomposition of tetraethyl lead, and corrosiveness. The protective action of soybean lecithin helps to retain the octane of high-leaded fuels, and counteract corrosion and clogging of fuel tanks and lines, particularly on aircraft.[88]

It was stated previously that choline and inositol are found in soybean phosphatides.[58, 28] It appears that phosphatides are widely distributed in nature, and indeed are present wherever oil is found. As such it is not surprising that phosphatides should be of great importance in the vital and reproductive processes. Extensive investigations have shown, for example, that choline and inositol, as found in complex organic combination in soybean phosphatides, have important therapeutic properties. Choline has such decided physiological importance that it is provision-

ally classified as a member of the vitamin B group.[16] It has been shown that choline has definite lipotropic activity, promoting phospholipid turnover and preventing fatty livers.[24] In addition it protects against hemorrhagic kidney degeneration, and has an important function in the conversion of hemocystine to methionine. Further, choline in conjunction with manganese acts as a preventive of perosis in turkeys and chickens. It was also discovered that mice fed a purified diet containing the known members of the vitamin B group ceased to grow and became hairless over the trunk. The substance causing this deficiency disease was later found to be inositol.[54] It is now estimated that the normal adult requires 1 gram of inositol per day to maintain proper health. Specifically, soybean lecithin has been found effective in the treatment of hypercholesterolemia [41] and psoriasis.[15]

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The Colloid Chemistry of Insecticides

O. A. Nelson and C. M. Smith

Bureau of Entomology and Plant Quarantine, Agricultural Research Administration, United States Department of Agriculture

If colloid chemistry is regarded as the chemistry of small particles, and the meaning of "small" is not defined too rigidly, many insecticidal preparations may be regarded as colloidal systems. Solid insecticides generally consist of very fine powders, which during application are dispersed in water as sprays or in air in the form of dust clouds. Liquid insecticides, such as petroleum oils, are dispersed directly into air to produce mists or are emulsified with water and then atomized. The particles and droplets are in general larger than in those substances which are strictly colloidal, but there is almost always some colloidal material. Certain colloids find application as accessory spray materials, namely, as wetting and spreading agents and as adhesives. Finally, various other colloidal phenomena are observed, such as adsorption of fumigants by fumigated products, the protective action of one aerosol upon another, and so forth.

For convenience of treatment, systems in which the dispersed phase is solid will be considered first, and systems with liquid dispersed phases next, followed by colloidal adjuvants and miscellaneous observations.

Systems with Solid Dispersed Phases. Solid insecticides are commonly prepared in dry powdered form with the grain size of the powder as small as is commercially practicable. Almost all the common inorganic products pass completely through the tightest available sieves (US #325, openings 45 microns square), and only the fibrous organic materials, such as powdered derris root and powdered pyrethrum flowers, show fractions of appreciable sieve size. Therefore, other less direct methods of particle-size determination must be used. Such determinations have been made microscopically,[1] by sedimentation and elutriation in both air and liquids,[2] and by air permeation.[3] By all these methods the dispersion around the mean size is found to be relatively large, and many products may contain an appreciable proportion of truly colloidal particles. A designation of the mean size is troublesome because of the many concepts upon which a mean value may be based, and also because every method has a limit on the low side, which leaves a fraction, sometimes of considerable proportion, which is not sufficiently well characterized to be accurately allowed for in calculating the mean.

In the permeation method,[3] developed by Gooden, an inexpensive and easily constructed apparatus is used which furnishes a so-called surface mean particle diameter. In principle the machine actually measures permeability, from which the total surface area could be deduced; the calibration is such, however, that the value read is the uniform spherical particle diameter corresponding to the total surface area. This value then may be expected to be correlated with the speed of chemical action of an insecticide. That there really is some such correlation is shown by the work of McGovran, Cassil, and Mayer[4] and others. For the few insecticides that have been examined for particle size by this method Gooden has obtained the results given in Table 1.

Table 1. Particle Size of Some Common Insecticides as Determined by the Air-permeation Method

Insecticide	Number of Samples Examined	Surface Mean Particle Diameter in Microns
Paris green	3	10-14
Lead arsenate	4	0.5-0.8
Calcium arsenate [5]	81	0.5-1.5
Sulfur [6]	54	5-25
Sodium fluosilicate [7]	52	6-33
Sodium fluoride [7]	17	4-66
Derris	28	4-9
Cube	11	5-10
Pyrethrum	2	6

The question now arises as to whether the toxicity of insecticides is correlated with the particle size, and if so whether anything is to be gained by an attempt to reduce the size still further. Considerable information on this subject has recently been accumulated, and has been summarized by Smith and Goodhue.[11] In a study of paris green, for example, McGovran, Cassil, and Mayer separated it into fractions of different particle size, in which there was practically no overlapping, and determined the relative toxicities of these fractions against Mexican bean beetle adults. Table 2 summarizes their results.

Table 2. Effect of Particle Size of Paris Green on Mortality of Mexican Bean Beetle Adults

Particle Diameter (microns)	Deposit (micrograms per sq cm)	Insecticide Ingested by Insect, (micrograms)	Surface Area of Insecticide (sq cm)	Mortality in 48 Hours (%)
		Sprays		
22.0	32	208	0.18	29
12.1	31	121	0.19	40
1.1	32	35	0.59	53
		Dusts		
22.0	110	449	0.42	43
12.0	105	238	0.37	61
1.1	105	34	0.52	88

The chemical composition of the three fractions was almost identical, except for the water-soluble arsenic (As_2O_3), which increased from 1.60 to 4.68 per cent between the coarsest and finest fractions.*

Nelson, working with J. H. Pepper and E. B. Hastings at Montana State College, found finely divided sodium arsenite much more toxic to Mormon crickets than the coarser fractions of the same product, and Siegler and Goodhue [12] have shown that finely divided phenothiazine is decidedly more toxic than the coarser material. Further work (unpublished) by several investigators in the Bureau of Entomology and Plant Quarantine showed a still greater toxicity when the so-called "micronized" phenothiazine was used.

There appears to be little doubt that in a material as coarse as ordinary paris green the finer particles are more toxic than the coarser ones, and by an extension of this idea it might be presumed to be desirable to prepare insecticidal materials in truly colloidal form.†

The cause of the increase in toxicity with decrease in particle size is probably the larger surface area of the finely divided product. In the case of contact poisons the finely divided powders adhere much better to the surface of the insect, and because of greater solubility are absorbed faster and in larger quantities through the integument or fleshy portions of the body. McGovran and co-workers noted a green coloration of the insects dusted with paris green of 1.1 micron diameter, but not with

* In general, solubility of substances is increased by fine subdivision. See paper on "Solubility and Size of Particles" by Geo. A. Hulett in Vol. I of this series. J. A.

† See "Colloid Chemistry," by J. Alexander, 4th ed. 1937, also earlier ed. (Van Nostrand Co., N. Y.).

coarser fractions; Nelson, Pepper, and Hastings observed that fine sodium arsenite powder covered the bodies of Mormon crickets more completely than did the coarser products.

A colloidal suspension of paris green might be more toxic than the finest commercial material now available, but there are other considerations that may make this an undesirable goal. As pointed out by McGovran, Cassil, and Mayer, the greater insecticidal effect of small particles is probably due to their greater solubility in the digestive tract of the insect. For the same reason we might expect finely divided material to be more harmful to plant foliage. A beneficial insecticidal effect, therefore, will be produced by finer subdivision only if there is a differential between the two changes in favor of the phytocidal action. Furthermore, mechanical difficulties are encountered with extremely small particles. When applied as dust clouds in air they envelope the plant better, but at the same time they drift too readily in air currents, and the energy with which each particle strikes a plant surface is too small to make it adhere well. In sprays extreme fineness of subdivision aids in keeping the material suspended in the liquid, which is advantageous until the spray leaves the pump; but upon contact with the sprayed surface delayed settling leads to excessive run-off, so that it is difficult to build up sufficient deposit to protect the plant fully from insect attack.

Recently, interest has been revived in the possibility of controlling the granary weevil in stored grain by incorporating in the latter one per cent or less of certain powdered mineral substances which would ordinarily be classed as non-poisonous. The physico-chemical aspects of this problem have been investigated, among others, by Briscoe and co-workers,[8] Parkin,[9] and Wigglesworth.[10] It appears that the really effective fraction of such dusts is that portion comprising the particles below 10 microns in diameter, and that the effectiveness increases with decrease in diameter, at least down to some limiting subdivision, 1.8 micron material proving most effective against *Sitophilus* (*Calandra*) *granarius* (L.). The effectiveness is rather markedly correlated with hardness of the mineral substance. Several theories have been advanced concerning the way in which dusts cause desiccation of insects; (1) that by close contact with the body surface the dust acts as a conductor of the body water, the loss of which is increased by capillary action; (2) that the dust increases body surface and consequent evaporation therefrom; (3) that the dusts adsorb the lipoid covering of the insect's cuticle, thus causing breaks in it through which the moisture evaporates at an abnormal rate; and (4) that the waxy, protective coating of the body surface is abraded by the hard, sharp, crystalline particles of the dust, thus allowing more rapid evaporation.

Particles of a powdered insecticide, when suspended in a liquid, assume charges which make them subject to cataphoresis and to adsorption on surfaces. Moore[13] has shown that most of our common arsenical insecticides become negatively charged when put into water; and because plant surfaces in general are also negatively charged, the adsorptive effects are slight. The presence of iron and aluminum compounds reverses the charge on the powders, and various attempts have been made to obtain more adhesive products by incorporating the hydroxides of these two metals. Following a rather unwarranted extension of the principle of favorable electrical charges, several studies have been made of the static charges produced during dusting of powdered insecticides, and efforts directed to increasing the naturally occurring effect. All such attempts have failed, however.

Powdered sulfur is extremely difficult to wet with water; hence certain manufacturers offer to the public so-called colloidal or wettable sulfurs, consisting of mixtures of dry sulfur with wetting agents or of pastes made by grinding sulfur with solutions of wetting agents. Lead arsenate has been marketed in several so-called colloidal forms, but careful tests have failed to show any marked superiority over the usual forms of that insecticide.

Systems with Liquid Dispersed Phases. Although most of the common insecticides are solid, certain liquid materials, especially petroleum oils, also find extensive application. They are usually applied either directly atomized as sprays, or as emulsions in water. In most emulsions the oil constitutes the dispersed phase, and in some types, such as the so-called miscible oils, the degree of dispersion may approach the colloidal. These miscible oils consist of oil, an emulsifier, such as soap, and a third substance, such as cresol, which renders the emulsifier soluble in the oil. Dilution of this clear mixture with water causes spontaneous emulsification of the oil into droplets of very small particle size. Such colloidal suspensions of oil, however, are recognized as being less useful as insecticides than emulsions with larger drops, which, being less stable, deposit the oil on the sprayed surface much more readily.

Smith and Goodhue [11] have reviewed the question of the dependence of insecticidal effect on droplet size. Beran [14] concludes that in coal-tar emulsions the finest droplets are the most toxic, but the claim of deOng,[15, 16] that the large-droplet, quick-breaking emulsions are better has been substantiated by Griffin, Richardson, and Burdette.[17]

When oils are applied directly in mist form, however, the evidence seems to be in agreement that the effectiveness is proportional to the degree of subdivision. Burdette [18] found that oil droplets 1 to 10 microns in diameter were more toxic to honeybees than larger droplets, and suggested that this effect was due to the completeness of the oil coating of the integument or of the penetration of the spiracles. Searles,[19] however, carried out experiments which he considered to indicate that there is a limit to the desirable fineness of spray droplets, because such droplets do not have enough energy to bring about contact with the insects.

In recent years a new type of dispersion of liquid insecticides in extremely fine form has been devised; insecticides dispersed in this manner are referred to as *aerosols*. The degree of dispersion is so great as to make the aerosol act very much like a fumigant; it is readily distributed throughout a space to be fumigated, and the active particles remain in suspension for a long time. Goodhue, Sullivan, and Fales have developed several methods of producing aerosols, one of which [20, 21] involves the spraying of a liquid insecticide, such as orthodichlorobenzene, onto a surface maintained at 375°. Veach and McCauley [22] have devised an insecticide-dispersing machine which operates on the same principle. A second method [23] consists in dissolving the insecticide in a liquefied gas, such as difluorodichloromethane (Freon) or methyl chloride, contained in a cylinder, and releasing the mixture from the cylinder under high pressure. The sudden evaporation of the solvent leaves the insecticidal liquid dispersed in minute droplets. By either of these methods the insecticidal effect of orthodichlorobenzene can be greatly increased over the effect attainable with ordinary spray apparatus.

Colloidal Adjuvants. The most direct application of colloid chemistry to insecticides is encountered in the use of adjuvants or supplementary materials which greatly enhance the value of insecticides, frequently without exercising any toxic effect themselves. Such materials include emulsifying agents, which induce the formation of emulsions; wetting agents, used to displace the air film from difficultly wettable materials and to make a spray spread over the surface; dispersing agents, to make powdered insecticides disperse readily and remain suspended for long periods in water; deposit builders, which increase the amount of active ingredient that can be made to adhere to foliage; and adhesive agents, which protect the insecticidal deposit from premature removal by the action of wind and rain.

It is difficult to classify such materials exactly. They are usually organic colloidal substances, such as soaps, gums, gelatin, and casein, or inorganic colloids, such as bentonite and aluminum hydroxide. In recent years great use has been made of

wetting agents such as are used in textile manufacture, and Cupples [24] has issued a comprehensive bibliography on them.

Colloidal adjuvants have also been used in overcoming undesirable chemical reactions between two insecticides which otherwise are incompatible when used together. For instance, when lead arsenate is added to dilute lime-sulfur solution, the mixture rapidly turns black because of the formation of lead sulfide, and the arsenic originally combined with the lead is transformed into more soluble and hence more plant-destructive combinations. The introduction of casein into the mixture stops, or delays, this reaction so that the combination can be successfully used under some circumstances.[25, 26]

In the making of dry lime-sulfur the ordinary liquid preparation is spray-evaporated, but excessive decomposition occurs unless sugar or some other macromolecular product is added. Likewise, some copper fungicides containing cupric hydroxide, which without protection are converted on standing to the inactive brown oxide, have additions of sugars or colloidal materials to prevent this conversion.

Miscellaneous. During the growing season it is essential that sprays or dusts adhere to the surfaces of the leaves or fruits. The residues must, however, be removed before the products can be marketed. A numbr of preparations more or less colloidal in character have been found of value in residue removal. De Sellem [27] found sodium silicate in concentrations of 53 to 130 pounds in 100 gallons of water to be effective in cleaning apples. The cleaning efficiency increased when foaming occurred, and the waxier the fruit the more easily it was cleaned. McLean and Weber [28] used textile wetting and degumming agents in addition to sodium silicate to increase the efficiency of washing. Diehl *et al.*[29] found that kerosene emulsion with kaolin effectively cleaned fruit which had been treated with sprays containing oil and lead arsenate, and Diehl and Fahey [30] removed fresh oil residue from apples with phosphatic alkali wash (probably trisodium phosphate) at the concentration of 60 pounds per 100 gallons.

The phenomenon of adsorption is frequently encountered in the use of insecticidal fumigants. Many fumigated food products adsorb sufficient fumigant to render their use immediately after fumigation hazardous. Fortunately, the adsorption is an equilibrium phenomenon, and usually the adsorbed poisonous material is easily removed by aeration, with quicker results obtainable by one or more exposures to reduced pressure. Adsorption is also frequently the unsuspected cause of lowering of the effective concentration in a fumigation chamber.

Proposals have been made to adsorb insecticidally active, but too soluble substances on powdered inert materials as a means of producing acceptable insecticides. Thus it has been suggested that arsenious oxide, itself too harmful to plants, be adsorbed on powdered coal.[31] One new and important product has been considered by some investigators as an adsorptive combination. This is nicotine bentonite, in which nicotine is held in relatively insoluble form by means of the colloidal clay called bentonite. C. R. Smith,[32] however, believes that this is a stoichiometric combination of nicotine with the silicoaluminic acids of the bentonite. Markwood [33] has developed a similar product in which nicotine is "adsorbed" on peat to form nicotine peat. Here again the combining power may be ascribed to the humic acids of the peat rather than to adsorption.*

Other examples of the use of supplementary inert colloids are furnished by the work of Goodhue, Sullivan, and Fales.[34, 35] They found that effective aerosols of rotenone could be produced by burning a mixture of derris, cornstalks, and sodium nitrate. The smoke appears to protect the rotenone from agglomeration into larger, less effective particles. The protective action of smoke was confirmed when naphtha-

* The experimental facts are more important than the scientific language used to describe them. Adsorption is based on a residue of the same electronic affinities that are responsible for chemical combination. J. A.

lene was used in place of the derris. When naphthalene is vaporized and condensed by itself, it first forms minute crystals, but they grow rapidly and settle out of the air. If, however, the naphthalene is vaporized in the presence of smoke from burning organic material, the crystals that form by condensation are extremely small, and grow very slowly if at all, so that a permanent and effective aerosol is produced.

The further adaptation of aerosols to insecticidal practice has been greatly promoted by the introduction of the use of solutions of insecticides in liquefied gases, such as Freon-12 (dichlorodifluoromethane) and methyl chloride.[86] These solutions are packaged in small metal containers fitted with easily operated valves. When the liquid is released into the air the sudden and complete evaporation of the extremely volatile solvent leaves the insecticide suspended in the air in the form of droplets or solid particles much smaller than those present in ordinary sprays. A fog or a smoke is produced which suspends for a long time and readily drifts into cracks and crevices and behind obstructions, so that the ultimate action approximates that obtained from fumigants. Pyrethrum extract, DDT,* and nicotine have been applied in this manner, with superior results.

* Dichlorodiphenyltrichloroethane, long known, has recently been found to be a potent insecticide and repellent. It is termed DDT for short. J. A.

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Developments in Electrical Precipitation of Suspended Particles in Gases

HARRY V. WELCH

Western Precipitation Corporation, Los Angeles, California

No observable phenomenon in science has been known to the peoples of the world for a longer time, or in more intimate form, than the discharge of high-potential electricity through gases. The picturesque nature, the brilliance, the hazards, the danger and distinctiveness of a thunderbolt discharge have been evident to the most primitive of peoples, as well as the most highly developed, from before the Stone Age to the present day. Not only has mankind observed the violent explosive type of atmospheric electrical discharge, but has, on occasion, noted the luminous areas of a darkened sky, and observed the "glow" discharge. The arc, flash or spark, and the glow are characteristic electrical phenomena of practical dust, fume, fog, and smoke electrical precipitation plant operation.

Thus, a public and common interest exists for everyone in high-voltage dust, fume, fog, and smoke precipitation. In the last quarter of a century, however, a new and really enlightened point of view has developed in our consideration of smokes, dusts and fumes in mines, industries and city communities, and this is with respect to health hazards, prevention or utilization of wastes, and conservation of our resources. The greater mankind's understanding and effective handling of these factors, the greater his intelligence and civilization. Further, in these health, waste and conservation considerations, as affected by suspended particles in air or gases, colloidal states of matter always appear in some stage or form, and constitute problems, the solutions of which may be expected to fill many new chapters in the succeeding volumes of this treatise.

One of the most visual and distinctive states of matter is that of the gas dispersoids. Discussion of this field of particles suspended in gases (aerosols or dispersoids), and their deposition and recovery by electrical precipitation, constitutes the major portion of the following sections of this chapter.

It would be anticipated that scientific and practical observation and studies in the precipitation of minute or colloidal particles by means of high-potential electrical discharge through gases would necessarily be of relatively late development, and would follow the great discoveries of Faraday, Maxwell, Lord Kelvin, and other great physicists of the nineteenth century. However, it may be noted that an Italian, G. Beccaria,[1] as early as 1771, recorded observations on electrical discharges in "smoke-bearing" gases. This discovery of the precipitation effect of high-potential discharge through smoke-containing gases was rediscovered in 1824 by Hohlfeld in Germany, again forgotten and then rediscovered by Guitard [2] in 1850, once more forgotten and finally rediscovered by Sir Oliver Lodge [3] in 1884. This discovery and work by Lodge led to the first attempt at commercial plant installation at the Dee Bank Lead Works [4] in North Wales, and to the first patents [5] in this field of applied science. At about the same time of Lodge's work in England, Dr. Karl Moeller,[6] in Germany, was exploring this same field of electrical precipitation of smoke, and obtained a patent in 1884.

Fortunately, shortly before Lodge began his work, Wimshurst succeeded in developing his electrostatic high-potential generator. Undoubtedly, the availability of Wimshurst's machine provided a most significant reason for the practical and public interest in electrical precipitation and the resulting activity in patents and attempted commercial operation.

This machine made available a vastly greater supply of high-potential unidirectional electrical current than had been known to any previous investigator. While most striking in its visual effect, it was nevertheless, as extended investigation made evident, totally inadequate to effect precipitation in a commercial installation. For example, tests have disclosed that a first-class four-plate Wimshurst machine is capable of energizing less than a foot of electrode in a test pipe precipitator, and the requirement in a typical commercial installation may run to thousands of feet of pipe electrode, or its equivalent in plates.

Thus, it came about that from a commercial point of view, the most important contribution was that of Cottrell.[7, 8] He incorporated electrical equipment of the electromagnetic type in his precipitator with ample power supply both to charge the suspended dust, fume, or fog particles present in the gases between "discharge electrode" and "collecting electrode," and to cause them to migrate.

Since "electrodes," "treaters," "precipitators," and similar terms, must occur frequently in further discussion of this subject, it is as well to define them briefly. A "precipitator" is a recovery unit for suspended solid or liquid particles in gases, in which the particles are caused to "precipitate" by high-potential electrical discharge between the electrode, termed "discharge electrode," and a second electrode termed the "collecting electrode." The discharge, or negative, electrode is always the electrode of relatively small surface and large angle of curvature, *e.g.*, a wire, an edge, or small rod, while the collecting or positive electrode provides a large surface, relatively small or no angle of curvature, *e.g.*, pipes or plates. Precipitators are also termed "treaters" or "Cottrells." Collection of suspended particles from a gas and onto an electrode surface is termed "precipitation," and the entire operation of removing the dust and/or fume from a gas stream and collecting it in hoppers is often termed "Cottrelling" the gas.

Commonly, four types of particles appear in the gas stream: dust or "fume," and spray or mist (fog), the first two being solid, the last two liquid particles. Dust is defined as the very fine product resulting from fragmentation of large masses; its particles always irregular or angular in form, and are commonly considered to range from 3 to 50 microns in diameter. Of course, it is not possible to define precisely the dimensional limitation for dust, as fragmentation may go to extreme subdivision under unusual conditions of rupture. A special consideration in dusts is that of suspended particles in furnace gases which are sufficiently fusible to reach a plastic, or molten, condition in the gases passing combustion or furnace chambers. The suspended fused particles tend to assume a spherical shape, and for conditions which exist under a gaseous release at fusion temperature during furnace operation, for example, combustion of powdered coal, often have a hollow interior.

"Fumes" are the solid product resulting from condensation of a vapor to solid which has taken place within a body of gas and without contact with containing walls. These particles are normally of minute size, often a fraction of a micron (*e.g.*, zinc oxide 0.3 micron), and in general show a rounded form of apparently amorphous material, although no doubt crystallization has occurred within the apparent noncrystalline exterior form. Fume and fog particles are subject to Brownian movement, which necessitates a mean diameter not exceeding 0.5 micron; the usual expression for range of fume particles is given as approximately 0.3 to 3 microns.

Spray in liquid particles corresponds in dimension to dust in suspended solids; mists (or fogs) in liquid particles correspond to fumes in suspended solid particles.

The collection of a suspension of fume, dust, or mist, as dispersed in a gaseous

medium, is essentially a modern problem. It is of interest from a scientific point of view as a widely prevalent problem in colloidal particle mechanics or chemistry, and industrially from the several points of view of material loss and value, health hazards from inhalation of dust and fumes, factory cleanliness or good housekeeping, and community or public relationship and interest. Our knowledge of today, and our means of testing and investigation, have greatly raised the standards of hygienic and health conditions; at the same time our development and extensive use of high explosives in rock work and our highly centralized, large and hard-driven industrial operations have enormously increased the amount and concentration of particles in all size ranges, from colloidal dimension up to gravity-settling coarse particles, as dispersed in gaseous mediums. The fraction which does not readily settle is usually designated as "smoke" [9] and may be defined as an aerosol, a dispersoid or suspensoid.

Electrical precipitation is not the only means at our disposal of collecting and recovering suspended particles in a gaseous medium, and if we are properly to judge its value for present conditions, and its possible future contribution to applied science, it is in order briefly to set forth the several other means of collection at present practiced, or which have served as a collection means in the past.

Anderson [10] considered five, and only five, procedures or methods of separation of suspended particles from gases: (1) gravitational method, illustrated by ordinary settling chambers, (2) inertial procedure, illustrated by baffle chamber and centrifugal apparatus, (3) filtration, illustrated by the baghouse and bag collectors, (4) sprays, as illustrated by scrubbing towers, and (5) electrical precipitation, as illustrated by the Cottrell process. Settling chambers are of reasonable efficiency on coarse particles (a 50-micron particle approximates a settling rate of 0.5 foot per second); but as industry is ever proceeding toward furnacing of finer and finer materials, they have been little used in recent years. Cyclones, as representative of the second class, are widely used, being relatively cheap and effective to a certain degree. As the efficiency of this type of equipment increases with decreasing diameter and increasing angular velocity, later years have seen the development of apparatus having a multiplicity of small and usually tubular cyclones, all serving in parallel. This development in mechanical and centrifugal apparatus has been more particularly discussed by Lissman [11] and Anderson.[12] This equipment finds wide usage in problems of dust (not fume) abatement. It is available in economical forms for both small and large gas volumes, and while requiring an appreciable pressure drop across apparatus for both capacity and efficiency, it is within the range of the general run of induced fans or exhausters on the market, and in a few cases, and with elevated temperatures, is satisfactorily operated by the draft from high stacks.

Baghouses can be built to collect very close to 100 per cent of suspended solids in gases (either dusts or fumes), but they are bulky, good ones being relatively expensive, both as to power requirements and first cost; they are strictly limited to that temperature and nature of gases which are reasonably well resisted by the usual cotton or woolen fabric used. Glass cloth and asbestos cloth bags have not come into wide use, probably due to first cost, and lack of the same degree of efficiency in cleaning and laundering as experienced with cotton or woolen materials. In general, baghouses meet the needs of many industries but are never very popular because of inherent characteristics of woven fabrics, their relatively short life, and gradual building up of deposits in filter-cloth openings, the latter either restricting capacity or increasing pressure requirements.

Spray towers, scrubbing towers, and the like, if of the more usual simple open construction, are fairly efficient only on relatively coarse dusts. To increase efficiency it is required to decrease the size of the spray particles and greatly increase their number, or provide an extensive surface of contact such as is found in a packed tower. The latter usually operates at a high pressure drop and is readily choked; the former requires greatly increased power to break up the larger droplets into the fine par-

ticles. In general spray, or scrubbing, towers are relatively inexpensive to build, simple to operate, and where there is no objection to wet collected material, find a field of broad usefulness.

Electrical precipitation is used for both wet and dry collection of dust, fume, spray and mist. Its application extends throughout the industries, both metallic and non-metallic, for chemical and power plants, and for both materials recovery and gas purification.

Considering the fact that in many metallurgical operations weight of furnace gases is from 5 to 20 times the product made, it is evident that as a machine or apparatus, electrical precipitation installations do handle an exceedingly large tonnage of material, which perhaps is not so evident at first glance. Examples of its service are to be found, for the field of metallurgy, in iron and steel plants,[13] copper smelters,[14] lead and zinc reduction works,[15, 16] metal refineries, [17, 18] and in the recovery of by-products such as arsenic [19] and sulfur.[20] In the non-metallic industries, precipitation installations are associated with cement mills [21, 22] by-product potash [23]; dryer installations [24]; power plants,[25, 26] and the like. In pulp and paper mills, soda and sulfate fumes are recovered from black liquor recovery furnaces.[27, 28] In chemical plants, electrical precipitators recover mists of sulfuric and phosphoric acids; and in the special field of gas purification [29, 30, 31] for subsequent use, for example, the treatment of gases containing So_2 for contact-acid manufacture,[32] the purification of iron blast-furnace [33] gas for gas engines and stoves, and removal of tar fogs [34, 35] from manufactured gas plants, electrical precipitators function most satisfactorily and find a field of ever-widening usefulness.

Theory, development, and practice of electrical precipitation have been covered by many investigators and for many special considerations. Cottrell [36, 37, 38] has offered discussions of the widest interest in this country, and many other investigators [39, 40, 41] here, as well as in Europe [42, 43, 44] and Great Britain [45, 46] have added to the literature. Strong [47] offered a rather extensive study in Vol. 3 of this series.

His consideration provides a good deal of mathematical treatment of the phenomena of electrical discharge in gases with special reference to the conditions existing between electrodes in an electrical precipitator. Wolcott [48] investigated the effect of varying characteristics of deposits on collecting electrode, developed the theory of "back ionization," and the descriptive terms of "porous dielectric," "semi-" and "non-conducting" deposits, and the like. Schmidt [49, 50, 51] has contributed to the literature of electrical precipitation over a period of many years. His earliest work reported effective precipitation of dusts and fumes in hot cement mill gases by higher potentials, and the utilization of smooth or "fine"-wire ionizing or discharging electrodes,[52] as distinguished from the earlier pubescent [37] or serrated ionizing electrodes of Cottrell; his later work [53] opened up the field of two-stage precipitation. Anderson [54, 55] reported studies in the field of satisfactorily conducting gases and precipitated deposits. These studies led to a precipitation equation involving a constant for given material and gas conditions. Berthelot [56] and Lind [57] have discussed chemical activity as associated with corona glow or electron emission.

An exceedingly large literature prevails in the special field of definition, control and effect of suspended particles in gases with respect to matters of health and growth. Such investigations [58, 59] cover metallic and non-metallic dusts and fumes, factory smokes, organic plant products, such as pollen and spores and air-borne bacteria and virus, many of which are submicroscopic in character. Of these reported studies, a representative constituent part is devoted to precipitation by electrical means.

In theory, electrical precipitation requires two successive or simultaneous physical phenomena: first, such an electrical source as will cause a particle, either solid or liquid suspended in a gaseous medium, to become electrically charged, *i.e.*, carry an electrical charge; second, provision of a unidirectional electrostatic field sur-

rounding such a charged particle—both of sufficient magnitude to cause migration of the particle to the electrode of opposite polarity and deposition of particle upon it. When this occurs, the particle should, in the ideal case, immediately lose its electrical charge and then become integral with the collecting electrode. However, in practice, additional physical factors at the electrode surfaces must be given consideration, as such factors and their variation greatly affect capacity, efficiency, and operating characteristics.

The several physical characteristics of precipitation phenomenon may be briefly described as follows:

Charging of suspended particles in gases: Since the fundamental phenomenon of electrical precipitation is based on mechanical movement of an electrically charged particle by the force existent in an electric field, it is essential that the suspended particle be electrically charged. Undoubtedly it was lack of knowledge or underestimation of this factor that delayed the technical development of electrical precipitation for so many years after the work of Sir Oliver Lodge. In fact, it was the thorough realization of this important factor that enabled Cottrell to accomplish his successful development. Current flow from an electrode into a gaseous medium occurs under proper adjustment between voltage and angle of curvature of the electrode. It is an electron emission, a Coulomb force effective only in an area adjacent to a metallic electrode surface. The overall effect of the emission of electrons is to charge gas particles; that is, under usual operating conditions with discharge electrodes negative, electrons constitute the electrode emission. On leaving the electrode they immediately contact neutral gas molecules and ionize them. Then the negatively charged gas particles, under the influence of the electrostatic field existing between the two electrodes, begin migration to the opposite electrode, termed the collecting or grounded electrode. The movement of charged gas particles under the steep potential gradient with it along numerous uncharged gas particles, the effect producing a windage commonly designated the "electric wind."

Charging of suspended particles is accomplished by collision of charged gas particles and neutral dust particles; as a result of this impact a portion of the electronic charge is transferred from gas particle to suspended solid particle; and under the influence of the electrostatic field between the positive and negative electrodes these charged dust particles immediately begin a migration to the electrode of opposite polarity.

It is usual practice in a precipitator, within which both charging of the particles and their electrostatic migration under influence of the high-potential field are accomplished simultaneously (*i.e.*, single-stage precipitation) to have the negative electrode of high angular curvature (*e.g.*, fine wire or edge), and the positive electrode of low angular curvature (*e.g.*, pipe) or zero angle of curvature (*e.g.*, plate). In precipitation of dusts and fumes, and where production of ozone is a matter of no consequence, a more copious ionization prevails, or a greater electron discharge exists for a maximum prevailing voltage when the discharge electrode is negative than when it is positive. The further fact that from one-fourth to one-third higher potential difference between electrodes may be normally maintained in a satisfactorily conducting gas with a negative discharge than with a positive discharge electrode is of significant importance in commercial installations. In effect, as is the case with other forms of energy utilization, the product of the pressure (*i.e.*, voltage difference between electrodes) and the quantity flow (*i.e.*, ionization effect or electron discharge, or corona loss, all expressing a current flow between electrodes) provides a means of measuring efficiency and gas volume capacity in given units. In a physical interpretation it is found that for each specific set of conditions (for example, type of dusts, temperature, state of condition or relative conductivity of dust and gases, type, size, and kind of electrodes), a definite quantity of precipitating energy will be emitted per unit length of discharge electrode, *e.g.*, wire edge or small

rod. Such energy discharge as corona glow or loss, or electron emission and ionization in gases, is the precipitation current flow; other conditions remaining constant, this is a measure of the efficiency of suspended particles removed from the gases. Thus, since a fraction only of the ionized or charged gas particles encounters dust particles and transmits charge thereto, actual charging of particles is a percentage effect. Thus, disregarding the effects at electrode surfaces and of deposits thereon, precipitation under a given set of conditions follows a logarithmic relationship between percentage recovery and length of effective electrode; the latter expresses time of contact of gas within the electric field. Thus, Anderson [55] expressed the relationship in the following formula:

$$1 - E = CK^t$$

where $E =$ precipitator efficiency
$t =$ time of treatment of gases and suspended particles in electrical field or time of passage of gases through precipitator
$C =$ type of precipitator
$K =$ a constant; expressing precipitation characteristics of gases suspended and precipitated particles

Regarding the equation of precipitation, W. A. Schmidt [50] makes the following comment:

"It should be emphasized that the equations pertaining to precipitation efficiency apply only while normal precipitation is being performed. If a porous dielectric deposit is accumulated upon the electrodes, and back ionization is established, normal precipitation is obviously interfered with, and these equations can no longer be applied. It should also be emphasized that the precipitation constant is in itself a variable and that its value is only constant for a specific set of fume and gas conditions, and shifts with changes in gas composition, temperature, fume composition, fume concentration, physical state of subdivision of dust or fume, etc."

Taking as an example a mist precipitator wherein no complications exist at the collecting electrode, since mist particles are immediately discharged on precipitation and are continually removed as a liquid discharge from electrode to sump, Anderson [55] offers the following table as illustrating the consistency of the precipitation constant K over a wide range of plant efficiencies. Data for equation $1-P = K^t$ are from precipitation tests:

P % Eff.	t seconds (gas passage)	$K \times 10^3$ (Calculated)
73.7	0.46	55
80.0	0.56	56
86.8	0.69	54
93.4	0.93	54
95.2	1.05	55
98.1	1.40	59

However, in the practical field of electrical precipitation only a minor proportion of the plants, built to meet the existing collection problem, is confined to precipitation of substantially perfect liquid mist conductors, such as weak alkali or acid mists or tar fogs. The great majority of precipitation installations, or probabilities and possibilities, are associated with collection of suspended solid dusts and fumes; and in this field of solid deposits on electrodes we encounter phenomena of a very special order. It is an obvious observation that if charged particles migrate across the electric field and to the collecting electrode, and upon deposition there do not lose their charge, actual precipitation will very quickly come to a stop and ionization current and effect will be suppressed. In practice, however, no such deposit is ever completely lacking in some electrical leakage to ground; so it could be stated theoretically that a sufficiently large precipitator would always permit the desired degree of efficiency to be obtained. Nevertheless, a practical limitation on size for any given

gas volume and efficiency is evident, and much study has been given to means which may be utilized to vary characteristics of the deposits in a favorable manner; this has been termed "conditioning" the deposit.

In the above consideration it is the rate of loss of charge from the collected deposits, for given gas volume and precipitator size, that determines efficiency, rather than the available normal energy flow from the discharge electrode, expressed as feet of discharge electrode, as first discussed and under which immediate discharge of collected particles at collecting plant surface was assumed. Thus, since the rate of discharge of collected deposit is dependent upon the area of the collecting electrode, the general formula still holds, with the time t now representing, for example, the cubic feet of gas treated per second per square foot of collecting electrode surface.

Wolcott [48] was among the earliest investigators studying and reporting effects of deposits in the electrical precipitation process. He expressed the character of the deposit as a porous dielectric of three characteristic forms as far as electrical conductivity is concerned, *viz.*, "good," "poor," and "non-conducting" deposits. These three significant types of deposits merit particular description and discussion.

"Good" conducting deposits indicate themselves by smooth and continuous uniformity of operation, with inappreciable difference as to whether electrodes are dust-covered or substantially free of deposit. That is to say, the precipitated deposits immediately lose their electrical charges and become electrically integral with the collecting electrode. Such operation is characteristic of the collection of dilute to moderate-strength sulfuric acid and phosphoric acid mists, suspended solids in gases from sulfide roasters, such as copper and zinc sulfide concentrates, oil and tar mists, etc.

"Poor" conducting or "semi-"conducting deposits constitute the vast majority of suspensoids in the commercial field. Satisfactory precipitation of these is brought about in a practical way, by two procedures: first, conditioning of suspended particles to increase their conductivity; and second, by providing a relative increase in precipitator size. Semi-conducting deposits are actually a kind of porous dielectric which, in an electrical field such as exists in the usual type of precipitator, produces a condition commonly termed "back-discharge." It is illustrated by points of glow, *i.e.*, ionizing centers, appearing on the collecting electrode deposit. With their extension over the deposit the effective voltage (defined as sparking and not arcing) which can be maintained between the two electrodes is reduced 30 to 50 per cent, the current increases very substantially, and precipitation tends toward the zero point. It may be inferred that the deposit, producing such effects as above enumerated, is discontinuous in nature and that between the precipitated particles, or rather agglomerates of particles, there exist minute open spaces, or pores, which persist as a more or less continuous interstitial medium to the wall of electrode. The latter, at the high potential between the electrodes and in view of the exceedingly sharp angle of curvature at these minute openings, provides a favorable condition for electrical discharge and gaseous ionization to develop at the positive or collecting electrode. The effect of an ionization discharge from both the discharge and collecting electrodes is first, that a readily ionized gas is provided between electrodes, whereby a major portion of the available electrical energy is dissipated without beneficial use in precipitation; secondly, that negatively charged suspended particles moving toward the collecting electrode have their charge neutralized by positive ionized gas molecules coming from the positive electrode, with the result that the migration of the moving particles is arrested and they then escape as neutral, uncharged particles; thirdly, that a certain proportion of the suspended particles relatively close to the positive electrode are positively charged, and on migration toward the opposite electrode encounter negative migrating particles. From the mutual attraction and collision of such negatively and positively charged suspended particles neutral, uncharged particles result.

While a porous and poorly conducting dielectric is typical of the majority of deposits, a few are known which under very special conditions of dry gas and dry deposit do give a non-porous or non-conducting deposit so uniform as to function as a nearly perfect electrical insulating layer. Zinc oxide fume received directly from a combustion chamber in which metallic zinc vapor has been burned offers an example. Starting with a clean precipitator pipe, a prevailing reasonably high voltage (*e.g.*, 60 KW) and typical switchboard readings on a primary supply of say 350 volts and 8 amperes, it would be noted that the first minute or two of operation shows no escaping zinc fume at exit of pipe; after this there is a visible discharge increasing with time, until in the course of 10 to 15 minutes the entire fume content of the gases is escaping. In the meantime, and corresponding to increased loss to the atmosphere, the primary current flow will have decreased to a figure too small to be read, the primary voltage will have reached the line voltage of 420 volts, and the voltage between electrodes will have reached a transformer ratio of approximately 75,000 volts. This set of readings is almost the reverse of the experience with a porous dielectric where, as the test proceeds and efficiency decreases toward the zero point, the primary amperage increases to maximum transformer capacity, the primary voltage falls, and the voltage between the electrodes decreases very substantially.

While freshly made and directly treated dry zinc oxide fume shows the special character of deposit discussed above, it should also be pointed out that in general commercial furnace gases carrying zinc fume show, upon precipitation, the characteristics of a semi-conducting, rather than a non-conducting, electrode deposit. This is due to increased quantities of other constituents present, to additional time factors, to some increase in humidity, and the like, all of which promote agglomeration between suspended particles; and it is the large accumulation of precipitated agglomerates that appears to promote the semi-conducting character of deposited layer.

It has been known for many years that the presence of water vapor and water particles within the gas undergoing treatment in an electrical precipitator serves greatly to increase the conductivity of the deposit. This is interpreted as effecting a layer of water molecules which provides a conductivity around and/or through the suspended particle. For example, Wolcott [48] found in laboratory tests that a content of 1 per cent moisture in zinc oxide fume was sufficient to render the dust conducting and to prevent a lowering of the arcing voltage. On elemental sulfur dust, 2.25 per cent moisture was insufficient and 2.91 per cent was sufficient to change the electrode deposit from a non-conducting to a conducting deposit. However, in practical plant operation it is not possible to secure the same ease or control or uniformity of surface distribution as in laboratory technique, and so in general such plants as lead smelters, various reclaiming zinc and lead furnaces, operate in such manner that a minimum of about 2½ per cent moisture appears in their collected product.

While water vapor and water fog are the most widely used and usually the cheapest means of conditioning inlet gases to Cottrell Precipitators, such operation is not limited to water alone. It has been found that, in special cases, oil mists have been particularly effective in conditioning, and in other cases mere traces of acids added to the gas stream have provided astonishingly good results. The addition of good conducting dust (such as graphite, or metallic and oxide compounds of iron), cooling, mixing of two gases, one carrying favorable, the other less favorable suspended solids, all have their interest and special cases of beneficial use.

For a time a good deal of argument was forthcoming as to whether conditioning (or the bettering of conditions for the maximum precipitation) was required within the gas or on the surface of suspended particles. While operations at numerous plants widely varying in character of gas and nature of suspended particles have not always shown concordant results, the general trend of experience has indicated a

desirable advantage in maintenance of high voltage between electrodes and minimum of arcing with appreciable percentages of water vapor present in the gases. For example, the gases from "wet" process cement plants with perhaps 33 per cent water vapor content, show much less irregularity in electrical effects than do gases from "dry" process cement plants with only a few per cent moisture present at operating temperatures much above the boiling point of water, say 600 to 700° F. Nevertheless, the effect of conditioning gases is a minor consideration compared with the beneficial effects derived by conditioning the electrode deposit. For example, Wolcott observed that with a certain lead smelter fume containing appreciable quantities of free sulfur with 2.25 per cent moisture present there occurred a lowering of the arcing potential to nearly half that obtainable with 2.91 per cent moisture present in the gases. Similarly, zinc oxide fume was a poor conductor with moisture content below 1 per cent but above this figure it became a good conductor; *i.e.*, back-ionization and lowering of arcing voltage prevailed below 1 per cent moisture but not above that point.

It is not always essential that the conditioning medium be present in the form of particles admixed with the precipitate. For example, beneficial effects of water as a conditioning agent may exist well above its boiling point; its nature and effect are those of condensation upon the particles of precipitate; the condensation need be only one or two molecules thick for a satisfactory effect. An assumption of a molecular condensation upon precipitated particles seems essential to explain the striking effects sometimes observed on precipitator operations by mere traces of an acid such as SO_3. Certain oil- or tar-conditioning agents such as mist or vapor also fall in this same field of probable condensed films.

Even with such provisions as above enumerated providing for maximum efficiency of precipitation, it is to be observed that in maintaining an ionizing or corona glow, current flow at effective potential between discharge and collecting electrode, and the like, certain physical or practical considerations are involved which may be further discussed here. Corona glow or electron emission from the discharge electrode, which is the "precipitation current," is dependent upon the angle of curvature of the discharging electrode and the voltage between electrodes. In the laboratory and even in smaller commercial units with relatively stable operating conditions, such as in building-ventilation air streams, it is possible to use exceedingly fine wire discharge members and thereby reduce spacing and potential necessary to effect precipitation; but in larger industrial plants a degree of ruggedness is required to permit vigorous rapping of the electrode system to remove deposits and to tolerate the sparking and occasional arcing to which such units with their widely varying conditions of operation are subjected. A wire $\frac{1}{16}$ inch in diameter is about the smallest that commercial practice will justify, and twice or three times this diameter or its equivalent in sharp-edged (*e.g.*, twisted square rod) discharge members is preferable. Such requirements necessitate a voltage minimum of the order of 35 to 40 KV and a minimum spacing between electrodes of the order of 3 inches. It is true that Cottrell in his early commercial work, wherein he was limited to power units of about 25 KV, secured a satisfactory ionization effect by using at first his "pubescent electrode" [37] —a compound electrode of asbestos fiber held between twisted wires—and later his "serrated electrode," [37] likewise a compound electrode of two wires or strips of metal with serrated mica strips mounted between. In these two electrodes the angle of curvature premitted by the asbestos fibers or the sharp edges of the mica offered a high degree of curvature and thus provided for electrical discharge. However, for service in hot gases such as prevail in the exit flue from copper smelters and cement plants, such compound electrodes proved unsatisfactory, and at a higher voltage difference between electrodes, a smooth small or "fine" wire discharge electrode member was substituted.

Horne [60] has shown at higher voltages that the separation between the sparkover

and arcover voltage with increasing voltage continually widens, with the arcover always the higher voltage. For practical operation this matter of the difference between sparking and arcing potential is of appreciable importance, since it is common practice to operate a precipitator at its sparking potential. The greater the difference between sparking and arcing potential the less detailed attention the plant will require. Horne has also shown that the difference between the maximum voltage which can be maintained between discharge electrodes, negative and positive, also increases with the voltage applied, and that the negative is always roughly a third to a fourth higher. It may be noted that at relatively low voltages, under 5 KV, the positive and negative curves intersect, and that at still lower voltages the positive is even slightly greater. It is important to maintain the maximum operating voltage, that is, the sparking voltage between the discharge and collecting electrode, as the efficiency of precipitation roughly varies with the potential which is consistently maintained.

Of all the varied industries in which electrical precipitation has found, or yielded, a service, no single application is so near that of a classical example as is the service it performs in the purification of mineral sulfide roaster gas for contact-acid manufacture. In the gases coming from the roasting of copper, zinc, lead, and iron sulfide ore, there are nearly always minor amounts of many other elements and compounds. Of these arsenic is the most objectionable and the most difficult to remove to a sufficient degree for contact sulfuric acid manufacture. It is common practice to use the minute particles of arsenic trioxide as centers of nuclei for liquid mist formation, the latter resulting either from spraying the gases in one or more spray towers or from passing the gases through a packed tower fed at its top with an abundant water or dilute acid supply. Usually such precipitators are entirely of sheet lead for shell, collecting electrodes and headers, of lead-covered iron wire with star-shaped circumference for discharge electrodes, and with electrical insulation effected through oil seals and outside porcelain supports. Such a type of precipitator is made to operate so completely for the removal of suspended particles that a Tyndall beam passing through a thickness of 5 meters of the purified gas will not make visible any floating particles. This is a considerably higher degree of cleanliness or freedom from suspended particles than the ordinarily quiet air of room or yard. Such quality of gas to a contact mass means its continual functioning over long periods of time at high percentage conversion without the usual ill effects of arsenic poisoning.

In purification of iron blast-furnace gases, particularly for gas-engine utilization, but also to insure most beneficial and continuous use of blast furnace stoves, practically as good a degree of cleaning is secured in steel pipe precipitators with the walls of such pipes continuously flushed by a water film, *i.e.*, a film-type precipitator.

The previous discussions have been confined to that particular type of precipitator in which both charging the dust particles (through an electron emission from discharge electrode) and their migration under the potential difference between electrodes and in the direction of the collecting electrode and grounding thereon, have been accomplished simultaneously between the same pair of electrodes. This is termed single-stage precipitation. Electrical precipitation is not limited, however, to this procedure, but may also be accomplished by charging the particles in one section of equipment and following this up by an electrostatic field between two plates (or at least with neither electrode functioning as an ionizing electrode) in which the charged particles are moved to the collecting electrode and there deposited. Since the secondary or precipitating section is without a high degree of ionization in the gaseous medium, such effects as back-ionization, lowering of arcing voltage, and the like are materially reduced, if not entirely absent, and it should be possible to treat most types of suspended particles regardless of whether they are dust or fume. Such a precipitator has been termed a "two-stage precipitator." [58] Two-stage precipitation has found effective service in air-cleaning in small units, as witness the

wide distribution of the Westinghouse development of an electrostatic precipitator, now known as the "Precipitron." This unit is used for home, office building, hospital and factory ventilation service.[41, 58, 59, 61, 62, 63, 64] In handling the often serious dust menace of pulverizing and grinding plants of mines and loading equipment a special type of two-stage water-film precipitator has been developed by Western Precipitation Corporation. No doubt when due recognition is given to the obligation that each unit of production must control its own dust and fume problem, much new equipment and many modifications of old equipment will find some degree of usefulness; and certainly much promise exists in the field of precipitation by electrical particle-charging and static-field precipitation.

The "Precipitron" unit has been designed primarily for ventilating air where collection of solids is almost infinitesimal in amount compared to the gas volume treated. Westinghouse, therefore, uses wetted or oiled collecting plates, a very small spacing between plates, and consequently a relatively low potential; the particle charging is effected from a very fine wire ionizing stage preceding the collecting stage. At relatively low electrode potentials (small spacing between electrodes) positive discharge from the ionizing electrode shows less ozone formation and a more favorable position of sparkover to arcover at maximum operating potentials than does the negative discharge. This arrangement is practiced in the "Precipitron."[41, 62] As mentioned earlier, this type of operation with minimum spacing and corresponding electrode potentials is the reverse of that found most effective in cases of heavy dust loading, which necessitate greater spacing and voltages for advantageous precipitation such, for example, as is the case in copper, iron, and lead smelters.

While a large proportion of electrical precipitators have been installed purely as commercially productive pieces of equipment and are based on value of reclaimed material, a lesser number have found their justification in the betterment of health and living conditions, effected by prevention or suppression of the discharge of the noxious products of a hard-pressed, driving and centralized industry into the atmosphere we live in and breathe. The future will probably see this ratio of commercialism to good housekeeping reversed, and withal of much real net profit in health, as well as material reclaimed for the community.

If one may be permitted to look to the future, and to the type of industrial enterprise and city environment that seems right and fair, we shall behold our cities free of the grime, smoky haze, acid, tar and chemical fogs (*e.g.*, "London Fog"), and the eternally settling ash and soot. Moreover, tunnel and hard rock miners using large quantities of explosives will be reasonably free from fine rock dust and its accompanying health hazard (silicosis); and the wear and deterioration of homes, factories and other structures and all manner of moving equipment and machinery will be lessened. This is all a possibility today, including in our sources of control all other means of dust collection as well as electrical precipitation. The latter, with construction at present too bulky and expensive, and operation requiring skilled service and attention, has not been able to meet these pressing needs of our modern civilization at a price that industry and householders could or would be willing to pay. However, in the several well staffed research and development laboratories now pushing forward investigations covering both scientific and applied scientific studies in electrical precipitation of suspended particles in gases, there is much promise of future achievement and of results that will eventually be a source of satisfaction, enjoyment and improved health conditions.

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Dispersions of Finely Divided Solids in Liquid Media

EARL K. FISCHER † AND DAVID M. GANS ‡

Interchemical Corporation, New York

The branch of colloid chemistry which deals specifically with the solid-liquid interface is of great industrial importance. Pigment, paint, and printing ink are examples of the products. The audience for helpful laboratory data and theories is composed of technicians who of necessity maintain quality control by empirical testing procedures, and their need for background information of greater scientific exactness has increased within the past decade. Methods for the study of the solid-liquid interface, drawn from all the resources of physics and chemistry, have been greatly improved in this period. In particular, the conception of the dimension of dispersed particles has been clarified by electron-microscope and gas-adsorption techniques. Rheological measurements, too, have contributed to an understanding of the mechanical processes of dispersion and the working properties of various products during application.

This chapter is a resumé of the physical attributes of these solids and liquids and the modifying agents commonly brought together by a variety of instruments for mechanical dispersion. The review will necessarily touch on the following topics: (a) terminology, for some of the words have very special meanings and not all investigators are careful to distinguish subtle differences and connotations; (b) a visualization of the states in which finely divided solids may be found in liquid media; (c) an examination of the dimensions or particle sizes of the dispersed phase; (d) the physical properties of the dispersion media which have been found thus far to have a significant bearing on the character of the solid-liquid system; (e) commercial instruments and operating methods for the comminution of the particles to their final or ultimate sizes; (f) the physical and colloidal properties of the dispersions so prepared; and finally, (g) illustrative examples drawn from industrial practice.

The continuity of this account will, of course, be broken by uncharted regions where at present there are gaps in recorded knowledge, but this inevitable deficiency is also an asset, for it points to profitable fields for research. It will be desirable at the start to interpolate a glossary, so that there will be no uncertainty in the meanings of the terms used.

GLOSSARY [88]

Body: A practical term widely used to give a qualitative picture of consistency. For Newtonian liquids, it is synonymous with viscosity.

Consistency: That property of a material or composition which is manifested by its resistance to flow. Consistency is an unresolved composite of several properties, each well defined and measurable as plastic viscosity, yield value, and thixotropy from the complete, force-versus-rate-of-flow curve. Consistency is a term applied to a variety of materials. For Newtonian liquids, it is simply viscosity. While consistency is an accepted rheological term it has qualitative meaning only, and is used with qualifying adjectives, such as "buttery," "thin," "high," etc., in describing plastic flow.

Deflocculation: State of a dispersion of a solid in a liquid in which each solid particle remains geometrically independent and unassociated with adjacent particles. A deflocculated suspension shows very low, even zero, yield value.[50]

† Present address: Institute of Textile Technology, Charlottesville, Virginia.

‡ Present address: Quaker Chemical Products Corporation, Conshohocken, Pennsylvania.

Dilatancy: Property of certain suspensions in which the resistance to flow increases at a greater rate than the increase in rate of flow. (See *Newtonian Flow, Plastic Flow, Pseudoplastic Flow, Thixotropy,* and *Yield Value*). Quicksand or wet sea sand is a familiar and spectacular example of dilatancy. If the surface is struck sharply, the sand is rigid and solid; but slow, sustained pressure causes the sand to flow and an object to sink into the mass. Dilatancy in a pigment-vehicle system commonly results from high pigment loading.

Dispersion: Any composition, process, or state, relating to heterogeneous systems composed of solids, gases, or liquids. This term is sometimes used loosely with special meanings which are often implied but not defined, especially when it is modified. For example, in paint and printing ink technology a "good" dispersion usually means one in which a pigment is not only finely divided but also deflocculated in the vehicle. If aggregates are present in the dispersed phase, the material is considered without exception a "poor" dispersion regardless of the state of flocculation. If the pigment particles are finely divided but flocculated, the material has been called variously a "good" and a "poor" dispersion.[41]

False Body: A practical term generally synonymous with thixotropy (*q.v.*). When a composition "thins down" on stirring and "builds up" on standing it is said to exhibit false body. The term "false body" is also used in practice for "buttery" materials characterized by a relatively low viscosity and high yield value.

Flocculation: The formation of clusters of particles separable by a relatively weak mechanical force or by a change, as in chemical composition, at the interface between the particles and the suspending phase. Flocculation is often visible as a "Jack Frost" pattern in a flow-out of a dispersion; microscopically, it appears as a lace-work or reticulation of loosely clustered primary particles. A flocculated dispersion of sufficiently high pigment concentration shows yield value. Surface-active agents are often useful in reducing the extent of flocculation and hence the yield value.

Flushing: The process by which pigments in aqueous dispersion are transferred directly to oil dispersion by agitation with oils, accompanied by displacement of water. The terms *flushing* and *flushed* colors have been applied to nearly every variety of the process and have become associated with dispersion procedures which avoid the procedure of drying of the pigment pulp, dry grinding, and grinding the dry color in oil.

Newtonian Flow: The type of flow characterized by a rate of shear that is directly proportional to the shearing force. Newtonian flow can occur, at least ideally, under the influence of an infinitesimally small force. It is to be distinguished from plastic flow which occurs only when a finite minimum force is exceeded. Oils, at sufficiently low rates of shear, exhibit Newtonian flow. The curve obtained for a Newtonian liquid on a rotational viscometer of the Couette type (rpm vs. deflection of torsion dial) passes through the origin.[53]

Oil Absorption: The quantity of oil required to wet completely a definite weight of pigment to form a stiff paste, when mechanically mixed. The oil absorption number is the grams of oil per 100 grams of pigment or pounds of oil per 100 pounds of pigment to form a stiff paste when mechanically mixed. The quantity described by the term "oil absorption" is frequently used as a measure of plastic viscosity. As such it is an indication of the crudest sort and its use can lead to unpredictable results, since oil absorption as measured bears little relation to the rheological properties of a finished mill-ground pigment dispersion. Oil absorption has meaning of a qualitative sort, however, in relation to a preliminary mixer operation.

Plastic Flow: The type of flow which occurs in materials possessing yield value (*q.v.*).

Plasticity: That property of a material which enables it to be continuously deformed without rupture when acted on by a force sufficient to cause flow and allows it to retain its shape after the applied force has been removed. Plasticity, like consistency, is a qualitative term, representing a composite of physical properties. The word stems from Greek and Latin roots that translate to "mouldable." It is a word closely allied with the historic ceramic arts.

Pseudoplastic Flow: The type of flow where the rate of flow increases faster than linearly with shearing stress, typified by a consistency curve which shows no intercept on the force axis. Certain types of materials, such as solutions of rubber, resins, and cellulose esters, give non-linear curves when sufficiently concentrated. Bingham has called these substances pseudoplastics and Ostwald refers to them as having "structural viscosity."

Seeding: Spontaneous formation of particles of comparatively large dimensions in a solid-liquid suspension.* The formation of "seeds" in a suspension can arise from two chief causes: (a) localized gelation of the continuous phase (vehicle) as in unstable resin solutions; (b) the flocculation and subsequent cementation of the discrete solid particles, usually as a result of the selective interfacial adsorption of a third component or phase, perhaps with concomitant chemical reaction.

* This seems analogous to "island formation" referred to in the paper of J. V. N. Dorr and Lasseter in this volume. J. A.

Surface-active Agent: A compound which in small relative quantity modifies the physical properties of a heterogeneous system by adsorption at an interface. The change is considerably greater than any law of mixtures would predict. This term is generic, and since these compounds are employed in many different industrial operations, a variety of terms has become associated with the subject. The most widely used, next to surface-active agent, is *wetting agent*—to indicate improved spreading qualities of a solution or a suspension over an initially repellent surface. *Penetrating agent* suggests an increased degree or more rapid passage of liquid into a porous solid. Often, in connection with powdered solids dispersed in liquids (pigment in a paint vehicle, for example) the term *dispersing agent* is used with the meaning of *deflocculating agent*. If the process is primarily cleaning or soil-removal, *detergent* is the term applied. An *emulsifying agent* is a compound which stabilizes the dispersion of one liquid in another liquid where the two are immiscible; an oil-in-water emulsion is a common example.[36, 41]

Tack: Pull resistance exerted by a material adhering completely to two separating surfaces.[52] In liquids, tack is a function of viscosity; in non-elastic plastic materials, tack is a function of plastic viscosity and yield value. Cohesion becomes negligible since rupture occurs at very small areas. Tack is measured in dynes.

Thixotropy: The property of a material which causes it to undergo an isothermol gel-to-sol-to-gel transformation upon agitation and subsequent rest.[53] A complete transformation from a gel to a true sol is not a prerequisite for thixotropy; partial transformation is all that is necessary. Thixotropic breakdown on mechanical agitation can be obtained by prolonging the time of agitation at a constant rate of shear until an equilibrium is reached. To obtain further breakdown, the rate of shear must be increased. For a complete discussion of this phenomenon see the chapter by H. Green and R. N. Weltmann in this volume.

Viscosity, Plastic: The resistance to flow in excess of the yield value in a plastic material. The coefficient of plastic viscosity is the force, in dynes/cm^2, in excess of the yield value, tangentially applied, that will induce a unit velocity gradient.

Wetting: The formation of a solid-liquid interface. This term, like *dispersion*, is used loosely with implied but undefined meanings. A solid-liquid suspension with the solid particles deflocculated is usually designated as "well wetted" or as showing "good wetting," while one in which the dispersed phase is flocculated is described as "poorly wet."[41]

Yield Value: The minimum shearing force which must be applied to a plastic material to start laminar flow. It is measured in dynes/cm^2 and is the shearing force producing infinitely slow rate of flow between adjacent planes.

The Liquid Phase

Many of the properties of the final dispersion are governed by those of the liquid phase. The viscosity of this phase, for example, will in general set the lower limit of the viscosity of any dispersion in which it forms the continuous phase. Illustrative viscosity data for some of the types of vehicles which find application in the paint and ink industries are given in Table 1.

Table 1. Lithographic Varnish Viscosity *

Commercial Varnish Number	Viscosity at 25° (poises)	Commercial Varnish Number	Viscosity at 25° (poises)
00000	2.0	1	20.
0000	3.0	2	30.
000	4.5	3	60.
00	7.0	4	100.
0	12.	5	150.
		6	200.

* Standards recommended by the New York Printing Ink Production Club.[54]

While the dispersion of a sufficient quantity of a second phase in a liquid will greatly modify such properties as the consistency of the system, a number of other attributes of the liquid phase may be only slightly affected, if at all, when this liquid becomes the continuous phase of a dispersion. The surface tension of the dispersion and its angle of contact fall into the latter category. However, it becomes more difficult to measure these attributes than is the case for the pure liquid. To take the angle of contact as an illustration, its determination by means of the contour of a drop of the dispersion on a selected surface may give a result different from that of a drop

of the continuous phase on this surface, only because the yield value of the dispersion prevents the attainment of the equilibrium shape of the drop; where the surface tension of the dispersion and its interfacial tension against the supporting surface dictate the formation of a flatter drop, the yield value of the dispersion may prevent further flow-out of the drop to its proper shape by opposing the surface forces involved. What is meant to be a determination of the angle of contact is thus merely an approximation of some function of the yield value.

Vegetable oils which have been "bodied" often form the outer phase. The viscosity to which an oil has been bodied by heating is an indication of a complicated series of chemical changes: iodine number decreases while density and acid number increase with viscosity. These properties are reflected to some extent by the data for spreading coefficients on water. Most of the vegetable oils and their partially polymerized derivatives have spreading coefficient values in the range of 20 to 30, placing them in an intermediate position between strongly hydrophilic substances such as alcohols, and hydrophobic materials like mineral oils. Such bodied oils (lithographic varnishes) in many respects are ideal media for the dispersion of pigments.

Synthetic-resin solutions constitute an increasingly important class of raw materials. These products exhibit a very wide range in physical and chemical properties. They are often marketed as solutions, generally 50 per cent resin in solvent. Many resin solutions and in particular the oil-modified alkyd resin types exhibit characteristics somewhat similar to the lithographic varnishes, with this important difference, however, that the volatile solvent (usually of low polarity) makes them less versatile as pigment dispersion media. The resin solutions occasionally exhibit pseudoplastic flow characteristics.

It is possible in nearly all cases to produce pigment dispersions directly in the substance intended for the binder in the finished composition, although economic, manufacturing, and safety considerations may render such a procedure unfeasible.

Such properties as the surface tension and the angle of contact of the dispersion may be affected by the dispersed phase, if the specific surface of the internal phase is so great (because of the amount of the dispersed phase or because of its extremely fine state of subdivision) that the continuous phase nowhere is thicker than a small multiple of its molecular diameter. When the continuous phase is divided into such thin layers, its colloidal properties begin to approach those of the interface, as compared with those of the material in bulk.

Small quantities of many materials often present as impurities in the liquid or introduced into it from the dispersed phase greatly influence the properties of the final system. These small quantities exert so powerful an effect as to be classed as surface-active materials. The greatest influence is ascribable to impurities which are more heteropolar in nature than the main constituent of the liquid phase. Traces of water, often difficult to exclude from a commercial product, are particularly active in this respect, and may transform what was designed to be a free-flowing dispersion into a heavy paste.

The Comminuted Phase

The solid intended for dispersion in industrial compositions, such as paints, is often a naturally occurring material which has been treated to isolate the desired ingredient, or has been purified from minor contaminants. Often the utility of such a powder must be increased by pulverization, involving the subdivision, by actual fracture, of the solid particles. But this treatment gives only a small proportion by weight of individual particles in the particularly useful sub-sieve range. The 44-micron aperture of the standard 325-mesh sieve may be considered to fix the upper size limit of this range.

In the great majority of cases, it has been found economically possible to obtain the comminuted phase as a sufficiently finely divided powder only by chemical reac-

tions involving precipitation, almost always in aqueous media. The manufacture of carbon black by deposition from the flame is one of the notable exceptions to this generalization.

The particles precipitated in these aqueous reactions are the primary particles of the system. They are much smaller than sieve sizes and range in diameter from less than 0.1μ to sizes over 1μ for different materials. When the primary particles of a precipitated solid in an aqueous medium do not clump together but maintain their isolated individuality, washing by decantation becomes difficult because of the slow settling rate, and filtration is often impossible because the deflocculated particles pass through the filter. Hence it is desirable to flocculate the powder to some extent by changing its interfacial characteristics as, for example, by proper adjustment of the pH or the addition of surface-active materials. This process of flocculation also yields a softer filter cake, which after drying is more readily pulverized.

The aqueous slurries of precipitated particles almost always contain soluble salts which are not completely removed by washing. In addition, the finishing agents often added for flocculation or to impart some desired property to the finished material also remain in traces in the filter cake. During drying, these dissolved substances tend to cement the particles of the powder together. Commercial chrome yellow pigments, for example, frequently contain up to 3 per cent of soluble residual salts. In the precipitation of organic colors by dilution of an acid paste, and in the wet-grinding of natural materials and of artificial color masses such as ultramarine blue, the retention of soluble salts, giving rise to cementation, is equally possible. For some colors, sintering occurs during drying of the filter-press cakes and this also contributes to the formation of aggregates. Barium lithol toner to which has been added an appreciable amount of a fusible metallic resinate is an example of this class.

The extent of cementation is reduced by subsequent pulverization of the dried material, but the strongest aggregates persist. Excessive aggregation is undesirable, although aggregation to a limited extent aids in isolation of the powder and subsequent handling. Thus carbon black is marketed in the form of small beads or spheres, since this form contributes greatly to economy and cleanliness in transport and storage (Figure 1).

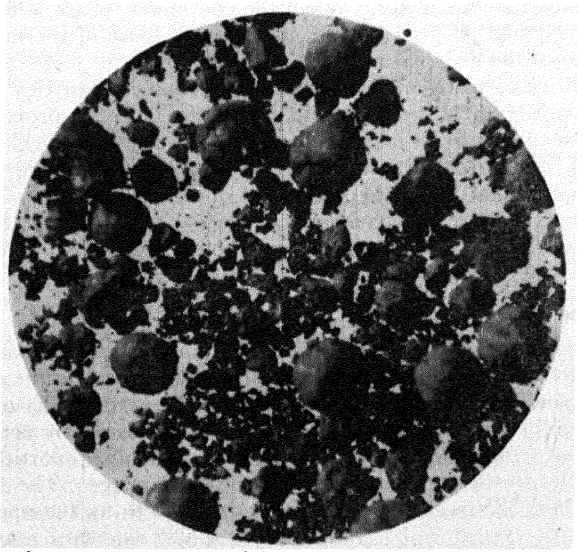

FIGURE 1. Photomicrograph of commercial carbon black pigment in bead or pellet form (X 16).

Any aggregates which are not broken down during pulverization after drying, or during the dispersion procedure adopted for the incorporation of the powder into the selected vehicle, remain as distinct entities in the resulting dispersion. These residual "hard aggregates" act as units in the scattering of light, for example, and therefore make a contribution to the optical properties of the system, not in relation to the size of the primary particle, but instead to that of the coarser aggregate. What was originally a finely divided pigment may thereby become the equivalent of a coarser material. Excessive aggregation then necessitates prolonged milling in an attempt to bring the maximum aggregate size to limits necessary for satisfactory performance.

For some purposes it takes very little of excessively coarse aggregate to ruin a material. As an illustration, consider a high-gloss lacquer film 25μ thick and containing 10 per cent by volume of a pigment whose ultimate particle size is 0.1μ, which is small enough not to interfere with the surface smoothness of the finish. Now if only 0.1 per cent of this pigment is in the form of aggregates 30μ across, then on the average 10 of these aggregates will perforce protrude through each square centimeter of the surface, form nuclei for blemishes, and destroy the quality of the lacquer. In practice, a lower content of even smaller aggregates will cause as much harm.

Manufacturers of pigments and colors in recent years have expended considerable effort in producing "soft-grinding" products. In addition there have been numerous patented procedures involving the coating of the pigment particles designed to avoid cementation, and the "flushing" of the particles directly from the aqueous phase into a constituent of the ultimate vehicle, which avoids the pigment-drying step altogether. The manufacture of pigments of controlled particle size is complicated by the existence of some powders so soft that even the ultimate particles are fractured during pulverization or dispersion.

Since the aggregate content and aggregate size distribution may vary with the severity of different dispersion techniques, any study of the effect of particle size must be made on the material after it has undergone the dispersion manipulation selected.

The available information concerning primary or ultimate particles and their aggregates has been greatly enlarged recently by the disclosures of the electron microscope.[48] * Additional information also has become available through the adsorption-isotherm technique developed by Emmett and his co-workers.[31] A compilation of primary particle-size data for representative pigments is given in Table 2, and electron micrographs are reproduced in Figs. 2-5.

With few exceptions the commercial pigments supplied currently are capable of comminution to primary particle sizes near or below the lower limit of resolution of the average microscope. Dispersed particles of such dimensions are also below the

Table 2. Particle Sizes of Representative Pigments *

Pigment	Diameter (d_3) (micron) †
Carbon black ("high color")	0.010-0.020
Carbon black (news-ink type)	0.030-0.060
Carbon black (blue tone)	ca. 0.12
Lampblack	ca. 0.10
Iron blue	0.06-0.08
Barium lithol toner	ca. 0.08
Zinc oxide (rubber grade)	0.10-0.12
Titanium dioxide (anatase)	0.20-0.35
Chrome yellow (medium)	0.17-0.26
Ultramarine	0.30-0.6
White lead (basic carbonate)	0.66
Whiting (calcium carbonate)	0.85

* Values selected from the literature.[7, 8, 25, 62, 86, 87]

† The d_3 diameter is the average diameter computed from the surface and volume of the particles:[26, 61, 62, 76] $d_3 = \Sigma nd^3/\Sigma nd^2$.

* See papers on the electron microscope by A. F. Prebus in Vol. V of this series, and by V. Zworykin and J. Hillier in this volume. J. A.

FIGURE 2. Electron micrograph of a medium chrome yellow (x 40,000).

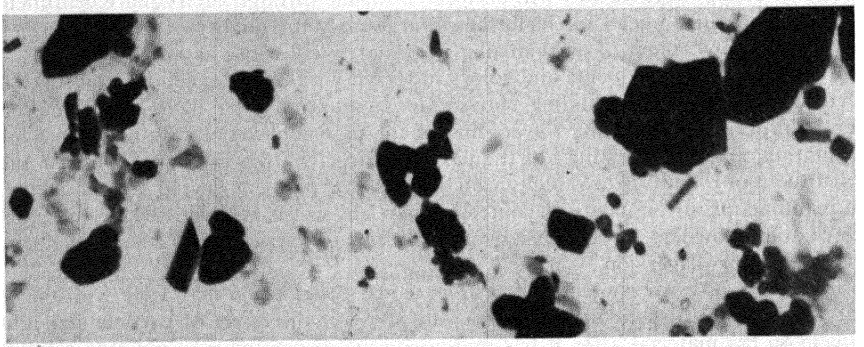

FIGURE 3. Electron micrograph of a dispersed chrome green pigment (x 30,000).

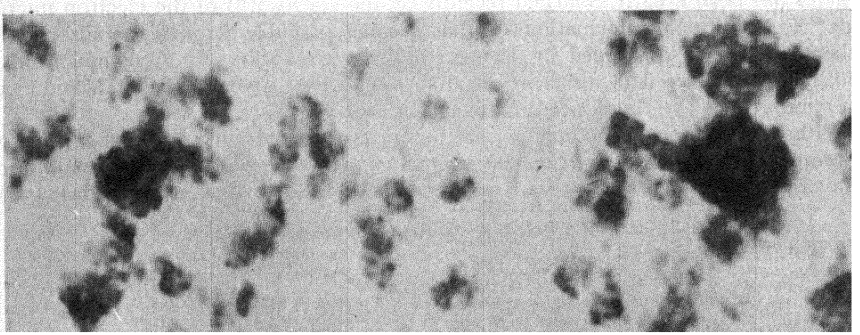

FIGURE 4. Electron micrograph of a dispersed "high-color" carbon black (x 55,000).

range in which difficulties in application would arise. An estimate of the quality of the dispersion thus resolves itself into a rating based chiefly on the presence of residual aggregates of primary particles. As has been shown, such aggregates may be present in only a fraction of a per cent of the total, but the composition may be unsuitable for applications with exacting demands, such as fine-screen half-tone printing or high-gloss enamels. The evaluation of dispersion is thus chiefly directed toward the estimation of the quantity and size of pigment aggregates. For this purpose the mill operator frequently uses a simple spatula test performed by slowly drawing the pigment dispersion down on a glass plate or polished metal surface, and ob-

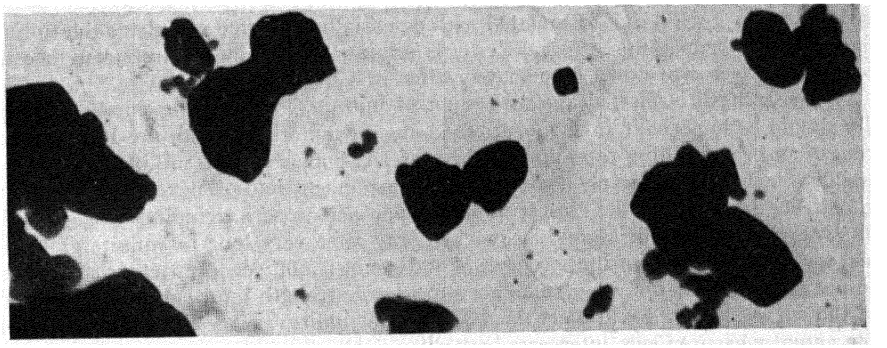

FIGURE 5. Electron micrograph of a dispersed lithopone. (x 30,000)

serving the gloss and smoothness of the film at the edge of the receding spatula; the presence of a large quantity of sizeable aggregates shows as a roughness and lack of gloss. In the hands of a skilled operator this method is surprisingly effective and reliable.

A somewhat more refined technique is the "wedge-grit" method, described by Craig.[24] Here a carefully machined, off-axis cylindrical bar is used to draw a wedge-shaped layer of the finished composition over a uniform surface, such as a glass plate. The position in the wedge at which the presence of aggregates shows makes possible an arbitrary grading on a scale from 0 to 20.

Carefully prepared mounts for microscopic examination supply a still better idea of the actual dimensions of over-size aggregates. A very small quantity of paste is placed on a drop of the vehicle and gently mixed with the end of a small stirring rod. A cover glass then is placed over the diluted ink and carefully pressed to a film thickness suitable for observation. It is essential that only a small quantity of the ink be used and that a representative sample be obtained. When the microscope is equipped with a calibrated scale in the ocular, it is possible to note the dimensions of the particles. Usually the field of view contains a background of finely dispersed particles, even after an initial pass on a grinding mill, together with some large aggregates. Progressive size reduction of the aggregates on extended milling can be observed by samples taken at intervals.

For the majority of pigment dispersions the technique of diluting the composition with a thinner and passing it through a fine-mesh sieve has very limited use. Such a procedure has value only in gauging mixer operation or some initial stage in mill operation. Any particles retained by even the finest screen are so coarse as to be entirely outside a satisfactory range.

A convenient and widely used method for evaluation of a pigment dispersion consists of mixing a small quantity of the pigment dispersion with a white base, usually formulated with zinc oxide and a lithographic varnish. Deviation from a standard, taken as 100 per cent, is made visually or photometrically on a "drawdown" of the two pastes, side by side. Computation of the relative "strength" of the dispersion is made from the proportions of white and tinting materials.

The use of such bleach tests for determining the relative degree of dispersion is not without objection.[34] Rapid change in the apparent strength of a bleach has frequently been noted. For carbon black, as an example, this change is usually less than 2 per cent, but in some cases may be as large as 5 per cent. In part the cause has been traced to differential flocculation, either of the carbon black or of the white pigment in the bleaching ink. For example, flocculation of the black reduces the relative tinting effect of the black, and the bleach appears weak on drying. On the other hand, flocculation of the white pigment makes the black appear stronger. It has been found

desirable to use a white ink formulated with essentially the same vehicle as the tinting composition to reduce this effect. Error is minimized also by basing strength estimates on the wet drawdown immediately after it is made.

When strength is plotted against extent of milling, the resulting curve theoretically should be hyperbolic in shape, approaching asymptotically both the 100 per cent strength and zero milling-time limits. In practice, however, zero milling time is impossible to achieve, for simple hand stirring of a pigment into oil develops a small but finite strength, which is the closest possible approach to zero grinding time. While full strength theoretically should be reached only after very long or infinite grinding time, the determination of the strength of the grind is subject to an error of at least one per cent, so that infinitely small increments of strength gain cannot be detected, and the curve as drawn will meet the 100 per cent limit. Hence the curve as drawn from actual measurements intersects both axes.

The task of reducing the aggregates of primary particles (several hundred microns in size) to the primary particles themselves is accomplished by mechanical means (Fig. 6). This process, properly termed comminution, is described in the next

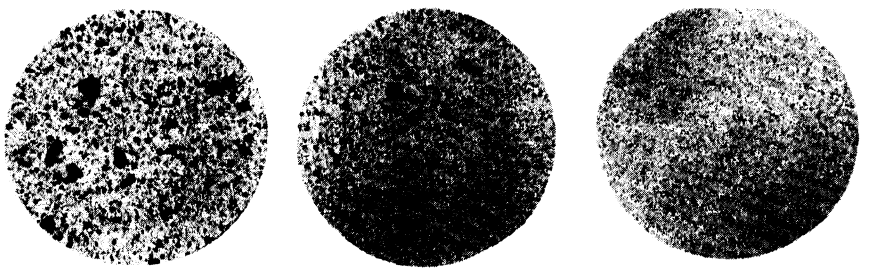

FIGURE 6. Photomicrographs showing progressive reduction in aggregate size with milling in a laboratory ball mill, iron blue pigment in linseed oil, (X 75).

section with a detailed discussion of three important commercial instruments: roll, ball, and colloid mills.

Mechanical Dispersion

Although many techniques have been devised for the preparation of dispersions of solids in liquids such as, for example, the Bredig arc method,* these are of limited academic and scientific interest only. The bulk of industrial products is produced by the application of mechanical force to viscous suspensions of solids in liquids, and for this purpose a variety of mills is in use.

The mill of today is a direct descendant of the mills used by primitive man for grinding grain, and it thus bears the distinction of being, in some respects, the world's oldest machine. The similarity in form of the stone mill, the iron mill (pot mill) and some types of colloid mills to these prototypes is striking. The putty-chaser mill, for example, consisting of two vertical stones, set to an axle in a shaft centered in a grinding well, has come down to us with no major changes in mechanical principle. The earliest mills operated by crushing grains between two surfaces set close together. All these mills were presumably used for dry grinding, and the pulverization of solids (size reduction of ores) continues to be an important industrial process. The maximum change in size for this type of dry grinding is roughly from pieces several inches in any given dimension to particles in the range of sieve sizes. The addition of water to the dry material, however, resulted in wet grinding, which was the analog of the dispersion of pigments in vehicles.

* See paper on "Inorganic Ferments" by G. Bredig in Vol. II of this series. J. A.

The reduction in size of the aggregate to that of the primary particle evidently calls for some process in addition to that of crushing between surfaces, for it is apparent that however precisely a machine were to be made, grinding surfaces spaced only 1μ or less would be impracticable. By subjecting the particles to intense plastic-shearing forces, size reduction to the region of the primary particle results. It is thus possible to picture the aggregates of the pigment particles ripped apart by violent friction with the viscous vehicle and by attrition against one another as the solid-liquid mass is subjected to shearing.

All mills operate first as crushers and secondly as instruments for the application of plastic-shearing forces. This distinction has often been made, but the importance as a principle for mill operation is not always kept in mind. More important, it supplies a connecting principle for all types of mills, explaining their function and guiding their proper use.

Diagrams of various commercial mills are shown in Figs. 7-13. The uni-roll mill,

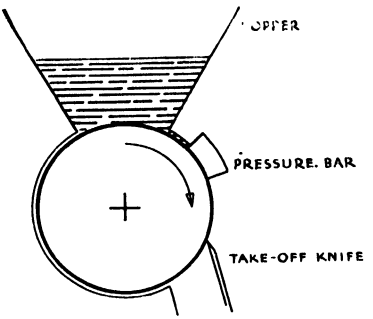

FIGURE 7. The uni-roll mill.

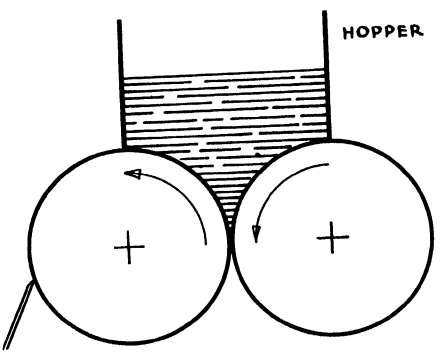

FIGURE 8. The two-roll paste mill.

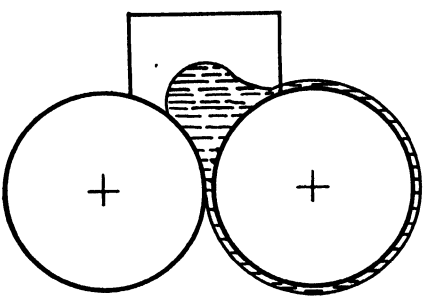

FIGURE 9. The two-roll rubber mill.

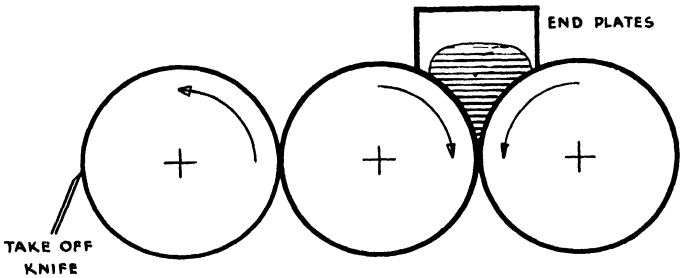

FIGURE 10. The three-roll mill.

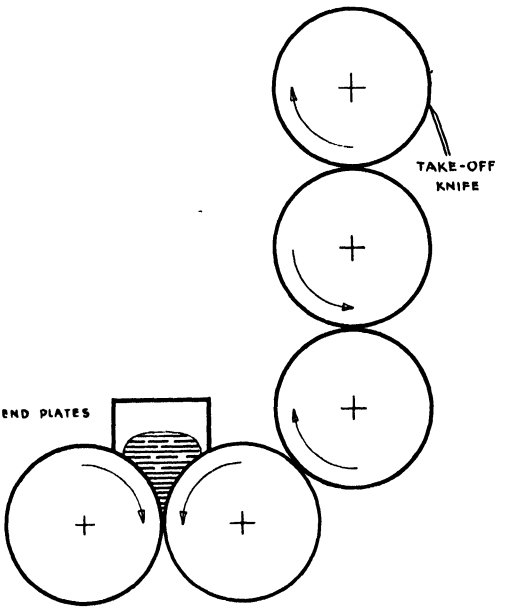

FIGURE 11. The five-roll mill.

widely used abroad, is employed to only a small extent in this country. In several respects this mill is similar to the colloid mill with a stator or pressure bar against which the roll shears the mix. Unlike the colloid mill, it is capable of handling pastes of high plastic viscosity, and the internal shearing is consequently higher.

The two-roll mill is of two types: one is fitted with hoppers and take-off apron and is intended for pastes; the other type is used for milling of rubber with compounding ingredients, and operates at comparatively large clearance on highly viscous or plastic compositions. The multi-roller mill is one of the most important instruments for pigment dispersion. In the form of the three-roll and five-roll mill, it has found wide and increasing favor. Ball and pebble mills are also of great commercial utility. The buhr-stone mill is shown in Fig. 12.

Three factors need consideration in a comparison of mills of different construction and operation: (a) clearance between surfaces; (b) the relative velocity with which the surfaces are moving in relation to each other; and (c) the plastic viscosity of the composition. These define the limits in which a mill acts as a crusher and indicate the magnitude of the shearing forces within the mixture.

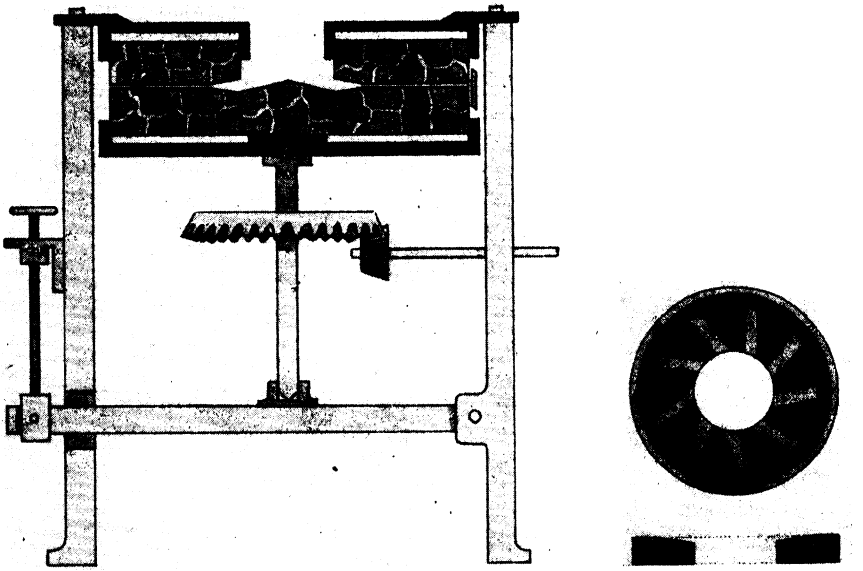

FIGURE 12. The stone mill, left; pattern of dressing a grinding stone, right.

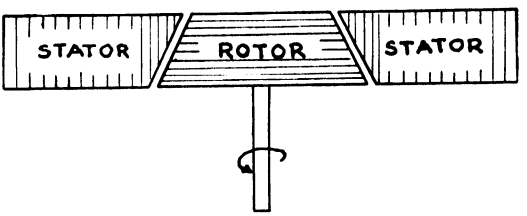

FIGURE 13. Cross-section of a colloid mill.

A little reflection will show the qualitative relationship between these factors. If a material is of extremely high viscosity—carbon black in rubber for example—the internal friction when the combination is kneaded in bulk is large. This accounts for the long use of the Banbury mixer and two-roll mill for rubber compounding. If we step to a lower plastic-viscosity level, represented by carbon black in No. 3 lithographic varnish, bulk shearing no longer suffices to separate the carbon black aggregates; but by passing the mixture over a three-roll mill, where the clearance is small and the shearing forces correspondingly large, a satisfactory breakdown or comminution of particles is obtained. At the low end of the plastic-viscosity scale in this analysis is the colloid mill. This mill operates at a comparatively low plastic viscosity and at large mechanical clearances; although the velocity at which the mill surfaces are passing each other is great, the rate of shear within the mixture is small and the comminution for a hard pigment is correspondingly low.

Estimates of the range of operating factors for commonly used mills, as based on a variety of source data, are given in Table 3. The ball and pebble mills in some respects are special cases, for in these mills the distance between contacting ball surfaces is variable and is a function of the probability of an aggregate being caught between two ball interfaces and crushed. High turbulence in the interstices in the ball mass contributes to plastic shearing. Mixing of pigment and vehicle preliminary

to grinding on a mill varies considerably in the extent to which the aggregates are initially comminuted. Light-duty dough or change-can mixers working on low-viscosity pastes produce only slight breakdown of the aggregates; this is reflected in comparatively poor color strength development: in several laboratory cases this has been found to be of the order of 25 per cent of maximum. What might be considered as a preliminary "wetting" is effected in such cases. On the other hand, heavy-duty mixers can apply high shearing forces through mixtures of high plastic viscosity. In the latter case, further milling is of the character of finish or blending passes.

Table 3. Estimated Clearance and Viscosity Limits for Various Mills

Mill	Clearance		Plastic-Viscosity Range (poises)
	Mils (0.001 inch)	Microns (0.001 mm)	
Roller (3,4,5 roll) *	0.2-1.0	5-25	10-5,000
Rubber (2-roll)	50-250	1250-6200	100,000-50,000,000
Dough Mixer	∞	∞	100-1,000,000
Banbury	∞	∞	100-50,000,000
Colloid	1-10	25-250	1-100
Uni-roll *	Variable	Variable	1-1,000
Ball (steel)	—	—	1-100
Pebble (flint)	—	—	1-50
Buhrstone	1-10 (?)	25-250	1-100
Iron ("pot")	1-10 (?)	25-250	1-100

* Where settings are maintained by hydraulic pressure, operating clearance depends primarily on viscosity.

It will be instructive to examine in some detail the operation of three types of mills: roll mills, ball and pebble mills, and the colloid mill. Each has distinct and special qualifications fitting it for pigment dispersion.

Roll Mills. For many years roll mills have been the standard instruments for the production of paints and printing inks. In the form of the three-roll and five-roll mills these are probably the most versatile of all mills, working over a wide range of viscosities and producing pigment dispersions with a minimum of aggregates when the mill is in good condition and properly operated.

The roll mill consists of a series of rolls set to operate at differential speeds. The first two rolls are the feed rolls and the mixture of pigment and vehicle introduced at this point follows along the second roll and is subjected to an initial shearing at the interface. Meeting the more rapidly moving third roll, the mix transfers to this roll and, in the case of the three-roll mill, is removed by the blade. The five-roll mill subjects the mix to two additional interfaces for grinding.

The roll mills in use today are distinguished from their forebears by superior steel rolls, more rugged construction, ease of adjustment, and most important, by the higher precision with which the roll surfaces have been ground. The roll surfaces of modern mills are reported to be finished to ±0.0001 inch. The importance of this point is easily seen. The roll clearance during operation is an important point on which there is little information to be found in the literature. Experiments in the authors' laboratory gave some indication of the separation of the rolls.

The steel of the frame and rolls of the mill is subject to elastic deformation. With the rolls illuminated from below it was possible to obtain visual evidence of this effect. A shim gauge (0.002 inch) was clamped between the feed rolls at the mid-point, and the two hand-setting wheels were tightened gradually. It was observed that the rolls could be deflected longitudinally, as shown by a smaller clearance at the ends of the rolls than at the center, which was spaced out by the shim gauge.

In tests with an unusually hard-grinding experimental carbon black on a three-roll laboratory mill, it was found that the particle size of the aggregates which came through the mill in a high-viscosity mix were never larger than 10μ. This corre-

sponded to a very "tight" mill setting and with a plastic viscosity estimated as about 5,000 poises. Another laboratory mill of more rugged construction on the same material left no aggregates larger than 6μ. It is inferred from these experiments that in normal operation the mill clearance is in the range of 5-10μ; in other words, the mill acts as a crusher to this minimum clearance.

A rough check of this value was obtained in an entirely different way. The mill delivery was measured as a function of the viscosity of the mix. An empirical equation was set up correlating the output with viscosity, mill dimensions, and the clearance, which was the unknown factor. By substituting known values in the equation, it was possible to compute the clearance. It was found in a pertinent case that the clearance was 0.00023 inch, or about 6μ. A diagram showing comparative dimensions of the pigment particles in relation to roll clearance is reproduced in Fig. 14.

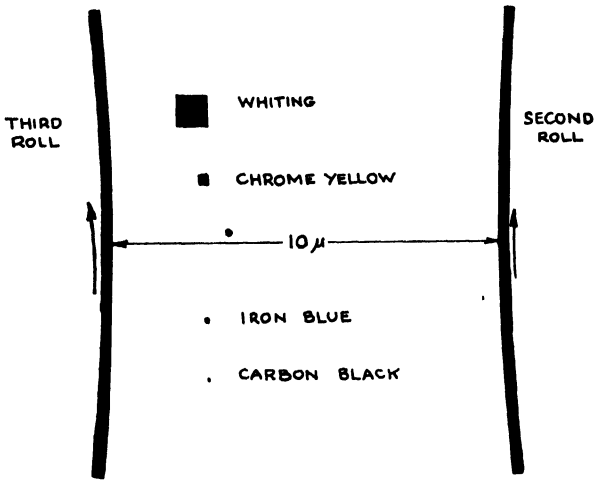

FIGURE 14. Diagram comparing mill roll clearance and size of primary pigment particles.

It may be seen that the clearance at which the mill is operating under load cannot be precisely determined, and the attempt to use shim gauges to obtain reproducible settings is virtually useless. Even if it were possible to make an accurate setting to a fraction of one-thousandth of an inch with the rolls stopped, the clearance when the mill is operating would be greater by an indeterminate amount which is related to the plastic viscosity of the mix and the mechanical rigidity of the mill.

That the output volume of the roll mill is a direct function of the viscosity is a fact which has long been known in a qualitative way, but the importance of viscosity as a factor has not been given sufficient attention. The way in which the production is related to plastic viscosity is shown in Fig. 15. These data were obtained from experiments on a 5 × 11-inch laboratory three-roll mill with both unpigmented litho varnishes and pigment dispersions. Plastic viscosities were measured on a rotational viscometer.*

The output of a roll mill was found to follow an empirical equation of the form

$$t = \frac{A}{dws\ U^k}$$

where t is the grinding time for unit volume of material;
A is a parameter based on roll dimensions and the driving gear ratios;
d is the clearance between the rolls during operation;
w is the width of the rolls;

* Experiments with C. W. Jerome

s is the peripheral speed of the rear roll;
U is the plastic viscosity in poises; and
k is an empirical constant.

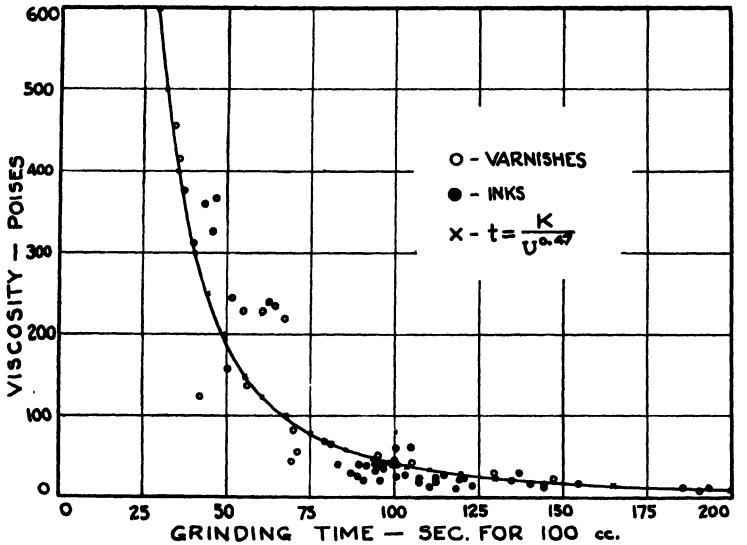

FIGURE 15. Curve showing relation between output on a laboratory three-roll mill and viscosity of composition.

This equation for a laboratory mill with rolls 5 inches in diameter and 11 inches long reduced to

$$t = \frac{0.35}{d\,U^{0.47}}$$

The quantity, dws, is the volume of material which would be extruded per unit time through an orifice of w length, d thickness, at s velocity.

It will be noted that the output reaches abnormally low levels as the plastic viscosity drops below 25 poises, and that a many-fold increase in output is achieved by raising the viscosity to about 300 poises. For all dilatant materials, the output has been observed to be high, corresponding to high equivalent plastic-viscosity at the great shearing stresses of the mill.

Yield value was found to have a negligible effect on the rate of milling. High yield value, shown in a stiff, non-flowing paste, however, may keep the material from entering the nip of the feed rolls properly and for this secondary reason decrease output.

Factory results on a wide variety of compositions have been reported by the New York Paint and Varnish Production Club [73] which bears out these results. The data in this paper have been abstracted in Table 4. While only qualitative consistency

Table 4. Relation of Output to Paste Consistency of Production Roll Mill [73]

(Five-roll Mill, High Speed, 13″ × 32″)

Consistency Rating	Output (lbs per hour)
Very thin	30-130
Thin	80-230
Medium stiff	120-180
Stiff	550-1400

ratings are given, it will be noted that the same mill varied in production from a low of 30 lbs per hour to a high of 1400 lbs per hour as the consistency ranged from ratings of "very thin" to "stiff."

Ball and Pebble Mills. These mills have several advantages which give them a special place in industry. The mills consist of a horizontally placed drum partially filled with steel or porcelain balls or flint pebbles. The mill is charged with the ingredients of the composition and rotated for periods which range usually from a few hours to about 100 hours, depending upon a variety of special conditions. Ordinarily it may be run without attention until the desired dispersion is obtained. Volatile components in the vehicle are retained without loss. These advantages are offset to some extent by the high initial cost of the mill and the contamination introduced by wear of the grinding surfaces.

Distinction should be made between different types of ball and pebble mills. Classified on the basis of the free grinding medium there are three main types: (a) The steel ball mill which is charged with alloy steel balls usually of sizes ½ to ⅝ inch in diameter; (b) the porcelain-ball mill, which is loaded with somewhat larger balls fabricated of a porcelain-type material, and is usually lined with bricks of a composition similar to the balls; and (c) the pebble mill, which is charged with selected flint pebbles ranging roughly from ¾ to 1½ inch in diameter.

The principles of operation are essentially the same for all types, but the contamination and efficiency are different. Porcelain balls have the highest rate of wear, approximating 2 per cent per hundred hours; for steel balls the range is from 0.1 to 0.5 per cent per hundred hours; flint pebbles wear at approximately the same rate as steel. Porcelain balls and pebbles do not affect the color of the dispersion, but the steel seriously contaminates light colors, and this result is especially marked where high infrared reflectance is necessary in the finished composition. The abraded material is extremely fine, however, and unless the mill is being used for abnormally abrasive materials or is improperly charged, these particles do not exceed the minimum size limits required for exacting applications.

The manner in which the mill is charged determines the efficiency of production. In a study of the optimum conditions for operation by one of the authors,[84] the following factors were considered: (a) relative charge volumes of balls and mix; (b) ball size and rate of dispersion and contamination; (c) mill diameter and rates of dispersion; (d) viscosity of charge.

Several terms used specifically for ball mill work follow. "Cascading" refers to the motion of balls in a rotating mill in which the balls are rolling over one another in a continuous coherent, mobile mass. This is distinct from "cataracting" in which individual balls are thrown clear of the ball mass and move independently, and "slipping" in which the ball mass moves as a static unit in relation to the walls of the rotating mill. The term "critical speed" is defined as the number of revolutions per minute at which the balls are held by centrifugal force at the interior periphery of the drum without motion relative to the drum; it has been defined also by the equation,

$$\text{C.S.} = \frac{K}{\sqrt{R}}$$

where C.S. is the critical speed in rpm,
R is the radius of the mill; and
K is a constant.

Relative Charge Volumes of Balls and Mix. On theoretical grounds the optimum grinding conditions are obtained when the pigment aggregates are exposed to the maximum number of contacting ball surfaces, and this result is achieved when the mix volume does not exceed the volume of the interstices or voids in the ball mass. The crushing force applied to a fine particle trapped at the interface of two balls is

of the order of several tons per square inch, on the average, in a typical production mill, while the portion of the mix within the interstices of the ball mass is subjected only to viscous shear from turbulent flow. Any excess of mix above the grinding media receives merely a tumbling action, quite incapable of disintegrating pigment aggregates.

A consideration of the relation of the gross volume of the grinding media (balls or pebbles), the volume of the interstices of the charge of the grinding media, and the total mill volume will serve to clarify the point.

Recommended charges of grinding media in relation to the mill volume vary (Fig. 16), but fairly general practice is based on a one-third charge for steel balls and up

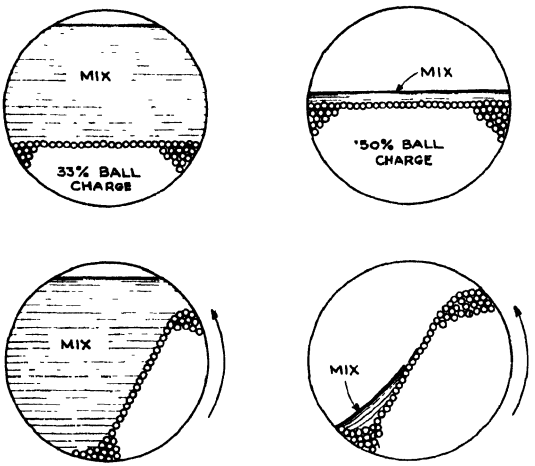

FIGURE 16. Diagrams showing ball mill charging practice.

to a 50 per cent charge for pebbles and porcelain balls. The maximum effective loading is of the order of 55 per cent. Larger loadings result in a marked decrease in power consumption, which indicates that ball mobility is lessened and the work done on the pigment particles is correspondingly reduced. Experimental evidence at hand indicates that a ball charge of 45 to 50 per cent of the total mill volume is a practical optimum loading.

The manner in which the balls pack determines the volume available for the mix. The limiting packing volume for spheres of a single size has been calculated as 26 per cent voids and 74 per cent solids. This figure holds for spheres of any given uniform diameter, but not for mixed sizes or shapes which depart from spherical. Actually, however, the balls do not pack so closely and the volume of the interstices of the balls and pebbles as used in milling operations varies generally between 38 and 42 per cent; 40 per cent may be taken as a representative average.

The volume of the mix in commercial practice, however, usually exceeds the volume of ball voids by a large amount. Several explanations can be given for adherence to this loading procedure. It has been suggested, for example, that the highest point of the ball mass in an operating mill should be immersed in the mix at all times; hence, a relatively large volume of fluid will lie above the balls. Such considerations imply that the mix drains rapidly from the ball voids, and while correct as an assumption for extremely low-viscosity grinds (which are not usual), in general the mix follows the balls closely and only slowly drains from the interstices. A second explanation lies in the desire to grind in one charging as large a volume of product as possible, although over-all efficiency may be greatly reduced thereby.

Experimental evidence for the advantage in charging the mill only slightly above the ball surfaces is given in Table 5 and Fig. 17. In the examples in Table 5 the pro-

Table 5. Relative Mix Volume and Grinding Rate

(Iron blue, 30% by weight in linseed oil; laboratory ball mill, ball size 0.6 inch, gross ball volume 50% of mill volume)

Relative mix vol	Filling ball voids	Excess over ball vol, mill filled 80%
Charge of mix, grams	510	1200
Strength, %		
7.8 hr.	81	65
24 hr.	99 *	83
48 hr.	100	89
102 hr.	100	99 *
Output for equivalent product, grams/hr.	21.2	11.8

* Basis for calculation of output.

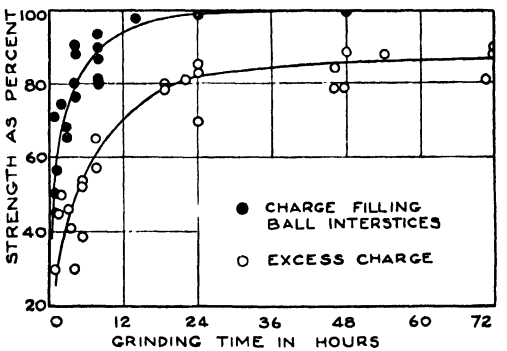

FIGURE 17. Rates of dispersion and relative charge volume, iron blue in linseed oil.

duction was doubled for equivalent dispersion for a given milling time. Thus, at 24 hours iron blue was carried to 99 per cent maximum strength with charges equal to the ball voids, whereas at the same time with conventional loading, the strength developed was of the order of 92 per cent. A milling time of over 100 hours was required in the latter case to equal 99 per cent strength. In Fig. 17, plotted from a number of experiments, the rate of comminution with conventional loading practice was markedly slower.

Ball Size and Rate of Dispersion and Contamination. The attrition produced by the balls increases as the number of contacts increases. For small balls, 0.13 inch in diameter, the number of points of contact in a given volume is 56 times that of balls 0.50 inch in diameter, and the rate of dispersion is proportionately more rapid. A calculation of the number of contacts of balls of different sizes, assuming the minimum theoretical packing of twelve points for each sphere, equivalent to six grinding interfaces is given in Table 6. The increased rate of dispersion obtained with small-size balls is shown in Table 7.

Table 6. Calculated Number of Contacts of Steel Balls

Av. Size (Inch)	No. per Pound	Calcd. No. Contacts per Pound *	Av. Size (Inch)	No. per Pound	Calcd. No. Contacts per Pound *
0.131	2840	17,040	0.65	24	144
0.250	435	2,610	0.75	16	96
0.375	130	780	1.0	6.4	38
0.50	53	318	2.0	0.8	4.8

* In close packing, each ball touches a total of twelve adjacent balls Since each contact is formed by two balls, the theoretical number of grinding interfaces is half the number of contacts or six times the number of balls.

Table 7. Relation of Ball Size to Rate of Color Strength Development

(Iron blue, 30%; No. 0 Litho (linseed) varnish, 70%; viscosity, 2.2 to 3.9 poises; yield value 0)

Ball Size (Inch)	Strength as % of Maximum			
	2 hr.	8 hr	24 hr.	72 hr,
0.131	78	98	98	98
0.250	65	86	95	100
0.375	46	71	87	92
0.50	55	71	85	90

The advisability of mixing balls of various sizes for batch milling of pigment dispersion is doubtful. Experiments indicate that a mixture of two or more sizes is additive in effect. Thus a mixture of 0.5-inch and 0.25-inch balls effects a rate of dispersion intermediate between that obtained when the same volume of each size is used independently. During grinding, the balls classify partially according to size, and theoretical advantages of mixed sizes are not realized. In unusual milling conditions, however, the addition of a relatively small number of larger balls may serve to prevent localized cementing of the grinding media and the mix.

Although the efficiency of milling may be increased by the use of small balls, practical difficulties inherent in their use for grinding media are not to be overlooked. Discharging the mix, separation of balls accidentally carried into the product, greater heat development, rate of wear, and possibly other problems attend the application of such grinding units. It is postulated that rate of wear, however, is a constant for all ball sizes, for a product carried to the same dispersion levels. Thus the longer grinding period with 0.5-inch balls may introduce the same contamination as that of 0.25-inch balls, provided the mill is operated only long enough to produce the same fineness.

Mill Diameter and Dispersion Rates. The rate of dispersion is generally considered to be directly proportional to the mill diameter, and accordingly production mills are often rated as of higher efficiency than small laboratory mills. This differential in grinding time is a reflection of the charging volumes of balls and mix, and the influence of the different radii of curvature of the large and small mills on the mobility of the ball. It is reasonable to assume that for low-viscosity grinds, differences in operation will be small. With relatively high-viscosity grinds, the ball charge in the small mill will to some extent pack together and result in a lessened grinding action; the mass of balls in a large mill, however, will retain a high mobility with undiminished grinding action. As a consequence, the rate of dispersion with equivalent ball mobility (which may necessitate an adjustment in viscosity of the grind) should be constant for ball mills of all sizes, provided an excess of mix is not present. From present experimental work this deduction appears valid.

Data on the dispersion of carbon black beads in mineral oils are given in Table 8

Table 8. Rate of Dispersion and Mill Diameter

(Carbon Black Beads in Mineral Oil Mixtures)

Mill Diam (ft)	Strength at 4 Hr. (%)	Pigment (%)	Viscosity (poises)	Yield Value, (Dynes/Sq Cm)
0.49	96	15	3.3	160
0.49	95	15	19	750
1.25	94	15	15	400
2.0	96	15	15	180
5.0	95	20	8.3	340
5.0	93	25	23	360

for four different mill sizes. The color strength developed after 4 hours of grinding varied from 93 to 96 per cent in mills that ranged from 6 inches to 5 feet in diameter. The range in viscosity was from 3.3 to 25 poises.

These experiments show that mill diameter is not the predominant factor in setting the rate of dispersion, and that for most purposes a laboratory mill will give a reasonably close approximation of the required grinding time for large mills.

Viscosity of Charge. The plastic viscosity of a grind of pigment and vehicle generally increases as the comminution increases, and may thus be considered a measure of the new surface exposed at the oil-pigment interface. Yield value measurements in most cases show a rapid change to a constant value which remains essentially unchanged for the duration of the grind. The power consumed by the mill is a function of the viscosity of the mixture, as shown in Fig. 18. Yield value

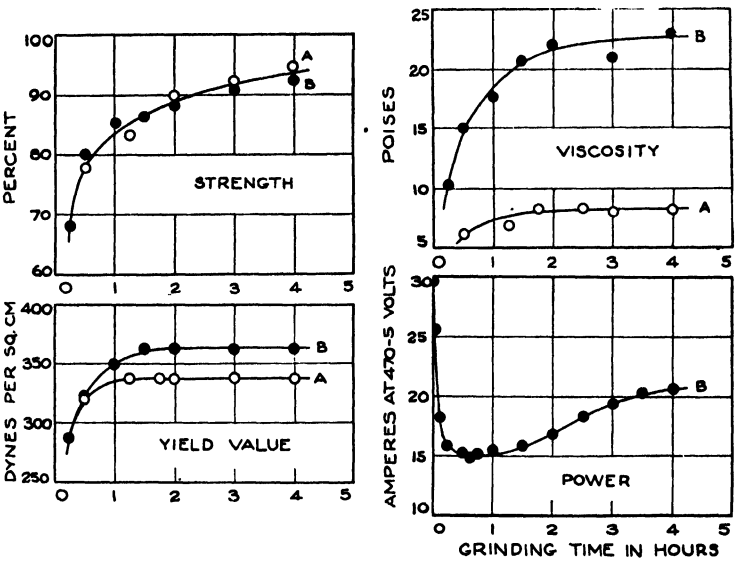

FIGURE 18. Dispersion of carbon black beads in mineral oils. Production mill, diameter 5.0 feet.

presumably is of some consequence in the estimate of power used, but inasmuch as it is nearly constant for the major portion of the grind, the relative effect on power consumption is additive.

There are, of course, maximum and minimum limits to the flow characteristics of mixes for best operation conditions in the mill, but such limits cannot be precisely placed. The noise of the operating mill is sometimes used to standardize conditions for optimum performance. A quiet mill is obviously not grinding, and one in which the balls are cascading with abnormal velocity and consequent high noise level is operating with excessive wear. The solution is difficult and necessarily based on a measure of empirical judgement.

It has been found convenient in preliminary tests to start a mill with a charge slightly higher in viscosity than is judged desirable for maximum ball mobility and to examine the charge at intervals. Additional vehicle or solvent can then be added in increments, until optimum grinding conditions are obtained.

Unusual milling conditions sometimes result in abnormal wear of the grinding medium. Where the viscosity of the mixture is too low, defective balls with 12 flattened areas are often to be found in the mill. This kind of wear can be explained on the basis of the following hypothesis: balls under pressure of several tons per square inch in a large mill will seize at the contacting surfaces unless the viscosity of the mix is high enough to provide a drag on the ball surfaces, and thus disturb their

orientation. Continued operation with each deformed ball leads to orientation of the flat areas against the spherical surfaces of adjacent balls, and eventually concavities are ground into the balls.

The Colloid Mill. This mill occupies a peculiar position in industry. Partly because of its name, academic writers with few exceptions discuss this mill in textbooks to the exclusion of all others. Attendant publicity has given the colloid mill —in some quarters—a reputation for utility which practice cannot justify; an equally erroneous view is that the colloid mill has very restricted usefulness.* Actually, the colloid mill in its present commercial forms is a rugged instrument, and it has a permanent place in the field of pigment dispersion. It is necessary to know the niche filled by this mill and its capabilties.

The colloid mill is characterized by high peripheral speed between the mill surfaces. It consists essentially of a conical stator and a closely fitting rotor. In some mills the rotor or stator or both are fluted (grooved). The mechanical arrangement is such that the rotor can be operated at speeds from several thousand rpm to about 20,000 rpm, depending on the size of the mill. The mechanical details of commercial mills can be found in the catalogs of manufacturers. A history of the development of the colloid mill is given by Travis.[93]

It can be seen from the geometry of the colloid mill that the intensity of the shearing forces applied to the material passing between the moving mill surfaces is related to the following factors: (a) clearance between rotor and stator; (b) rpm of rotor; (c) diameters of rotor and stator; (d) viscosity of the material.

Data on the rotor speeds for one type of colloid mill are given in Table 9. The

Table 9. Relation of Rotor Diameter and Speed to Peripheral Speed of Rotor Surface

Peripheral Speed Rotor Surface (ft/min)	Rotor Diameter (inches)				
	3	6	10	15	21
	RPM of Rotor				
5,000	6,400	3,250	1,950	1,300	925
10,000	12,800	6,500	3,900	2,600	1,850
15,000	19,200	9,750	5,850	3,900	2,775
20,000	25,500	13,000	7,800	5,100	3,700

data show the peripheral speed (feet per second) of the rotor in relation to the rotor size and speed (revolutions per minute). It will be noted that a three-inch mill has to be run at approximately 19,000 rpm to equal the peripheral speed of a 21-inch mill turning at 2,775 rpm. This speed represents something of an upper limit for operation, and for mechanical reasons it is generally advisable to run the mill at more conservative speeds.

Possibly one of the outstanding features of the colloid mill is the large production volume for all sizes. A small mill of the size suitable for laboratory use is actually large enough for production requirements. For example, a dispersion with a plastic viscosity of 1 poise was given one pass at the rate of 100 pounds per hour.

The rate with which a paste is ground on the mill is closely related to the viscosity of the mix. As a general principle, the higher the viscosity, the lower the output. Naturally if force-feed methods are employed, this generalization is not necessarily valid. Representative data illustrating this point are given in Tables 10 and 11.

For gravity-feed colloid mills, the yield value of the mixture has an important bearing on the output. The effect is simply that of impeded flow into the mill port, and an expedient solution for this problem is achieved in some cases by increasing

* See discussion in J. Alexander's "Colloid Chemistry," D. Van Nostrand Co., 4th ed., 1937, and earlier editions. See also paper by A. Chwala in Vol. III of this series. J. A.

Table 10. Relation of Output of Three-Inch Laboratory Mill to Viscosity and Clearance

Material	Initial Viscosity (poises)	Clearance (inch) 0.002	0.004	0.008
		Output (lbs/hour)		
Mill RPM: 10,000				
Water	0.01	670	1800	2400
Linseed oil	0.33	85	280	—
Litho varnish	4.5	60	160	250
Litho varnish	18.0	52	94	220
Litho varnish	62.0	44	48	108
Mill RPM: 7,200				
Ink (carbon black mineral oil)	0.56	100	—	—
Ink (carbon black mineral oil)	1.1	104	—	—
Ink (carbon black mineral oil)	2.4	78	—	—

Table 11. Dispersion of Pigments on Three-Inch Laboratory Colloid Mill (Mill Speed 7200 RPM)

Pigment	Vehicle	Pigment Content (% Weight)	Viscosity (poises)	Yield Value (dynes/cm²)	Strength (%) Clearance (inches) 0.002	0.004	0.008
Iron blue *	Mineral oil A	35	5.8	870	65	40	28
	Mineral oil B	30	64.0	330	67	43	38
	Linseed oil	35	3.1	20	83	66	40
	Litho varnish	35	20.0	32	71	57	50
Ultramarine	Mineral oil A	40	2.3	0	92	91	89
	Mineral oil B	25	11.5	60	93	95	
	Linseed oil	50	4.9	0	95	94	94
	Litho varnish	25	9.9	20	96		82
Carbon black †	Mineral oil A	7.2	1.0	240	91	87	81
	Mineral oil B	7.2	12.0	290	93	93	93
	Linseed oil	7.2	1.7	20	95	87	86
	Litho varnish	7.2	10.7	40	100	100	100

* "Hard-grinding" type
† Flow black

the height of the feed hopper, resulting in a greater mass of material pressing into the intake port. Alternates are the use of deflocculating agents in the mixture and force-feed pumps.

Dilatant pigment mixtures are usually perplexing to the operator. A dilatant mixture will feed into the mill without trouble, but the motor will labor and stall. A dilatant mixture at high rates of shear acquires an extremely high equivalent viscosity, and the load on the mill then exceeds the rated motor load. Compositions of high pigment content are apt to show dilatant flow; the most likely are those formulated with alkyd resin solutions or highly loaded water dispersions. Dilatant materials are almost invariably deflocculated, showing high fluidity at low rates of shear. The solution for the problem is the addition of more vehicle, thinning the mixture to the point where it no longer exhibits dilatant flow at the rates of shear produced by the mill.

The relation of the plastic viscosity of the mixture to the final tinting strength of colloid-mill dispersions is shown in Table 11. The increment of strength gained for carbon black in litho varnish is the most clear-cut of the cases cited, represented by 5 per cent at 0.002 inch clearance. Larger clearances for the other two pigments show the same effect quite markedly: 10 per cent for iron blue in both mineral oil and linseed vehicles at 0.008 inch.

It will be noted that the iron blue showed low final strength, with the maximum at 71 per cent. This was a particularly "hard-grinding" material, deliberately selected for this property. The presence of large aggregates in the iron blue grinds was readily noted visually, but the carbon black and ultramarine appeared smooth and quite free of aggregates. Centrifuging the ground products, however, disclosed a small percentage of oversize particles.

The clearance of the mill surfaces has a profound effect on the extent of comminution. This is shown by the data in Tables 11 and 12. These results are for a

Table 12. Dispersion of Pigments on Three-Inch Laboratory Colloid Mill

(Carbon Black in Mineral Oil; Viscosity, 1.7 poises, Yield Value, 20 dynes per cm.; Mill Speed, 7200 RPM)

Setting (inch)	No. of Passes	Strength (% of Maximum)
0.001	1	95.8
0.002	1	93.0
0.003	1	92.5
0.002	1	91.0
0.002	2	95.0
0.002	3	95.0
0.004	1	87.0
0.004	4	89.0

laboratory mill operating at 7200 rpm; and the shearing forces represented are approximately equivalent, for example, to those imparted by an 8-inch production mill at 3600 rpm. The output rate is greatly increased by the use of larger mill settings. For most purposes it is mechanically impracticable to set the rotor and the stator closer than 0.002 inch. Production-size mills are frequently operated at wider clearances, from 0.004 to 0.008 inch. Repeated passes of the same material through the mill at the same setting produce a slight gain in tinting strength, as shown in Table 11.

Heating of the mixture occurs when it passes through the mill; the temperature rise is directly related to the shearing forces imparted. Low-viscosity materials show a negligible rise in temperature; when the plastic viscosity exceeds 20 poises, however, it is not uncommon to find that the mixture has reached temperatures between 70 and 100° in a laboratory mill. In general, large clearances lead to lower final temperatures. The actual temperature for any given mill is, of course, a function of many additional factors: length of time the mill has been running; temperature and volume of cooling water; room temperature, etc.

Excessive temperature rise can lead to many untoward effects, and it is necessary to be aware of potential consequences such as loss of volatile components, bodying of oils, "dirtying" of pigments (*e.g.*, chrome yellow), and loss of strength (iron blue, PTA colors). For completely inert pigments such as carbon black, temperature rise is usually of no consequence.

The Solid-Liquid Interface

The process of grinding, discussed in the preceding sections, is the application of mechanical forces to effect a size reduction of the aggregates of the primary particles. Simultaneously, the liquid displaces air, moisture, or other substances adsorbed by the solid, and a new interface between the solid and the liquid is formed. The properties of the composition depend entirely upon the nature and extent of this interface.*

* The statement is sometimes made in the literature that "Mills do not grind; they merely 'wet' the pigment." A little reflection will show that this is a play on words used with specific but undefined meanings. The statement should be emended to the following: "Mills effectively produce a size reduction of the aggregates of pigment particles by grinding, and facilitate the wetting of the comminuted particles by the vehicle."

The "wetting" of solids is a subject on which many have worked,[1, 6, 10, 11, 13, 15, 47, 82, 91] and in which the experimental data are fragmentary and rarely suitable for cross comparisons. The hypotheses and theories which have been devised to explain apparently divergent observations likewise do not form a concordant picture. It is possible, nevertheless, to obtain an impression of the inter-connection of the various attributes of a dispersion if a practical viewpoint is adopted. In this analysis a synthesis will be presented, built from the simplest visual observations to the more complex thermodynamic concepts.

Rheological Properties. Inspection of the properties of a solid-liquid dispersion in bulk quantities leads to several commonplace characterizing phrases. It may appear, for example, as "stringy" or "long" as molasses; or it may be as fluid as water. The composition, on the other hand, may be a stiff paste such as painter's putty, or a soft paste such as mayonnaise or whipped cream. These properties are apparent on stirring the dispersion; for some applications, an impression of "tack" is obtained by tapping a film of the composition between the forefinger and a smooth surface. These visual and tactile impressions describe flow properties (consistency) which are too complex to permit of a single unit mathematical expression; however, it is fairly common practice to note that the solid in a free-flowing composition is "well wetted," while that in a non-fluid paste is "poorly wetted."

In spite of this coarseness of expression, this kind of description has wide use, for it permits a comparison of properties in ordinary parlance. These terms can be given a rough quantitative charting by means of rheological measurements[35] (Table 13).

Table 13. Terms Commonly Used to Describe Flow Properties or Consistency of Pigment Dispersions With Approximate Ranges in Absolute Units [35]

Descriptive Terms Frequently Used	Plastic Viscosity		Yield Value		Example
	Magnitude	Range (poises)	Magnitude	Range (dynes per sq cm)	
Watery; thin; soupy; highly-fluid; non-tacky	Low	0.1-1.0	Low	0-10	Spraying lacquer; gravure ink
Pasty; stiff; buttery; high-consistency; non-fluid; non-tacky; short	Low	0.1-5	High	1000-5000	Textile color pastes; stipple paints
Fluid; low-tack	Medium	5-50	Low	0-1000	Black news ink
Buttery; stiff; pasty; salve-like; short	Medium	5-50	High	1000-5000	
Long; molasses-like; tacky; highly-viscous	High	100-1000	Medium	100-10,000	Rotary press ink
Long; heavy-bodied; high consistency; tacky	High	100-1000	Medium high	1000-30,000	Paper litho, job press inks
Leathery; tough; rubbery; sticky	Very high	1000-10,000,000			Resin melts, rubber, asphalt

The rotational viscometer has been of great assistance in analyzing the complex flow properties of solid-liquid systems, since it distinguishes between viscosity and yield value, provides a measure of thixotropy, and offers a means of detecting anomalous flow properties, such as pseudoplasticity and dilatancy. Details of the rheological properties and measuring methods for solid-liquid dispersions are presented by Green and Weltmann elsewhere in this volume; in this discussion it will be sufficient to supplement their chapter with several points which apply to the practice of pigment dispersion.

It has been noted previously that the disintegration of aggregates is facilitated by maximum viscosity, obtained by the use of viscous vehicles and comparatively high pigment loadings. Under the conditions usually prevailing for two-roll mill and

Banbury mixer operation, and occasionally for multi-roll mill dispersion, the solid content of the paste may be sufficient to obtain dilatant flow. Crowding of the particles of the dispersed phase contributes to the efficiency of aggregate size reduction, by attrition of the particles against one another. Although dilatant flow provides for efficient mill operation, it is undesirable for most applications of the finished product; it impedes, for example, transfer of printing ink from the roller to the plate and impairs the brushing of paint.

At pigment concentrations which fall in the range where most products find application, plastic flow is commonly observed.[40] The increase of plastic viscosity with pigment volume follows an exponential law.[95]

Sedimentation Equilibria. Rheological measurements on solid-liquid compositions with relatively high solid contents are of great value, particularly since these measurements can be correlated closely with the application qualities of the product. For complementary information, however, it is usually desirable to resort to other experimental devices, and the techniques of sedimentation equilibria of solids in liquids have been employed by a number of investigators with significant results.

The technique for this work is basically quite simple. A definite quantity (volume) of the solid is suspended in a liquid, and the time for the suspended phase to reach an equilibrium volume is determined. The preparation of the materials for this work requires considerable care, however, especially with respect to the retention of residual moisture. The technique of desorption of the solid under elevated temperatures and high vacuum, together with precautions in handling, have been described by Harkins and Gans.[61]

Experimental data illustrating typical results are presented in Table 14. One of

Table 14. Sedimentation Equilibria of Solids in Liquids

Liquid	Spreading Coefficient against Water	Titanium dioxide [88] (Untreated anatase)	Titanium dioxide (Water-dispersible anatase)	Titanium dioxide	Silica [63]	Glass spheres [18]	Blue clay [65]	Ultramarine	Iron blue (Milori)	Iron blue [72]	"Organic red" [72]	Carbon black (Newsink grade)	Carbon black (Flow black)	Carbon black [65]
	Specific Packing Volume (cc of sediment per gram of solid)													
Water	—	—	1.1	1.3	0.66	0.73	1.8	2.6	2.5	1.8	6.0	7.8	6.3	15.2
Ethyl alcohol	50	0.89	—	—	—	0.75	—	—	—	—	—	—	—	—
Propyl alcohol	49	0.89	—	—	—	0.78	—	—	—	—	—	—	—	—
Butyl alcohol	48	—	1.9	1.3	—	1.7	—	1.7	2.0	2.5	4.3	8.5	7.7	—
Amyl alcohol	44	—	—	—	0.68	2.6	1.3	—	—	—	—	—	—	13.0
Ethyl ether	45	1.6	—	—	—	2.0	—	—	—	—	—	—	—	—
Octyl alcohol	37	—	1.7	—	—	—	—	1.9	2.3	—	—	6.1	7.2	—
Butyl acetate	35	—	—	—	0.72	—	2.1	—	—	2.6	5.3	—	—	12.7
Oleic acid	25	—	1.6	—	—	—	—	—	—	—	—	—	—	—
Chloroform	13	—	3.3	—	0.79	—	2.5	6.2	4.1	—	—	8.5	8.5	—
Benzene	9	2.0	2.1	3.2	0.80	2.7	2.6	5.4	3.6	4.6	5.8	6.7	7.8	12.0
Toluene	7	—	2.0	—	—	3.6	—	—	—	4.8	4.9	—	—	—
Nitrobenzene	4	1.7	—	—	0.82	2.8	2.4	—	—	—	—	—	—	—
Chlorobenzene	2	1.9	2.0	—	—	—	—	—	—	—	—	—	—	—
Carbon tetrachloride	—	1.9	2.5	—	—	3.2	—	5.5	5.3	6.8	4.6	8.9	8.0	—
Carbon disulfide	−7	1.9	2.5	—	0.86	—	2.8	—	—	—	—	—	—	11.5
α-Chloronaphthalene	−10	—	2.1	3.9	—	—	—	5.6	5.1	—	—	7.4	8.0	—

Note: Column 6, glass sphere 15.2 micron radius; theoretical packing volume 0.60 cc per gram.

the most spectacular observations of this work is embodied in the following generalization: flocculated particles settle rapidly to high volumes and deflocculated particles settle slowly to low relative volumes. The rate of settling may be predicted (in this case approximately only) by Stokes' law.* For ideal systems, where the particles are settling under gravity in liquids of equal density and viscosity, the equation reduces to the following:

$$V = r^2 K$$

where V is the velocity of settling;
r is the effective particle radius; and
K is a constant.

The velocity of settling, related to the square of the radius, is greatly increased by particles flocculating into units which then function as single particles of complex shape with increased effective radii.

The equilibrium volumes of solids in liquids are determined by the character of the solid, the polarity of the liquid, and adsorption of substances at the interface. If the liquid is pure, the equilibrium volumes for a given solid have been correlated with the interfacial tension of the liquid measured against water, and the function derived from this measurement, the coefficient of spreading of the liquid on water.

For hydrophilic pigments suspended in liquids of high interfacial tension against water, the sedimentation volume is high, but in liquids with low interfacial tension, the sedimentation volume is low. This generalization for solid-liquid systems which contain water has been noted repeatedly.[14, 16, 44] Mack [68] found a straight-line relationship between sedimentation volume and spreading coefficient for three hydrophilic solids. Carbon black exhibited a negative slope, a result attributed to the hydrophobic characteristics of the surface. Murray and Bartell,[72] working with mixed liquids, found a straight-line relationship between the amount of liquid adsorbed preferentially and the interfacial tension of that liquid. For solids which may be characterized by the term hydrophobic, the opposite effect was noted: high sedimentation volumes were associated with high spreading coefficients (low interfacial tension).

Mardles [69] in a series of papers has studied the sedimentation equilibria of various solids in liquids, correlating these data with viscosity measurements made on a capillary-tube plastometer. The suspensions which showed high anomalous viscosity (thixotropic flow characteristics) also exhibited high sedimentation volumes. The degree of flocculation determined the viscosity of the suspension as measured, but the experimental technique used did not distinguish clearly between viscosity and yield value of the suspensions, and the values reported for the viscosity ratio are thus some composite measure of the non-Newtonian flow factors.

Experiments of Ostwald and Haller on sedimentation of talc, fullers' earth, alumina, silica, magnesia, chalk, iron oxide, graphite, and activated carbon showed a correlation between dielectric constant of the liquid and final volume of the solid. The trend was toward lowest volumes in liquids of highest dielectric constant.[28]

The final settling volume for dry solids is only slightly affected by the liquid. Gallay and Puddington noted this result with starch, magnesium oxide, ferric oxide, and talc suspensions.[44] Bloomquist and Schutt conclude that the sedimentation volumes of dry glass spheres in a series of liquids are nearly the same.[16] The data of Ryan, Harkins, and Gans show markedly smaller differences for dry solids in dry liquids in comparison with the same suspensions which were not kept under anhydrous conditions.[80] Because of the extraordinary difficulty in maintaining completely anhydrous conditions during handling of the ingredients, it is likely that trace quantities of water persist in experiments on hydrophilic solid suspensions.

The adsorption of a surface-active material (oleic acid) from solution by titanium

* Stokes' law is based on spherical particles falling in a homogeneous fluid medium. Air was no longer "homogeneous" to the tiny oil droplets on which R. A. Millikan weighed the electron. See his paper in Vol. I of this series. J. A.

dioxide was studied by Harkins and Gans.[61] Oleic acid deflocculated the suspension of the powder in benzene, and the quantity required was that amount required to form a unimolecular film at the solid-liquid interface. In the presence of water, anomalous effects were observed, and it was deduced that water partly replaced the oleic acid adsorbed. With dry materials, however, the method was found sufficiently precise to determine surface areas of titanium dioxide.

The presence of residual traces of water profoundly affects the final sedimentation volumes of hydrophilic solids, and the qualitative correlation of the final sedimentation volume with the interfacial tension of the liquid against water, although not entirely satisfactory, is nevertheless fairly clear. Commercial pigments ordinarily are not specially treated before use and the moisture adsorbed on the solid may reach values as high as 5 per cent for most pigments and 10 per cent for carbon black. The properties of the solid are conceivably determined in some measure by the presence of this moisture.

The experimental results of sedimentation equilibria studies are significant, but the complexities of the experimental method render them semi-quantitative only. The technique of shaking to effect dispersion does not result in any appreciable comminution of aggregates, so that a variable quantity of the solid remains in the sediment; the settling volume is determined to some extent by the dimensions of the graduate or cylinder used for the experiments; the time for equilibrium settling may extend to excessive time intervals (months) and readings taken before the final volume has been reached are, accordingly, high; preliminary desorption of the solid and maintenance of anhydrous conditions throughout require extreme precautions, and even under the best circumstances are subject to some doubt. As a consequence, it is necessary to interpret the results only in relative terms.

The extent of flocculation of the dispersed particles, determined by rheological measurements and sedimentation equilibria, furnishes a comparatively simple and easily visualized picture of the grosser structure of the internal phase. A more fundamental approach is through the energy relations at the liquid-solid interface. It will be instructive to examine the experimental and theoretical devices employed to explore this subject. These include procedures based on contact-angle differences and calorimetric data on the heats of immersion of a powder in a liquid.

Contact-angle Relations. Detailed attention has been given in the literature to the thermodynamic relationships governing interfaces. From a technological viewpoint, some of these relationships are of more immediate interest than others. Two of the problems which concern us are the mixing of a powdered solid into a vehicle, and the spreading of the resulting dispersion on a flat surface, as in painting.

Consider a finely divided solid thrown onto a liquid in a mixer. We may ask what condition determines whether the powder will form a stable dispersion in the liquid, that is, will be "wetted" by the liquid, and under what condition the powder will remain unmixed. The powder may be considered to have been in proximity to the liquid for a sufficient time to achieve equilibrium with the vapors from the liquid. When mixing takes place, the surface of the powder is transformed into an equal area of interface between liquid and solid, while the extent of the surface of the liquid exposed to the air may be considered as unchanged. Hence the free energy change per square centimeter after solid is mixed into liquid is:

$$-f_1 = \gamma_{S'} - \gamma_{SL}$$

where γ represents free interfacial energy per square centimeter, S' refers to the solid surface in equilibrium with liquid vapor, and SL refers to the solid-liquid interface. The difference $\gamma_{s'} - \gamma_{sL}$ has been designated by Harkins * as the "spreading pressure" $\phi_{L/s'}$. Neither $\gamma_{s'}$ nor γ_{sL} has yet been determined directly. But, at equilibrium:

* See paper by W. D. Harkins in Vol. I of this series, also his paper in Vol. V. J. A.

$$\gamma_S' = \gamma_{SL} + \gamma_L \cos\theta$$

where γ_L is the free surface energy of the liquid (numerically equal to its surface tension) and θ is the contact angle between the liquid and the solid particle. Hence

$$-f_I = \gamma_L \cos\theta$$

For values for θ over 90°, then, cos θ is negative, so that $-f_I$ is negative and the powder resists the mixing operation. For values of θ under 90°, the dispersion is more stable than unmixed liquid and powder.

If we consider $-f_I$, which is a measure of the tendency of the solid to remain mixed in the liquid, to be also the criterion of the "wettability" of this solid by this liquid, it follows that liquids showing a contact angle of less than 90° against a solid "wet" that solid, whereas poor immersion wetting obtains if the contact angle exceeds 90°. Since θ, as well as γ_L, is experimentally determinable, relative and absolute "wettability" may under these circumstances be determined in terms of the sign of cos θ and of the value of $\gamma_L \cos\theta$.*

When a dispersion, such as that just discussed, is applied to a solid surface, as in painting, a somewhat different set of conditions prevails. Here we desire a composition which will remain in the painted-out state and not tend to crawl back. Since the applied films are relatively thick, and since there is rarely so much dispersed powder in the liquid that the surface energy and the interfacial energy of the dispersion are appreciably different from the vehicle, the three energy quantities involved are γ_S', which is the surface energy per square centimeter of the substrate in close contact with the film-forming composition, and therefore practically saturated with its vapors; γ_L, which is the free surface energy of the composition, equal to the free surface energy of the vehicle with rare exception; and γ_{SL}, which is the free interfacial energy between dispersion and substrate. On spreading, the substrate disappears and an equal area of interface and dispersion surface both appear. Thus the net free energy change on spreading, $-f_P$, is:

$$-f_P = \gamma_S' - \gamma_{SL} - \gamma_L$$

Since

$$\gamma_S' - \gamma_{SL} = \gamma_L \cos\theta$$
$$-f_P = \gamma_L(\cos\theta - 1)$$

which again involves the same measurable quantities, γ_L for the vehicle (or dispersion) and θ between the vehicle (or dispersion) and the surface to be covered. This relationship shows that $-f_P$ is negative for all values of θ except 0°, and that therefore, the composition will spontaneously resist the spreading operation for $\theta > 0°$.

Heat of Immersion. When a powder is immersed in a liquid, the surface of the solid becomes an equal area of interface, and this change is accompanied by a heat effect. If E_S represents the total energy per square centimeter of the powder and E_{SL} that of the interface, then this heat effect on immersion $h_{I(SL)}$ is:

$$h_{I(SL)} = E_S - E_{SL}$$

The magnitude of $h_{I(SL)}$ throws considerable light on the relationships involved, although it does not give us a direct determination of the values of the more important quantities E_S and E_{SL}. This subject has received detailed treatment by Harkins and his collaborators.[17, 57, 58, 59]

Many attempts have been made to measure the heat of immersion (or heat of wetting), but the fragmentary data available from the work of different investigators

* Another school of thought bases its criterion of "wettability" not on this thermodynamic approach but on considerations involving adhesion and cohesion which lead to the viewpoint that wettability is zero at $\theta = 180°$, improves as θ decreases, and becomes complete at $\theta = 0°$.

are not satisfactorily comparable. This deficiency can be traced to several factors: (a) methods of varying precision; (b) differences in sample preparation; (c) incomplete description of samples or the state of their surfaces; (d) incomplete particle-size information; and (e) limited surveys by each investigator; thus while comparisons within one set of measurements are valid, conclusions for other physical systems are by inference only.

The method calls for highly refined precision calorimetry, since the quantities of heat liberated are of the order of one calorie per gram of powder. The experimental procedure described by Harkins and Dahlstrom,[59] for example, is based on the use of a specially designed calorimeter equipped with a 36 junction thermopile, stirrer, and arrangement for introducing the powder. The temperature change is measured potentiometrically to 0.00001°.

When a hydrophilic pigment such as titanium dioxide or zinc oxide is immersed in a vehicle of high spreading coefficient, corresponding to high polarity, the heat of immersion is high, as shown in Table 15; liquids of low polarity (*e.g.*, benzene) show

Table 15. Heats of Immersion of Pigments in Pure Liquids [33, 58, 59]

Pigment	Liquid	Heat of Immersion (Calories per gram)
Titanium dioxide	Water	1.2
	Ethyl alcohol	1.2
	Butyric acid	0.88
	Ethyl acetate	0.85
	Butyl alcohol	0.83
	Nitrobenzene	0.67
	Carbon tetrachloride	0.57
	Benzene	0.35-0.39
	Iso-octane	0.25
Zinc oxide	Water	1.1; 1.18
	Ethyl acetate	0.74
	Butyl alcohol	0.69
	Nitrobenzene	0.66
	Benzene	0.30
	Nujol	0.20
Graphite	Water	1.79
	Ethyl alcohol	1.69
	Carbon tetrachloride	1.31
	Benzene	1.53
Carbon black (Acetylene black)	Carbon tetrachloride	0.7
Carbon black (Micronex)	Carbon tetrachloride	1.1
Carbon black (Super Spectra)	Carbon tetrachloride	6.5

minimal values. The correspondence of high heat of immersion to low sedimentation values, representing a deflocculated state, is apparent.

The data quoted are for rigorously purified systems. A suspension of titanium dioxide in benzene is remarkably sensitive to traces of surface-active materials. Harkins and Dahlstrom found, for example, that additions of 0.10 per cent of boiled linseed oil raised the heat of immersion from 0.39 to 0.71 calories per gram, and that, in general, the quantity of heat increased with the oil adsorbed until the quantity required for a unimolecular film was reached. Ewing [33] found that the heat liberated when zinc oxide was immersed in linseed oil was 2 calories per gram, or nearly seven times that for pure benzene. The presence of water increased the heat of immersion of titanium dioxide until a value of 1.12 calories per gram was obtained, which approaches the value for the immersion of this pigment in water.

It will be instructive to recall these measurable effects when discussing the utility,

at present still largely empirical, of surface-active materials for pigment dispersions, in the sections below on surface-active agents and flushed colors.

Adsorbed Water. The effect of moisture adsorbed on the pigment, noted so frequently by investigators, indeed may be the main factor influencing the final rheological and dispersion characteristics of commercial pigments. It must be emphasized that the pigment stocks as used are only rarely given an oven drying immediately before use. Consequently, the pigment is generally used with an adsorbed film of moisture, the magnitude of which may be judged from data for the water content for various materials as given in Tables 16 and 17. For titanium dioxide samples, water

Table 16. Moisture Content of Commercial Pigments

Pigment	Water Toluene Extraction (Wt. %)	Water Oven Dry 24 hrs., 105° (Wt. %)
Titanium dioxide (Anatase, Sample A)	0.1	0.06
Titanium dioxide (Anatase, Sample B)	0.3	0.23
Titanium dioxide (0.1% Al_2O_3)	0.4	0.36
Titanium dioxide-barium sulfate (composite pigment)	0.2	0.24
Chrome yellow (primrose)	0.8	—
Chrome yellow (medium)	0.5	—
Iron blue (Milori-type)	4.	—
Ultramarine blue	1.4	—
Toluidine toner	0.4	—
Hansa yellow	0.1	—

Table 17. Moisture Content of Carbon Blacks

Carbon Black Type	Initial Oven-Dry, 105° C 24 hrs. Water (%)	Water Content (%) at Relative Humidity of 12-15%	36%	58%	74%	80%	95%
News ink (rubber) grade	0.0	1	1	2	3	3	9
Halftone ink ("flow") grade	0.0	3.5	7	7	8	8	12
High color (lacquer) A	0.0	1	6.5	15.5	16	18	20
High color (lacquer) B	1.0	1	8	11	13	14	15

to the extent of 0.1 to 0.4 per cent has been found adsorbed; for chrome yellow the figure of 0.3 per cent is a representative average. Carbon black with greatly increased surface area and adsorptive capacity holds considerably larger quantities—to 10 per cent under normal storage conditions. Water present to this extent actually acts as a diluent and observed variations in strength of the pigment can be attributed to this factor alone.

The quantity of water adsorbed is roughly equivalent to that necessary to form a unimolecular film on the solid surface. For example, assuming 10 square meters as the area per gram of titanium dioxide, and 10 square Angstroms as the adsorbed area of the water molecule, a monomolecular film requires 0.3 per cent by weight on the pigment. Carbon black with a specific surface of 100 square meters per gram requires 3.0 per cent water, and for high-color blacks, with surface areas reported as high as 800-900 square meters per gram, close to 30 per cent adsorbed moisture corresponds to the dimensions of a monomolecular film. These computed quantities are in the range of the analytical values noted in Table 16 for commercial pigments.

During dispersion on the mill some of this moisture may be lost, but only if the milling temperature rises sufficiently. Hot mill operation has been advocated by Gardner and others.[29, 48] Highly plastic mixes in the Banbury mixer and two-roll rubber mill develop sufficiently high temperatures on prolonged mastication, and it has been observed that with carbon black, especially, the water is visibly vaporized, rising from the hot rolls as steam.

A generalized summary of the properties discussed above is given in Table 18.

Table 18. Generalized Summary of Physical Properties of Solid-Liquid Dispersions

Property	Deflocculated	Flocculated
Appearance, visual	Fluid	Paste
Rheological properties	Low or zero yield value	High yield value
Sedimentation volume	Low; equilibrium volume attained slowly	High; equilibrium volume attained rapidly
Heat of immersion	High	Low
Work of adhesion	High	Low

Surface-active Agents

The addition of small quantities of reagents to provide desirable working properties for paints and printing inks is a practice extending back to the origins of the industry. Commonly used materials include soaps, tallow, stearin pitches, waxes, gilsonite, etc. While the function of these substances is neither entirely clear nor simple, one important result of their addition is the change in flow properties of the composition, either rendering it more fluid or contributing to an increase in consistency or yield value.

In recent years a large number of patents [9] has been issued on the addition of synthetic surface-active agents to facilitate pigment dispersion, and some of the art is listed here for illustration.

For the dispersion of pigments in water or aqueous vehicles such as casein, glue, or methylcellulose solutions, most of the water-soluble reagents are of advantage. Hydrophilic pigments such as water-dispersible titanium dioxide will ordinarily form a deflocculated dispersion without special reagents, but for hydrophobic pigments such reagents are essential. Carbon black, for example, forms deflocculated dispersions on the incorporation of the sulfonated condensation product of a naphthalene derivative and formaldehyde. Water-dispersible colors have been made by admixture of a relatively large quantity of readily water-soluble substances. Sugars, dextrine, molasses, glycerin, and soluble salts are frequently used and in combination with the newer surface-active agents, superior self-dispersing qualities are obtained.[25] The principle is that of a protective colloid and in the procedure shown by Alexander,[5] maximum effect was obtained by precipitating the color in the presence of the stabilizing substances.

For pigments dispersed in non-aqueous vehicles, a wide variety of compounds and processes have been described. The simplest combination is that of a pigment with fatty acids.[75] Variations include soaps, such as the stearates of aluminum, lead, and zinc patented by Meister,[71] and naphthenates of the alkaline-earth metals described by Brizzolara [18] and Sullivan.[89] Esters and amides of naphthenic acid are given in the work of Erskine and Perkins.[82] Cationic-active materials listed by Sloan include quaternary ammonium, sulfonium, and phosphonium compounds.[84]

A special group of reagents has been used for carbon black. Copper soaps were patented by Sweitzer [90] and nickel soaps by Zapp.[93] Vogel [94] and Wiegand [96] list a number of amines as deflocculants; benzidine, ethylene diamine, and triethanolamine are examples. These amines are used to advantage in oils containing fatty acids; if the oils have low acid numbers, it is necessary to add fatty acids.

The phthalocyanine pigments are noted for poor working properties, and the use of metal resinates was patented by Siegel [68] to correct this difficulty.

An investigation of the role of surface-active agents in pigment dispersion was undertaken by Fischer and Jerome.[41] Representative surface-active agents were selected from each of the several classes of the commercial types available. The effect of these compounds on typical pigment vehicle combinations was studied in relation to the pigment and vehicle types, concentration of the pigment, and method of addition. The rate of dispersion and final tinting strength of the mixtures were measured.

The change in rheological properties of the dispersion was taken as the primary physical criterion of the effect of a given surface-active agent. The results obtained have been an aid in selecting surface-active agents for specific formulations of analogous systems.

The quantity of reagent estimated to form a monomolecular film on the pigment particle may be considered the minimum to register a decided change in properties of a dispersion.[39, 61] Calculations of this quantity for commercial pigments on the basis of a number of arbitrary assumptions have been made. While these figures are only estimates, they serve as a rough guide. For many pigments less than 1 per cent by weight is sufficient; for pigments of small particle size, such as organic toners and carbon black, 2-3 per cent is required. In one series of experiments the effect of concentration of different surface-active agents was determined. An observable change in yield value was obtained in most cases at 0.5 to 1.0 per cent, with the maximum result at approximately 3 per cent. Large excesses of surface-active agents are of little advantage, since insoluble reagents act as an addition to the dispersed phase, while fluid and soluble substances merely extend the vehicle.

The data in Tables 19 to 23 show the viscosity and yield value changes produced

Table 19. Relation of Pigment Strength to Plastic Viscosity (Three-Roll Mill Dispersions)

	No. of Experiments	
	Colors *	Carbon black †
Increase in plastic viscosity	76	64
Increase in strength	74	104
Decreased or unchanged plastic viscosity	87	152
Decrease or no change in strength	89	112

* Includes toluidine toner, iron blue, ultramarine blue.
† Includes "long" and "short" carbon blacks.

Table 20. Change in Flow Properties of Titanium Dioxide Dispersions on Addition of Water

Reagent *	Before Water Addition		After Water Addition	
	U †	*f* ‡	*U*	*f*
25.8% TiO_2 by Volume in Mineral Oil				
None (control)	§	§	§	§
Zinc naphthenate	35	2900	53	4400
Lecithin	22	1300	18	1500
Aerosol OT	40	3600	31	3200
31.3% TiO_2 by Volume in Linseed Varnish				
None (control)	58	740	§	§
Zinc naphthenate	44	780	60	1440
Lecithin	68	8200	50	10000
Aerosol OT	61	3400	55	6400

* 3% by weight on pigment.
† Plastic viscosity in poises.
‡ Yield value in dynes per sq cm.
§ Stiff paste; could not be measured.

by the addition of surface-active agents on dispersions of pigments in different vehicles. Where the yield value of a dispersion is high initially, as in the case of toluidine toner in glycerol, a number of reagents decrease this value. The magnitude of the change is large. In the glycerol system, compounds with some solubility are most effective. Somewhat similar results can be noted for carbon black. Iron blue and ultramarine, however, show high initial fluidity without surface-active agents, and the addition of these reagents merely serves to increase the yield value in the majority of cases.

In litho varnish, all pigments appear to show comparatively high fluidity, and added reagents act rather to increase yield value and thus reduce fluidity. When mineral oil is used as vehicle, however, the dispersions are of lower fluidity than similar

Table 21. Effect of Surface-Active Agents on Flow Properties of Ultramarine Blue and Iron Blue

	Ultramarine Blue					
	39.7% by vol. in glycerol		32.0% by vol. in mineral oil		43% by vol. in linseed varnish	
Reagent	U *	f †	U	f	U	f
None (control)	41	0	46	1900	100	580
Aerosol OT	20	0	28	530	160	890
Aresket 300	41	0	46	6700	130	890
Daxad 23	32	0	..	...	131	880
Duponol ME	51	0	50	7200	130	2300
Lecithin	65	7700	23	74	110	3500
Nacconol NR	37	0	..	...	161	1370
Santomerse D	..	...	..	....	...	...
Sapamine KW	42	4500	41	1250	110	1200
Tergitol 7	30	0	90	1400	110	960
Zinc naphthenate	60	1970	35	180	145	590
Water	..	...	§	§	§	§

	Iron Blue					
	29.8% by vol. in glycerol		20% by vol. in mineral oil		28% by vol. in linseed varnish	
Reagent	U	f	U	f	U	f
None (control)	8.3	37	106	6900	90	2600
Aerosol OT	8.3	260	32	5500	78	2200
Aresket 300	8.6	830	81	6350	98	2200
Daxad 23	14 ‡	0	61	9000	92	2400
Duponol ME	8.8	130	38	2700	83	2300
Lecithin	57	1400	23	410	85	2400
Nacconol NR	8.8	130	74	6600	84	1800
Santomerse D	9.9	350	69	5200	81	1700
Sapamine KW	70	8000	77	4400	81	2300
Tergitol 7	7.3	300	89	9300	114	1700
Zinc naphthenate	§	§	47	4400	78	2200
Water	..	...	§	§	§	§

* Plastic viscosity in poises.
† Yield value in dynes per sq. cm.
‡ Calculated at low r p m on rotational viscometer; dilatant at standard measuring speeds.
§ Too high to measure.

Table 22. Effect of Surface-Active Agents on Flow Properties of Barium Lithol Toner and Carbon Black

	Barium Lithol Toner					
	19.8% by vol. in glycerol		34.2% by vol. in linseed varnish		20.8% by vol. in mineral oil	
Reagent	U *	f †	U	f	U	f
None (control)	31	1120	90	3080	40	2100
Aerosol OT	38	6050	110	6800	39	1680
Aresket 300	13	4380	120	5310	37	2640
Benzidine	..	...	...	...	..	...
Copper oleate	..	...	...	...	..	...
Daxad 23	27	865	105	7080	42	2880
Duponol ME	7.3	220	110	7520	43	2600
Gilsonite	..	...	...	...	..	...
Ink Lengthener EE	..	...	...	...	..	...
Lecithin	44	8260	79	2690	35	1100
Nacconol NR	22	4380	116	5020	42	2840
Santomerse D	6.1	0	127	2060	41	2450
Sapamine KW	69	12,700	63	4370	45	2550
Tergitol 7	43	7120	...	...	41	1780
Zinc naphthenate	95	19,100	66.8	8400	48	2260
Water	..	...	168	7360	56	6540

Reagent	Carbon Black: 9.7% by vol. in glycerol U	f	11.6% by vol. in mineral oil U	f	15.3% by vol. in linseed varnish U	f
None (control)	3.0	3800	45	7300	57	10,400
Aerosol OT	3.1	2000	48	6000	55	8650
Aresket 300	8.4	1550	44	7100	69	8260
Benzidine	17.0	5870	47	7700	53	770
Copper oleate	4.8	2600	41	4230	64	2500
Daxad 23	6.2	1780	37	6300	56	10,900
Duponol ME	5.6	1200	44	8650	75	9880
Gilsonite	..	...	46	3760	63	7300
Ink Lengthener EE	14.0	3080	43	6060	55	7930
Lecithin	12.0	6640	34	6250	68	6000
Nacconol NR	6.1	1390	40	7500	66	7200
Santomerse D	6.9	1250	42	7020	53	9620
Sapamine KW	7.8	2600	38	6250	57	8650
Tergitol 7	4.4	820	40	7100	65	10,700
Zinc naphthenate	21.0	4100	38	5960	69	8060
Water	..	...	...	...	70	8850

* Plastic viscosity in poises.
† Yield value in dynes per sq cm.

Table 23. Method of Incorporating Surface-Active Agents

Composition No.	Pigment	Pigment Concn. (% by Vol)	Vehicle
1	Ultramarine	20.8	Mineral oil
2	Ultramarine	37.0	Phenolic resin varnish
3	Toluidine toner	22.0	Glycerol
4	Toluidine toner	27.3	Mineral oil
5	Iron blue	24.3	Mineral oil
	Carbon black		
6	Short	13.7	Linseed varnish
7	Long or flow	9.0	Phenolic resin varnish
8	Short	9.8	Mineral oil
9	Long or flow	13.7	Linseed varnish

Composition No.	Reagent	Yield Value in Dynes/Sq Cm*: Control	Method A	Method B	Method C	Method D
1	Zinc naphthenate †	3000	120	90	100	0
2	Santomerse †	3800	120	0	240	710
3	Santomerse †	620	0	0	0	0
4	Lecithin †	1150	550	660	560	220
5	Lecithin †	10,000	2580	1770	2600	770
6	Benzidine ‡	1100	330	260	400	430
7	Lecithin ‡	620	160	160	140	500
8	Gilsonite ‡	970	660	430	770	970
9	Zinc naphthenate‡	350	290	290	260	660

* *A*, all ingredients mixed and ground; *B*, reagent in vehicle; *C*, reagent added to dispersion after grinding; *D*, coating pigment.
† 3% on pigment by weight.
‡ 5% on pigment by weight.

dispersions in litho varnish, and surface-active agents produce reduction in yield value. In some cases the reduction is marked, as shown, for example, on the addition of lecithin to an iron-blue dispersion. Ultramarine in mineral oil shows a striking reduction in yield value with the addition of lecithin and zinc naphthenate.

The change in flow characteristics as measured is apparent even on casual examination. A marked reduction in yield value, such as that shown by the addition of lecithin to iron blue in mineral oil, represents the difference between a heavy non-fluid paste and a product which will pour readily from the container.

Several advantages can accrue from the use of surface-active agents. Not only is it possible in some cases to increase the pigment content of a dispersion while retaining necessary flow properties, but also to decrease the flocculation to a point

where a composition changes to a fluid from a condition initially highly plastic. Such an application is found in printing inks, which must show maximum obscuring power at low film thickness and yet be sufficiently fluid to follow the fountain rollers on the press at high speeds. The opposite result may also be obtained, for should an increase in yield value be desired, as in certain paints, a suitable surface-active agent may be added.

FIGURE 19. Deflocculated, right, and flocculated titanium dioxide dispersion in linseed varnish (photomicrographs x 600).

Some pigments when dispersed in vehicles are water-sensitive and form stiff, pasty masses on chance contamination with water. Surface-active agents serve to prevent this large increase in yield value, and a spectacular example is that of dispersions of titanium dioxide (Table 20). In mineral oil a trace of moisture added to the dispersion increases the yield value to such an extent that a stiff paste results. If, however, zinc naphthenate, lecithin, or Aerosol OT (as examples of possible reagents) is added during grinding, subsequent addition of water increases the yield value to a much smaller degree.

In pigment dispersions of comparatively low pigment volume, the rheological effect of surface-active agents is much less marked. This result is readily understood, for where the particles are widely spaced, flocculation (when present) shows microscopically as a loose reticulum of clustered particles which can be disturbed at low shearing stresses. If, on the other hand, the particles are crowded, the force of flocculation produces a structure which on shearing in the viscometer is reflected in a yield value of appreciable magnitude.

Settling of the dispersed phase on dilution, however, is a more sensitive test. Where a surface-active agent has effectively deflocculated the pigment particles, the settling volume is small and the cake of settled pigment difficult to re-disperse. Such hard settling in paints is a recurrent difficulty, and can be largely prevented by addition of surface-active agents which promote flocculation.

In formulation problems, the selection of surface-active agents can be facilitated by the use of compounds indicated for analogous systems. This procedure is not infallible, but it has the advantage of reducing the amount of empirical testing necessary. For example, reagents effective for ultramarine blue can be tested with lithopone, titanium dioxide, and most types of chrome yellow. Because there is a measure of specific action associated with the use of surface-active agents, the procedure suggested for routine testing is to select different types of compounds for a quick experimental survey, and then to test more thoroughly related species of the compounds giving the most effective results.

The rate at which aggregates of a dry pigment disperse in a vehicle to the maxi-

mum fineness, is of primary importance in manufacturing operations. That surface-active agents increase the rate of comminution of aggregates is a frequent claim, but the complexity of the process excludes any simple generalization; in addition to specific pigment and vehicle factors the evaluation must be based on (a) type of milling operation, (b) rate of mill output as compared with a control dispersion, and (c) rheological properties of the dispersion.

For roll-mill dispersion, as typified by the three-roll mill, disintegration of aggregates is accomplished first by an actual crushing of particles 10μ and larger in size, at the start of a batch-grinding operation, and finally by shearing within the plastic mixture; the latter reduces the aggregate size to the dimensions of ultimate pigment particles less than 1μ in diameter. Internal friction resulting from flocculation of the pigment particles is of small comparative magnitude and may be considered negligible.

Since the output of a roll mill is proportional to the viscosity of the mix when roll clearance and operating speeds remain constant, surface-active agents which increase the plastic viscosity act to increase mill output rates. The addition of these reagents is thus a useful production device. Essentially the same result may be obtained, however, by formulation with higher-viscosity oils, by increase in the pigment content, or both, using preferably a deflocculating combination of vehicles and reagents. When the dispersion is satisfactory, the product can be extended with additional vehicle to give the desired pigment-vehicle ratio.

Somewhat different considerations apply to colloid mill and to ball and pebble mill operation. The mixture fed into a colloid mill should be fluid, since any appreciable yield value will markedly reduce the rate at which the dispersion will flow into the mill. In ball and pebble mills the mixture should allow cascading of the grinding medium, and if the yield value is excessively high the balls or pebbles will pack, especially in small mills, with consequent reduction in attrition.

It is evident that an improved dispersion rate resulting from an increase in mill efficiency by the addition of surface-active agents is a secondary effect of such reagents. Final pigment tinting strength appears to be directly related to the change in plastic viscosity of the mixture produced by the addition of surface-active agents. This is shown by the statistical data in Table 19. The strength differences were in the range of 2 to 10 per cent, sufficiently large to be outside the errors of the measurement. Although no direct experimental evidence has been obtained to show that surface-active agents facilitate the mechanical breakdown of pigment aggregates, such a result is not unlikely. The data for carbon black suggest that with this pigment at least a favorable effect is found.

Of considerable practical interest are the several ways in which surface-active agents may be incorporated in a dispersion. Except where noted, the experiments were performed by mixing all ingredients of the formulation and then grinding. This procedure, designated *A*, follows manufacturing operations where a premix of all ingredients is made in a pony mixer or dough mixer. Alternative methods included: *B*, solution or dispersion of reagent in vehicle; *C*, addition of reagent to pigment dispersion already prepared; *D*, treatment of dry pigment by mixing with a solution of surface-active agent in a volatile solvent to form a paste, followed by evaporation of solvent at low temperatures. Each of these methods has an analog in commercial practice.

Experimental results are shown in Table 23. Of the four methods of adding surface-active agents, the chief differences noted were in the degree rather than the direction of change in flow properties. Coating the pigment before incorporation in a dispersion is effective and practical from the standpoint of the color manufacturer, but essentially equivalent results are obtained if the reagent is added at the time the preliminary mixture of pigments, vehicles, and other components is made. The latter method is preferred in many manufacturing operations.

Flushed Colors

The manufacture of pigment-in-oil pastes directly from aqueous pulps without the intermediate steps of drying and dry grinding is an old art and one that has found a large measure of economic exploitation. In recent years, the terms "flushed colors," "flushed inks" and less frequently "pulped colors" have come into use, and these terms have included nearly every variant of color and paint manufacturing in which direct grinding of dry color and vehicle is avoided.

The process in its simplest form consists in mixing filter press cakes of a pigment (comprising pigment, water, dissolved and adsorbed salts, excess reagents, etc.) with an oil by means of a dough mixer. The pigment is preferentially wetted by the oil and the water is displaced from the mixture and may be separated by decantation. Some water remains in the pigment-oil paste, and further dehydration may be effected, mainly through evaporation, by repeated passes on a roll mill. Numerous modifications of this procedure have been in use and other variants have been proposed.

The transfer of a pigment from aqueous to oil dispersion may be analyzed by a consideration of the interfacial energies, represented by vectors, acting on the particle. This is based on the classical treatment described by Maxwell,[70] Adam,[4] and others, and is directly analogous to the theories of mineral flotation derived by des Coudres and Hofmann.

For convenience in visualizing the manner in which the transfer from one liquid phase to another may occur, consider a single particle momentarily placed at the oil-water interface. It is possible to postulate that the particle caught in the interface encounters a resolution of forces such that it is held immobile. This equilibrium state may be represented by tensions, diagrammed in Fig. 20, according to the following relation:

$$\gamma_{SO} = \gamma_{SW} + \gamma_{OW} \cdot \cos\theta$$

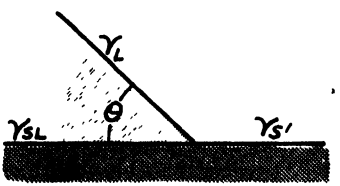

FIGURE 20a. Contact-angle relations air-liquid-solid system.

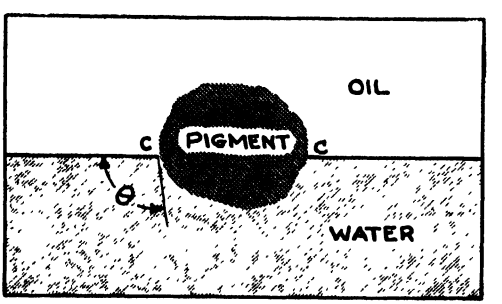

FIGURE 20b. Contact-angle relations in the oil-water-solid system.

If the interfacial-tension relations are changed by the addition of a surface-active material or by reaction of the pigment with some component of the oil, then the equilibrium is disturbed, causing the point *C* to move toward the water phase with

the particle moving toward the oil phase; if flushing takes place the particle becomes engulfed by the oil. This condition is represented by

$$\gamma_{SW} > \gamma_{SO} + \gamma_{OW}$$

The opposite case, that of transfer from oil to water dispersion ("water flush") may be described in similar terms. Then the contact angle θ approaches zero, the point of contact C moves toward the oil phase, and the particle enters the water phase. This condition is represented by

$$\gamma_{SO} > \gamma_{SW} + \gamma_{OW}$$

The actual operation of flushing may be pictured in the following manner. Oil is added to filter-press cakes of pigment in which the pigment is dispersed in the water. Mixing results in an emulsification of the oil and the consequent formation of a large area of interfaces at the junction of emulsified oil, dispersed pigment, and water. Particles of pigment transfer into the oil particles. As the mixing continues the transfer is gradually completed, and the water, which originally served as the dispersion medium for the pigment, is depleted of the pigment particles. The oil particles now containing the pigment coalesce into a paste, adhering to the mixing surfaces because of their greater viscosity and tackiness. The water separates and may be decanted; some water remains in the paste as a water-in-oil emulsion which must be removed by further processing.

An elementary form of the process is described by Jessup [67] in a patent granted in 1885 which consists merely in mixing pigment pulp with oil and evaporating the water by heating in open kettles. Ramage [78] 25 years later modified this procedure by adding a stearate or oleate soap to a concentration of 30 per cent on the pigment, heating to fusion, and adding oil. Later the soap concentration was reduced to 5 per cent and decantation of the water was effected after initial stirring with the oil. This last variant is the procedure which is largely followed at the present time.

Various emulsification processes were developed around vat and color-slurry operations. Paint oils may be emulsified with the pigment slurry, the emulsion broken by addition of "electrolytes," and the pigment-oil paste separated from the water; this is the general form described by Acheson.[2, 3] A number of variations followed which include the use of heat-coagulable proteins for emulsifying agents [55]; conversion of the soluble soap to water insoluble soaps by Schroeder[81]; and the use of specific reagents to break the emulsion, *e.g.*, formic [49] and citric [65] acids. A pigment-oil combination which is similar to a dry pigment in general physical properties, but which may be readily converted to an oil paste is described by Gessler.[49] Preparation of the colors and pigments in the presence of oils, resins, or waxes, or cellulose derivatives is the basis of patents by Whatmough,[90] Hucks,[65] Hailwood, Shepherdson, and Stewart.[56] Simplification of all the foregoing processes and avoidance of the addition of emulsifying and other reagents is claimed by Denslow, Erskine, and Horning,[27] who pass the mixture of slurry and oil through a mill capable of high shearing action.

Plastic mixing is the more generally described or implied method of operation, and to facilitate the liberation of water from the mixture, surface-active or other reagents are employed, with special techniques for manipulation. The earliest uses of soaps have been noted; further development led to the use of amine and hydroxyamine soaps by Ryan and Fischer,[79] triethanolamine by Holton,[64] lead soaps together with high-acid linseed oil by Brown,[21] inorganic salts, presumably to form soaps with fatty oils, such as magnesium oxide, barium and calcium hydroxides by Broeker,[19] and manganous borates by Fletcher.[42] Sloan and Patterson[85] describe the use of cationic surface-active agents, such as sulfonium compounds, pyridinium halides, and quaternary ammonium bases.

Special manipulation techniques are given by Acheson,[8] who adds the oil to the pigment paste "at a rate not substantially exceeding that at which the oil is absorbed, continuing such addition until separation of water occurs." Use of a previously prepared pigment-in-oil paste as a "seed" to which the aqueous pulp is added is the basis of the patent obtained by Todd and Silvermann.[92]

Removal of residual water, retained in the paste as a water-in-oil emulsion is the feature of another group of patents. An early patent by Ismay[66] describes a pug mill for treating white lead with oil, decanting the separable water, and removal of the residual water by heating under vacuum. Later Hochstetter[68] and Cajar[22] in similar disclosures used vacuum-jacketed mixers for the final dehydration of pigment-oil combinations especially suitable for printing inks. Gradual addition of the aqueous pulp to the vacuum-jacketed mixer at a rate at which the water is volatilized is the basis of patents by de Stubner.[88] Distillation of the water from the pigment-water-oil mixture is accomplished by the addition of a solvent such as toluene and heating in a still is also described by de Stubner.[88]

All these procedures have this principle in common: the color or pigment is not isolated as a dry product independent of the vehicle. Manufacturing advantages may be inherent in certain procedures, but the products are essentially similar to those obtained by regular methods.

Certain colors may be processed to advantage by direct transfer. One of the best known is alkali reflex blue, and this product has been manufactured and sold as a color paste for many years. Another color which is flushed is phloxine toner (lead salt). Photomicrographs reproduced in Figs. 21 and 22 show a comparison of dry-grind dispersions with the flushed pulps; both were of identical composition after processing. The presence of aggregates in the dispersions made from dry color attest to the difficulty in comminuting these aggregates by mechanical means. Processes for other colors, satisfactory only if flushed, are described by Gans,[45] and Fischer, Gluck, and Reynolds.[87]

The majority of colors and pigments when dispersed from dry color by mechanical means are equivalent to flushed colors. The data presented in Table 24 show

Table 24. Strength Changes in Flushed Color Dispersions
Average Values Based on Bleach Tests

Iron blue	−5 to −10%	(Note 1)
Chrome yellow	0 to + 2	
Barium lithol	0 to + 5	
Toluidine toner	+5 to +10	
Victoria blue (P.T.A.)	0 to + 5	
Malachite green (P.T.A.)	0 to + 5	
Peacock blue (Hydrate lake)	0 to − 5	(Note 2)
Phloxine toner	+5 to + 8	
Hansa toner	0 to + 5	

Note 1. Loss of strength attributed to incomplete oxidation of color in vat or reduction reactions during flushing in presence of oxidizable oils or both. Strength frequently develops to 100% on oxidation (drying) of film.
Note 2. Loss of strength attributed to desorption of dye and consequent color loss in decanted water.

average values of strength determinations on the two types of compositions. For most cases, skilled formulation of finished products minimizes any differences.

In a general way the advantages and limitations of flushed pigments may be outlined as follows: (a) with few exceptions flushed colors retain the particle-size characteristics of the color as prepared in the aqueous system, and sintering of the particles or cementation by residual soluble salts during drying is avoided; (b) flushed color dispersions in a few cases have a higher tinting strength than equivalent dry colors, where the color is either deleteriously affected by drying or the particles form excessively hard aggregates which require an impracticable amount of grinding to develop full strength; and (c) the presence of a small residual amount of moisture in the ink accelerates livering reactions and increases the extent of flocculation of

pigments, especially neutral or hydrophilic pigments. This has led to the frequent but not invariable observation that flushed color pastes are of "higher consistency or body" than equivalent dispersions made from dry colors; the charge has also been made that "seeding" is more frequently found in paints formulated with flushed colors.

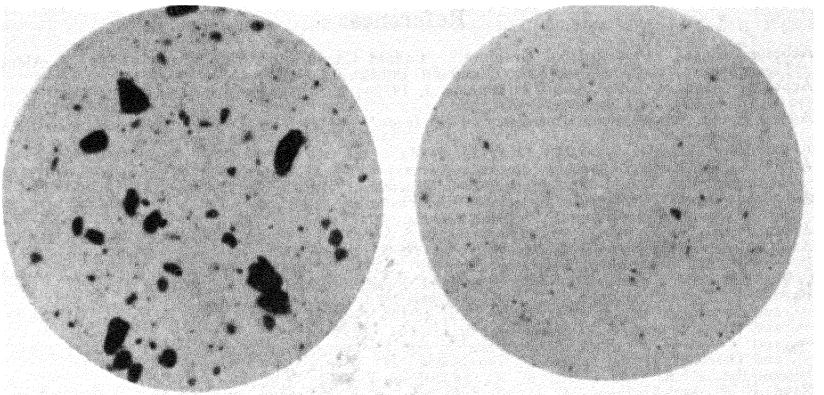

FIGURE 21. Photomicrographs of dry-grind alkali blue toner, left, and the same pigment in flushed form, right (X 600).

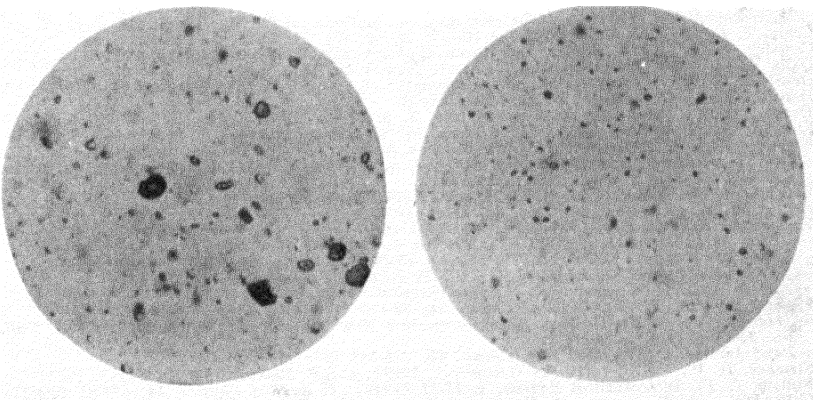

FIGURE 22. Photomicrographs of dry-grind phloxine toner, left, and the same pigment in flushed form, right (X 600).

Summary

In the products represented by the pigment, paint, and printing ink industries the colloid chemist is faced with a complicated and challenging array of physical properties. Emphasis can rightly be placed on the extent and nature of the solid-liquid interface represented by dispersions of a great variety of solids in an equally great variety of liquids.

This review has been concerned primarily with the practical, empirical aspects of such dispersions and the theoretical background for the manufacturing operations which are commercially practicable. Mechanical comminution methods with roll, ball, and colloid mills are widely employed to obtain the particles of the solids in a required fineness, but the physical properties of the dispersions so prepared are determined by the chemical properties of the ingredients of the heterogeneous system.

These are capable of experimental analysis by procedures based on rheological, microscopic, sedimentation, contact-angle, and calorimetric measurements. From the data from these techniques a theoretical picture is emerging which supplies an understanding of the industrial performance of many products based on solid-liquid dispersions.

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Thixotropy

HENRY GREEN AND RUTH N. WELTMANN

Research Laboratories, Interchemical Corporation

One of the phenomena frequently encountered in the realm of colloid science is the ability of certain suspensions to lose part of their consistency when agitated and to regain their original consistency when allowed to rest. This reaction, which is isothermal, was known for a number of years before it was given a name. It was not until 1927 that Peterfi [87] with the agreement of Freundlich, called it "thixotropy." * The word means *to change by touch.*

Structure

The thing changed by touch is structure. In the case of simple thixotropic materials like ferric oxide suspensions in water, the structure is apparently formed by a linkage of the colloidal particles of oxide. In the more complex examples found in materials like printing inks, for instance, it is conceivable that the structure might reside entirely in the large polymerized molecules of the vehicle.

Thixotropic Structure. When thixotropic suspensions such as paints and printing inks are examined under a microscope, they are almost invariably found to possess a flocculated structure. This type of structure can exist, however, whether the material is thixotropic or not; consequently, no definite conclusion can be drawn, at least from visual evidence, as to the relationship between flocculation and thixotropy. It seems to be fairly well established that thixotropy cannot exist without flocculation; but the converse of this proposition is not necessarily true.

Various types of structure capable of producing thixotropy can be imagined. For

* Pryce-Jones states that thixotropic behavior was first recorded in 1863 by Kuhne,[80] who described a nematode which wandered through a muscle cell and traversed the cross-striated fibers without any apparent effort. The implication is that the cell wall was thixotropic. The thixotropy of cytoplasm was also noted by Freundlich.[10, 17]

According to Copley,[6] the phenomenon of thixotropy was first described by Howell,[29] in 1910. This was done in regard to the conversion of fibrinogen to fibrin by the addition of thrombin. Howell also referred to the same phenomenon as early as 1892, when he observed it in the plasma of horse's blood.

Chambers [4] observed in 1921 that protoplasm frequently becomes fluid upon stirring and gelatinizes on standing. Minot and Lee in 1916 [85] observed thixotropic action with blood coagula of hemophiliacs and called it "reclotting phenomenon."

Barus in 1893 (according to Pryce-Jones) observed a rapid fall of steel spheres in a gelatin sol when shaken, against a slower fall in the undisturbed gel, indicating that shaking destroyed structure.

An interesting case that might be attributed to thixotropy is the ceremony of "The Liquefaction of the Blood" held semiannually in the Cathedral at Naples. During the ceremony two phials, said to contain the dried blood of St. Januarius, are placed on the altar. If the blood liquefies it is regarded as a good omen; otherwise, it is considered a sign of misfortune to be visited upon the city and its people. It was suggested to the authors in a private communication from Dr. E. Newton Harvey, who has witnessed the ceremony, that the dried blood is now perhaps a thixotropic suspension of iron oxide.

The authors feel that the above idea is not so impossible when it is realized that blood contains iron and that almost any change could have taken place in it since the time in which St. Januarius lived, that is, during the third century.

instance, if simple flocculation is not sufficient, it is conceivable that particle orientation or some form of particle alignment is the necessary factor. Again, it is possible that cases exist where the thixotropic structure resides in the vehicle molecule by the formation of molecular chains or bridges existing between the particles. The part played by flocculation, in this case, would be simply to bring the particles sufficiently close together so that such linkages could be formed. The presence of flocculation with the absence of thixotropy would mean that no molecular linkages are present. Freundlich [17] believed that the magnitude of the flocculating force is the deciding factor; it must be neither too large nor too small.

Because there are various ways to account for thixotropic structure, it is impossible to say that anything very definite is known about it. Only one fact remains generally acceptable, and that is that the phenomenon of thixotropy is the result of an internal structure so constituted that when broken down it can rebuild itself, if not prevented from doing so by externally applied forces.

Methods of Studying Structure. Perhaps the most obvious ways of studying the structure of suspensions are by microscopy and by rheology. Even though microscopy has not revealed the ultimate nature of thixotropy, it can give, in many cases, sufficient information for a general classification of structure. With suitable technique [21] it is easy to see whether a structure is flocculated or deflocculated and, in the former case, whether the force of flocculation is weak or strong. It is also possible to observe whether a suspension is likely to be plastic, pseudoplastic, dilatant, or Newtonian. This branch of microscopy is a fairly large subject in itself and cannot readily be discussed in detail in the present article. Photomicrographs of various types of structure are shown in Fig. 1.

The electron microscope makes possible a new development in the study of structure. The limit of resolution of this instrument is in the neighborhood of 20 to 40 Ångstroms (1 Å = 0.0001 micron), which figure is quite small in comparison with the various distances quoted in the literature as existing between particles of thixotropic structure.[16, 17] It is the interparticle space that contains the desirable information and the electron microscope, with its high revolving power and depth of focus offers the first opportunity for a truly close-up inspection of it. The total revelation may ultimately turn out to be simply that interparticle distances in a flocculate are less than the resolving power of the instrument, but if that is so, it will still constitute a step in advance by eliminating some of our present ideas as faulty. So far no particular technique has been developed for carrying out this kind of work, but electron micrographs of flocculated pigment have indicated that the interparticle distance can be exceedingly minute. An inspection of Fig. 2 will confirm this conclusion. Here the pigment has been taken in an oil vehicle. This causes a slight loss in resolution, but the interparticle spaces are still very small.

Rheology,* the science of flow, offers a second method for the study of structure.

* This name was coined by Professor John R. Crawford, of Lafayette College. The literature on rheology is extensive; most of it, however, is in the form of individual papers. Professor Bingham has often stated that his own private collection consists of over ten thousand different papers. On the other hand, the number of textbooks on rheology is still relatively small. The first of these to appear was by Bingham,[3] in 1922. This book is particularly valuable for its treatment of Newtonian viscosity and for its extensive bibliography. Naturally, it does not discuss thixotropy, which was hardly recognized at that time as a property of rheological importance.

During 1931-32, Markus Reiner [48] gave a course in Mathematical Rheology at Lafayette College and a similar course at Princeton University, 1932-1933. In 1937, he lectured on Theoretical Rheology at the Hebrew University, Jerusalem. These lectures, covering a period from 1931 to 1937, have been collected and have appeared in book form. It is a mathematical treatise on the fundamentals of rheology and is well illustrated with diagrams that add greatly to the value of the book.

The most exhaustive treatises so far published are the two reports on viscosity and plasticity (1935 and 1938), both being the work of the Committee of the Academy of Sciences at Amsterdam for the Study of Viscosity.[45] Neither of these reports however,

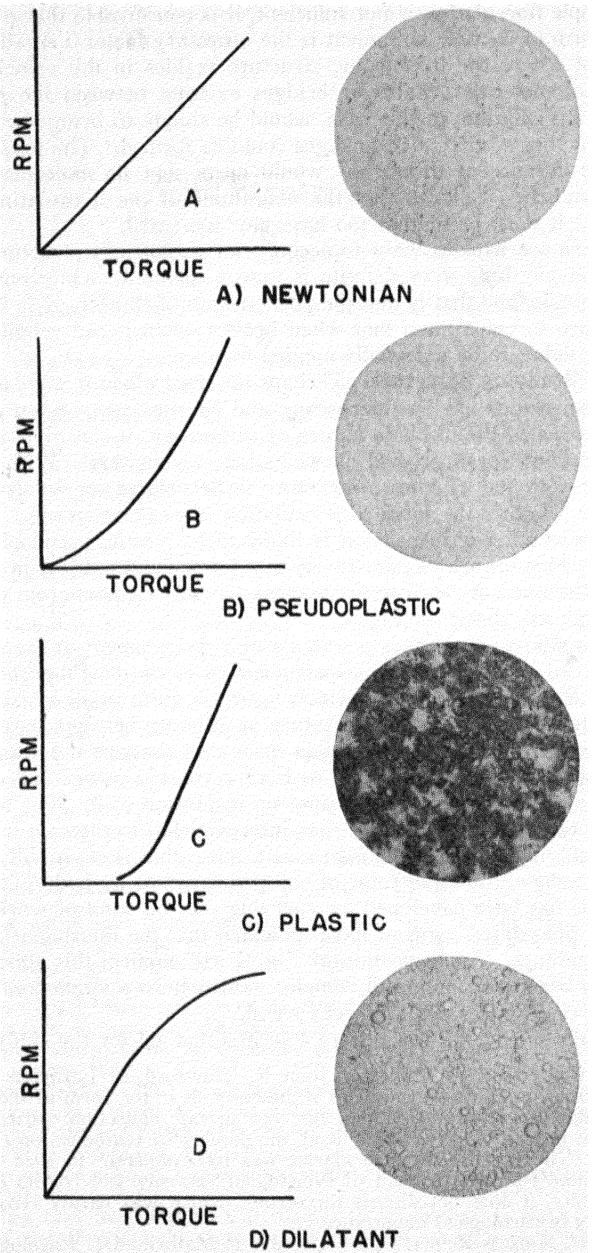

FIGURE 1. Pigment structures in suspensions and their corresponding consistency curves. Suspensions are slightly diluted to get sufficient light through for photomicroscopy. The layers photographed are fairly thick; hence the lack of sharpness in definition. A, a Newtonian suspension. Particles too far apart to form a connected structure. B, a pseudoplastic material. Particles deflocculated and nearly submicroscopic. C, a plastic suspension. The flocculated structure is clearly evident. D, a dilatant material. Particles packed together but completely deflocculated. (Magnification 834 x.)

This is accomplished by means of the consistency curve. This curve is obtained with a viscometer constructed in a manner that makes it possible to vary the force used to induce flow over a wide range. The consistency curve is obtained by plotting shearing force versus rate of shear. When thixotropy is involved the viscometer must be of the rotational type, as explained presently.

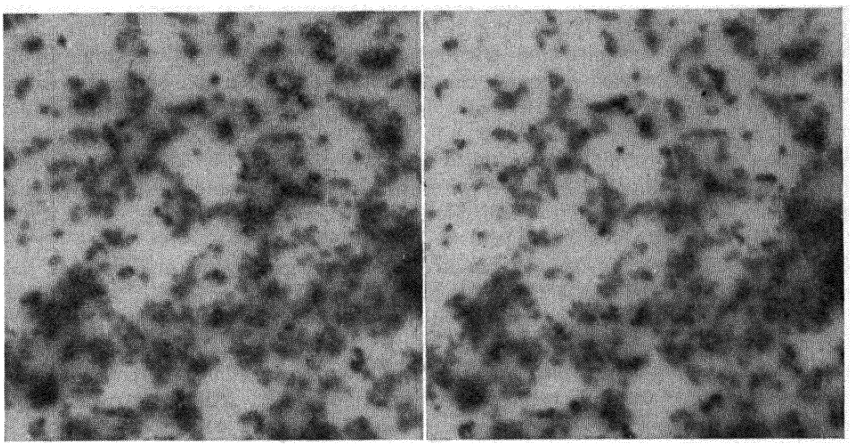

FIGURE 2. Stereoscopic electronmicrograph of an Iron Blue pigment. In estimating the distance between flocculated particles, care should be taken that both particles are in the same horizontal plane, otherwise overlapping might invalidate the results. The amount of diffraction is very small. The particles, however, cannot be any farther apart than the distance between their centers. Even this exaggerated distance is much smaller than interparticle distances usually quoted in the literature. A study of this picture will show that interparticle distances can be less than 0.03 micron. (Magnification 15000 x.)

Each kind of structure produces its own kind of consistency curve. If the structure is that of a simple Newtonian liquid and the molecules and particles do not align themselves under high rates of shear, the curve will be linear and intersect the origin. (Fig. 1a.) If the molecules or particles are not linked together and are elongated sufficiently so that their long axis tends toward an alignment parallel to the direction of flow, the flow curve will be convex toward the force axis; the material is then classified as *pseudoplastic,* (Fig. 1b). Typical examples of such substances are rubber solutions, nitrocellulose solutions and resinous and asphaltic materials. If the structure is flocculated and sufficiently concentrated [59] to be continuous and interlocking throughout the mass of material, then the curve will be of the kind shown in Fig. 1c. Reiner [42, 43] has called this type of material a *Bingham body* because Bingham [2] first stated his law of plastic flow from its consistency curve. This law has since become the foundation upon which much of modern rheology has been erected.

makes any attempt to discuss the subject of thixotropy. In 1937, R. Houwink [28] published a book on elasticity, plasticity and structure of matter. A chapter was contributed by W. G. Burgess. This work covers a wide variety of subjects related to rheology and discusses, though briefly, the subject of thixotropy.

G. W. Scott Blair [52] in 1938 published a book on industrial rheology which is valuable for any investigator who is more or less unfamiliar with the subject. A second book by Scott Blair [53] was published in 1944. This is not an elementary treatise. It devotes a number of pages to thixotropy. The book is a valuable contribution to rheology and has an extensive bibliography. Certain books on colloidal chemistry have chapters on thixotropy which are of value to the student in this field. Hauser's work in this connection is particularly well known.[27]

Dilatancy. In 1885 Osborn Reynolds [46] described a type of suspension to which he gave the name *dilatant*. A suspension becomes dilatant when the force of flocculation is quite small or entirely absent and the amount of the liquid phase is just sufficient to fill the spaces between the particles when the particles are in the position of minimum or nearly minimum voids. Any attempt to force such a material to flow rapidly disturbs the position of the particles, resulting in a dilation of the voids. Since there is not enough liquid present to fill the expanded voids, the material as a whole becomes dry and hard and develops an unexpectedly high resistance to flow. When the applied force is removed, the substance returns to its original condition, again becomes wet, and will flow readily enough if not forced to do so too rapidly. That is Reynolds' own theory. It seems to account for all the facts. There are other investigators who have not been able to accept it.[17] Reynolds gave, as an example of a dilatant material, sand in water where the ratio of the ingredients is such that a pressure applied to the material causes it to become dry. Examples of this are found readily enough along the seashore.

Dilatancy is of rather common occurrence in the paint and printing ink fields. Paints of the enamel type that have been allowed to stand for a long time will deposit a hard, tough layer of dilatant material at the bottom of the can. On account of the dilatant nature of this layer it is difficult to stir it back into the liquid above. On the other hand, if the pigment is flocculated, settling will occur; but the settled layer will not be dilatant and can be stirred back with relative ease.[48] A dilatant material gives the type of consistency curve shown in Fig. 1d. This is the same form of curve that is produced by turbulence; it often requires considerable rheological experience to tell whether such a curve is the result of dilatancy or turbulence.

Pseudoplasticity. In the case of pseudoplastics an applied shearing force produces a change from a disorganized particle (or molecular) arrangement to one of particle alignment with the long axis turned in the direction of flow. Since the particles are not joined together, this alignment does not constitute a structural breakdown; consequently, no buildup time is required when the shearing force is removed; that is, the particles return almost immediately to their original disorganized state. If the material is thixotropic, however, an actual breakdown in structure ensues from an applied shearing force. When this force is removed, the structure commences to rebuild; but the complete reforming of the structure might require hours or even days. On account of this time lag, a change in consistency can be recorded by plotting two consistency curves instead of one. If these two curves comprise an upcurve and a downcurve taken with a rotational viscometer, the result will be a consistency curve having the form of a loop. This will be described in detail later.

Thixotropy in Industry

The colloidal phenomenon of thixotropy is of importance to those industries that manufacture or use materials composed of particles (like pigments, clays, etc.) suspended in liquids. The industries concerned include the paint, the printing ink, and the ceramic industries. So far very little attempt has been made to use thixotropy commercially. A notable example, however, has been in the production of thixotropic paints for the purpose of obtaining a short set-up time. In respect to such paints reference should be made to the works of Gamble [18] and of Williamson.[60] Another example [8] where use has been made of thixotropy is in the petroleum industry, where the drilling muds * are prevented from settling because they possess a certain amount of thixotropic structure. In general it might be stated that interest in thixotropy from the industrial viewpoint more often lies in the fact that the phenomenon has a decided nuisance value. For instance, it would be of considerable advantage to the printing ink industry if it were possible to manufacture heavy printing inks completely free from thixotropy, giving stable viscosity on the press, while retaining

* See paper on drilling muds by D. H. Larsen in this volume. J. A.

printability. The solution of such a problem would require first some laboratory procedure for measuring the thixotropic magnitude, if such a magnitude actually exists.

Measurement of Thixotropy

Methods for studying thixotropy can be classified, briefly for convenience, into four categories:

(1) Single-point measurements, where there is often the implication that the material is Newtonian; (2) deflection-time curves; (3) single-consistency curves; (4) and double-consistency curves. This paper will be devoted mainly to the last-named procedure.

Single-Point Method. The most generally used single-point method of measuring thixotropy is by measuring the time a material requires to solidify after having been liquefied by agitation. Freundlich,[13, 14, 15] Freundlich and co-workers,[9, 11, 12] Heller and Roeder,[26] Roeder,[47] and Schalek and Szegvari [50] used this method. The thixotropic magnitude is assumed to be proportional to the time of solidification in a test tube after the material has first been liquefied by thorough agitation. The end point is determined by inverting the tube. When no material flows out, the solidification is assumed to be complete.

Engelhardt [7] and Winkler [61] used another single-point method. Their value of thixotropy is determined by the ratio of liquid volume to solid volume required to give a solidification time of one minute subsequent to thorough agitation, in a vessel of specified dimensions.

Deflection-Time Curve Method. This method for evaluating thixotropy has been used by Pryce-Jones,[38, 39] Gamble,[18] Saal and Labout,[49] McMillen [32, 33, 34] and others. Some of these investigators plot the deflection against the so-called "relaxation time." This "relaxation time" is not the same as Maxwell's. A pendulum or bob or any other torsion device is deflected through the material to a desired degree, and then released. On release, the deflection decreases in a certain time frequently referred to as "relaxation time," which depends on the physical properties of the test material. For true Newtonian liquids the deflection-relaxation time curves are logarithmic, whereas the presence of thixotropy or yield value causes these curves to deviate from the logarithmic function. For the same material various measurements are obtained after the material has been agitated to different extents. For non-thixotropic materials all curves coincide, whereas for thixotropic materials the curves for the same material differ widely, depending on the amount of thixotropy and on the state of agitation in which the material was before the test started. Traxler [55, 56] and others showed that asphalt is thixotropic by keeping it under strain for a period of time. Traxler used a Mooney [36]-type rotational viscometer and plotted the velocity of the rotor versus the elapsed time. The velocity of the rotor increases until it reaches its maximum, where the asphalt is broken down completely for the applied shear. After a rest period, the velocity of the rotor returns to its original slow speed. This behavior is typical of thixotropic materials.

Since the single- and double-consistency curve methods are of such nature that if either one is correct the other must be wrong, both will be discussed here in detail.

The Single-Consistency Curve Method. The single-consistency curve method developed by Goodeve and Whitfield [19] is one of the best known in this category. It has many adherents both here and abroad. For a complete description, reference must be made to their original article. Their work is not easy to follow, and the present authors realize that their analysis might be at variance in places with Goodeve and Whitfield's own ideas.

Goodeve assumes that the spontaneous buildup, given as rate of structural increase, dx/dt, is proportional to the structural concentration x, the maximum concentration being x_m. Then,

$$\frac{dx}{dt} = k''(x_m - x)^a \tag{1}$$

where a is the order of the reaction. Next it is assumed that the rate of structural breakdown is proportional to the shear, s.

$$\frac{-dx}{dt} = Ksx \tag{2}$$

At equilibrium, breakdown is offset by buildup. By equating the above expressions and assuming that x is negligible compared to x_m, the following expression is obtained.

$$x = \frac{k'' x^a_m}{Ks} \tag{3}$$

The concentration, x, of the thixotropic structure, is assumed to be proportional to the difference between the apparent viscosity, η, and the "residual viscosity" η_0, so that

$$\eta - \eta_0 = k'x \tag{4}$$

Substituting (4) in (3) gives,

$$\eta - \eta_0 = \frac{k'k'' x^a_m}{K} \cdot \frac{1}{s} \tag{5}$$

where the constant $\frac{k'k'' x^a_m}{K}$ subsequently written as θ, is called the "coefficient of thixotropy." An analysis of this constant shows that it is the rate of *viscosity* increase when the material is undisturbed divided by the rate of *structural* decrease when a unit structure is subjected to a unit shearing stress.

Though it is difficult to obtain a mental picture of such a coefficient, Goodeve feels justified in calling it such because it contains, as he says, the two factors, which are necessary for a coefficient of thixotropy to have, *i.e.*, a time factor and a factor indicating the strength of the structure. In carrying out their experiments, Goodeve and Whitfield plot η against $1/s$ and obtain an intercept on the η axis which is equal to η_0. The tangent of their curve is θ. However, the Goodeve equation can also be plotted in the usual manner, that is, as a force-rate of shear curve. If F is the shearing force per unit area, then $F/s = \eta$ and eq. (5) can be written

$$F = \eta_0 s + \theta \tag{6}$$

Eq. (6), like eq. (5) holds only for the linear part of the curve, *i.e.*, the portion where flow is completely laminar.

Refer to Fig. 3. If it is possible to picture the material being run in a hypothetical rotational viscometer where the distance between the bob and cup is the thickness of only two layers of the material, then nothing but laminar flow can take place and eq. (6) must hold down to s equals zero. When s becomes zero, F equals θ; this shows that θ is the shearing force that will produce an infinitesimal rate of shear between two adjacent layers of the material. In other words, Goodeve's θ is defined exactly as Bingham's yield value, f. Goodeve and Whitfield admit the identity of θ and f. They state, however, that θ cannot be a "yield value," as originally visualized by Bingham, for if it were, they argue, it would not remain independent of shear, as shown in Fig. 3, but would be affected, because thixotropic structure is something that breaks down on being disturbed. Yield value, which arises from structure, would have to decrease as a consequence.

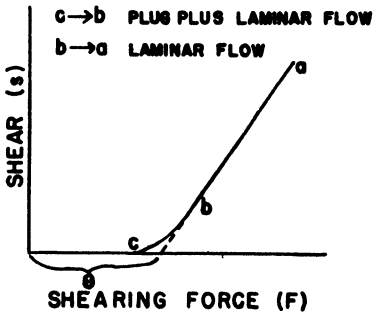

FIGURE 3. Showing the parts of a consistency curve for a plastic of the pigment vehicle type. Plug flow starts at c. Total laminar flow starts at b. From c to b is a mixed regime. From b to a, the flow is completely laminar.

The present authors believe that it is impossible to determine from a single curve like Fig. 3 whether yield value has been changed by thixotropic breakdown or not, for such a curve gives only the consistency *after breakdown has taken place;* consequently no comparison can be made with any previous state in order to see what changes, if any, have occurred; hence the authors are unable to accept θ as a coefficient of thixotropy; θ is still, as far as can be seen, a Bingham yield value, and as such is not directly related to thixotropy. Goodeve's eq. (6) can be written

$$\eta_0 = \frac{F - \theta}{s} \tag{7}$$

which is identical in form to Bingham's original equation for plastic flow through a capillary tube

$$\eta = K\frac{P - f}{v} \tag{8}$$

Other investigators like Sheets [54] and Mardles [31] measure single-consistency curves on a rotational viscometer and conclude from the curvature of the rate of shear-shearing stress curves (decreasing apparent viscosities) that the materials are thixotropic. Roeder [47] pulls a sphere through the test material at various speeds and so obtains a single-consistency curve by plotting the speed of the sphere against the weight which is used to pull it through the test material. Scott Blair [51] used the capillary and falling-ball viscometers to obtain measurements before and after stirring. This represents also a kind of single-consistency curve of only two points. De Waele [6] and many other investigators measured single-consistency curves on capillary-type viscometers and assumed that the curvature of the flow curve might be caused by thixotropy. However, all these single-consistency curve tests fail to distinguish between plug flow, pseudoplasticity, and thixotropy.

Double-Consistency Curve Methods. Pryce-Jones [39, 40, 41] was probably the first investigator of thixotropic systems to realize the inadequacy of a single-consistency curve. He stated that thixotropy cannot be determined from a single curve; he also published a graph of the hysteresis loop. Other investigators like Hatschek [25] and McMillen [32, 33, 34] were aware of the existence of such loops, but evidently made no serious attempt to study them.

In order to measure thixotropy, or at least some attribute of it, it is evident that the material must be examined both before and after a thixotropic change in consistency has been induced. This will give measurements in two states, or at two thixotropic levels. The magnitude of the difference in consistency between these levels will be some function of the thixotropy of the system. *If there should be no difference, then there is no thixotropy, even though the material is plastic.* This is the basic principle upon which the double-consistency curve method is founded. In contrast with this conception, the single-consistency curve method involves the idea

that the existence of plasticity without the coexistence of thixotropy is impossible. If thixotropic materials were Newtonian, a single-point measurement would be sufficient. Thixotropy, however, is invariably associated with non-Newtonian behavior and so consistency curves (F versus s) must be employed. The advocates of the single-consistency curve method believe that the effect of thixotropic breakdown is sufficiently recorded in one curve—the before and after states (the two different levels) being respectively at the bottom and at the top of the F versus s curve (Fig. 3, b and a).

Extrusion Type of Viscometer Not Suited for Thixotropy Measurements

Consistency curves can be obtained with any type of viscometer so constructed that *the shearing force can be varied over a sufficiently wide range.* Both capillary tube and rotational viscometers have been developed along this line. There is, however, a fundamental difference between them when the measurement of thixotropy is involved, which so far has not been emphasized in the literature. It is necessary that this difference be understood. In the capillary viscometer the material passes from the container A (Fig. 4) through the capillary B into the receptacle C. Any agita-

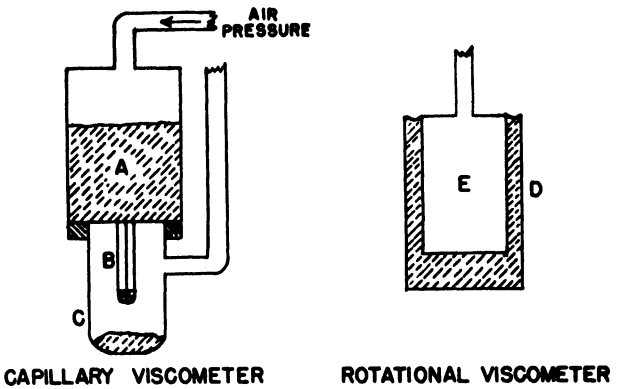

FIGURE 4

tion to which the material in A has been subjected during the measurement is negligible. Consequently, if a second consistency curve is to be run on the same sample, it will be carried out with the material in A in which no thixotropic change in consistency has occurred. The two curves will, therefore, coincide. There will be no difference in consistency recorded. This does not mean that there is no thixotropy present; it simply means that in this instance, the experiment was not carried out correctly, *i.e.,* at two *different* thixotropic levels.

In the case of the rotational viscometer, the situation is quite the opposite. The material is not extruded during the measurement of each point of the curve but remains in the cup, where it is subjected to a substantial and known rate of shear. As will be shown, advantage can be taken of this fact so that consistency curves can be run at different thixotropic levels, and a measurement of the thixotropic magnitude thus obtained.

The Authors' Method

The Hysteresis Loop. It is well known that if a thixotropic material is subjected to an increasing rate of shear, it will undergo increasing thixotropic breakdown. It is not so well known that, if such a material at this point is next subjected to a decreasing rate of shear, there is no further change in the thixotropic structure during the period of decreasing shear. It should be noted that by "thixotropic breakdown"

is meant a decrease in plastic viscosity; it does not refer to "apparent viscosity," which naturally must decrease whether the material is thixotropic or not, if the rate of shear increases.

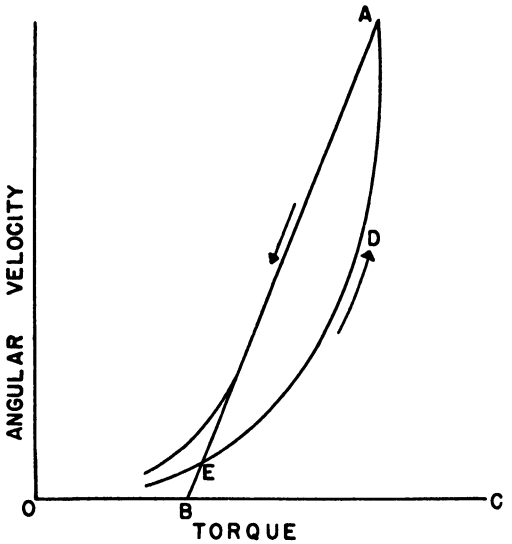

FIGURE 5. A hysteresis loop of a thixotropic plastic taken with a rotational viscometer.

As a result of the above mentioned facts, if up-and-down curves obtained with a rotational viscometer [20] (not with a capillary viscometer) are plotted together, a so-called "hysteresis loop" is formed (refer to Fig. 5). The bending of the upcurve is the result of a structure continuously breaking down. The linearity of the downcurve (except at the lower end where the flow is a mixture of laminar and plug) indicates a temporarily stable structure. The plastic viscosity, U, is obtained from the cotangent of the angle ABC; and the yield value, f, from the intercept OB. The thixotropic breakdown is a function of the area of the loop, $EDAE$. A large loop indicates considerable thixotropy; no loop, no thixotropy.

The upcurve, EDA, is obtained by passing through, not one, but many levels. The only level actually drawn in is the last one measured, AB. The upcurve is, in a way, the "before" state and the downcurve the "after" state. In order to measure thixotropy it is necessary to have a record of both states. One of the first things revealed by a study of the loop is the fact that thixotropic breakdown can occur from two different procedures. The first of these will be called the "breakdown with time." This is shown graphically in Fig. 6.

Commencing at point A and increasing the angular velocity, ω, the material will continue to break down along the curved path ABC. If upon reaching C, the downcurve CDA is started immediately, no further breakdown occurs. On the other hand, if the downcurve is not started at C but the shearing rate at C is maintained, the material will continue to break down until an equilibrium point is reached where the rate of buildup equals the rate of breakdown. This point is designated by E. If the downcurve is now run, it will follow the path EFA. In other words, only a certain amount of breakdown can be obtained from any given shearing rate no matter how prolonged the time of application may be.

Further breakdown can be had only by increasing the rate of energy input, *i.e.*, the power. This type of breakdown will be referred to as breakdown by "rate of shear." The breakdown by successively raising the rate of shear (angular velocity, ω) is shown in Fig. 7. Three different degrees of breakdown are shown, ω_1, ω_2, and

ω_3. The breakdown is evident from the decrease in plastic viscosity, *i.e.*, the cotangent of the angle between the T axis and the downcurve decreases as the rate of shear, or angular velocity, ω, is increased from ω_1 to ω_2 and from φ_2 to φ_3.

The Downcurve. In Fig. 7, three different thixotropic levels are shown by three different downcurves. In Fig. 5, a single downcurve is shown in more detail. It

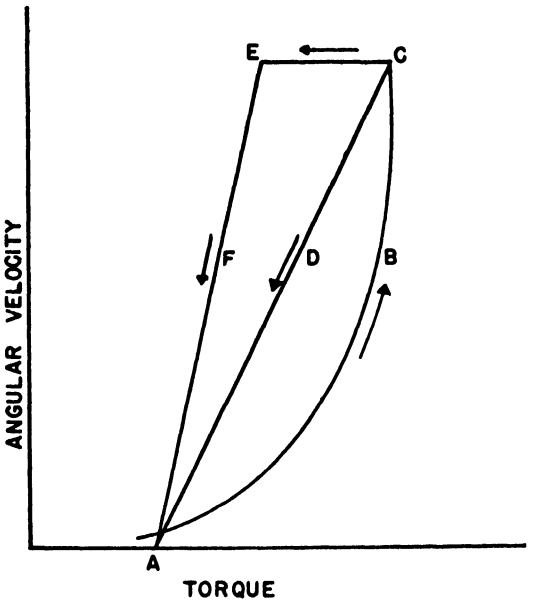

FIGURE 6. Thixotropic breakdown with a constant shearing rate over a period of time. The downcurve shifts from CA to EA.

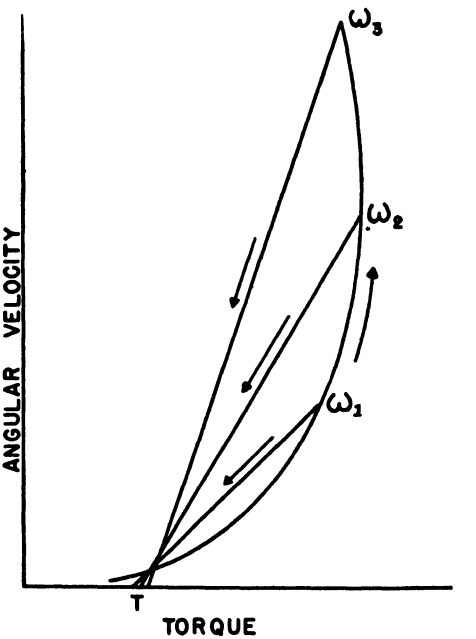

FIGURE 7. Thixotropic breakdown affected by increasing the angular velocity or rate of shear.

will be noticed that throughout the greater part of its length the downcurve is linear. At the extreme lower part, it curves toward the left.

In 1927, Reiner and Riwlin [44] predicted that just such a curve should be obtained from a plastic material (referred to as a Bingham body), if run on a rotational viscometer. They based their deduction on the supposition that the material in no way changes in consistency during shear. It is evident, then, that their equation of flow should be applicable to the downcurve of the loop. From the Reiner and Riwlin equation it can be shown that

$$U = \frac{(T - T_2)S}{\omega} \tag{9}$$

and

$$f = CT_2$$

where U is the plastic viscosity, f the yield value, T the torque at angular velocity, ω; T_2 the intercept on the torque axis, obtained by extrapolating the linear part of the curve; and S and C are constants of the apparatus.

$$S = (1/R_b^2 - 1/R_c^2)/4\pi h \tag{11}$$

$$C = S/\ln (R_c/R_b) \tag{12}$$

when R_b is the radius of the bob, and R_c the radius of the cup. It should be noted that eq. (9) is of the same form as Bingham's eq. (8).

The Coefficients of Thixotropic Breakdown. The expression, "coefficient of thixotropy," implies that "thixotropy" can be quantitatively defined. The authors doubt that thixotropy is a phenomenon that can be placed on a quantitative basis and have discussed their reasons for being unable to accept the only coefficient of thixotropy so far offered, *i.e.*, the one given by Goodeve and Whitfield. On the other hand, "thixotropic breakdown," is a physical reaction involving in some way a redistribution or change in those forces within the system that are the cause of resistance to flow. Looking at it as a *reaction*, the problem becomes easier to handle. It is necessary only to express the extent of this reaction under the conditions that induce it. There may be more than one kind of reaction involved, in which case it will take more than one quantitative expression to define it, *i.e.*, there will be more than one coefficient of thixotropic breakdown.

The Coefficient M. It has been shown [22] if breakdown is induced by change in rate of shear, a coefficient of thixotropic breakdown, M, exists which *is the loss in shearing force per unit area per unit increase in velocity gradient.* Referring to Fig. 8, it can be seen that when the rate of shear is raised by increasing the angular velocity from ω_a to ω_b, the torque will increase from T_a to T_c, if no thixotropic breakdown occurs. With breakdown, the torque will increase from T_a to T_b. The net result is that the final torque is less than it would be in the absence of thixotropy by an amount $T_c - T_b = \Delta T$. The quantity ΔT is the loss in torque corresponding to the "loss in shearing force" in the above definition of M. Assuming that the total loss in torque is proportional to the top velocity gradient, it can be deduced that

$$M = 2(U_1 - U_2)/\ln(\omega_2^2/\omega_1^2) \tag{13}$$ [22]

M is known to be independent of the time employed in obtaining the upcurve. In Table 1 the experimental decrease in plastic viscosity with increase in rate of shear, and the M coefficients determined by eq. (13) are tabulated for various printing inks.

Equations for the upcurve and the area of the loop can be deduced by using the same assumption of proportionality that was employed in obtaining eq. (13) for M. These three equations can be checked experimentally, indicating the correctness of the proportionality assumption.[22, 28]

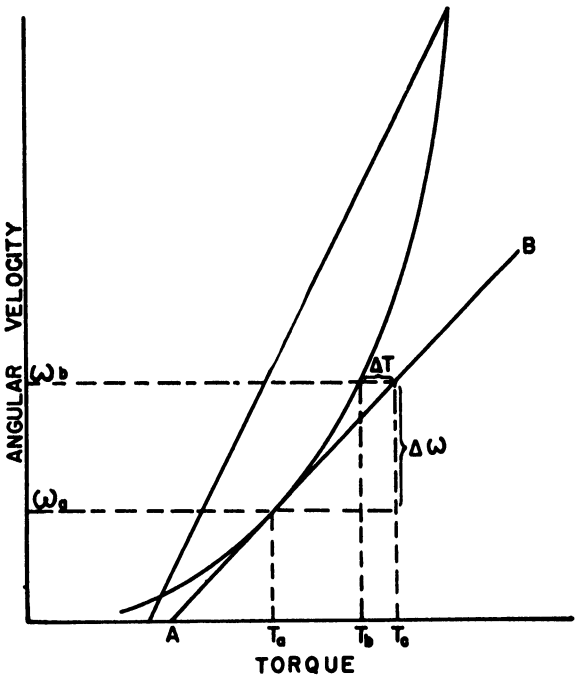

FIGURE 8

Table 1. Decrease in Plastic Viscosity, U, and Increase in Yield Value, f, with Increase in Rate of Shear, dv/dr, and the Coefficients of Thixotropic Breakdown, M and V.

Material	Top rpm	dv/dr (sec.$^{-1}$) *	U (poises)	f (dynes/cm^2)	Coefficients of Thixotropic Breakdown M (dynes sec/cm^2)	V (sec.$^{-1}$)
#1	100	73	990	11000		
	200	146	645	23000	490	39
	300	219	455	32000		
	400	292	335	37000		
#2	100	73	675	11000		
	200	146	440	20800	346	41
	300	219	305	26500		
	400	292	190	31000		
#3	100	73	99.5	1800		
	200	146	84.0	2500	22	45
	300	219	75.0	2900		
#4	100	73	230	200		
	200	146	183	1400	68	26
	300	219	156	2100		
#5	100	73	483	16000		
	200	146	346	17700	190	13
	300	219	270	18700		
	400	292	224	19400		
#6	100	73	600	13300		
	200	146	440	17600	232	27
	300	219	345	20200		
	400	292	280	22000		

* Rate of shear [38] at midpoint of clearance between cup and bob is, $(dv/dr)_{(mid.)} = 4 \text{ rpm}/60\ kS\ (R_c + R_b)^2$.

The Coefficient B. If a thixotropic material such as a pigment suspension is subjected to a constant rate of shear for a period of time it will break down, rapidly at first, then more slowly, until equilibrium is attained. If the plastic viscosity is determined at various intervals during the breakdown, it will be found that the plastic viscosity plotted against the logarithm of the time of breakdown gives a linear relationship [57] (refer to Fig. 9).

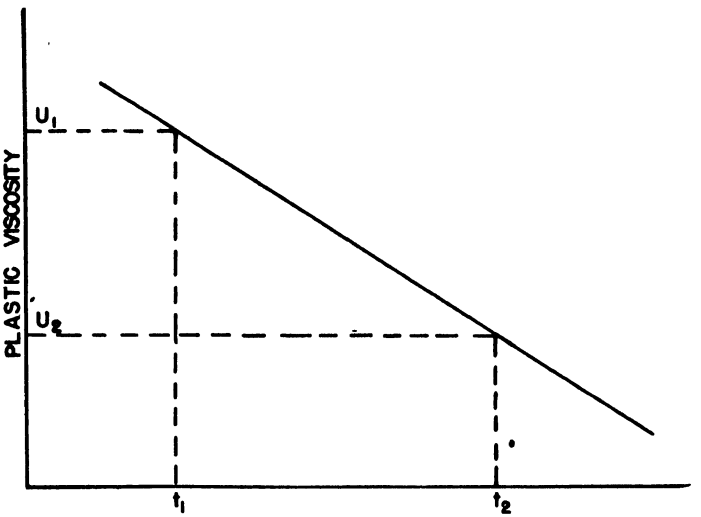

FIGURE 9

If B is the slope of the curve, then

$$B = \frac{dU}{dt}t \tag{14}$$

It can be seen from eq. (14) that the rate of breakdown multiplied by the time of breakdown is a constant.

Integrating the equation between limits gives

$$B = (U_1 - U_2)/\ln(t_2/t_1) \tag{15}$$ [57]

by means of which B can be determined experimentally. B is the coefficient of thixotropic breakdown that shows the relationship between the rate of breakdown and time of agitation. Table 2 shows the experimental decrease in plastic viscosity with time of agitation at different constant rates of shear and the B coefficients for various printing inks.

The Coefficient V. If a thixotropic material is allowed to remain undisturbed, it builds up in both plastic viscosity and yield value until maximum values for both factors are attained. If this material is put into a rotational viscometer and then subjected to a definite rate of shear, breakdown will commence immediately. From the appearance of the stirred material, breakdown seems to occur in both yield value and plastic viscosity. Unfortunately, the nature and extent of this initial breakdown cannot be measured, for the maximum values, which exist only in the undisturbed state, are never known.

If the "definite rate of shear" mentioned above is next increased, further loss in consistency takes places. This is manifested by a drop in plastic viscosity. Paradoxically, the yield value intercept increases at the same time. This increase is shown

Table 2. Decrease in Plastic Viscosity, U, with Increase in Time of Agitation, t, for Various Constant Rates of Shear dv/dr and the Coefficient of Thixotropic Breakdown, B.

Material	top rpm	dv/dr (sec.$^{-1}$)		Experimental Results							B (dynes sec/cm^2)
#1	100	73	U (poises)	1080	1010	953	899	850	825	780	77
			t (sec.)	6	16	30.5	70.5	128.5	166.5	298	
#1	150	110	U	870	780	735	670	617	570		77
			t	7.5	22.5	42	87	184	350		
#1	200	146	U	700	643	600	566	522	498	469	77
			t	11	22	37	62	107	157	235	
#2	100	73	U	794	785	740	696	645	580		62
			t	12	17	30.5	67.5	143.5	413		
#2	150	110	U	622	580	550	520	482			62
			t	16	29	48	80	152.5			
#2	300	219	U	420	370	311	282	253	242	220	62
			t	8.5	17.5	42.5	61.5	98	128	178	
#3	100	73	U	105	103	99.5	94				2.5
			t	3	8	26	266				
#3	200	146	U	86.8	85.2	81	78.8				2.5
			t	9	19.5	76	200				
#3	300	219	U	79.2	77.6	76	73.9	71.6	68.5		2.5
			t	7.5	11.5	20.5	50.5	128	430		
#4	100	73	U	250	235	218	198	177			18
			t	13	22	61.5	170.5	770.5			
#4	200	146	U	200	187	168	148	131.5	128.5		18
			t	11	25.5	73.5	200.5	530	710		
#4	300	219	U	175	162	150	134	120	110	102	18
			t	10	21	45.5	98	225.5	422.5	700	

in Fig. 7, where the angular velocity increases from ω_1, to ω_2. The ratio of the increase in intercept to decrease in plastic viscosity is a constant for any given thixotropic material. This constant, V, is independent of time.

$$V = (f_2 - f_1)/(U_1 - U_2) \qquad (16)^{23,\,24}$$

The experimentally obtained plastic viscosities and yield values for different top rates of shear and the V coefficients calculated from eq. (16) for various printing inks are given in Table 1.

It is difficult to associate any kind of structural breakdown with an actual increase in yield value. Anything like a facile explanation of this problem is impossible. However, the following analysis (which is purely conjectural) might help to visualize what is happening within the thixotropic material.

A Possible Explanation of the Mechanism of Breakdown

Let it be assumed that in a thixotropic pigment suspension two different structures exist simultaneously. One is formed from the flocculation of the pigment, shown as large round particles in Fig. 10a. The other, which causes the suspension to be thixotropic, arises from some quite unknown factor. This factor is represented schematically as long, thin micelles, also in Fig. 10a. Let it also be assumed that the pigment-vehicle ratio is sufficiently high so that the average distance between the pigment particles cannot be increased during flow.

In addition two more assumptions must be made. They are: (a) As soon as two pigment particles come in contact with each other (in the suspension) they must adhere, that is, no time is consumed in having the particles turn and face each other in some definite way. (b) When the thixotropic micelles touch, they will not adhere unless certain particular parts of the micelles form the point of contact, *e.g.*, like the

positive and negative poles of magnets coming together. Hence, if these particular parts do not touch at the moment of micellar contact, time will be consumed before Brownian motion or some other disturbing force brings them into position so that they do touch at the right points. It is this time consumed that manifests itself as the "setup time" in a thixotropic material.

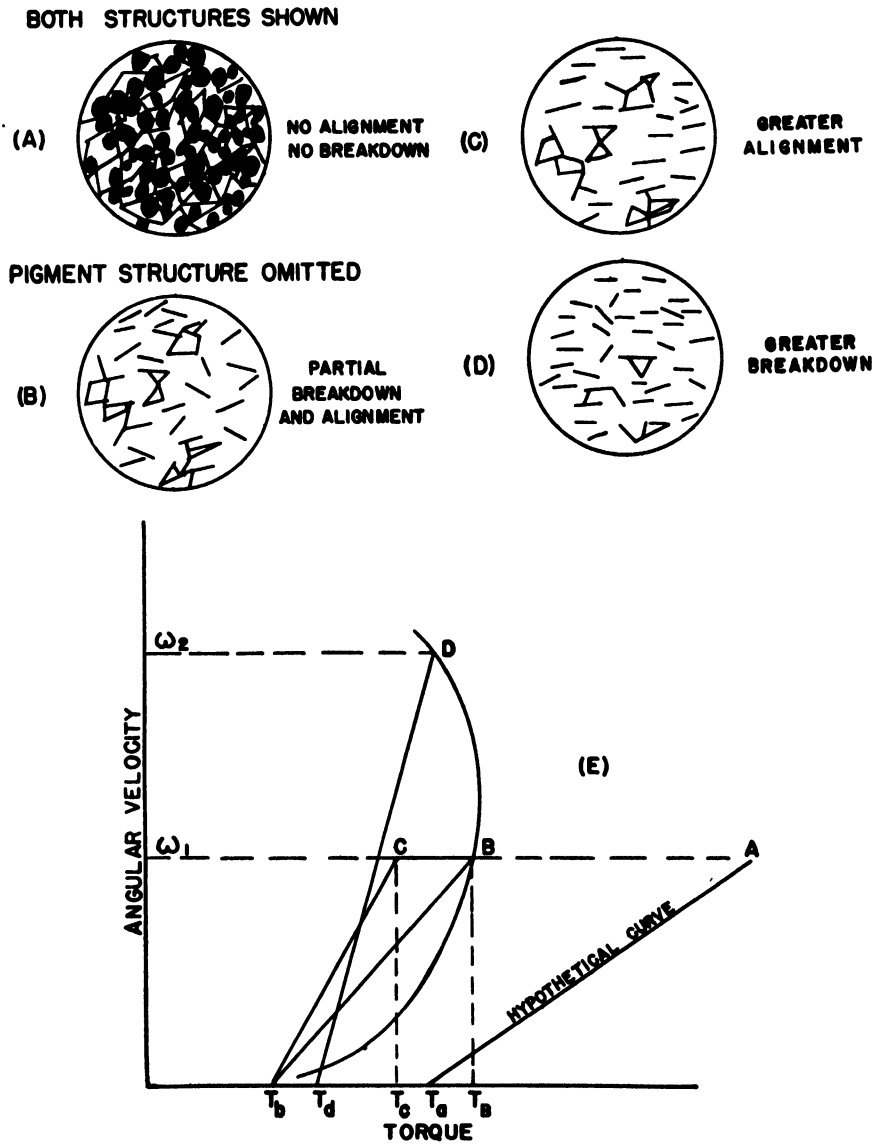

FIGURE 10. A possible explanation as to what happens in a thixotropic material when broken down by time and rate of shear. The schematic pictures (A), (B), (C), and (D) correspond to the points A, B, C, and D in diagram (E). In order that the hypothetical change in the micellar structure would not be obscured, the pigment structure was omitted in (B), (C), and (D).

The above model, in order to be satisfactory, must be able to answer the following questions:

(1) Why is the dynamic yield value intercept T_b, T_d, etc. (Fig. 10E) smaller than the static yield value intercept T_a?

(2) Why, at a constant top rate of shear, does the intercept T_b remain constant as the consistency curve drops from BT_b to CT_b during the time of application of the shearing force?

(3) Why does the yield value intercept increase from T_b to T_d when the top rate of shear is increased from ω_1 to ω_2 (Fig. 10E)?

Before attempting to answer these questions, it is first necessary to try to visualize what takes place when the two hypothetical types of structure are forced to flow. In the case of the flocculated pigment structure, any layer as it flows by its adjacent layer will maintain constant contact with it. Such layers remain in contact while the particles in one are changing their positions with respect to the particles in the other. That is, as a particle in one layer is breaking contact with its neighboring particle in the adjacent layer, it is at the same time forming a new contact with a new neighbor in the same adjacent layer. Since particle attraction in this hypothetical model does not depend on orientation, nothing fundamentally is changed when such a flocculated system is made to flow, and therefore no drop in yield value occurs.

The situation is different when an oriented thixotropic structure flows. Here, as one micelle is forced to break contact with its neighboring micelle (in its adjacent layer) it will not necessarily adhere to the next micelle with which it comes in contact, because it might not be oriented in a way that makes adherence possible. (The positive and negative poles of the magnets might not constitute the points at which they touch.) Consequently, flow induces a state akin to internal rupture, without the material as a whole actually falling apart. Naturally, the resistance to flow offered by structure will decrease, if the structure is ruptured and there is present no equal counteracting effect; thus structural breakdown can appear as a decrease in the yield value intercept.

Pryce-Jones [39] and many others, including the authors of this paper, have found that the breakdown in a thixotropic material is relatively easy and rapid in the initial stages, where the thixotropic setup time is comparatively long; however, as the amount of breakdown increases it becomes more and more difficult to maintain the more highly broken down state, where the setup time has become short. At the equilibrium point detectable buildup can often be found in a fraction of a second after the breaking force ceases to act. In contrast to this, in the early stage of breakdown, a detectable buildup might not be noticeable for hours or even days after the breaking force has been removed.

It should now be evident why the static yield value intercept, T_a, (Fig. 10E) is greater than the dynamic yield value T_b. As soon as a shearing force is applied, the initial resistance to flow is that offered by *both* structures, that is, by the flocculated pigment structure and by the thixotropic structure. Naturally, this condition will give the maximum yield value intercept. As soon as flow starts, the thixotropic structure begins to break; and, because the rate at which energy can be put into the system (by the rotation of the cup) is greater than that required to maintain the broken down state *in the initial stages of breakdown*, there is a very rapid decrease in the intercept. This decrease continues until equilibrium is established, that is, until the rate of breakdown equals the rate of buildup. The intercept at that stage will be equal to T_b for a top angular velocity ω_1, and so the dynamic yield value will be smaller than the static yield value.

In Fig. 10E, the curve T_aA is entirely hypothetical; it is the consistency curve that the thixotropic material would have if shear produced no breakdown. Shear does produce breakdown, however, and the curve drops very rapidly from T_aA to some position T_bB, the extent of the drop depending on the time the shearing rate

at ω_1 has been applied. At point B the total energy consumption per revolution is $2\pi T_B$. The energy used in overcoming viscous resistance, and consequently employed in producing laminar flow, is $2\pi(T_B - T_b)$. The residual energy, $2\pi T_b$, is the amount required for performing all other operations within the system such as overcoming structural resistances, maintaining the state of breakdown, rotation of particles, and inducing and maintaining particle alignment in the direction of flow.

Apparently there are only two conditions under which the yield value intercept is reducible; one, where a deflocculating agent can permanently decrease or destroy the flocculated pigment structure; and the other, described above, where the thixotropic breakdown takes place in a region where buildup is so slow that measurements can be made before the structure has time to reform.

At the point where the breakdown in consistency is given by the position of the curve BT_b, structural buildup equals structural breakdown; and so no further decrease in T_b can be expected from structural change. Something, however, happens if the constant shearing rate at ω_1 continues to be applied; for the curve gradually changes its position from BT_b to CT_b, where equilibrium in plastic viscosity is finally attained (for ω_1).

It is necessary to explain this shift. Structural breakdown is compensated by structural buildup, and so is eliminated as an explanation. Apparently this leaves but one possibility—micellar alignment. When a thixotropic structural unit is destroyed by shear, there come into existence a number of disconnected micelles (Fig. 10B). Assuming that these particles are elongated they will align with their long axis in the direction of flow, Fig. 10C. It is reasonable to assume that in the aligned state they will offer less resistance to flow than otherwise: hence a drop in plastic viscosity can be expected, and that is what actually happens.

It requires the use of energy, however, to perform the work of alignment. Since energy used for this purpose is not employed in producing flow, it must exist in the consistency diagram as part of the intercept T_b. At first it would seem that this should increase the intercept. Since the intercept remains constant, the reasonable assumption can be made that it takes exactly as much energy input per second to maintain a given aligned state during flow as that required to produce it originally. Though the intercept T_b does not change, there is a falling off in the amount of energy consumed in producing plastic flow. This decrease in energy is equal to $2\pi(T_B - T_C)$.

Now as to the third question: Why should the intercept increase when the top angular velocity is increased? It must not be forgotten that the top ω is the factor that controls the amount of thixotropic breakdown for the *entire* down curve. In going from a top ω_1 to a top ω_2 (Point B to Point D, Fig. 10E) there is an increase (with certain theoretical exceptions *) in the amount of energy put into the system per second. This extra power is divided, some of it being used to increase the rate of plastic flow, and some for performing those operations that ultimately govern the size of the intercept (when the downcurve is finally completed). This increase in power makes possible a further breakdown in thixotropic structure (Fig. 10D); that

* In actual practice, where the speed of the cup must be kept within practical bounds, there will be in all probability an increase in power with increase in ω. From a theoretical viewpoint, however, if it is assumed that thixotropic breakdown is proportional to the rate of shear, it follows that when breakdown attains a certain limit, a further increase in ω will result in an actual decrease in the power involved. Reference should be made to the original paper [22] where the equation of the upcurve is shown to be: $T = \omega \ln k/mS - 2\omega \ln k/mS + T_z$. S is an instrument constant; k and m are constants of the material. The power involved at T is $T\omega$. Multiplying the right-hand side of the equation by ω gives the power for any ω. When power is plotted against ω it is seen that power passes through a maximum. The authors have some experimental evidence that in certain cases they have actually attained this maximum power and that beyond this point there follows a decrease in T_z. Such work requires a viscometer capable of giving rates of shear sufficiently high to cause the necessary structural breakdown in the thixotropic material.

is, in that part of the structure that previously had a buildup time so short that the power available at ω_1 was insufficient to destroy it. Again the continuous input of this extra available energy per second is required in order to maintain the extra thixotropic breakdown, the net result being an increase in the yield value intercept. Experimentally, this is easily shown to be the case.

Briefly summarized: It requires energy to overcome the structural resistance of flocculation; it requires energy to break thixotropic structure and to maintain the broken down state; it requires energy to enforce particle alignment. Since none of these energies produces flow they must jointly appear as the yield value intercept. When the power is increased, more energy becomes available for further breakdown. This manifests itself as an increase in the yield value intercept. The same argument applies also to the energy necessary to maintain alignment.

It is not the intention of the authors to make any emphatic claims of correctness for the preceding explanation. The foundation of the argument, however, is one that seems to be universally accepted, that is, that loss in consistency arises from a temporary breakdown in structure. If this conclusion is granted and the three experimental facts given above are accepted, then one is practically forced in the direction the authors have taken. As a matter of fact, there seems to be no second choice under the circumstances. Unfortunately, thixotropic structure cannot be studied microscopically; no direct visual evidence of breakdown can thus be seen; and so an element of uncertainty enters. It is quite possible that new evidence which will not fit into the present scheme, will alter our concepts. The authors feel that this possibility is at present sufficiently remote to make the above analysis worthy, at least, of some consideration.

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Rubber Latex Technology

R. W. Albright and R. A. Lees

American Anode, Inc., Akron, Ohio

Production of Latex

Rubber latex, the milky white fluid obtained from rubber trees, is a typical colloidal dispersion, and the principles of colloid chemistry are applied at practically every stage in its industrial utilization. At the same time, it exhibits many unique properties attributable to vagaries arising out of its natural origin, so that successful commercial use of latex ordinarily involves much more than mere routine application of known principles of colloid chemistry. It is only natural, therefore, that workers in this field should have been concerned more with the practical than with the theoretical aspects of this very interesting material; and the fact is that, while great strides have been made in adapting it to a variety of commercial uses, there has been relatively little study of the basic colloid chemical aspects of latex.

In keeping with the history of the art, this discussion will be concerned primarily with the technological principles and procedures which have been developed for utilizing rubber latex in industry, and no attempt will be made to delve thoroughly into its more purely scientific and in many instances still controversial aspects.

Primarily, it should be noted that a number of excellent works on latex have been published in the last few years, among which are, "The Chemistry and Technology of Rubber Latex" by C. F. Flint; "Rubber Latex" by H. Stevens and W. Stevens; "Latex in Industry" by R. J. Noble; "The Science of Rubber" by Prof. D. K. Memmler; and the book entitled "Latex" by E. A. Hauser in 1930, as well as the series entitled "Latex and Rubber Derivatives and Their Industrial Applications" by Frederick Marchionna.

Although liquid latex has been known to man since rubber was discovered, it is only since the turn of the century that it has been more than a scientific curiosity. Early commercial interest was centered in its function as a source of dry rubber, and not as a commodity of trade. The principal reasons for such lack of interest were (1) that latex putrefied rapidly, (2) that the products of putrefaction coagulated the latex into an unusable mass, and (3) the cost of transportation was high because of the large proportion of water present.

As the rubber industry grew and developed, the idea of producing rubber articles directly from latex became more attractive. New methods for the direct utilization of liquid latex were devised and, in order to supply the resulting increased demand, improved methods of preserving, concentrating, and shipping were developed. As a result, the latex industry grew rapidly, and the demand for liquid latex increased steadily. More than 60 million pounds of dry rubber in the form of latex were imported into the United States alone in 1939, 75 million pounds in 1940, and if shipping facilities had been available, 1941 imports would have exceeded these figures.

Rubber trees, from which latex is obtained, were first discovered growing wild in the tropical South America, especially in the Amazon valley. Here was found *Hevea Braziliensis,* the most important latex-producing plant. Most of the early rubber

was obtained from these regions, but the rapid growth of the rubber industry forced the search for latex deeper and deeper into the jungles of the interior, and it soon became apparent that shortage of easily available wild rubber would result in exorbitant prices. To relieve the shortage, it was proposed to start cultivating the plant; and after much difficulty, seeds and plants were transported to British Malaya, Java, Sumatra, Ceylon and India. Thus were started the vast plantations of the Far East, from which we have obtained most of our rubber, both dry crude and latex.

The growing and collecting of rubber on the plantation is carried out in much the same manner as is scientific farming in America. Trees are selected, fertilized, cultivated, tapped and rested according to the latest known methods to obtain maximum production with minimum damage to the trees. Tapping begins when the trees reach the age of seven or eight years. Tapping consists of making a spiral slice in the bark of the tree. The first slice is started at 4½ to 5 feet above the ground and extends downward and to the left as it proceeds around the trunk. A small cup is placed at the lower end of the cut to receive the latex. A small amount of ammonia is placed in the cup to prevent putrefaction of the fresh latex. Tapping begins early in the morning. Each coolie is assigned 200 to 400 trees and, as the latex flow lasts for only an hour or so, he is able to start collecting as soon as he has completed his round of tapping. Each tree yields about ⅛ pint of 30-50 per cent latex, (the average being in the neighborhood of 40 per cent), so that the daily crop per coolie is 5 to 10 gallons of latex, or 12 to 25 pounds of dry rubber. The coolies collect the latex in pails which they transport to the central station or "godown." Here the latex is weighed and strained into bulking tanks to await processing for market. The next day the coolie removes the dried rubber from the previous cut and renews the surface by removing a thin ribbon of bark, whereupon the latex starts to flow again.

The latex thus collected may reach the market either in liquid form or as dried crude rubber. To produce the latter, the latex is placed in rectangular tanks equipped with separators or dividers. A calculated amount of dilute formic or acetic acid is added to induce coagulation. The soft, spongy coagulum is removed, washed to eliminate the impurities and worked on a mill to produce sheet or crepe rubber.

When the latex is destined to reach the market in liquid form, a different procedure is followed. First, it is treated with preservative to prevent both putrefaction and coagulation. The most useful substance for this purpose is ammonia, ½ to 1 per cent being sufficient. Other chemicals such as formaldehyde, sodium hydroxide, potassium hydroxide, and more recently, sodium pentachlorophenate, have been used successfully (Stevens and Stevens). The preserved latex may then be shipped as "normal" (38-42 per cent) latex, or may be further processed to produce the concentrated or 60 per cent commodity.

Concentration of latex may be accomplished commercially by one of three important methods: namely, centrifuging, creaming, or evaporating (Stevens and Stevens; Hauser).

Centrifuging consists of passing 40 per cent latex through a high-speed centrifugal machine very much like the familiar milk separator. The latex is separated into two fractions, the "cream," rich in rubber, and the "skim," poor in rubber. Separation is accomplished by centrifugal force. The rubber globules, which are lighter, collect in the inner layers, while the heavier serum is forced to the outer portion of the spinning bowl (Utermark, B.P. 219,635). The cream contains 60 per cent dry rubber and about 38 per cent water, the remaining 2 per cent being composed of ammonia and serum constituents occurring naturally in latex. The skim contains a small amount of rubber and much larger amounts of serum constituents. Still greater purification of the latex may be accomplished by diluting the cream with pure water and repeating the centrifuging.

Creamed latex is produced by treating normal latex with a creaming agent such as glue, gelatin, Iceland moss, and other vegetable mucus substances (Noble). The

treated latex is allowed to stand at somewhat elevated temperatures, whereupon it separates into two layers. The rubber collects in the upper layer and is removed in the form of concentrated latex. The lower layer becomes rich in non-rubber constituents and contains very little rubber.

The third commercially important means of concentration is by evaporation. In this method, normal latex is treated with sodium or potassium hydroxide, together with an alkaline protective colloid. It is then heated to 160 to 180° F. while being constantly agitated. The vapors are removed from above the surface of the latex by the passage of a slow stream of air (Petersen, U.S.P. 1,670,900). By this method of concentration, it is possible to produce a much higher concentrate than by other methods. Stable pastes of concentrations up to 80 per cent solids are easily produced. The disadvantages of the method are that the impurities are all retained in the concentrate and that the alkalinity of the product is high and cannot be reduced except by careful neutralization with acid.

Latex may also be concentrated by passing through filter paper especially treated to reduce the size of the pores to such an extent that they will retain the rubber particles. The method is slow and requires special pressure equipment, so that it has no commercial importance at present (Stevens and Stevens).

Still another method which has been proposed for concentrating latex utilizes the electro-endosmotic properties of latex. A cell containing a series of semi-permeable membranes is filled with latex and an electric current is passed through it. Rubber particles move toward the anode and concentrate at the surfaces of the membranes, forming concentrated latex. The concentrate is decanted, and fresh latex is added continuously to replace it. The method is said to be economical and continuous (Pauli and Stamberger, U.S.P. 2,247,065).

After processing at the plantation or bulking stations, the latex is packed in wax-lined steel drums for shipment to American or European markets. More recently it has become customary for large shipments to be made in bulk. Large tanks containing as much as 150,000 gallons are installed in the holds of steamers and the latex is pumped into these. At the destination, it is transferred to storage tanks and thence to rail tankers for transportation to the consumer.

Nature of Latex

Hevea latex is a bluish-white emulsion having a viscosity comparable to that of table cream. It is composed of rubber in the form of minute globules, dissolved sugars, proteins, resins, etc., and water. The rubber globules are generally considered to be pear-shaped and to vary from about 0.5 to 3.0 microns in diameter (Hauser).* Latex particles exhibit Brownian movement, and viewed under a powerful microscope, they give the effect of a miniature snow storm. Henri states that 1 cc of 8.7 per cent latex contains 50 million particles. Each particle carries a negative electric charge, causing it to repel other particles in its vicinity. The Brownian movement and the negative electric charge of the particles, in addition to the presence of protective colloids and preservatives, account for the stability of latex. This is destroyed either by extremely high or low temperatures, by electrolytes or by dehydrating agents. Freezing coagulates latex through the crystallization of water, which forces the latex particles into such close contact that they eventually stick permanently together. Boiling removes both water and ammonia and alters the

* Francis F. Lucas of Bell Telephone Laboratories states [*Ind. Eng. Chem.*, 34, 1371-81 (1942)] that most latex particles are spherical. He explains the presence of pear-shaped, egg-shaped and other irregular particles by stating that two or more particles become attached to each other in a chain to form a larger particle, which then slowly changes in shape until it eventually becomes spherical again. To support the theory, latices of rubber, balata, Buna S and neoprene were studied by means of motion pictures of magnified specimens of latex. The film, presented at the A. C. S. meeting (Sept., 1942) actually showed particles changing in shape from chains of three or four particles toward the spherical.

nature of the protective colloids, thereby causing coagulation. Once the rubber particles have coalesced into a coherent mass, they cannot be separated again except by special mechanical and chemical treatment.

Latex Compounds

Before latex can be utilized for the manufacture of rubber products or rubber-coated articles, it is necessary to incorporate substances capable of improving the physical and chemical properties of unvulcanized rubber. In addition to sulfur, accelerators and activators of vulcanization, it is common practice to add to the latex a wide variety of fillers, colors, age resisters, softeners, etc. There are limitations, however, as to the substances which may be added. Certain salts and all but the very weakest acids are incompatible with latex, as they cause serious instability, if not instantaneous coagulation. Other substances having strong dehydrating action are likely to cause flocculation or complete coagulation.

In order to obtain homogeneous mixtures of the latex and the compounding ingredients, it is essential to dissolve the latter, or, if they are not soluble in water, to grind them in water suspension to a particle size comparable with that of latex. The grinding is usually carried out in ball mills or in commercial colloid mills of various types. These ground materials, or dispersions, should have an alkalinity similar to that of latex, and it is advisable to incorporate in them suitable dispersing agents and protective colloids. Liquids, semi-solids, and some low-melting solids which are immiscible with water are prepared for incorporation into latex by emulsification. Satisfactory emulsions are produced by means of several types of commercial homogenizers and colloid mills. In some cases a high-speed mixer which provides violent agitation may be utilized.

Latex compounding is an art in itself. While it follows the general lines of the familiar crude rubber compounding procedure, there are some vital differences which must be observed. The quantities of various ingredients required to obtain a desired result are sometimes greatly different, and each compound or combination must be studied carefully to determine how to obtain the optimum result.

Latex in Industry

Once a satisfactory latex compound has been produced, it may be utilized in a wide variety of processes. Large quantities of latex are used in the textile and paper trades as binders for the fibers and waterproofing of the finished fabrics. Rubber thread is produced by extruding the liquid latex compound through an orifice submerged in a coagulating liquid. Latex may also be used for spreading, impregnating, casting, spraying and dipping. Rubber articles and rubber-coated articles may be manufactured by dipping forms into latex compounds. The desired thickness of rubber is built up either by repeated dips or by utilizing the coagulating action of various acids and metallic salts previously applied to the form, as in the Anode Process (Klein & Szegvari 1,825,736; Twiss 1,996,051). Rubber articles and rubber coatings may be produced by electro-deposition of latex in much the same manner as metals are deposited. This process for a time appeared very promising, but is now used only in the manufacture of specialized articles such as labels, figured corset blank deposits, rubber-coated screen, etc. Lack of more extensive application is due to several shortcomings of the process. In order to produce a solid deposit by this process, the anodes must be made of either zinc or cadmium (with other metals the deposits are spongy because of the liberation of gas at the anode), and these metal forms waste away rapidly in use as a result of the action of the electric current, and must be replaced frequently. Also it is necessary, in order to produce a uniform deposit, that cathodes be positioned equally distant from all portions of the anode so that the current flow between cathode and anode in all areas will be uniform. For articles of complex shape, such as gloves, this is a practical impossibility. Standard

electro-plating equipment cannot be used, and special expensive equipment is necessary.

The method of producing articles by the use of chemical coagulants came into greater use shortly after 1930, and before the end of the decade was responsible for the production of a large proportion of the articles made by dipping methods.

In the chemical coagulant dip processes, forms are coated with coagulant salts such as calcium chloride, calcium lactate, calcium nitrate, zinc chloride, zinc sulfate and numerous others (Klein and Szegvari 1,825,736; Twiss 1,996,051). These polyvalent metallic salts, when applied to the form and dipped in the latex, dissolve and ionize in the water phase of the latex adjacent to the form, liberating positively charged metallic ions. The rubber particles, which bear a negative charge, are neutralized by the positive charge of the metallic ions and coalesce into a semi-rigid film around the form. The thickness of the film can be controlled by the length of immersion in the latex and by the salt concentration of the coagulant. The latex compound used contains sulfur, accelerators, activators, age resisters, colors or any other pigments essential to the product desired. After the deposit is made, the form is withdrawn and the latex deposit is washed in lukewarm water for a short time to remove excess coagulant and protein matters. Then the resultant deposit is dried to within a small fraction of 1 per cent of moisture, after which it is either stripped from the form, or placed in the vulcanizer while on the form. Since the process is entirely cold until after the rubber deposit is formed, very high-powered accelerators may be used, and as a result, much of the vulcanizing is done in hot air at low temperatures (220-250° F). Steam and water vulcanization, of course, are also utilized.

Another method of manufacturing by dipping forms in latex, which utilizes the coagulating action of acids and salts, involves first dipping the forms into latex, then coagulating the films adhering to the forms by exposing them to fumes of a volatile acid such as formic or acetic acid, or by dipping them into solutions of suitable coagulating substances. Heavy-gauge articles are produced by repeating the cycle a number of times until the desired thickness is obtained. The deposits obtained by this method may then be washed, dried and vulcanized as described above (Teague 1,719,633). Although the method is slower than the one previously explained, it is somewhat more rapid than straight dipping and drying methods, as the coagulant sets the latex film on the form in a shorter time than is required for simple drying.

Latex is now finding wide commercial application in the manufacture of high-grade gloves (surgical, household, electricians', acid, and general industrial), baby pants, dress shields, tobacco pouches, drug sundries, catheters, tubing, drains, blood-pressure bags, anesthesia equipment, oxygen equipment, balloons, (toy and meteorological), dolls of all shapes and sizes, diaphragms, and the like.

In addition to its extensive use as a raw material for the production of rubber articles by electro- and chemical-coagulation methods and by multiple dipping and drying methods, latex is being used extensively in a wide variety of other manufacturing operations. In many of these it is used by itself, but in many others it is incorporated in compositions containing other materials, or is used as a coating or protective sheath.

Latex Sponge

Latex has been used for some time to produce sponge rubber, but the product was given impetus when the Dunlop Company in England introduced their "Dunlopillo" to the motor industry about ten years ago. Their commercial adaptation was primarily that of dispersing air in the latex to form a foam by whipping the latex in much the same manner that cream is whipped (B.P. 332,525, B.P. 332,526). In the United States, the early work on this method was done by Untiedt (U.S.P. 1,777,945). A beater was used to stir air into properly compounded latex mixes.

Just before the foam was complete, a delayed-action coagulant such as sodium fluosilicate was added. This foam was then poured into molds where it set and was vulcanized. Another method of producing sponge rubber from latex consists of incorporating a low-boiling liquid, such as butane, into the latex compound to form a composition which is stable so long as it is maintained in the bulk at ordinary temperatures. A drum is then partially filled with the composition and rolled to spread it in thin films on the walls of the drum and thus reduce its bulk state. The liquid thereupon vaporizes and a latex foam is formed which may be poured into molds, coagulated, and vulcanized. (Harrison and Gould, U.S.P. 2,278,441). Automobile seats, railroad car cushions, upholstery of all kinds, and mattresses, have been the industrial applications of this sponge rubber.

Numerous other methods of making cellu-rubber have been used, but the Dunlop method is the one most popularly employed.

Rubber Thread

Another use of latex, which has become very extensive, is in the manufacture of rubber thread. "Lastex" thread, as produced by U. S. Rubber Co. and in England by Dunlop, is made by extruding latex from spinning nozzles, immersing the filament thus formed in a coagulant, and conducting it thence through washing, drying and vulcanizing operations (Hopkinson, U.S.P. 1,545,257; Dunlop, B.P. 311,844). Another method of producing rubber thread entails the making of a latex sheet and then slitting the sheet into threads (Beal, U.S.P. 2,061,749; Hansen, *et al.*, U.S.P. 2,086,616). The "Controlastic" thread is made by depositing a thin narrow band of latex on a moving belt, removing the rubber band and forming it into a thread by passing it obliquely over a sheave (Alderfer, U.S.P. 2,054,354). Other methods of producing threads involve flowing latex into a groove in a belt or drum (International Latex, B.P. 400,846; Kratz, U.S.P. 2,037,031), or depositing latex on a flat wire and cutting the edges, thus forming two threads simultaneously (B.P. 244,931). The diameter of threads has been reduced by stretching before vulcanization (B.P. 441,799). Special covering machinery was devised to enclose the rubber threads in silk, cotton, rayon, etc. Threads as fine as 150 to the inch are commercially in use.

Molded Latex

By thickening latex it has been found possible to mold it into rubber objects in somewhat the same manner as the ordinary crude rubber molding process, except that pressure is not essential to cause the flow of the rubber; a setting up or coagulation is the essential feature. There are many disadvantages in molding latex, however, and the primary one is that of shrinkage, which causes deformation upon drying.

The Kaysam process overcomes some of these disadvantages, primarily by incorporating in the compounded latex substances which cause gelling at a predetermined time upon the rise of temperature. The latex so treated is poured into a mold and allowed to gel, after which the object is removed from the mold and dried (B.P. 391,511; B.P. 391,853; B.P. 391,868). Unless the gelling agent is washed from the deposit, an inferior finished product may result. A variation of the Kaysam method consists of making articles on the inside of a hollow form. A pre-determined amount of latex is treated with a gelling agent and introduced into a hollow form. The form is rotated about several axes, the mix coagulates on the inside of the form, and upon the removal of the form, the resultant rubber product is washed, dried and cured. The above methods are frequently spoken of as latex casting, and have been popular to some extent in the manufacture of balls, bulbs, and certain forms of medical rubber apparatus and toys.

Another distinctly advantageous variation of this process is in the manufacture of sounding balloons. The balloons are made in a similar manner, enough latex

being used to produce a heavy wall. While the deposits are still wet, the balloons are inflated to increase their diameter and reduce their wall thickness. While so inflated they are dried and vulcanized. So handled, they do not return to their former size, but retain the diameter at which they were vulcanized. Such balloons may then be inflated a second time to a diameter very much greater than would normally be the case. Thus a balloon made on a form no bigger than a few inches in diameter may be inflated to about 36 inches, where it is vulcanized, and from that point it is possible to inflate it to 12 feet.

Insulation

Latex has been used for coating wires for electrical purposes, especially where a light insulation is desired. In this way great economy in weight is effected.

Latex which has been centrifuged or creamed three times has been found to be most satisfactory from a water absorption standpoint, and is most generally used in this form of insulation (McGavack, *Ind. Eng. Chem.*, 894 (1935).

Metal Coating

In addition to the production of all-rubber articles, latex has found a rapidly increasing utilitarian value as a permanent coating for metal. These coatings are used where cushioning or insulating properties are desired. Such a coating may be produced by the Anode Process, by more or less the same steps as previously described, except that in this case the form on which the deposit is made becomes a permanent part of the finished article, and also that an adhesive coating is applied to the metal and becomes the bonding agent between the metal and the rubber deposit.

Metal may also be covered with latex by spraying or brushing, if temporary protective coating is desired. Highly polished metal surfaces have been protected by covering them with paper which had previously been coated with latex to adhere the paper to the metal. Thin coatings of latex alone have also been used to protect fragile articles from damage during fabrication and shipping (Copeman, U.S.P. 2,020,255).

Fabrics

Various methods of wetting fibers and impregnating them with latex have been devised and are being used in treating tire cords. Rayon cords are especially improved by impregnation with latex [Hopkinson, U.S.P. 1,411,786; Jury, U.S.P. 1,470,924; Hancock, B.P. 5,045 of 1824; Dieterich, *Ind. Eng. Chem. Anal. Ed.*, **2**, 102 (1930); and Trobridge, B.P. 309,321]. Several of the large tire companies in the United States have been utilizing these methods commercially.

The spreading of fabrics with latex is carried on by using concentrated latex containing various compounding ingredients. The danger of coagulation at the doctor knife is acute, and extreme care and skill must be used to avoid the setting up of the latex particles at this point. Pre-treatment of the cloth to prevent striking through is essential; also the cloth must be relatively free of oils, waxes, fats, copper and manganese. The spread fabric is dried by passing it over platens or steam-heated drying drums. (Reference between 35-48, page 537, of Flint.) Nettings, sacking, fishnets, and covers for miscellaneous specialty items have been made by this method. Insoles for shoes and artificial leathers may also be made by spreading fabric. Prefabricated cotton gloves in large numbers have been treated with latex to render them waterproof and increase their life. Vulcanization of fabrics treated as noted above is generally effected with hot air. One of the very largest single uses of latex has been the treating of the backs of carpets and mohair upholstery. The pile fabric is woven double with a backing on each face, and is then split by a knife into sections, which are then strengthened with latex on the outside (*India Rubber World*, April, 1932; U.S.P. 1,842,746). Mohair upholstery, in which the

fibers in the V-weave of the pile are fastened primarily by means of compounded latex, was used in tremendous quantity during the last decade (U.S.P. 2,065,937; U.S.P. 2,070, 335).

It might be well to remark in passing that the familiar Kaye process for adding latex to beaten pulp is still being used in manufacturing certain types of paper (Kaye, B.P. 167,935; U.S.P., 1,500,500). Latex-treated papers or paper pulps are, as noted above, used in the manufacture of artificial leathers.

Latex-Bound Upholstery

Latex as a binding agent for pig bristles, horsehair or similar material has been used for some time (Weber and Howard, U.S.P. 1,906,028; B.P. 355,004; B.P. 341,383). An improved and unique type of upholstering material composed of hair and latex is produced by the "Nukraft" method. The product is made by coating a layer of hair or bristles with latex and folding the resulting sheet, while still tacky, in such a manner as to form a series of parallel tubes. As the folding is carried out, the rubberized sheet adheres to itself at both the upper and lower surfaces of the resulting slab. The slabs are next vulcanized to strengthen the bond and remove the tack from the rubber coating. The vulcanized slabs may be used singly or, if required to support great weight, may be cross-plied one upon another to increase their strength. Such material has great strength and is easily fabricated into cushions, arm rests, padding, etc. (Heldenbrand U.S.P. 1,988,843; 2,029,370; Leguillon, 2,023,273.)

Can Sealing

In sealing cans, latex is flowed around the well of the can bottom and dried. The resulting tough film cushions and seals the edge of the can when the body is applied and the rim edge turned over ("Rubber Latex," H. Stevens, p. 83).

Road Surfacing and Flooring Compositions

Latex has been used to a considerable extent for the expansion joints on roads. It has also been incorporated with various mineral materials as a road surface (B.P. 464,562).

A latex composition containing Portland cement, sulfur, zinc oxide, and a miscellany of other necessary vulcanizing ingredients and fillers, makes an excellent floor covering. One successful application of this type of latex composition was as a substitute for teak wood on decks of vessels. The material is handled very much like plaster (B.P. 369,561; B.P. 384,030).

Rubber chemists are now turning their attention to production and utilization of synthetic rubber latex, and we are on the threshold of a tremendous new development, in which colloid chemistry will play a role of ever-increasing importance. Many of the above noted Hevea rubber latex applications will be displaced with synthetic rubber. With a large production of synthetic rubber available after 1944, and eventually the output of increased acreage in South and Central America, and the whole acreage in the Far East, we should have an abundance of rubber and rubber-like materials. Commercial application of these elastomers will be far-reaching, and it challenges the vision of the rubber technologist as never before.

Synthetic Rubber

E. A. HAUSER

Associate Professor, Chemical Engineering, Massachusetts Institute of Technology

and

D. S. LE BEAU

Research Associate, Department of Chemical Engineering, Massachusetts Institute of Technology

GENERAL CONSIDERATIONS

In general the term "synthetic" has been applied to man-made substances which not only exhibit the same properties as the natural product, but which are also chemically identical therewith.* If this definition for a synthetic product is upheld, and there is really no reason why it should not be, the term "synthetic rubber" as now used is somewhat misleading. Even the simple man-made isoprene polymer, although identical in its strictly chemical composition with natural rubber, does not deserve to be called synthetic rubber because it differs noticeably from the natural product in its structural make-up as revealed by x-ray diffraction, as well as in its physical properties. Offhand it would seem, therefore, more to the point to term such synthetic products as exhibit rubber-like properties "artificial rubber."

Recently it has been suggested that such synthetic products which have many properties similar to rubber be called "elastomers." However, this term now emphasizes primarily the physical properties without regard to the chemical composition. As a result, we find in the literature certain synthetic resins listed as elastomers; for example, polyvinyl chloride, which in combination with certain plasticizers like tricresyl phosphate can be converted from a white powder to a material exhibiting many properties akin to rubber. These materials (Koroseal and Flamenol) which may contain up to 60 per cent of the plasticizer cannot be vulcanized and show a much slower recovery than rubber.

The terms "artificial rubber" and "elastomer" would seem satisfactory if they referred only to those synthetic products which in their pure state, *i.e.* without any admixture, exhibit properties for which natural rubber has become known. For the same reason rubber derivatives—for example, chlorinated rubber or rubber hydrochloride—should not and actually have not been classified as synthetic rubbers.

To sum up, only those substances should be classified as artificial rubbers or elastomers which exhibit in their pure state without the addition of any softener, plasticizer or the like, at least two of the most striking properties of natural rubber, namely, elasticity and vulcanizability. Vulcanization in the sense here applied is not limited to the incorporation of sulfur, but is intended to embrace any reaction which will result in an irreversible change of such properties of the substance as increased elasticity, increased resistance to solvent and temperature changes, reduced plasticity, etc.

* Often natural products contain "impurities" which exert an important influence on their behavior. J. A.

Therefore, the following discussion will include only simple and copolymerized derivatives of butadiene and chloroprene as long as they come under the definition just outlined: copolymers of olefins with diolefins (Butyl rubber), and condensation products of halogenated aliphatic compounds with alkali polysulfides (Thiokols).

The previously mentioned plasticized polyvinyl chlorides and the like will not be considered. Polyisobutylene (Vistanex), which according to the above definition cannot be classified as artificial rubber, will be discussed only because of the importance of butylene as an olefin in copolymerization with diolefins.

However, since the term "synthetic rubber" has been so widely used in the past, it does not seem opportune to confront the reader with a sudden change in terminology at this moment. Therefore, it will be used throughout this presentation.

Historical Facts

Faraday in 1826 was the first to study the composition of rubber.[67] Himly [72] in 1847 described two liquids obtained by pyrogenetic decomposition of "caoutchouc" which he named *faradayin* and *caoutchine*, respectively. It has since been fairly well established that these two liquids consisted chiefly of isoprene and dipentene.

In 1860 Williams [223] succeeded in isolating the parent substance of rubber by destructive distillation. He found it to be composed of five atoms of carbon and eight of hydrogen and termed it *isoprene*. He also noted that isoprene, if subjected to distillation, increases in viscosity and may even be converted into an elastic mass. Although Williams does not state precisely, we have good reason to believe that he considered rubber and gutta-percha to be what are today called polymers of isoprene.

In 1879 Bouchardat [28] reported that he obtained a product of rubber-like properties upon treating isoprene with fuming hydrochloric acid. However, all these and many more studies were primarily directed toward evaluation of the chemical constitution of rubber.

The first investigator really to recognize the commercial importance of the synthetic production of rubber from isoprene was Tilden [202] (1882). He also pointed out that isoprene could be obtained from turpentine and that upon polymerization a product similar to India rubber in its behavior resulted. Several investigators continued this work during the following years, but with comparatively little success. The methods for the polymerization of isoprene as described by them were very indefinite and frequently not even reproducible. The yields of synthetic rubber were small. In 1900 Kondakoff [119, 120] gave new impetus to the work when he described a synthetic rubber obtained from dimethylbutadiene; it was shortly thereafter that Thiele [198] reported the polymerization of piperylene to a rubber-like product.

The realization that isoprene as well as dimethylbutadiene can be considered a derivative of butadiene started experimental work on the polymerization of the butadiene series of compounds. In 1909 a British concern, Messrs. Strange and Graham, Ltd., was formed which eventually worked exclusively on synthetic rubber for the purpose of developing a process for the production of butadiene rubber. Not long thereafter, Matthews,[148] as a result of previous work by Weizmann,[221] discovered a method for the polymerization of isoprene using metallic sodium as catalyst. At about the same time extensive research on synthetic rubber was started in Germany. Harries and Hoffman [16, 68, 69, 76] synthesized various derivatives of butadiene and upon polymerization obtained products more or less resembling rubber.

Up to this time synthetic rubber had been considered only as a substitute for natural rubber, and any special properties it might have possessed had not been recognized. Consequently, when the price of natural rubber dropped very substantially in 1911, interest in the production of synthetic rubber decreased rapidly.

During World War I, Germany was by necessity forced to find a substitute for natural rubber and started on the production of "Methyl rubber." The decision to produce it was not made because of its excellent qualities, but rather because the

materials and equipment then available permitted more rapid production of it than of any other then known synthetic product. The polymerization was effected either by heating dimethylbutadiene for several hours to 60-70°, or simply by storing it at room temperature for several months. However, polymerization was extremely unreliable both at elevated and room temperatures, and a great number of experiments had to be carried out to determine the influencing factors. Further difficulties were encountered during vulcanization. The finished products were very much inferior to those made from natural rubber. An interesting review of the difficulties encountered in the manufacture of "Methyl rubber" during the first World War has been given by the Austrian chemist, K. Gottlob,[55] who was one of Hoffman's closest collaborators.

Two different grades of "Methyl rubber" were produced: "Methyl rubber W," polymerized at elevated temperatures, suitable for soft rubber goods, and "Methyl rubber H," polymerized at room temperature, used for the production of ebonite or hard rubber.

Developments after World War I

After World War I the production of synthetic rubber was discontinued until about 1925, when as a result of the Stevenson Restriction Scheme [193] an abrupt rise in the price of crude rubber occurred. Ever since then an increasing number of patents have been issued covering the various stages in the production of synthetic rubbers. At first the greatest difficulties consisted of producing the necessary raw materials on a commercially and economically acceptable basis.*

The first practical process for making butadiene from coal and limestone was worked out in Germany in 1927. This process is still today the backbone of the production of synthetic rubber in that country. Another raw material for the production of butadiene is ethyl alcohol. This method is in use in Russia and was practiced to a smaller extent in Poland prior to its occupation in World War II. The United States is able to obtain butadiene in great quantities and at lower costs from petroleum and natural gas. Thus, the United States definitely has an advantage over other countries in regard to the availability of raw materials, inasmuch as it also produces large quantities of butadiene from farm crops.

Production of Synthetic Rubber

The commercial production of synthetic rubber entails two distinct steps: the production of the chemical building units known as monomers, and their subsequent combination by polymerization or condensation to form high molecular compounds resembling rubber in many of their properties.

Production of Monomers

Butadiene ($CH_2{=}CH{-}CH{=}CH_2$). The production of butadiene as carried out in Germany can be summarized by the following schematic equations:

$$3\,C\ (Coke) + CaO\ (limestone) = CaC_2 + CO$$
$$CaC_2 + H_2O = CH{\equiv}CH + CaO$$
$$CH{\equiv}CH + H_2O = CH_3CHO\ (acetaldehyde)$$
$$CH_3CHO + CH_3CHO = CH_3CHOHCH_2CHO\ (aldol)$$
$$CH_3CHOHCH_2CHO + 2H = CH_3CHOHCH_2CH_2OH\ (1,3\text{-butylene glycol})$$
$$CH_3CHOHCH_2CH_2OH \longrightarrow CH_2{=}CH{-}CH{=}CH_2\ (Butadiene) + 2H_2O$$

Instead of producing acetaldehyde from acetylene, it can also be obtained from ethanol. The further reactions remain unchanged.

* An excellent survey of the many methods by which butadiene and isoprene were produced up to 1926 can be found in S. P. Schotz's book, "Synthetic Rubber," published by Ernest Benn (London) 1926.

Another process utilizes ethylene, which is first converted into synthetic ethyl alcohol. The latter is then partially converted to acetaldehyde. Thereafter a mixture of ethanol and aldehyde is catalytically converted into butadiene. It is evident that instead of first producing ethanol synthetically, ethyl alcohol obtained by fermentation of farm crops can be used.

The Russian and Polish processes using alcohol as raw material differ from the above by converting the alcohol into butadiene by a one-step catalytic process involving simultaneous dehydrogenation and dehydration.[4, 194]

Another method only recently developed in the United States for the production of butadiene is based on the well known conversion of certain farm products to 2,3-butylene glycol by bacterial fermentation.[50, 118] This compound is then acetylated. The glycol diacetate so formed splits when heated into acetic acid and butadiene of high purity.[37]

Another bacterial fermentation process with certain carbohydrates produces butyl alcohol and butylene as intermediary products in the catalytic formation of butadiene.

Large quantities of butadiene are now produced in the United States and Russia from liquid petroleum or natural gas by various processes, using butane, butylene, or ethylene as feed stock.

The most important methods for the commercial production of butadiene are compiled schematically in Fig. 1.

Isoprene ($CH_2{=}C(CH_3){-}CH{=}CH_2$). Although isoprene is no longer considered of any major significance as a basic monomer for the production of synthetic rubber, it has nevertheless retained its interest and value in certain synthetic rubbers where it constitutes one part of the copolymer.

It is obtained either from petroleum by cracking or from natural turpentine by heat treatment and fractional distillation. Another possibility is to obtain isoprene from acetone formed as a by-product in the production of butyl alcohol by bacterial fermentation. By reacting acetone with acetylene one obtains methyl butinol, which after dehydrogenation and dehydration yields isoprene.

The simplified chart (Fig. 1) offers a quick survey of the most common ways of producing isoprene.

Chloroprene ($CH_2{=}C(Cl){-}CH{=}CH_2$). Nieuwland [155] demonstrated the possibility of polymerizing acetylene to mono- and di-vinylacetylene by the use of catalysts. The E. I. duPont de Nemours Company immediately envisaged the possibilities of such a reaction in connection with the production of new high molecular organic compounds. Carothers [30] and his collaborators were able to convert monovinylacetylene into chloroprene (2-chloro-1,3-butadiene) by treating the former with hydrochloric acid in the presence of cuprous chloride. The following schematic equations account for the most important reactions in the production of chloroprene.

$$3C\ (coke) + CaO\ (limestone) \longrightarrow CaC_2 + CO$$

$$CaC_2 + H_2O \longrightarrow CH{\equiv}CH + CaO$$

$$CH{\equiv}CH \xrightarrow{\text{catalyst}} {=}C{=}CH_2$$

$${=}C{=}CH_2 + CH{\equiv}CH \xrightarrow{\text{catalyst}} H_2C{=}CH{-}C{\equiv}CH\ \text{(vinylacetylene)}$$

$$H_2C{=}CH{-}C{\equiv}CH + HCl \xrightarrow{\text{catalyst}} CH_2{=}CH{-}CCl{=}CH_2\ \text{(chloroprene)}$$

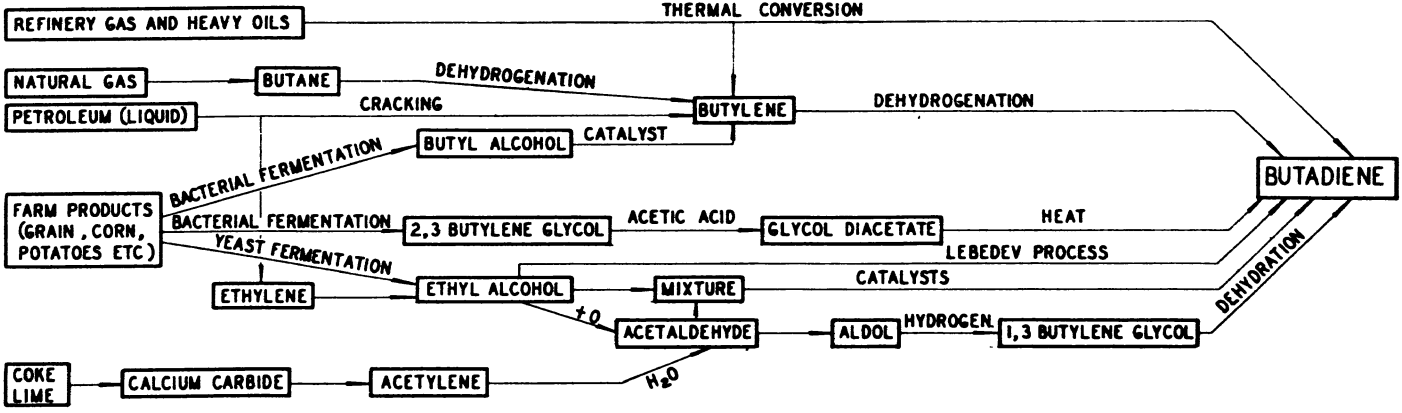


FIGURE 1. Production of Butadiene (schematic).

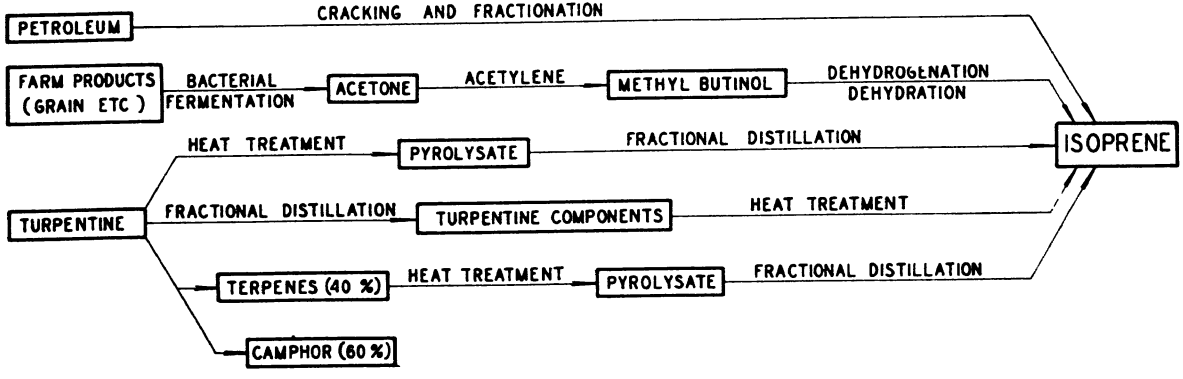


FIGURE 1. Production of Isoprene (schematic).

Isobutylene ($CH_2{=}C(CH_3)_2$.) Isobutylene is obtained as a by-product in the normal cracking operations of petroleum refining.

Styrene ($CH_2{=}CH{-}C_6H_5$.) Styrene can be manufactured by first reacting ethylene with benzene in the presence of a catalyst and then subjecting the ethyl benzene so formed to dehydrogenation (Fig. 2). Ethylene can be obtained either by cracking petroleum or from ethyl alcohol.

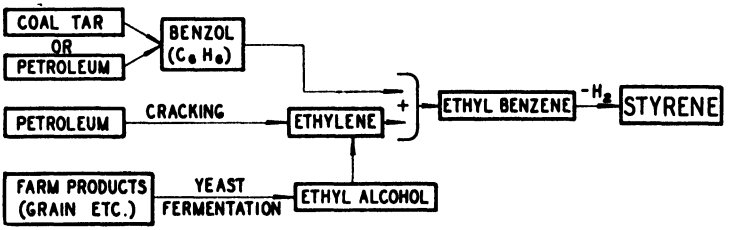


FIGURE 2. Production of Styrene (schematic).

Acrylonitrile ($CH_2{=}CH{-}CN$.) Acrylonitrile can be produced by either of the following reactions:

$$CH_2{=}CH_2 + HOCl \longrightarrow HOCH_2CH_2Cl$$
$$HOCH_2CH_2Cl + NaCN \longrightarrow HOCH_2CH_2CN \longrightarrow CH_2{=}CH{-}CN$$

or

$$HOCH_2{-}CH_2CN + CH_3{-}C(=O){-}O{-}C(=O){-}CH_3 \longrightarrow CH_2(OCOCH_3){-}CH_2CN \longrightarrow CH_2{=}CH{-}CN$$

Ethylene dichloride ($ClCH_2CH_2Cl$.) Ethylene dichloride can be obtained by chlorination of ethylene.

$$CH_2{=}CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl$$

Dichlordiethyl ether ($ClCH_2CH_2OCH_2CH_2Cl$.) Dichlorodiethyl ether can be prepared from ethylene:

$$CH_2{=}CH_2 + HOCl \longrightarrow ClCH_2CH_2OH \xrightarrow{H_2SO_4} ClCH_2CH_2OCH_2CH_2Cl$$

Polymerization of the Building Units into High Molecular Compounds Resembling Rubber in Many of Their Properties

Before discussing the methods by which the various synthetic rubbers are built up from monomers, and before surveying some theoretical considerations involved in

these reactions, a brief reference to the terminology generally used in this field, a resumé of the most important synthetic rubbers, country of production and a discussion of their industrial development up to the present days seems in place here.

However, the war and prevailing secrecy regulations still make it impossible to offer a really complete survey of the development at this time.

The production of synthetic rubbers entails two major steps: the production of the monomers, which has been discussed, and their subsequent polymerization.

Definition. The term "polymerization" * denotes the ability of certain compounds to increase the size of their molecules by self-addition, involving the action of primary valence forces and thereby forming a new substance with entirely different physical properties, while the chemical composition in general does not experience any radical change. This is to be understood in the sense that no elements present in the original compound are eliminated during polymerization. But it is likewise to be understood that the formation of molecular aggregates *without* chemical bonds cannot be considered to fall under this definition.

Copolymerization. The polymerizing molecules can be either of like nature or of different natures. To give a specific example we can say that natural rubber complies with the first case, whereas "Buna S" or "Butyl rubber" complies with the second case. It is generally assumed that polymers obtained by simultaneous polymerization of molecules of different natures do not consist of a mixture of the different polymers, but are mixed polymers in themselves. One molecule of such a polymer contains all the different original molecules combined by primary valence forces (copolymerized). However, the distribution of the original molecules is generally not uniform in the final product. The properties of the finished copolymer will be different from those of polymers obtained from each of the reacting components. The authors, however, feel that such an assumption may not be generalized. So far unpublished results of studies pertaining to copolymerization definitely indicate that certain factors, like the ratio of the monomer, have a very definite bearing on the question whether the polymer can be considered as a true copolymer or a mixture of polymers.

Condensation. An increase in the molecular size of a compound can also be obtained by condensation reactions. The term "condensation" is used here to denote any reaction whereby a new primary valence bond is formed between two molecules by elimination of parts of the reacting compounds. Again the reaction molecules may be alike or different in nature.

Bulk Polymerization. The term "bulk polymerization" is used when the monomers are present in a continuous phase during the polymerization reaction. The monomer can be present in the form of a liquid or dissolved in an appropriate solvent or even in the gaseous state. Bulk polymerization is the oldest of the polymerization methods.

Emulsion Polymerization. In emulsion polymerization the monomer or monomers are emulsified in an appropriate dispersion medium with the aid of emulsifying agents.

Tables 1-5 give a condensed survey of the most important synthetic rubbers known to be commercially produced in various countries.

Other butadiene copolymers manufactured in the United States, but not included in the Government Rubber program, are "Chemigum" (Goodyear Tire and Rubber Company), "Hycar" (Hycar Chemical Company), and "Butaprene" (Firestone Tire and Rubber Company).† Condensation products of organic halogenated aliphatic compounds with sodium polysulfides are known as "Thiokol" (Thiokol Corporation).

* See paper on polymerization by H. Mark in Vol. V of this series. J. A.

† For a more detailed description of the various types now available, see "Plastics Catalog" 1942, 1943, 1944, published by Plastics Catalog Corp., New York.

Table 1. Production of Synthetic Rubber in U. S. A.

Product	Gov't Designation	Monomer	Method of Production	Chemical Reactivity	Manufacturer
Buna S	GR-S	Butadiene + styrene	Emulsion Polymerization	Unsaturated	Gov't Controlled
Perbunan (Buna N)	GR-N	Butadiene + acrylonitrile	Emulsion Polymerization	Unsaturated	Gov't Controlled
Vistanex	.....	Isobutylene	Bulk Polymerization	Saturated	Standard Oil Co. of N. J.
Butyl Rubber	GR-I	Isobutylene + butadiene or isoprene	Bulk Polymerization	Somewhat unsaturated	Gov't Controlled—Standard Oil Co. of N. J.
Neoprene	GR-M	Chloroprene	Emulsion Polymerization	Unsaturated	Gov't Controlled—E. I. duPont de Nemours & Co.

Table 2. Production of Synthetic Rubber in U. S. S. R.

Product	Monomer	Method of Production	Chemical Reactivity	Manufacturer
S K A	Butadiene (from petroleum)	Bulk polymerization	Unsaturated	Gov't U.S.S.R
S K B	Butadiene (from alcohol)	Bulk polymerization	"	"
Sovprene	Chloroprene	Emulsion polymerization	"	"
Resinit	Halogenated org. aliph. compounds + sodium polysulfide	Condensation	Saturated	"

Table 3. Production of Synthetic Rubber in England

Product	Monomer	Method of Production	Chemical Reactivity	Manufacturer
Vulcaplas	Halogenated org. aliph. compounds + sodium polysulfide	Condensation	Saturated	Imperial Chemical Industries

Industrial Development of Synthetic Rubbers

The first large-scale production of synthetic rubber from butadiene was based on the use of sodium as catalyst. The origin of this development dates back to 1910 when Matthews and Strange obtained a British patent [144] for the polymerization of isoprene with sodium as catalyst. Shortly thereafter Harries obtained a similar patent in Germany, but the courts unanimously upheld the English claim for priority. In Russia work along similar lines was initiated by men like Lebedev,[127] Ostromislensky,[158] and others. The great interest in the possibility of producing rubber synthetically between the years 1907 to 1910 was largely due to the skyrocketing price of the natural product. However, as previously mentioned, when at the start of 1911 the market price for rubber rapidly declined, the interest in rubber synthesis vanished with the same speed, and practically all research work stopped. It was again revived in the 20's when the Stevenson Restriction Scheme for the exportation of crude rubber from the British plantation caused a new rise in its price. It was particularly

Germany and Russia who again set out to subsidize research with private as well as government funds.

Table 4. Production of Synthetic Rubber in Germany

Product	Monomer	Method of Production	Chemical Reactivity	Manufacturer
Buna 85 *	Butadiene	Bulk polymerization	Unsaturated	I. G. Farbenindustrie, A. G.
Buna 115 *	Butadiene	Bulk polymerization	"	"
Buna S	Butadiene + Styrene	Emulsion polymerization	"	"
Buna SS †	Butadiene + Styrene	Emulsion polymerization	"	"
Perbunan (Buna N)	Butadiene + Acrylonitrile	Emulsion polymerization	"	"
Perbunan Extra †	Butadiene + Acrylonitrile	Emulsion polymerization	"	"
Oppanol	Isobutene	Bulk polymerization	Saturated	"
Perduren	Org. Halogenated aliph. compounds + sodium polysulfide	Condensation	"	"

* Buna 85 and Buna 115 are rapidly disappearing from the market and have been mentioned only for the sake of completeness

† Buna SS differs from Buna S only in its higher styrene content The same is the case for Perbunan Extra in regard to acrylonitrile.

Table 5. Production of Synthetic Rubber in Japan

Product	Monomer	Method of Production	Chemical Reactivity	Manufacturer
Mustone	Chloroprene	Polymerization	Unsaturated	....
Thionite	Org. polysulfide	Condensation	Saturated	....

In Germany greatest attention was paid to the production of butadiene from acetylene, owing to that country's lack of natural oil resources and insufficient farm crops, whereas the Russians relied largely on the latter and only to a minor extent on natural oil. Furthermore, Germany made one important step forward when it started to develop emulsion polymerization on a larger scale. K. Gottlob of Bayer & Company had already obtained the basic patents therefor in 1912.[54]

Few people remember the excitement created by the announcement that tires made from synthetic rubber were exhibited at the International Automobile and Motor Show in Berlin in February 1936.[225] In 1939 the plant at Schkopau with an annual capacity of 25,000 long tons went into operation. This plant is the first large-scale unit to produce Buna S by emulsion polymerization. Since then other factories have been put into operation. It was of course impossible to even estimate Germany's war time production capacity, but it is certain that a production of 1-200,000 tons yearly was planned.

Russia, in contrast to Germany, retained its interest in the production of simple butadiene polymers by bulk polymerization. The Russian development has been dis-

cussed in detail by A. Talalay and L. Talalay [194] and also by E. I. Fulmer,[51] from whom the following is quoted:

"In 1918 the Russian Government provided funds for research on the production of butadiene from two sources:—(a) from a mixture of ethyl alcohol and acetaldehyde by the Ostromislensky process, and (b) from petroleum by the method of Buizov. By 1925 it was apparent that neither method met the requirements for the production of synthetic rubber as a part of the general program for economic independence. Therefore, in 1926 the Superior Economic Council announced an open competition for the best industrial method for the production of synthetic rubber, setting January 1, 1928, as the deadline. The qualifying conditions were very severe not only with reference to the quality of the rubber but they also involved the presentation of detailed plans for a complete factory setup. The plan presented by Lebedev won the prize after careful checking of all plans submitted. The Lebedev procedure involves the production of butadiene by the simultaneous catalytic dehydration and dehydrogenation of ethyl alcohol.

"A pilot plant was completed in 1930 and the first batch of synthetic rubber was produced in January, 1931. By the middle of 1931 three plants were under construction, each with a capacity of 10,000 tons per annum. By 1935 five large plants were in operation, and the plans for 1935-7 called for 14 additional plants.

"The progress of the synthetic rubber industry in Russia is shown by the data given in Table [6]. The amount of synthetic rubber produced increased from 5,600 tons in 1933 to 90,000 tons in 1938, and by 1940 the amount of synthetic rubber used was 73 per cent of the total rubber employed. The efficiency of the method for the production of butadiene from ethyl alcohol increased from 40 per cent of theory in 1935 to 70 per cent of theory during the later months of 1939."

Table 6. The Synthetic Rubber Industry in Russia

Year	Production (Long tons)	Butadiene from alcohol (% of theory)	Synthetic Rubber % of total new rubber
1933	5,600		4.7
1934	12,000		18.5
1935	20,000	40	40.6
1936	24,000		54.1
1937	50,000		73.1
1938	90,000	56	
1939		62	
1939	(later months)	70	

Since 1939 Russia has also been increasingly successful in the production of polybutadiene derived from petroleum.

No detailed figures for Russia's annual production capacity have been made public, but it can be assumed that it lies well above 100,000 long tons, since the output reported for 1938 already closely approaches this figure.

Because of the lack of the necessary raw materials and possibly also because of its great interest in natural rubber, England did not and, since the outset of hostilities, could not engage in any major industrial development of synthetic rubbers.

As far as Japan is concerned, it is known that Germany granted a license for the manufacture of Buna rubbers in 1938, but no information as to further development is available. However, with the Japanese conquest of Malaya and the Dutch East Indies, it is doubtful if Japan has taken any further interest in the production of Buna rubbers.

In the United States the production of all types of synthetic rubber was estimated by Wood [226] to be 2,500 tons in 1939, 5,000 tons in 1940 and 12,000 tons in 1941. These figures clearly demonstrate that the United States entered this war without any significant production capacity for synthetic rubber. This was still the situation when the Baruch Rubber Survey Committee submitted its report [181] in September 1942.

While the total production of GR-S for 1941 amounted to not quite 4,000 tons, the total production for 1943 had already reached 184,781 long tons and the total production for 1944 is estimated at somewhat over 700,000 long tons. The estimate for the first half of 1945 is 390,000 long tons. All this GR-S is produced by emulsion polymerization.[180]

No accurate figures for the production of other types of synthetic rubbers outside the United States are available at present. In this country the output of neoprene amounted to 33,603 long tons in 1943, the 1944 output is estimated at 57,453 and that for the first six months of 1945 at 33,500. The corresponding figures for Butyl rubber are: 1,373; 21,159; and 27,550; for Buna N, 14,487; 20,049; and 9,700.

If one considers that the United States alone consumed in 1940 about 640,000 long tons of rubber and in the first ten months of 1941 about 840,000, and compares these figures with the total production of the four basic synthetic rubbers in 1943, amounting to about 234,000 long tons, and a justifiable estimate of 811,000 long tons for 1944, one must admit that this development is close to miraculous.

Principles of the Production of Synthetic Rubbers

Present world conditions make it impossible for two reasons to discuss the industrial production of synthetic rubbers in complete detail. These reasons are the lack of information from foreign countries and the only too justifiable restrictions pertaining to the disclosure of details in this country. In the following, therefore, only the principles of the most important methods can be given.

Polybutadienes —CH_2—CH=CH—CH_2—CH_2—CH=CH—CH_2—*. In this field only the Russians and possibly to a very small extent Germany are still active.

The Russians have developed two methods for the production of polybutadiene which can be described as the rod or comb method and the vapor phase method.[2, 45, 194, 227]

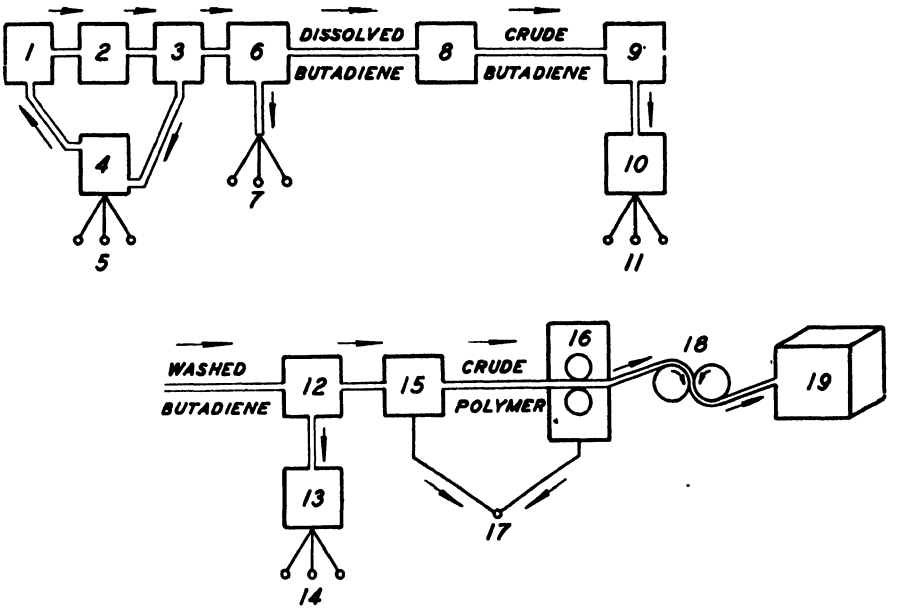
Rod Method: The rod method for the polymerization of butadiene is carried out in an autoclave whose walls and bottom are first coated with a paste consisting of glycerol and talc in equal proportions. Attached to the cover are a series of combs composed of iron rods of a length corresponding to the height of the reactor. These rods are coated with metallic sodium by dipping. Since the amount and available surface of catalyst is of predominant importance, special attention must be paid to its deposition. It has been ascertained that best results are obtained when the molten sodium is kept at a temperature of 105°. According to the Russian publications, the amount of sodium should be about 0.5 per cent by weight of the rectified butadiene used in the reaction. The rods so coated are then dipped twice into molten paraffin. To avoid oxidation during this coating procedure, the treatment is carried out in an inert atmosphere, preferably dry carbon dioxide.

After the autoclave has been assembled, it is filled with butadiene and the reaction started by raising the temperature of the autoclave to about 30°. Since polymerization is an exothermic reaction, a very rapid temperature increase sets in after the initiation period. It is, therefore, necessary to provide effective cooling so that the maximum temperature never exceeds 65°. The reaction is considered as complete when the temperature of the reactor drops to about 40° or the pressure below that of butadiene at the prevailing temperature.

After removal of the polymer, particular attention has to be devoted to the cleaning of the reactor and combs, because the presence of minor impurities will inhibit polymerization. A schematic flow sheet is shown in Fig. 3.

Vapor-phase Method: Although no detailed information on this process has so far been published, several indications point to the following basic details: A reactor is equipped with a series of trays covered either with cloth or fine wire gauze. These are then coated with a kerosene gel containing metallic sodium dispersed therein in as fine a degree as possible. The butadiene in vapor form is passed over these trays by an appropriate fan system. Polymerization is thus initiated on the surface of the coated trays and the reaction then is allowed to continue until a sufficient thickness of a polymer layer has accumulated. The excess butadiene is recycled. There also are

* The formulas used in discussing synthetic rubbers are schematic.



1. Ethyl Alcohol Storage
2. Catalyst Reactor
3. Condenser
4. Still
5. By-products
6. Solvent Scrubber
7. Gases Not Absorbed
8. Still
9. Washer
10. Still
11. By-products
12. Rectifier
13. Still
14. By-products
15. Polymerization Reactor
16. Vacuum Kneading Rolls
17. By-products
18. Refiner
19. Baled SK Rubber

FIGURE 3. Production of Polybutadiene (SK rubber) by the Lebedev process (schematic).

some indications that work in the U.S.S.R. now is along the lines of making this process a continuous one.

Experiments using the above-mentioned catalyst gel in the polymerization of liquid butadiene under pressure have demonstrated that the amount of sodium needed for the reaction is less than that used for the rod method. (For a discussion of the colloidal aspects of these methods of polymerization and their influence on the properties of the finished polymer, see p. 388.)

Polychloroprene $-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2-$. While the original chloroprene polymers were obtained by bulk polymerization, later development showed a definite trend toward the application of emulsion polymerization methods. Today practically all polychloroprene is produced by the latter method. Some of the main advantages of emulsion polymerization are the greater uniformity of the polymer obtained, the ease of removing the odor which was characteristic for the older types, and further that emulsion polymerization offers the possibility of producing copolymers with other monomeric substances, as for example, isoprene.

The emulsion is formed with the aid of sodium oleate or other wetting and dispersing agents. Ammonia or other alkalies are added during polymerization to neutralize the hydrochloric acid formed and thus avoid premature coagulation of the synthetic latex. The polychloroprene latex is coagulated by passing it over a rotating chilled drum. The thin film formed by freezing in this way is continuously removed with a doctor blade, washed, and dried by passing the film through a specially designed drying oven. This drying operation also serves to remove volatile polymers still included in the film and other matter causing disagreeable odor of the polymer.[192]

According to the degree of polymerization, four main types of polymers can be obtained. They are known as α, β, μ and ω polymers. The α-polymer is soft, plastic and readily soluble in most rubber solvents. It is comparable in these properties to crude rubber. It is formed by polymerization at normal temperature.

The β-polymer is obtained when polymerization of the chloroprene is carried out at temperatures above 60° and in the absence of air. It is an oily substance.

The μ-polymer can be considered as a product of progressive polymerization of the α-polymer. It can be obtained therefrom by prolonged reaction, by the influence of light or prolonged storage. Heating will convert the α-polymer into the μ-polymer in comparatively short times depending on the temperature used. This is the reaction which causes the α-polymer to change its properties into such resembling vulcanized rubber.

The ω-polymer is a hard, granular, non-elastic substance.

Polybutadiene by Emulsion Polymerization

Comparatively little information on the polymerization of butadiene by the emulsion method has been published. The Russians, however, have made a series of contributions, according to which technical butadiene containing between 14-22 per cent β-butylene is emulsified in water with the use of fatty-acid salts as emulsifiers, and peroxides, diazoamino benzene, etc., as catalysts. The reaction is carried out at temperatures between 40-70° for several days. The latex so obtained is of high stability and characterized by extremely small particles.

Buna S—CH_2—CH=CH—CH_2—CH_2—CH(C$_6$H$_5$)—CH_2—CH=CH—CH_2—. As has already been shown, by far the largest amounts of synthetic rubbers now produced are copolymers of butadiene obtained by emulsion polymerization with other unsaturated organic compounds. Buna S (synonymous with GR-S) leads this field.

In its production, rectified butadiene and styrene are first emulsified in water with the use of a few per cent of appropriate emulsifying agents like fatty acids or rosin soaps. The proportions of butadiene to styrene depend entirely on the desired properties of the end product. Although in standard Buna S the proportion is about 3:1, special Buna S polymers with ratios of 1:1 are also in production. These types are to some extent comparable to the German Buna SS. For purpose of additional stabilization, small proportions of protective colloids are frequently added. The catalyst and specific modifying agents are then added to the emulsion. The catalysts are usually oxidizing agents. The modifying agents are added to reduce branching and to induce linear polymerization. Besides this they also exert a controlling effect on the entire reaction. Various organic halogen compounds, alkyl mercaptans, have so far seemingly been most successful. However, just as in the case of accelerators of vulcanization, it is to be expected that continued research will result in the production and use of even more effective modifiers than are now known.

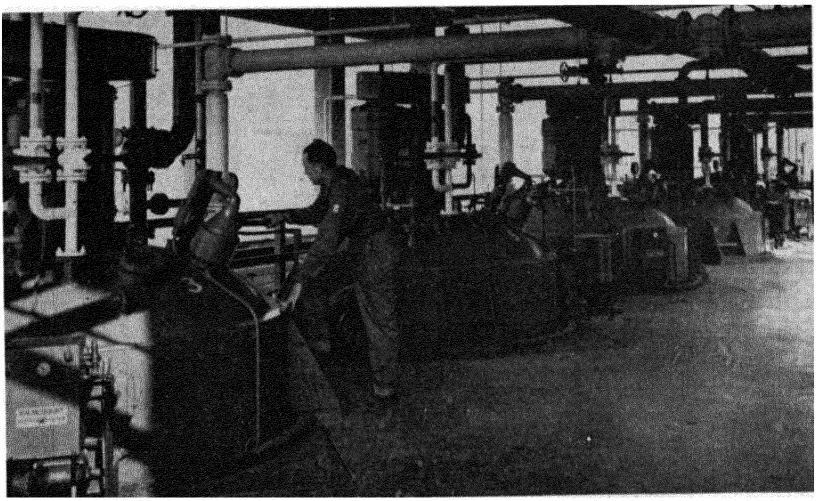


FIGURE 4. Polymerization reactors. (By courtesy, Office of Rubber Director)

The emulsion so prepared is then heated under constant slow agitation in a reactor to temperatures from 40 to 60° and retained at that temperature for 10 to 15 hours. (Fig. 4). The time of reaction actually depends on the desired properties of the polymer to be produced as well as on the temperature and on the amount of catalyst and modifier. The concentration of monomers present in the emulsion is another factor of importance. Best results are generally obtained with concentrations not exceeding 40 per cent.

After completion of the reaction, the synthetic latex so formed is subjected to a stripping operation for the purpose of removing the unreacted monomers which are recycled. (Fig. 5). To assure good aging of the finished polymer, antioxidants are added to the latex at this stage. Thereafter, the latex is coagulated, preferably by the use of electrolytes containing high-valent cations. (See p. 403.) The coagulum is then forced, while still in a wet and therefore soft state, through screens or perforated plates to remove water and coagulant. This procedure also assures a convenient subdivision of the coagulum before it is washed and conveyed into drying ovens. After drying, the crumb or wormlike polymer is sheeted out on a rubber mill, baled, and packed for shipment. (Fig. 6). A schematic flow sheet for the production of Buna S is shown in Fig. 7.

Buna N $-CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2-CH=CH-CH_2-$. The production of Buna N, a copolymer of butadiene and acrylonitrile, is identical in principle with that of Buna S. In the standard product, the ratio of butadiene to acrylonitrile is about 4:1, but copolymers with a ratio of 3:2 are also manufactured. The latter correspond approximately to the German designation Perbunan Extra.

Butyl Rubber $-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2-CH=CH-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}-$. Butyl rubber is in principle a copolymer of an olefin with small amounts of a diolefin. Specifically, Butyl rubber as now produced is a copolymer of isobutylene and isoprene or

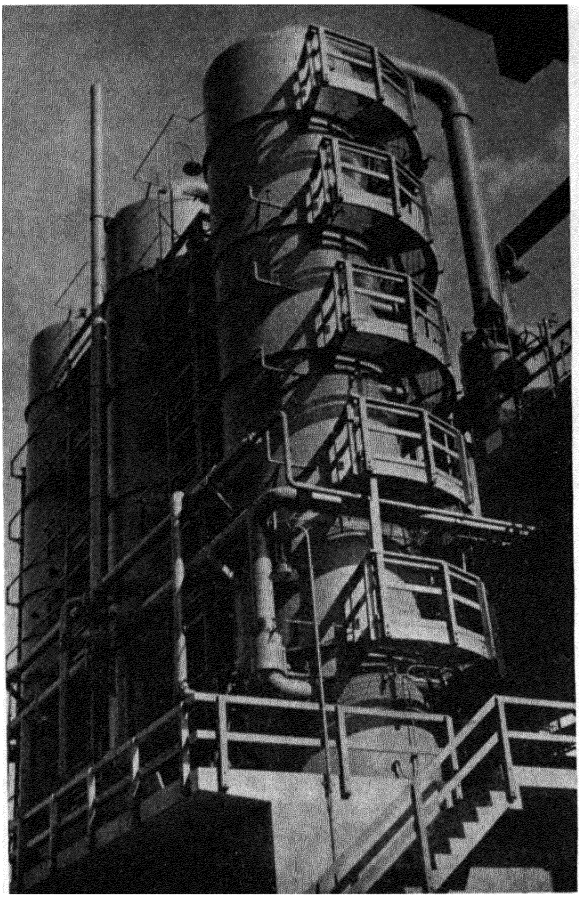


FIGURE 5. Latex stripping towers. (By courtesy, Office of Rubber Director)

butadiene. It is known that the Germans had developed in the 1930's a polymer of isobutylene which they called "Oppanol." [81, 159] In the United States, this product is manufactured by the Standard Oil Company of New Jersey under an agreement with I. G. Farbenindustrie—A. G., and is called Vistanex. In 1940 the Standard Oil Company of New Jersey announced the development of a new synthetic rubber obtained by copolymerizing isobutylene with small amounts of diolefins. This permitted the introduction of unsaturated bonds into the chain of the polymer, thereby producing a vulcanizable material.

The principle of this copolymerization consists of copolymerizing the olefin and the diolefin at low temperatures in the presence of a Friedel-Crafts reagent, as for example, boron trifluoride or aluminum chloride, the latter dissolved in ethyl chloride. The practically instantaneous reaction is now carried out at temperatures of liquid ethylene (−95°), which is used as refrigerant and solvent.

Although the ratios of olefin to diolefin permit a comparatively wide range, the standard Butyl rubber is composed of 95-98 per cent isobutylene and 2-5 per cent diolefin. A schematic flow sheet for the production of Butyl rubber is shown in Fig. 8.

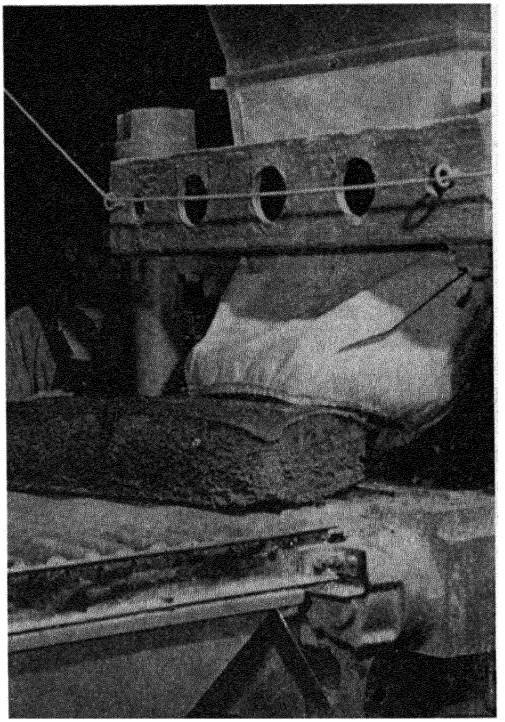


FIGURE 6. Bale of Buna S (GR-S) (schematic).
(By courtesy, Office of Rubber Director)

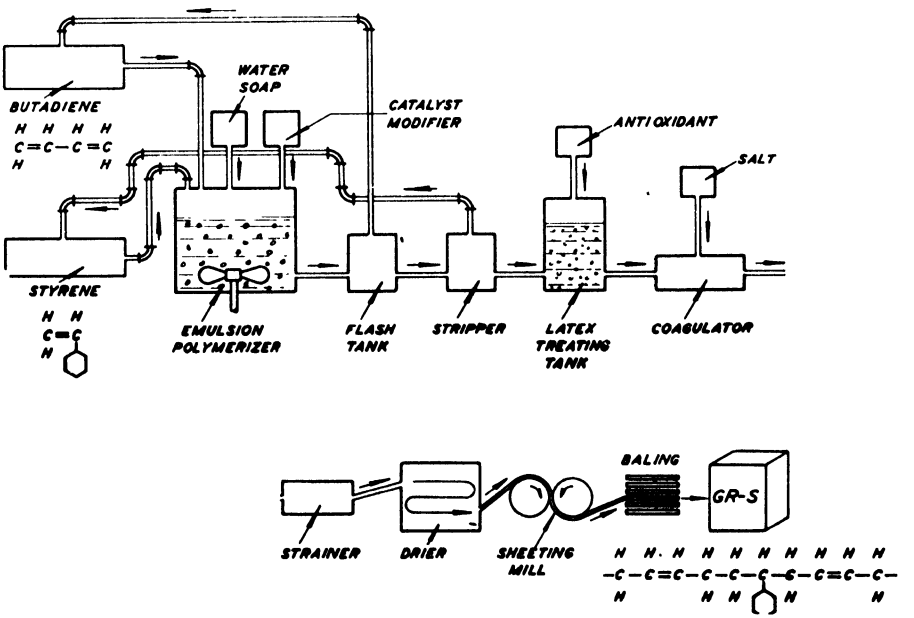


FIGURE 7. Production of Buna S (GR-S) (schematic).

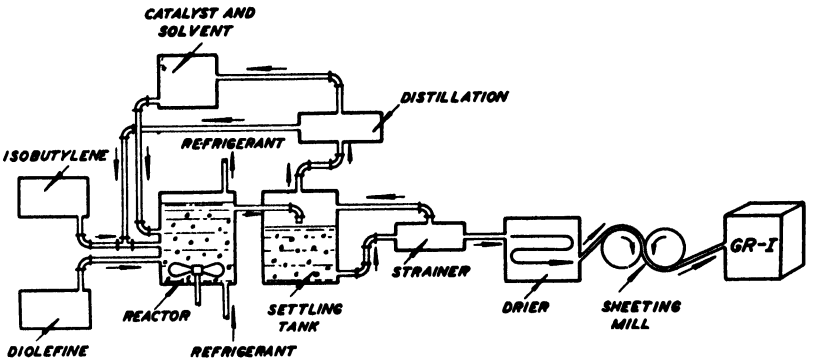


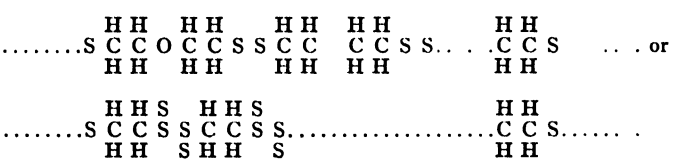
FIGURE 8. Production of Butyl rubber (GR-I) (schematic).

Thiokol. Thiokol, discovered in the early 20's by J. C. Patrick,[101] is the only polymer classified as synthetic rubber that has a chemical composition entirely different from rubber; it contains no diene building units in its molecule. Its formation is also different from that of the other synthetic rubbers. It is the result of a condensation reaction between dichloroethylether and sodium polysulfide, or between dichloroethylene and dichloropropylene and sodium polysulfide. The production of Thiokol can be easily demonstrated according to E. Baker [10] in the following way: Dissolve 4 g of sodium hydroxide in 100 cc of water, heat to boiling and add 7-10 g of flowers of sulfur under constant stirring until all sulfur is dissolved. Then add 20 cc of ethylene dichloride under constant agitation, keeping the mixture at a temperature below 83°. The Thiokol will slowly form at the interface between the two immiscible liquids and settle to the bottom of the container.

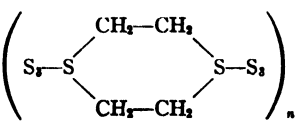
According to Patrick,[100] this reaction is assumed to proceed in principle in the following way:

$$ClCH_2—CH_2Cl + NaS_4Na \longrightarrow ClCH_2—CH_2S_4Na + NaCl$$
$$ClCH_2—CH_2S_4Na + ClCH_2—CH_2S_4Na \longrightarrow ClCH_2—CH_2—S_4CH_2—CH_2S_4Na + NaCl$$

This addition and splitting off of sodium chloride can repeat itself until long-chain molecules are formed. The process of condensation is the same in the case of dichloroethyl ether, the chain then containing oxygen in addition to the sulfur. Possible formulas for both types of such long chains may be:



Another structural possibility has been pointed out by Akobzhanov [8] based on the structure $Na_2S.S_n$ attributed to sodium polysulfides. It is, therefore, considered possible that the sulfur atoms in Thiokol occupy a similar position. This would then permit us to write the Thiokol formula as follows:



Polymers of the following building units show rubber-like properties:

$$CH_2\underset{SS}{S};\quad CH_2CH_2\underset{SS}{S};\quad CH_2CH_2CH_2\underset{SS}{S}$$

$$CH_2CH_2OCH_2CH_2S\underset{SS}{S};\qquad CH_2CH_2OCH_2CH_2\underset{SS}{S}$$

$$CH_2CH_2OCH_2CH_2OCH_2CH_2S\underset{SS}{S};\quad CH_2CH_2OCH_2CH_2OCH_2CH_2\underset{SS}{S}$$

It can be easily seen that the length of the carbon chain in the building unit has no influence on the rubber-like properties of the condensate. The ether-like building units need less sulfur to exhibit them than those which do not contain any ether oxygen. Condensates obtained from building units, as for example CH_2SS, do not show any rubber-like properties.*

The peculiarity of two sulfur atoms being found in the chain and the other two being attached to them has been proved by the fact that two sulfur atoms can be removed per building unit by treatment with potassium hydroxide. No rubber-like properties can be observed if only one sulfur atom is bound within the chain; three sulfur atoms are sufficient to promote these properties in compounds containing *no* oxygen. It is evident that various compounds can be produced, all of which have been classified as Thiokols. A whole series of different types of Thiokol are on the market. For a discussion of their properties, see p. 381.

The German Thiokols are Perduren G (condensate of dichloroethyl ether with sodium polysulfide), Perduren H (condensate of dichloroethyl formaldehyde acetal with sodium polysulfide), Perduren SP (a water suspension of Perduren H), and Perduren L, which is a special combination of Perbunan and Perduren.

Properties of Synthetic Rubbers

The following survey of the processing properties of synthetic rubbers and of the physical properties of their vulcanizates covers only the most outstanding general features and does not include a discussion of detailed compounding formulas and the like.

Sodium-catalyzed Polybutadienes

These polymers, if subjected to milling on a cold mill (not over 40°), break down very rapidly, forming a smooth, plastic sheet. The use of a hot mill results in a rapid conversion of the polymer into a very sticky, soft state which makes further processing impossible. Incorporation of compounding ingredients is easy and the entire compounding procedure requires less power consumption than that of natural rubber.

So far it has not been possible to produce pure gum stocks exhibiting good physical properties, but compounds containing reinforcing fillers are very satisfactory and are comparable with the compounds obtained with standard Buna S. However, the sodium-catalyzed polybutadienes, when compounded with reinforcing carbon black, show a pronouncedly superior tear resistance.

Compounds made from these polymers exhibit appreciable stickiness in unvulcanized condition, which is of great importance, for example in tire construction. Their oil resistance, however is poor, as is to be expected from their chemical composition.

For more details in regard to plasticization and compounding, see references.[32, 39, 43, 44, 195, 196]

* When sulfur is heated to about 400° and then chilled in liquid air there results a transparent and exceedingly elastic form of sulfur, which crystallizes on standing [P. P. von Weimarn, *Koll. Zeit.*, **6**, 250 (1910)]. It is possible that this elastic form of sulfur may be stabilized or determined by the influence of organic and other substances. J. A.

Neoprene

Neoprene is the only unsaturated synthetic rubber polymer that is vulcanized without the addition of sulfur and the regular rubber accelerators, although sulfur may be added as a modifying agent for certain specific purposes. This peculiarity of neoprene most probably is related to the presence of the chlorine atom at the double bond. However, neoprene possesses curing qualities, and irreversible vulcanization can be effected either by heat without the addition of any foreign substances, or by the addition of various metal oxides followed by subsequent heating of the compound. The latter process is preferred because it yields better physical properties than the former.

Vulcanization probably consists of a lengthening of the chains, whereby netting between them may take place. Our knowledge of this process is still too inadequate, and chemical analysis so far has not succeeded in enlightening us on this point. Determination of unsaturation has failed completely because of the presence of the chlorine atom bonded to the unsaturated carbon atom. Furthermore, that quality of vulcanized neoprene which makes it desirable for a number of uses, namely its comparative insolubility in organic solvents, has so far defeated customary analytical methods.*

The term "neoprene" has been applied to a great number of polymers possessing certain common characteristics. A whole family of "neoprenes" has at one time or another been on the market, their chemical differences not always being disclosed. Neoprene E, M, G (GCX and GCR), GN, I, and FR are the most familiar ones, Neoprene GN being generally in use at present in the United States. However, all these different types of neoprene show in general the same reactions toward vulcanizing agents, softeners, and accelerators, and have the same principle of vulcanization.

Neoprenes are extremely resistant to sunlight and oxidation, and exhibit good heat and oil resistance in comparison with natural rubber. Another important advantage is that they do not support combustion. They at one time showed slow but progressive polymerization without the addition of vulcanizing agents if stored above 20°, and hardening if stored at abnormally low temperatures. However, this has since been overcome to a considerable extent by the addition of polymerization inhibitors.

Processing. Neoprenes require hardly any breakdown, and speedy milling is often advisable. The optimum friction ratio of the mill rolls should not exceed 1:1.2 since at higher ratios an increased amount of heat is developed. For the same reason a fairly tight setting of the rolls is advisable. Peculiarities in the processing of certain types of neoprenes [83] can be found in the literature of the manufacturer.

Softeners of particularly salient properties are tricresyl-(triphenyl) phosphate, naphthalene, or chlorinated naphthalenes and chlorinated paraffins. At the same time they aid in making the stock more sticky. Others include vegetable oils and light mineral oils. In compounding, the choice of the softener will depend largely on the further application of the finished product. Starkweather and Walker [190] have carried out some extensive experiments in this field.

The effect of lubricating oils on finished neoprene goods has been studied by Fraser,[47] who states that it depends on the chemical characteristics of the particular oil as well as on the temperature, the volume increase of the neoprene compound being a logarithmic function of the viscosity-gravity constants. Kambara [111] explains the oil resistance of Neoprene on the basis of its complex structure and high polarization.

*W. S. Penn in an article published after this manuscript had been written [*India Rubber J.*, 107, 9 (1944)] discusses the possibility that the use of metal oxides for the vulcanization of neoprene results in the formation of oxygen bridges and the release of chlorine which combines with the metal ion.

Pigments generally used in the rubber industry can be used also in neoprene compounds. It is interesting to note that channel black affects tensile strength only slightly. The use of factice (rubber substitute *) is very beneficial for certain purposes such as extruding and calendering.

Certain neoprene types have responded to chemical plasticizers such as the guanidines, diorthotolylguanidine in particular.[192]

Certain metal oxides are found to increase the rate of cure extraordinarily, at the same time also increasing modulus and tensile strength. Starkweather and Walker [191] have made a detailed study of the influence of metal oxides on neoprene compounds and have come to the conclusion that zinc oxide, light calcined magnesium oxide, calcium oxide, and litharge show the most striking effects. In general use today is the combination of zinc oxide and magnesium oxide, the latter promoting an increase in modulus and tensile strength, preventing scorching and neutralizing small quantities of hydrogen chloride which might be liberated. For some neoprene types Bridgewater and Krisman [25] found the addition of wood rosin essential. Although it improves the physical properties of the vulcanized product, it cannot be considered as a vulcanizing agent.

A new group of substances which act as true accelerators of the vulcanization of neoprene has been found in the catechols and related compounds.[203] It must also be mentioned that neoprenes will not yield any ebonite-like products, a fact which probably is connected with its structural as well as its chemical composition (chlorine atom). Although neoprene can be mixed with natural or synthetic rubbers on a mill, it is not compatible with them from the point of view of vulcanization. However, a minor addition of neoprene to natural rubber is sometimes made to obtain flexible, less brittle natural hard rubber.

Properties. Aromatic hydrocarbons and chlorinated organic compounds will affect articles made from neoprene to about the same extent as those made from natural rubber. Neoprene, however, excels in its resistance to greases and oils, particularly at high temperatures. The degree of oil resistance also depends to a large extent on proper compounding.[71]

Properly vulcanized neoprene compounds are also characterized by their stability toward elevated temperatures, exposure to sunlight, or even to the influence of oxygen or ozone. These properties, therefore, distinguish neoprene compounds from those made from natural and even more so from other synthetic rubbers. Neoprene does, however, unless specifically compounded, harden at low temperatures more pronouncedly than natural rubber.

Applications. The fact that neoprene not only is comparable with natural rubber in regard to elasticity and tensile strength, but excels it in resistance to heat, abrasion, sunlight, oxygen, oils and many chemicals, makes it a synthetic, rubber-like material of extreme interest for a great variety of applications where rubber is not fully satisfactory. It is employed in the manufacture of tubes and hose used for the conveying of oil, in the construction of conveyor belts which are to come in contact with oil, as a coating for printers' rolls, for the insulation of cables, as protective coating for metal surfaces, fabric coating, gloves and aprons used in the chemical industry, and for all types of gaskets, packings and seals which are exposed to oil, to high temperatures, or to chemicals.

Its high resistance to abrasion has been demonstrated in tires, where its resistance to sunlight and high temperatures is an added advantage. The fact that the production of neoprene calls for ingredients essential in other war uses, and the demand for neoprene for so many special applications are most probably the reasons why its use in the building of tires has not reached beyond what one might call the advanced experimental stage.

* Factice is obtained by reacting vegetable oils with sulfur or SCl_2.

That neoprene must be considered as one of the most applicable man-made rubbers is also evidenced by the great interest the Russians have taken in it.

Buna Copolymers

Of all the synthetic rubbers, Buna S was first selected, in Germany and later in the United States, as the best overall substitute for natural rubber, whereas Buna N is used only where a rubber-like substance exhibiting exceptionally high resistance to oils and organic solvents is called for.

Some of the properties common to both types are the following:

(1) The breakdown of these Buna copolymers on the mill is more difficult and time-consuming than that of natural rubber. It has been demonstrated that breakdown is the more difficult the higher the percentage of styrene or acrylonitrile in the copolymer. To obtain satisfactory dispersion of the compounding ingredients and a smooth-running stock in general, the polymer must first be thoroughly plasticized on a mill. The question whether the compounding of Buna S, particularly with carbon black, is best achieved by incorporating the fillers in the customary way on a cool mill, or at elevated temperatures in an internal mixer has thus far not been conclusively decided. However, there seem to be indications that, in contrast to natural rubber, the latter procedure has advantages in the compounding of Buna copolymers.

(2) Vulcanization can be effected by the same methods as with natural rubber.

(3) No reversion takes place upon prolonged vulcanization, a constant increase in modulus and some decrease in tensiles and elongation being noticeable.

(4) The oil and solvent resistance of the Buna rubbers is generally superior to that of natural rubber. This holds particularly for Buna N.

(5) The resistance to heat and abrasion are superior to that of natural rubber.[107]

(6) The cold resistance of Buna rubbers is not as good as that of natural rubber.

(7) So far it has not been possible to produce pure gum stocks exhibiting physical properties at all comparable to those obtained from natural rubber. However, reinforcing pigments will exert such an effect that the breaking strength in most cases can be so increased that values comparable to those of reinforced natural rubber stocks are obtained. The rebound elasticity or resilience of these synthetic rubbers is inferior to that of natural rubber. Therefore, these rubbers, when subjected to frequent flexing, heat up considerably. This heat development still is one of the most serious problems in the performance of heavy-duty tires made from Buna S synthetic rubber.

The Germans, who were the first to encounter this difficulty, worked out a special plasticizing process for Buna S [62, 118, 170] whereby the copolymer is subjected to a combined heat-air-pressure treatment. To assure as uniform a product as possible, this treatment has to be carefully controlled, because the oxidation-temperature reaction, if carried too far, will cause hardening of the rubber.[52] This treatment is essentially the same as advocated several years ago for natural rubber. For Buna N, however, the treatment is ineffective.

In the United States this treatment has not found commercial application, and more emphasis is placed on the use of special softening agents.

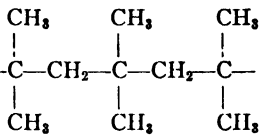
As far as compounding ingredients are concerned, the same fillers as used in the compounding of natural rubber can be applied. Although channel blacks cause a very pronounced reinforcement, they are not recommended for general use because they produce a very hard stock with short elongation and high heat build-up. The use of so-called semi-reinforcing or thermatomic blacks is preferred. Buna copolymers are inferior to natural rubber in regard to flex-cracking. However, partial replacement of the black with fine clays seemingly increases its resistance thereto.

For vulcanization, the same type and approximately the same amounts of vulcanizing ingredients, *i.e.*, sulfur, zinc oxide, accelerator, are used.

Buna S and Buna N permit the production of ebonite or hard rubber.

The applications of Buna S are nearly as manifold as those of natural rubber. Its largest application, of course, lies in tire production, where it has already—with the exception of heavy-duty tires and tires for large bombers—replaced natural rubber. It is also replacing natural rubber in most mechanical goods, rubber footwear, cable insulation, etc. Buna N is not only replacing natural rubber wherever its oil resistance is of primary importance, as for example in the production of hose, tubing, gaskets, fuel cells, self-sealing fuel tanks, printing rolls and blankets, but actually surpasses it.

Vistanex



Vistanex really should not be classified as a synthetic rubber, since it cannot be vulcanized. However, as it is an essential component of "Butyl rubbers," it will be discussed here.

Chemically Vistanex can be classified as a high polymer of isobutylene. (See p. 363). It resembles rubber only inasmuch as it has a regular distribution of short aliphatic side chains and consists of long chain molecules. However, one essential criterion of the rubber molecule, its unsaturation, cannot be found in Vistanex. It is completely saturated except for one theoretical double bond possibly occurring at the terminal group of every chain.

Various degrees of polymerization can be achieved. The consistency of the polymers ranges from a viscous, honey-like fluid to solid rubber-like, tough, colorless masses with a specific gravity of about 0.9.

Processing. The processing of Vistanex on a rubber mill causes a degradation of the polymer,[188] which is graphically represented by Fig. 9. Pigments are readily taken up. However, not even carbon blacks impart any reinforcement to the polymer.

Polyisobutylene has so far not been vulcanized by any of the conventional methods. Its treatment with sulfur monochloride, however, will cause a change in its solubility No satisfactory explanation for this phenomenon is yet available. Prolonged heating will cause a degradation of the polymer.

The tensile strength and elongation of polyisobutylene depend on the molecular weight of the polymer. Polymerization to a molecular weight below 80,000 yields polymers of such low tensile strength that it cannot be determined by the standard Scott rubber tester. It is interesting to note that if polyisobutylene is worked for about 5 minutes on a cold mill and then compressed for 15 minutes at a temperature of 141°, the tensiles will be very much lower than if it has been worked in a hot Banbury mixer (140°) for 20 minutes and then compressed as stated above. It has been assumed that some kind of mechanical vulcanization has taken place, compacting and at the same time aligning the molecules so that intermolecular forces come into play. However, this so-called vulcanization is reversible in that it is possible to remill the "cured" product without any difficulty.

Vistanex has a very wide temperature range of elasticity from −78° up to nearly 180°. The rebound resilience at room temperature is very low and does not quite reach that of rubber even at 110°.

Vistanex dissolves in liquid aliphatic hydrocarbons, carbon disulfide, and chlorinated hydrocarbons. It is stable toward esters, ethers, and alcohols.

It is inert toward any alkalies or acids except hot nitric acid, which produces a sticky oxidized polymer. It is also resistant toward ozone, and in mixtures with natural rubber up to about equal parts it has a very beneficial influence on the ozone- as well as steam-resistance of the compound.

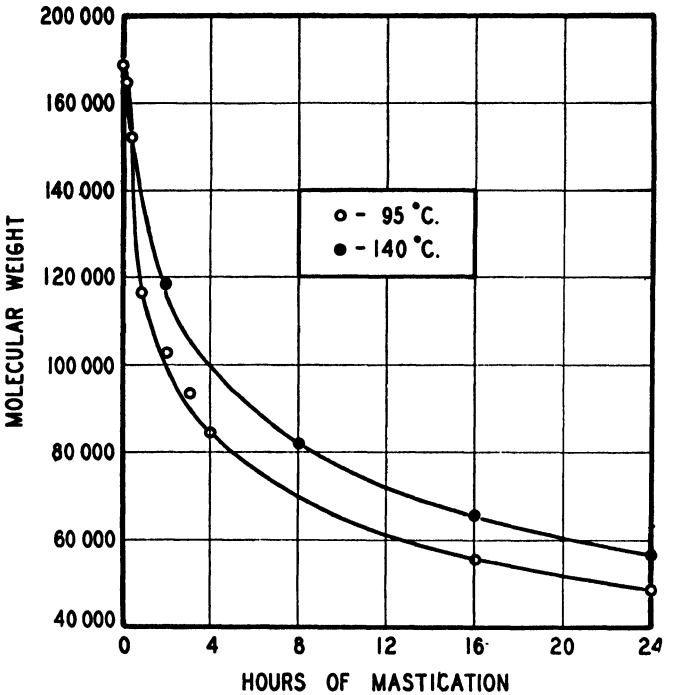


FIGURE 9. Molecular weight degradation versus time of Banbury mastication [W. J. Sparks *et al., Ind. Eng. Chem.*, 32, 732 (1940)].

The electrical properties are excellent even in its wet state.

Applications. Due to its peculiar properties, Vistanex is used in a somewhat different line of products than are the synthetic rubbers. If mixed with petroleum oils, it improves their viscosity index. It is added to greases and lubricants if stringy properties are desired. Its excellent electrical properties make it of value as a coating for high-tension cables, and its inertness toward chemicals favors its use for the coating of reaction vessels. If added to asphalt it improves the softening point-penetration relation. Added to paraffin wax it lessens the "strike through" tendency in that it does not allow the wax to penetrate the surface to be coated. Vistanex is also compatible with natural rubber and Thiokol. Mixed compounds with the latter will possess the desirable qualities of Vistanex if not more than 25 per cent of the former are present. Such compounds are resistant to chemicals and show improved cold flow. In almost all cases, Vistanex imparts a plasticizing effect to the substances to which it is added. It is highly impermeable to gases. Its combination with rubber in the manufacture of inner tubes, gas masks, and impregnated cloth, therefore, are self-evident applications.

Butyl Rubber

As previously stated, Butyl rubber is a copolymer of isobutylene and a diolefin. So far only a few publications pertaining to Butyl rubber have been published. In 1935 L'vov [133] described the copolymerization of isobutylene and butadiene. R. M. Thomas [200] stated that in the production of Butyl rubber the main effort was bent upon obtaining a material which, while having enough unsaturated bonds in the molecule to permit vulcanization, would not show the chemical instability of natural

rubber. After vulcanization, practically no unsaturation should remain in the molecule. This in turn implies that the amount of diolefin copolymerized with the olefin must be small. The unsaturation of the product before vulcanization is described as from 1-2 per cent of that of natural rubber, its molecular weight ranging between 40,000 and 80,000.

A British patent [201] specifies that polymerization of 10-20 per cent butadiene with 80-90 per cent of olefin is preferable, stating that higher proportions of butadiene reduce the elasticity and pliability of the product. The amount of diolefin now used in standard commercial types is below 5 per cent.

Although it is pointed out that the properties of Butyl rubber can be varied greatly by changing the proportion of the components, it seems as if copolymers with higher butadiene content impart more undesirable than desirable qualities to the product.

Considering what has been said about the properties of polyisobutylene, it is evident that the properties of the copolymer will correspond to a large extent to those exhibited by Vistanex, but with one added advantage. The small degree of unsaturation introduced with the diolefin will now permit vulcanization. Depending on the unsaturation—or to put it in other words—on the diolefin content of the copolymer, vulcanization can be so adjusted that a practically completely saturated vulcanizate of excellent mechanical properties is obtained. This result astonished many because it had been felt that the comparatively high unsaturation of natural rubber was primarily responsible for the elastic properties of its vulcanizates. However, Hauser and Brown [64, 65] had shown that vulcanizates of natural rubber exhibiting optimum physical properties call for a loss in unsaturation of only about 2 per cent.

It is not surprising that Butyl rubber has better aging properties and is more resistant to elevated temperatures than natural rubber, if we bear in mind that the former is a far more saturated compound than the latter. For the same reason, it becomes understandable why the addition of so-called rubber antioxidants has little if any influence on the aging of Butyl rubber.

Another important advantage of Butyl rubber over natural is the fact that the presence of such typical rubber poisons as copper and manganese compounds do not exert any deleterious influence. Since it is known that their action in rubber is largely that of an oxidizing catalyst, their inability to affect Butyl rubber can be fully explained by the above consideration. It is still disputable whether excessive heat, light, and air cause a noticeable softening of Butyl rubber stocks or not. Those who have taken an affirmative attitude suggest that such softening can be overcome by using stocks heavily loaded with carbon black. Because of its high degree of saturation, its remarkable resistance to ozone and acids is not surprising.

When discussing the properties of polyisobutylene, attention was drawn to its very satisfactory electrical properties, its low gas permeability, and its solvent resistance. It is, therefore, understandable that Butyl rubber has retained these properties, thus surpassing any other known rubber-like material in this respect.

Processing. Butyl rubber, probably due to its high content of isobutylene, needs practically no breakdown on the mill. Any pigment used in natural rubber compounding can be easily incorporated. Channel blacks, however, do not noticeably affect the tensile properties as they do in natural rubber. So-called semi-reinforcing blacks can be introduced to a far greater amount than into natural rubber without impairing the processing properties of the mixture. Such stocks show noticeable resistance to flex-cracking and abrasion.

Butyl rubber can be vulcanized in the usual way. It is interesting to note that rather high temperatures (307-311° F) are advisable and that no tendency to overcure is encountered over a wide range of time. The representative compounding formula for Butyl rubber as given by Thomas [200] contains what is today considered a rather high percentage of sulfur (3 per cent) particularly in view of the small amount

of vulcanizable diene present. Fig. 10 shows the effect of low unsaturation on the rate of the vulcanization reaction.

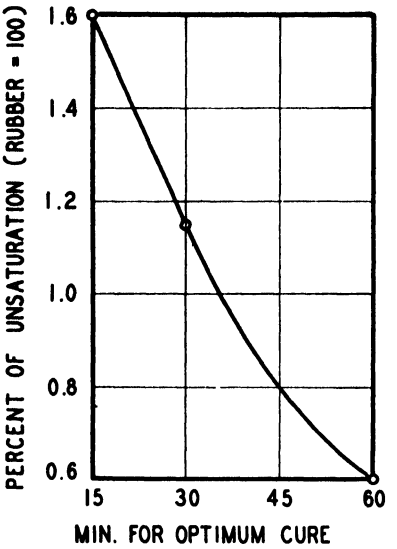


FIGURE 10. Effect of unsaturation of Butyl A on rate of cure at 155° C (311° F) [R. M. Thomas *et al.*, *Ind Eng. Chem.*, 32, 1287 (1940)].

More recent work on compounding and vulcanization reported by Lightbown [128, 129] gives improved compounding formulas containing 1.5-2 parts of sulfur. A combination of thiuram-type accelerators with thiazoles reduces the time of cure to that of natural rubber. This accelerator combination also exerts a beneficial effect on the heat build-up of the product and reduces the cold flow. Both these properties are of great importance.

The tensile strength of Butyl rubber compounds, even of pure gum stocks, is comparable to that obtainable with similar compounds of natural rubber. However, Butyl rubber differs markedly from natural rubber in its modulus at low and medium elongations (Fig. 11).

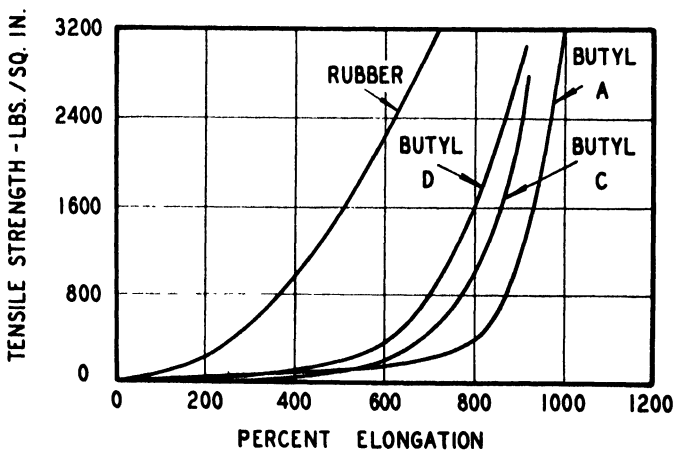


FIGURE 11. Stress-strain characteristics of three types of Butyl rubber as compared with natural rubber [R. M. Thomas *et al.*, *Ind. Eng. Chem.*, 32, 1287 (1940)].

It has been previously stated that the rebound elasticity of Vistanex is very low at normal temperatures but improves noticeably at elevated temperatures. The same phenomenon is encountered in Butyl rubber.

Applications. Largely due to its inertness to aging, chemicals, etc., as well as its resistance to the diffusion of gases, Butyl rubber is of outstanding importance in a great number of war applications, as for example gas masks, gas-resistant clothing, life rafts, inflatable pontoons and jackets, etc. Of particular interest is its excellent performance as an automobile tire inner tube, as was clearly disclosed in the Rubber Director's 4th Progress Report.

Polysulfide Rubbers

Polysulfide rubbers must be considered in every respect as specialty rubber, since practically none of the claims for their *general* applicability have materialized.

Polysulfide rubbers have a unique resistance to solvents, being practically unaffected by lubricating and fuel oils, greases, kerosene, gasoline, and—depending on the type—by a great number of chemicals. Besides this they are very resistant to sunlight and aging, and exhibit low permeability to gases.

One of their greatest disadvantages is the high plastic flow even in the vulcanized condition, their noticeable stiffening if exposed to higher temperatures, and their disagreeable odor.

The polysulfide rubbers are not easy to mill unless softeners are added at the very outset. In contrast to natural rubber, vegetable-oil plasticizers have no effect because of the inertness of the product toward them. However, certain organic accelerators, as for example benzothiazyl disulfide and diphenylguanidine in combination act very effectively.

Contrary to experience with natural rubber, channel black exhibits a reinforcing effect on only certain types of Thiokol (Thiokol FA). However, all of them can be reinforced by semi-reinforcing and soft carbon blacks.

Oils, resins, and well broken down rubber are compounded with Thiokol to improve its tackiness [141, 142] and extruding and calendering qualities; stearic acid is used to prevent adherence to the mill rolls.

Zinc oxide, cupric oxide, lead peroxide, as well as nitrobenzenes and benzoyl peroxide, can be used as vulcanizing agents. It is assumed that the vulcanization reaction involves an oxidation process whereby the length of the chains is increased. The curing range is extremely broad. Accelerators are not necessary in the curing of Thiokol. However, small amounts of benzoic acid or sulfur will act as such. For further details on compounding, the literature obtainable from the manufacturer should be consulted.[199]

Considering the characteristic properties of polysulfide rubbers as discussed above it is only logical that practically all their applications depend on their high resistance to solvents. Most of this material is used in the production of oil hose, seals for oil tanks, gaskets, diaphragms, etc., for equipment in contact with solvents, for self-sealing fuel tanks as well as for removable fuel tanks to be used in regular box cars. Fabrics coated with Thiokol are used for their low gas permeability in barrage balloons, inflatable life rafts, etc. The printing industry also uses considerable quantities for printing rolls and blankets.

SYNTHETIC LATICES AND ARTIFICIAL DISPERSIONS OF SYNTHETIC RUBBERS

During the last quarter of a century a new industry based on the use of natural rubber latex has been developed.* However, with the temporary loss of most of the plantations, importation of latex from the Far East immediately stopped. Therefore, interest in synthetic rubber latices increased rapidly, and the developments along

* See paper in this volume on "Rubber Latex Technology" by R. W. Albright and R. A. Lees. J. A.

these lines must be considered highly successful if one bears in mind that the time so far spent is extremely short.

The very first to really consider the idea of producing a synthetic latex was K. Gottlob who, as far back as 1912, had obtained polymerized isoprene emulsions by much the same methods as are now being applied in the large-scale production of synthetic latices and rubber.[80]

The first references to the production of synthetic rubber latices on an industrial scale date back to 1936 when the Russians described in detail the production of a *polybutadiene* latex.[11, 12] This fact is noteworthy, because the Russians, even today, are predominantly interested in the bulk polymerization of polybutadiene. Their attempt to make an emulsion polymer, therefore, clearly indicates the importance they attributed to the production of synthetic latex.

The butadiene they used was derived from petroleum and contained a considerable percentage of β-butylene. It was emulsified in ammoniated water, using oleic or stearic acid salts as emulsifiers. Diazoaminobenzene was used as catalyst and polymerization was carried out at 40-70° for several days.

When the production of neoprene was converted from bulk polymerization to emulsion polymerization, neoprene also became available in latex form. The first *Neoprene latices* available were of a concentration of about 45 per cent, whereas the types now on the market reach 60 per cent.

As has been discussed, the manufacture of butadiene copolymers passes through a stage where the polymerized copolymer is present in the form of an emulsion or a synthetic latex. The first detailed reference on *Buna S and Buna N latices* was published in 1937 [8] in Germany. At that time it was not possible to produce a Buna S or Buna N latex of high concentration. Today, however, concentrations up to 60 per cent are commercially available. The composition and properties of three standard type Buna S latices are given in Table 7.*

Table 7. Available GR-S Type Latices

Type No.	1	2	3
Formulas:			
Butadiene	75	75	50
Styrene	25	25	50
Treatment after Polymerization:			
Short Stopper *	0.1	0.1	0.0
Antioxidant	1.5	0.0	0.0
Properties:			
Polymer viscosity (Mooney)	45-55	45-55	65-85
Total dry solids (%)	24-28	24-28	35-40
pH	8.5-10.5	8.5-10.5	9.5-11.5
Viscosity (cps)	5-10	5-10	8-10
Yield value (cgs/cm^2)	0.5-1.0	0.5-1.0	1.0-1.5
Surface tension (dynes/cm)	57-61	57-61	45-57
Stability (minutes)	30+	30+	30+

* Polymerization inhibitor

Type No. 1 corresponds to the synthetic latex from which standard GR-S is obtained. As can be seen, it contains antioxidant, which is usually of the discoloring type. Type No. 2 has no antioxidant and contained less agglomerates than No. 1.* However, the film-forming properties of both were not very satisfactory for many purposes, because, as already mentioned in discussing Buna S rubber, pure gum stocks show low tensile strength. To overcome this drawback Type No. 3 was developed which has a higher styrene content. This latex results in films of satisfactory properties.

* Office of Rubber Director, Dec. 8, 1943; *India Rubber World,* 109 (6) 577 (1944).

Application

Whereas Buna S latices of low styrene content could be used for such purposes where film strength was of secondary importance, a Buna S latex containing more styrene than the standard product is necessary for most applications for which natural rubber latex has so far been used. Most important of these are container-sealing compounds, various products needed in the shoe industry, and special adhesive compounds.

A *latex type suspension of Thiokol* can be readily prepared if the experiment previously mentioned is carried out carefully and good agitation during the reaction is maintained. This *Thiokol latex* is then subjected to washing to remove impurities, which is easily accomplished because the comparatively coarse particle size permits rapid separation.

Artificial Dispersions

Artificial water dispersions of natural rubber have also found considerable application for specific purposes. Their production is based on a series of patents dating back to the early 1920's.[110, 165]

The first patent specifically mentioning the dispersion of synthetic rubber is U.S.P. 1,671,314 (1928) to W. B. Pratt. The method, which is essentially identical with that used for natural rubber, consists of mixing into the polymer a hydrophilic colloid, as for example casein, glue or colloidal clays, such as bentonite, characterized by a high swelling capacity when in contact with water, and then introducing water into this compound until phase reversal occurs. An excellent detailed description of this method was recently published by Madge.[134]

The technology of synthetic rubber latex and of artificial water dispersions of synthetic rubber as well as their application, is in principle identical with that of natural rubber latex and artificial rubber dispersions, and can be found in the literature of the various manufacturers. However, there do exist some differences due to dissimilarities in the colloidal state of natural and synthetic latices which will be discussed later.

Synthetic Rubber Reclaim

It is easily understandable that the question of reclaiming synthetic rubbers becomes of greater interest as the synthetic rubber production increases in volume. Standard methods for reclaiming natural rubbers have proved ineffective for synthetic rubbers. The first suggestions to make vulcanized synthetic rubber scrap reusable were attempts to plasticize it either by heat treatments or by the incorporation of softening agents. These products, however, exhibited such poor physical properties that they could be used only if blended with new polymers, and even then the resulting products had only limited applications.

So far, very few patents referring to the actual reclaiming of synthetic rubbers have been issued, but it is known that more have either been granted or have been applied for; but their publication is being held up for the duration of the war.

Bachle [9] claims the reclaiming of butadiene copolymers by heating them from 10-20 hours in the presence of a solvent to temperatures ranging from 100-140°, while bubbling an oxygen-containing gas through the mix in the presence of a monaryl hydrazine.

Gumlich's [56] process is very similar to the one mentioned above, differing only by the addition of condensation products of hydrazines with ketones or aldehydes. Another process of Gumlich describes the reclaiming of synthetic rubber of the butadiene type by heating in the presence of an aromatic mercaptan in an oxygen-containing atmosphere and at temperatures between 130-150°.

Kirby and Eliott [115] describe the reclaiming of neoprene by heating the scrap to

about 300-425° F in the presence of an acid of the formula R-COOH, where R is selected from the group consisting of H, OH, COOH and aliphatic hydrocarbon groups containing from 1-18 carbons. Kirby and Steinle [114] reclaim neoprene by heating it at a temperature from about 300-425° F in the presence of a sugar.

However, it must be admitted that our knowledge of the reactions involved in the reclaiming of natural rubber is still far from satisfactory, and that, therefore, all attempts in this direction so far are based on trial-and-error experiments rather than on a fundamental knowledge of these reactions.

Chemical Considerations

Ability to Polymerize

The reason for the ability of certain compounds to undergo polymerization has been examined by various investigators. The shortest explanation and also the one which seems the most plausible is given by Cohen,[84] who states that "the properties of undergoing polymerization are peculiar to unsaturated compounds from a natural tendency to saturate themselves." The occurrence of the reaction does not seem to be limited to a particular kind of double bond or, for that matter, triple bond present in the original compound. Isobutylene which contains only one double bond in its molecule can easily be polymerized to Vistanex, whereas the raw materials generally used in the production of synthetic rubbers, as, for example, butadiene and its various derivatives, contain conjugated double bonds. However, the difference will be noted in the reactivity of the polymer produced. Vistanex, being completely saturated, shows a remarkable resistivity toward many of the influences affecting natural rubber or polymers produced from conjugated double bonds and still containing some unsaturation in the molecule. From the point of view of the rubber chemist, the most important characteristic of such saturated polymers is their inability to be vulcanized.

Carothers [139] states that "under sufficiently drastic conditions almost any compound can be converted into a material of high molecular weight." He then cites the transformation of methane into higher hydrocarbons by loss of hydrogen upon the action of alpha particles or silent electrical discharge. However, this self-addition of methane cannot be considered as a polymerization of a saturated compound, since methane must first be brought into a state of activity, in this case by the action of the alpha particle, before it will dispose of hydrogen and, becoming an unsaturated compound, start the self-addition process. Therefore, it actually was not the methane which was converted into a high-molecular substance, but an intermediate product formed during the reaction. This in turn conforms to Cohen's definition.

Ever since the first experiments in this field, the literature on polymerization has grown enormously and the number of patents filed on this subject is formidable. This, however, does not imply that we have as yet any fully satisfactory knowledge as to the more exact details of polymerization. Although we have improved the control of the reaction from an empirical point of view, any new substance or even derivatives of known compounds will require different reaction conditions, which first have to be experimentally determined before any attempt for large-scale production can be made.

The reactions occurring during polymerization are manifold and varied, and the more this problem has been studied the more it has been found to be complicated and complex. In general the isolation of intermediate products formed during polymerization has not been possible, and the end product has so far offered only a few conclusions as to the course of polymerization. Many factors, as, for example, temperature and choice of catalyst, have marked influence on it. Excellent examples for the variability of the polymerization reaction are the self-addition products obtained from acetylene. If acetylene is polymerized by the use of catalysts containing copper or

magnesium, an insoluble amorphous powder of unknown structure is formed. Similar results are obtained by the action of cathode rays, ultraviolet light, and alpha particles. So far only of scientific interest is a method for the polymerization of dienes, which consists of subjecting the catalyst-polymerization compound to the resonance of radiation of the metal used as catalyst.[107] Silent electric discharge at low temperature yields considerable amounts of liquid compounds containing highly unsaturated open-chain products, whereas polymerization at elevated temperatures in the presence of activated carbon results in hydrocarbons containing great quantities of benzene and naphthalene.

As a matter of fact, the very first experiments in the synthesis of rubber showed that polymerization can be induced by radiation. The effectiveness of light increases with decreasing wave length. Butadiene is polymerized by light of a wave length shorter than 2,300 Å at 40-45° in 100 hours.[123] The effect of silent electrical discharges [73] has also been studied on solutions of natural rubber and Buna 85. In both cases further polymerization resulted. This kind of activation, as well as the one obtained from alpha particles or silent electrical discharge, is probably due to an increased activation of the reacting molecules.

Besides the different activity exerted by different catalysts, various other factors such as impurities, temperature, pressure, and chemical constitution of the original compound have to be taken into consideration, as well as surface effects and various other conditions. It is possible that these factors either decrease or increase the rate of polymerization, or possibly change the course of the reaction completely. Not all compounds can be influenced by the same factors, nor can it be predicted which factors will influence the reactions in one case or the other.

Of all these factors the action of the catalysts still seems the most striking. A satisfying and short definition of this action is rather difficult, particularly one which will include all the reactions taking place.* We might perhaps define a catalyst simply as a substance which, although influencing the reaction rate of a certain process, remains chemically unaffected by it. However, certain substances classified as catalysts are known to react with the molecules of the monomer, forming intermediary compounds.[22] Ipatieff [109] has accounted for the polymerization of butylene in the presence of phosphoric acid by the assumption that the formation of the phosphoric ester takes place first. Although this demonstrates that catalytic reactions, contrary to older concepts, do not necessarily follow a definite pattern, certain characteristics, however, seem to be common to all of them. The following are of special interest.

Usually only small amounts of catalyst are necessary to bring about a considerable reaction. Experience has also taught that the catalytic effect of a mixture of catalysts is very often greater than the sum of their separate effects. Unfortunately, however, all this does not impart conclusive information if any specific group or groups of chemical compounds exert a catalytic effect in the polymerization of molecules of a given chemical composition.

The following table lists some of the many catalysts † published for the use in the polymerization of butadiene, its derivatives and copolymers, and other unsaturated monomers.

As can be seen, the variety of substances studied for their catalytic action is rather impressive. However, for large-scale production the use of certain catalysts, specific for the methods of polymerization applied, has by now been standardized. The development of highly effective catalysts has permitted an appreciable reduction of

* See paper on "Catalysis as a Biological Factor" by J. Alexander in Vol. V of this series. J. A.

† It seems likely that many of these substances may not be the actual catalysts, but that they lead to the formation of catalysts in he reaction mixture, *e.g.*, by serving as what are known biologically as prosthetic groups. J. A.

the time necessary for polymerization. This is one of the steps in the process which has materially assisted in improving the economics of the production of synthetic rubbers.

Isoprene

Acetic acid [68, 69, 70, 217, 218]
Organic + inorganic acids [18]
Organic acid anhydrides [183]
Aldehydes [109]
Carbonyls, metal [5]
Carbonyls, iron, nickel [78]
Halides, ammonium chloride [7]
Stannic chloride [27]
Ketones [109]
Metals, alkali, liquid Na-K alloy [151]
Metals, alkali, Na [150, 162]
Salts of nitrogen bases [85]
Olefins [148]
Organo-metallic compounds [40, 230]
Manganese, lead, silver oxides [86, 149]
Oxidizing agents [88]
Peroxides [85, 94]
Soaps [20, 88]
Sodamide [74]
Sodium naphthalene sulfonate [206]
Sulfur [13]
Light-sensitizers [168]

Butadiene

Acetic acid [69, 70]
Biliary acids [108]
Trichloracetic acid [104]
Carbonyls, iron, nickel [78]
Cobalt, molybdenum, Tungsten, chromium [78]
Organic halides [18]
Hydrides, alkali, metal [79, 98, 106]
Ketones [99]
Metal, alkali [100, 205]
Metals, alkali or alkaline earth [41, 88, 101]
Metals, alkali, Li + Na [69, 231]
Metals, platinum [5]
Metals, Na [117]
Nitrogen bases and salts [19, 21, 122]
Olefins [148]
Organo-metallic compounds [40, 230]
Peroxides [53]
Manganese, lead, silver oxides [86, 149]
Mercuric oxide [149]
Oxidizing agents [102]
Soaps [20, 131]
Sodium naphthalene sulfonate [206]

Chloroprene

Nitrogen bases, NH_3 [122]
Oxygen [29]

Diolefins

Acids, sulfuric, phosphoric [90]
Ammonium persulfate [91]
Halides [92]
Unsat. ketones [93]
Metals, alkali [80, 82, 89, 98]
Organo-metallic compounds [105]
Oxidizing agents [132]
Oxygen [84]
Ozonides [95]
Soaps [96]
Albumin [94]

Erythrene

Metals, alkali or alkaline earth [18, 157]
Nitrogen bases, amides, urea [15]

Ethylene

Metals, mercury [197]

Isobutylene

Sulfuric acid [126, 154, 163]
Halides, boron fluoride [228]

Myrcene

Metals, alkali, Na [156]

Butylene

Metals, copper, followed by Na [163]

Substituted Olefins

Unsaturated esters [101]

While the Russians retained their interest in bulk polymerization, working hard to overcome the serious drawbacks of the early methods, as for example fire and explosion hazards and the difficulty of obtaining uniform polymers, the Germans were the first to shift to emulsion polymerization on a large scale. After a considerable effort had been spent, their method of emulsion polymerization not only had reduced fire and explosion hazards to a minimum, but had also permitted a very pro-

nounced increase in rate of polymerization at lower temperatures than had been previously employed.* This procedure also avoided the formation of oily by-products caused by local over-heating in high-temperature bulk polymerization. Applying lower temperatures without greatly impairing the rate of polymerization usually results in superior physical properties in the finished polymers.

There is ample evidence that if polymerization is carried out for too long a time, undesirable interpolymerization (cross-linking) occurs, causing tough products which are difficult to process. Therefore, the reaction is frequently interrupted before it has gone to completion, and the unreacted monomers regained by stripping. Copolymerization is greatly facilitated by the emulsion polymerization process. The question of the concentration of the emulsified part deserves special attention. It is a well-known fact that oil-in-water type of emulsions can be prepared with up to 90 per cent of emulsified phase. The possibility of using an emulsion of such high concentration in the polymerization of synthetic rubbers would be of extreme interest from an economic point of view. However, it has been demonstrated that the yield of polymer is adversely affected when carrying out polymerization in such high concentrations.

The catalysts usually employed in this process are oxidizing agents, benzoyl peroxide, tertiary butyl hydro-peroxide and potassium persulfate being among the most generally used. Complex organic compounds [107] such as hemin, sodium isobutyl-naphthalene sulfonate, ammonium thiouranyl persulfate, etc., have recently been suggested as catalysts, whereas organic sulfur compounds, selenium compounds, amines, quinones, phenols, and nitro-aryl [29] compounds are used as modifying agents to control polymerization. It is claimed that these compounds will prevent or at least reduce interpolymerization and branching, and propagate long-chain polymerization.

Numerous compounds have been investigated for use as emulsifying or stabilizing agents, following in a great many instances the knowledge gained from studies on natural rubber latex. Sodium butyl-alpha-naphthalene sulfonate, oleyl-beta-diethylaminoethylamine, and tetrahydronaphthalene-beta-sulfonic acids are mong those particularly specified for this purpose. Others include bile salts and derivatives, organic sulfonic acids, sodium linoleate and stearate, sulfite cellulose waste liquor, etc. For acidic emulsions the hydrochlorides of diethylamine, ethoxyoleyanilide, and pentadecylglyoxaldine are recommended.

Lately certain cationic soaps, such as cetyl- and stearyl trimethyl ammonium bromides, have been used for the production of positively charged chloroprene and bromoprene emulsions. Another class of compounds claimed to be emulsifying agents is recommended because it decreases the time of polymerization to one-third or one-fourth of that required when using known emulsifiers. They are saturated aliphatic open-chain compounds containing oxygen or sulfur in the chain and radicals of secondary amines, quaternary ammonium bases, and amides on the ends.

The addition of various hydrophilic colloids, such as gum arabic, glue, casein, blood serum, milk, starch, egg albumin, etc., has been recommended, and claims are made that they not only facilitate the emulsifications and stabilize the emulsions, but also improve the finished product. It must be said that the reasons for the latter are not quite understandable, unless the cause for the improvement in the finished polymer is to be looked for in the more stable emulsion produced by the addition of protective colloids, which in turn would induce more uniform polymerization.† The addition of egg albumin for this purpose was suggested by Gottlob [35] as far back as 1925.

* This recalls biological chemical changes, which take place in detail rather than in mass, and at relatively low temperatures, as a consequence of the great development of free surface. J. A.

† Rubbers, both natural and synthetic, have structures at levels of organization higher than those commonly considered, and adsorbed surface layers of proteins, etc., may exert an important influence. See, *e.g.*, paper by H. A. Winterkorn on soil stabilization and by J. Alexander on principles underlying plastics, in this volume. J. A.

It has also been claimed that the addition of appropriate solvents in connection with the above-mentioned colloids improves plasticity, workability, and strength of the resulting products. For example, less than one per cent of such compounds as hexachloroethane, chlorobenzene, dichloroethylene, and carbon tetrachloride in combination with glue, saponin, and casein are recommended.

Many more modifications of the polymerization process both in bulk or emulsion form are being constantly added to the list, as shown by the literature and patent surveys of Voge [209-216] and others.[171-179]

The Effect of Bulk or Emulsion Polymerization on the Properties of the Final Polymer

There are indications that bulk and emulsion polymerization produce polymers of different structure. The differences between the products can best be noticed when the product is processed. Butadiene rubbers produced by the old bulk polymerization method, using metallic sodium as catalyst, are fairly easy to work on the rubber mill. They break down in a way similar to natural rubber. Butadiene rubber obtained from an emulsion polymerization process is tougher, less tacky, and comparatively hard to work on a mill.

It seems probable that bulk-polymerized butadiene consists mostly of short and primarily straight chain molecules, whereas the product obtained from emulsion polymerization seems to contain chains which due to a 2,3 and 3,4 addition, as well as the 1,4 addition found in natural rubber cross-link. This branching occurs not only in one direction, but is tridimensional. A schematic formula (according to Staudinger [189]) may serve as illustration. (Fig. 12).

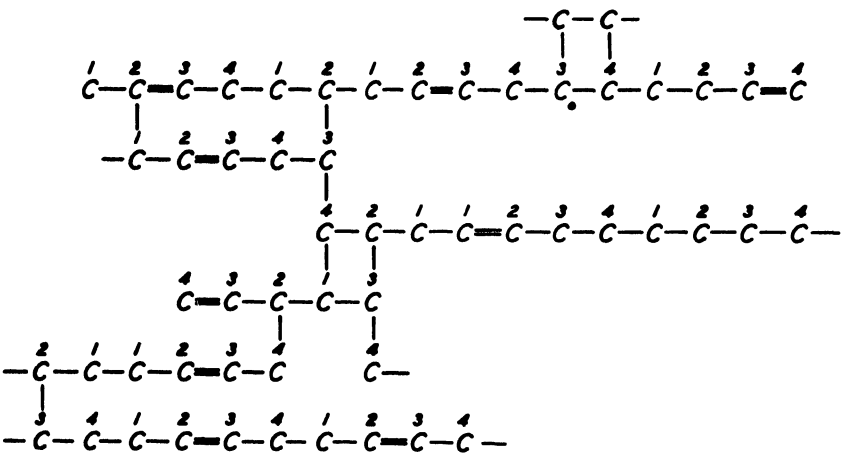


FIGURE 12. Branching in Polybutadiene [H. Staudinger, *Trans. Faraday Soc.*, **29**, 28 (1933)].

This formula clearly explains the behavior of this particular kind of synthetic rubber. Chain slippage will be much more difficult, if at all possible, than in a non-linked straight chain polymer, and breakdown on the mill will need much more force.

These difficulties encountered with polybutadiene obtained from emulsion polymerization led to further work in the search of products with better processing properties. By copolymerization of butadiene with other hydrocarbons, as for example, isoprene or dimethylbutadiene, certain improvements were obtained. Greater progress was made when using olefins for the copolymerization. Butadiene was copolymerized with styrene or acrylonitrile. Very soon it was recognized that copolymer-

ization had opened up a new field of tremendous possibilities. Any unsaturated compound can be used for this purpose as long as it polymerizes together with the dienes.

Chemical Composition of the Monomers

Although the degree of unsaturation determines the ability of a compound to polymerize, its chemical composition also has a great influence on the rate of polymerization. It has been found that the rate of polymerization generally increases with increasing unsaturation of the monomer.

As has been mentioned, saturated hydrocarbons will polymerize only if subjected to the action of a powerful energy source such as, for example, radioactive substances. The high kinetic energy of the alpha particles is capable of producing unsaturated hydrocarbons as well as ions and free radicals which are then actual polymerization monomers. Table 8 gives the number of reactive molecules per pair of ions produced (−) M/N and enables us to draw conclusions as to the differences in polymerization reactivity as related to unsaturation.* The reactions were carried out at 25° and the amount of radon per 30 cc of compound was a few hundredths curie.†

Table 8

Compound	(−) M/N	Compound	(−) M/N	Compound	(−) M/N
Methane	2.2	Ethylene	5.1	Propyne	8.3
Ethane	1.7	Propylene	4.9	Butyne-2	5.8
Propane	1.7	Butene-2	3.8	Butadiene 1,3	9.0
n-Butane	1.8	Acetylene	19.8	Isoprene	10.3

These results indicate that activation of the saturated hydrocarbons stops after the initial impact of the alpha particles, as expressed by the extremely low (−) M/N ratio. The greater polymerization reactivity of the unsaturated compounds is demonstrated by the increase in this ratio, the highest values being obtained with compounds of higher unsaturation.

Table 9, a compilation of straight-chain hydrocarbon compounds containing four carbon atoms, serves to emphasize this effect.

Table 9

Compound	Per cent Conversion under Given Conditions
Butene-1 $CH_2{=}CH{-}CH{-}CH_3$	39.6% in 52.5 sec. at 750°, stable at 200°
Butadiene 1,3 $CH_2{=}CH{-}CH{=}CH_2$	10 days at 150° in sealed tube "all polymerized"; 70% polymerized in one hour at 350°
Vinylacetylene $CH{\equiv}CH{-}CH{=}CH_2$	Explosive polymerization on contact with sulfuric acid or upon heating. Under pressure readily polymerized to a solid. Homologues form viscous syrup upon standing for 2-3 months.
Diacetylene $CH{\equiv}C{-}C{\equiv}CH$	Explodes at 35°. Definite polymerization in 5 min. at 0°.

It has been known for some time that if a polymerizing molecule contains more than one unsaturated linkage, its rate of polymerization will be greatest if these linkages alternate within the structure of the molecule. Such alternating unsaturated linkages are called conjugated linkages. They are present in the building units of rubber or synthetic rubber, as exemplified by the formula for butadiene, $CH_2{=}CH{-}CH{=}CH_2$.

* The data in this table and the following table were taken from Burk, Thompson, Weith, Williams, "Polymerization," pp. 15-6, Reinhold Publishing Corp., New York, 1937.

† "The quantity of emanation in radio-active equilibrium with one gram of radium by the laws of radio-active change is termed a curie." Crowther, J. A., "Ions, Electrons, and Ionizing Radiations," Longmans, Green & Co., New York, 1931.

If any of the hydrogens are replaced by alkyl groups, the effect of the latter on the rate of polymerization will depend on their position in the polymerizing molecule. Substitution occurring on carbon atoms in 2 and 3 position as, for example, in isoprene or 2,3-dimethylbutadiene, leads to an increase in the rate of polymerization. (See Table 10).

Harries pointed out that alkyl substitution on the end carbons decreases the rate of polymerization. However, it may be said in general that an increasingly complex structure of such a molecule will decrease its reactivity.

There also seems to be some difference in the rate of polymerization of ortho, meta, or para alkyl-substituted ring systems, as found by Shoruigin [187] and his collaborators in their work on styrene.

If hydrogen is present in an acetylenic bond, the rate of polymerization will be increased.

The substitution of hydrogen by halogens has been extensively studied by Carothers.[139] Chloroprene (2-chloro-1,3-butadiene) polymerizes much more quickly and readily than does 1,3-butadiene, and about 700 times as quickly as isoprene.

If bromine is introduced into the molecule instead of chlorine, the rate of polymerization becomes still more rapid. Substitution by iodine further increases the rate. However, the iodine polymer demonstrates rubber-like properties only under certain conditions. The polymerization product obtained from 2-bromo-1,3-butadiene is inferior in its rubber-like qualities to that of chloroprene. It has been assumed that the great weight percentage of bromine and iodine in the molecule is the main cause for this deficiency.

If a second chlorine atom is introduced into the diene compound forming 2,3-dichloro-1,3-butadiene, polymerization progresses even more rapidly than in chloroprene, but again the product is far inferior to the latter, as far as rubber-like properties are concerned. The reason for this can be two-fold: either polymerization proceeds too far, or the amount of chlorine in the molecule is too great.

The effect of the position of the chlorine substitution in the carbon chain is very pronounced; 1-chloro-1,3-butadiene polymerizes only slightly more rapidly than isoprene. If chlorine has been added to all four carbon atoms of the chain by substitution of four hydrogen atoms, no polymerization occurs.

Having obtained such striking results in the halogen substitution, Carothers investigated other constituents. 2-heptyl-1,3-butadiene and 2-phenyl-1,3-butadiene were studied but found to result in inferior products. 2-ethoxy-1,3-butadiene also yielded an inferior product, but 2-acetoxy-1,3-butadiene [$CH_2 = C(OCOCH_3) - CH = CH_2$] and similar compounds gave polymerization products of rubbery properties, the rate of polymerization of which was about the same as that of chloroprene.[222]

4-Cyano-1,3-butadiene ($CH_2 = CH - CH = CHC \equiv N$), although an end-substituted compound, polymerizes about 20 times as fast as isoprene. Presumably its increased conjugated unsaturation accounts for this effect. Its properties are inferior to those of rubber in that it shows considerable permanent set.

Lately a new patent was issued covering the copolymerization of chloroprene and 2-cyano-1,3-butadiene. In view of the above discussion we might expect that polymerization would proceed at least as rapidly as with chloroprene alone, if not faster.

This pronounced effect of chemical composition and substitution on polymerization has attracted other investigators to work in this field. The following table gives a compilation of data concerning the relative rates of polymerization of various dienes. Isoprene was used for comparison. However, the data on estimated rates should not be used for any quantitative considerations, since the rate of polymerization of these compounds depends to a great extent on the previous history of the samples, which is not the same in all cases. Carothers assumed that such variations are insufficient to change the order of magnitude of the estimated rates.

Table 10. Estimated Relative Rates of Polymerization of Various Dienes at 25° *

Position and nature of substituent C_1	C_2	C_3	C_4	Estimated Rate †	Character of Polymer
—	Cl	Cl	—	2000	Hard, not extensible
—	I	—	—	1500	Rubber-like under certain conditions
—	Br	—	—	1000	Good rubber
—	Cl	—	—	700	Excellent rubber
—	Cl	CH_3	—	500	Fair rubber but low extensibility
Cl	Cl	Cl	—	120	Soft, elastic
—	C_6H_5	—	—	90	Soft
CH_3	Cl	—	—	30	Soft
C_2H_5	Cl	—	—	30	Soft
C_4H_9	Cl	—	—	10	Soft
C_7H_{15}	Cl	—	—	10	Soft
—	C_7H_{15}	—	—	9	Soft
Cl	—	—	—	7	Soft, sticky
—	CH_3	CH_3	—	3	Fair rubber but low extensibility
CH_3	CH_3	Cl	—	1.5	Soft
—	CH_3	—	—	1.0	Fair rubber (Isoprene)
—	—	—	—	0.8	Fair rubber
CH_3	—	—	—	0.3	
CH_3	CH_3	—	—	Probably less	
$(CH_3)_2$	—	—	—	than 1	
CH_3	—	CH_3	—		
CH_3	—	—	CH_3		
$(CH_3)_2$	—	CH_2	—		
$(CH_3)_2$	—	—	CH_3		
CH_3	CH_3	CH_3	CH_3		
$(CH_3)_2$	—	—	$(CH_3)_2$		

* Collected papers of Wallace H. Carothers on Polymerization. Edited by H. Mark and G. S. Whitby, p. 396, Interience Publishers, Inc., New York, 1940.
† "The estimated rates are based on calculated unimolecular reaction velocity constants."

In general this table confirms the previous discussion, with the exception that a onsiderable increase in complexity of molecular configuration does not decrease the ıte of polymerization on account of the sluggishness of the molecule. The two subtitution derivatives show that the rate of polymerization of the methyl derivative is ›wer than that of the heptyl derivative.

Structural Considerations

In discussing the synthesis of rubber it seems first advisable to consider our presnt knowledge of the structure of the *natural* product. Destructive analysis has ıught us to consider isoprene as the ultimate building unit of rubber, and with the id of organo-chemical methods, x-ray, and electron diffraction, we have been able to raw certain conclusions as to how several such isoprene units combine to form ırger aggregates or "rubber molecules." We have also obtained some important ıformation as to changes in the position of the double bonds of isoprene during such ombination (polymerization). However, as objective scientists, we must admit that 're still have no positive indication that the plant produces the rubber hydrocarbon y polymerization from this diolefin. It even seems doubtful, inasmuch as it has not een possible to isolate isoprene or one of its low polymers from the plant.

There is good reason to believe that if isoprene is present, the combination of ɔveral isoprene units preferentially takes place in one direction, resulting in linear ıolecular chains; and it is furthermore known that this combination takes place in n orderly fashion (1,4 addition). Thus, x-ray diffraction studies have revealed that ıe isoprene units in natural rubber join to form molecular chains characterized by a *is*-configuration, whereas these same units are aligned in *trans*-configuration in the ase of gutta percha or balata.[49]

However, there is still no satisfactory picture as to what groups constitute the

ends of these chains and none of the suggestions so far advanced permit a satisfactory correlation with the various known properties of rubber.

What importance chain length and its distribution may have in regard to the physical properties of the substance, and what may be the effect of cross-bridging between chains, due to primary valence forces or sidegroups in the molecular chains, is not yet clearly understood. Therefore, it must be admitted that our knowledge of the structure of rubber is still far from being complete or fully satisfactory.*

That this is so despite the tremendous amount of experimental as well as theoretical work [1, 24, 28, 42, 57, 58, 59, 110, 124, 125, 136, 137, 164, 204, 207, 210] which has been done during the last thirty years should not be surprising if one recalls that natural rubber is far from being an ideal, uniform substance. Those attempting to solve the many remaining problems by rigid theoretical or mathematical analysis too frequently overlook the fact that not only is the raw material itself a non-equilibrium system, but also that minute changes in experimental procedure will cause appreciable differences in the results obtained. There is no doubt but that these two factors are mainly responsible for the many conflicting and frequently contradicting observations and results reported in literature.

Although it is possible to obtain rubber-like substances by polymerization of isoprene, so far none of these has even approached natural rubber in most of its properties. This indicates either that the plant produces rubber in other ways than by polymerization, as suggested above, or that we have so far not been able to control polymerization to obtain a product exhibiting the desired properties.

The fact that x-ray diffraction studies of synthetic poly-isoprene have not revealed patterns similar to those of natural rubber seems to indicate that the man-made polymer does not possess the uniformity of the individual chain structure which characterizes natural rubber. As a matter of fact, several properties, both chemical and physical, would indicate that the synthetic product contains *cis-* as well as *trans-*configuration. Furthermore, there is sufficient indication that the synthetic material is characterized by shorter average chain length and a different chain-length distribution, and that linking between chains is more frequent than in the natural product.

So far the only synthetic rubber which shows considerable regularity in polymerization is polychloroprene. The fact that its monomer differs from isoprene only in the substitution of the latter's methyl group by chlorine seems to indicate that this orderly polymerization (which takes place in *trans*-configuration) is attributable to the greater activity of the chlorine atom.

As previously pointed out, there is as yet no indication as to how nature accomplishes such an orderly combination.† There remains the possibility of preferential catalysis, or it may be that the rubber is formed in the plant not by polymerization, but by a condensation reaction from preformed carbohydrates. Inositol derivatives which have been found quite generally in natural rubber latex may constitute the basic components for such reactions.

Principle of Geometrical Configuration of Polymers

Most of the high polymeric compounds are built up from long-chain molecules by repetition of the building units. The number and chemical nature of these units determine the properties of the polymer. For a really complete description of the polymeric molecule, it would be necessary to specify the nature of the end units of the chain. However, so far we have not been able to do this either in the case of natural or synthetic rubbers.

* Possibly a consideration of successive levels of material structure in rubbers will be helpful here. See J. Alexander in Vol. V of this series. J. A.

† Biological catalysts are highly dispersed and natural reactions take place in regular detail, rather than in more or less disorderly mass. Protective colloids (impurities) usually greet naturally catalyzed products in their nascent state. J. A.

It also must be remembered that these chains will not all be of the same length, and that the properties of the polymer depend to a great extent upon the number and distribution of chains of an average length.

Some high-polymeric compounds are characterized by intramolecular ring formation. Such structures are, however, of little value for the rubber-like group of synthetics, although intermolecular ring formation may occur as a side reaction in high-molecular chain molecules.

Carothers' [189] work, his conclusions being based for the most part on probability considerations, shows the tendency of high polymeric compounds to form chain- rather than ring-like structures. Staudinger concurs in this view (Faden Molekule). Five-, six-, or seven-membered rings form quite easily and without strain on the molecule; but with increasing chain length there is less chance for ring formation. However, the probability of ring formation can be increased if substitution groups are introduced which restrict the mobility of such compounds.

Some Kinetic Considerations of the Mechanism of Polymerization

Kinetic considerations of the mechanism of polymerization and condensation reactions of synthetic rubber meet with considerable difficulty. The condensation reactions cannot be dealt with satisfactorily as long as the kinetics of esterification are not completely understood, whereas in studying the kinetics of polymerization reactions we have the advantage of knowing about the behavior of radicals and the reactivity of the double bonds. However, a distinct disadvantage can be found in the fact that many molecules do not polymerize in the vapor state, thus complicating the issue. The factors influencing polymerization are innumerable. Polymerization, and particularly co-polymerization, are extremely sensitive to the action of catalysts and the influences of impurities. Minute traces of impurities can change the regular course of the reaction quite drastically. Contact with air or the effect of light will greatly influence the rate of polymerization. Admittedly, decided progress has been made in the study of the kinetics of molecules polymerizing in strict chain fashion, like styrene.

Dimerization experiments afford an indication of the energy required to induce double-bond reactivity, but the data available for the time being do not permit any general conclusions as to whether a similar degree of activity is needed for the production of high-molecular compounds.

A further complication in kinetic considerations can be found in the various mechanisms of polymerization induced by the particular kind of activation of the double bond. The double bond can be excited, or a di-radical can be formed. The former is always accompanied by the migration of a hydrogen atom.

Many systems where polymerization reactions of special interest have been observed are in the liquid state, a fact which introduces still more difficulties in the evaluation of the reactions, since our knowledge of the liquid state of matter is still rather incomplete. For the evaluation of such systems it is often necessary to resort in part to the determination of viscosities. It is not within the scope of this chapter to discuss the theories of viscosity and the mathematical formulas worked out by various investigators.* However, the particular molecular constitution of high polymers certainly adds to the difficulties in evaluating them. Staudinger [189] has given his special attention to such effects and has worked out a viscosity equation wherein the shape of the molecule is taken into account. This equation was experimentally confirmed for very dilute solutions. However, several of his assumptions do not conform to our present ideas of shape and arrangement of long-chain molecules in solution. Staudinger contends that the molecules are represented by rigid rods, whereas others consider them to be snarled threads. Further serious complications

* See paper by H. Eyring and R. E. Powell in Volume V, p. 236.

for the evaluation of viscosities of synthetic high polymers will be encountered because of the occurrence of extensive branching. Branching and linking between chains of the polymer will decrease the solubility of the polymer to such an extent that in extreme cases any attempt to interpret experimental viscosity data becomes a hopeless task. Meyer and Mark [147] hold that a considerable amount of solvent is immobilized by attachment to the solute. Thus it is evident that in the case of high polymeric substances viscosity measurements have still to be regarded with some restraint, at least if they are to be used to evaluate other data.

Meyer [140] explained the anomalies in thermodynamic properties of solutions of high polymers in an interesting and original way. He visualizes a model in which molecules of the solvent are replaced by "elements" of the chains of the polymer. The polymer molecules are free to assume various configurations. The deviation of the entropies of mixing from the ideal values are attributed to these configurations. Huggins [77] seems to have assumed a model similar to that of Meyer in his concept of dilute polymer solutions.

Another difficulty in kinetic considerations of polymerization reactions can be found in the variety of reactions and reaction products which often occur during polymerization. Evidence has been presented that polymerization reactions do not occur between monomers alone. The existence of chain reactions is also conceivable. By "chain reaction" we understand a reaction where intermediate compounds are first formed which themselves are then able to act as additional catalysts, thus increasing the rate at which active molecules are formed. Such reactions are particularly sensitive to the influence of catalysts and inhibitors.

Montroll [152] applies statistical methods to obtain an indication of the molecular size distribution in long-chain polymers, developing a theory of depolymerization with the assumption "that all bonds connecting monomeric elements in the system have the same probability of being broken. The molecular size distribution at any time is given as a function of the initial distribution and the fraction of bonds split. Under the assumption that the rate at which bonds are cut is proportional to the number of uncut bonds in the system the time dependence of the degree of polymerization is discussed." Marei [135] develops mathematically the determination of polymerization constants.

Hydrogenation and dehydrogenation may occur during the polymerization reaction as well as the rearrangement of the compounds to form their isomers. Structural studies have given good evidence that branching occurs as well as interpolymerization between polymers.*

Melville [145] holds that "at present there is no published evidence pointing to any deviation in normal kinetic behavior which may be conclusively ascribed to branching, although products have been obtained which appear to be cross-linked. This may be due to the fact that most polymer growth stops by mutual deactivation in pure systems. But branching can only become noticeable if the reaction goes abnormally quickly as some parameter such as concentration or temperature is increased, and such an event only becomes possible if the kinetic order of the branching process with respect to the active polymer concentration is greater than the order of the reaction responsible for the destruction of the polymer. When active polymer destruction is already of the second order, it is thus impossible for this condition to be fulfilled. Unless, therefore, branching is brought about by the addition of some specific new component to the system, its detection kinetically seems unlikely."

The occurrence of branching is one of the greatest problems in the manufacture of synthetic rubber. It is probably the major reason for the toughness of the synthetic polymers. The above theoretical considerations seem to make it unlikely that kinetics alone will be helpful in solving this problem.

* Re branching structures in starch and glycogen, see paper by R. M. Hixon and R. E. Randle in Vol. V of this series. J. A.

The orientation of polymerizing molecules on surfaces may be another factor influencing the character of compounds formed during polymerization.[224] Kinetic considerations will have to take all these possibilities into account. But inasmuch as the course of the basic reaction is not yet fully elucidated, it is very difficult, at least for the time being, to draw general conclusions as to the reaction mechanism of polymerization.

Progress of Polymerization

Modern interpretations of polymerization tend to divide this reaction into three distinct phases occurring successively: the formation of nuclei, the reaction of growth and the termination.[138] * The formation of nuclei can be a reaction of monomolecular, bimolecular, or any other order. A very highly activated molecule is formed by adsorption of a photon or by impact with an energized particle (compare the polymerization of unsaturated hydrocarbons by raaon). This process depends to a high degree upon temperature and the presence of a catalyst. The second phase, the growth of the polymer, occurs if such a nucleus collides with another molecule resulting in their combination. This action starts the growth of the chain. The last phase, the termination, will occur if the active group at the end of the chain becomes deactivated. There are several reaction possibilities causing the deactivation of the polymeric molecules, three of which are most generally assumed:

(a) spontaneous loss of activity of the growing polymer;

(b) interaction of two growing polymers;

(c) destruction of the reactivity of the polymer by collision with a molecule of a monomer.

Other assumptions hold that a hydrogen atom may move along the chain toward its end and form a double bond at the end of the chain, or that the two free valencies at the end of the chain may react to form a ring. (However, as has been previously discussed, this seems rather improbable). Finally, the collision of the chain with a molecule, whereby a hydrogen atom jumps from the chain to the colliding molecule, while a double bond is formed at the end of the chain, might be considered as a possible explanation. Flory [46] accepts Mark's theory, except for the termination process.

Ziegler's [229] investigations on sodium-catalyzed polymerization processes have led him to the assumption that organic sodium compounds are formed during the first phase of the process. J. L. Bolland,[22] in his study on the polymerization of isoprene with sodium, concludes that the first phase of polymerization is complicated and involves adsorption of the isoprene molecule on the catalyst, followed by an activation and a desorption of the activated complex.

The induction period which has been found to occur in polymerization is supposedly due to the time required for the formation of an adequate number of nuclei.

X-Ray Studies and the Configuration of the Molecules of Synthetic Rubbers

The configuration of molecules has attracted the special interest of scientists during the last quarter of a century. Although chemical analysis will permit an insight into the composition of a "molecule," it cannot reveal its general configuration nor its particular configuration in relation to another "molecule."

X-ray diffraction patterns of crystals have enabled us to obtain, for the first time, an insight into the spatial arrangement of the ions, atoms, or groups of atoms which account for the chemical composition of the substance. Somewhat later it was found that fibrous substances like cellulose give an x-ray diffraction pattern which reveals a preferential orientation of the building units parallel to the fiber axis. Rubber, when stretched, also yields such a fiber diagram. At first it was assumed that these

* See paper by H. Mark in Volume V, p. 280.

patterns could be evaluated on the basis of the same assmuptions as patterns obtained from crystals. However, it soon became evident that this was not possible. Further work finally led to a new concept—the macromolecular lattice. (Fig. 13). In this

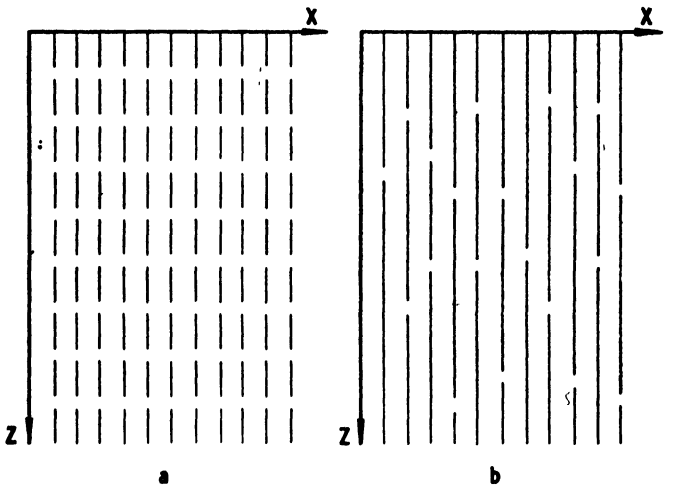


FIGURE 13. Plane through (a) an ordinary and (b) a macromolecular type of molecular lattice [C. S. Fuller, *Rub. Chem. Tech.*, 14 (2), 326 (1941)].

lattice the "molecules" are oriented only in one direction, but otherwise their distribution as well as their length is variable. The structure can be considered as an intermediate stage between a crystal lattice and a mesomorphic system.*

When rubber, which has been stored for a long time at low temperatures, is subjected to x-ray diffraction studies, a ring pattern is obtained. The radii of the rings correspond to the distance of the interference spots from the center in the fiber diagrams. This fact indicates that the macromolecular lattice is the result of a localized aggregation (micelles) of the long-chain molecules. These zones are randomly arranged, but on stretching have the tendency to align in the direction of strain. Since a single-chain molecule can be part of several such micelles, this concept is frequently referred to as the fringe structure theory. (Fig. 14).

However, synthetic rubbers have not lent themselves very successfully to such an investigation, and x-ray diagrams have been obtained only from comparatively few of their kind.

Polyhaloprenes (specifically neoprene)

Polychloroprene has been found to give a fiber pattern if stretched to about 500 per cent.[30, 49, 185] The pattern is not as clear as that obtained from natural rubber. Also, a much higher elongation is needed than with the latter, to obtain it at all. The identity period of polymerized chloroprene corresponds to that of beta-gutta percha, leading to the assumption that there is a *trans-* rather than a *cis*-configuration at the double bond. (Fig. 15).

Synthetic Polymers Prepared from Isoprene, Butadiene, and their Copolymers

No fiber patterns have as yet been reported for any of these polymers. In the case of isoprene, this was thought for some time to be caused by random polymerization of the monomer, so that the CH_3 group occurs at irregular intervals within the

* See paper by G. Friedel on mesomorphic states, in Vol. I of this series (1926). J. A.

chain, thus destroying any periodicity. However, this argument was disproved, since no fiber pattern could be obtained from pure butadiene polymers. Thus a random tri-dimensional polymerization had to be postulated whereby the chains were netted together by primary valence forces. This concept would also account for the greater stability of the butadiene polymers toward mechanical or chemical attack.

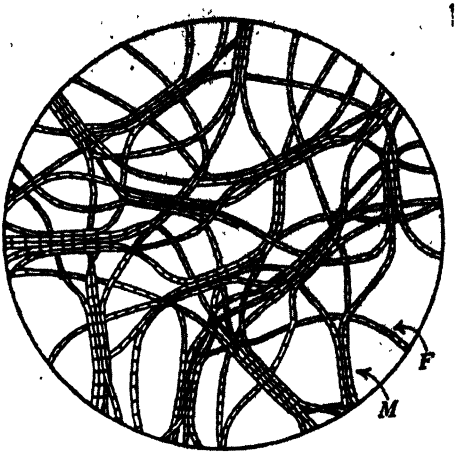


FIGURE 14. Fringe structure of rubber after Hermann and Gerngross. F = Fringes; M = Micelles (crystallites) [R. Houwink, "Elasticity, Plasticity and Structure of Matter," Cambridge Univ. Press (1937)].

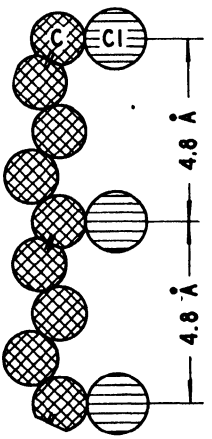


FIGURE 15. Chain configuration of Polychloroprene [C. S. Fuller, *Rub. Chem. Tech.*, 14, 337 (1941)].

That the polymerization of synthetic rubbers does not always follow the same direction has been brought out by the fact that the reaction itself is difficult to control, and polymerization products exhibiting different properties have been obtained only upon changing some one factor in the reaction set-up.

Thus Katz [112] reported that he studied isoprene polymers which gave exactly the same diffraction pattern as the liquid monomer if polymerized under certain conditions, whereas different polymerization conditions would yield different "liquid" patterns or none at all. He reported the same phenomena for methyl rubber.

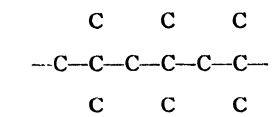
If one compares the results discussed above, it is interesting to note once more that polymerized chloroprene will show a fairly well defined diffraction pattern, even if not as good as that of natural rubber, whereas polyisoprene or polybutadiene show none. It is known that the chlorine atom in the molecule exerts a powerful influence

on the speed of polymerization and analogous effects can be found in the polymerization of vinyl chloride and propylene. In this case the chlorine atom also controls the polarity of the molecule. Thus, it can be assumed that the chlorine atom in chloroprene imparts to the molecule a greater polarity than, for example, the CH_3 group in isoprene, thereby controlling not only the speed of polymerization but also preventing irregular alignment of the chloroprene units in the chain during polymerization.

In the case of butadiene copolymers of the Buna S and Buna N types, the inability to obtain x-ray diffraction patterns even if the rubbers are stretched is possibly also accentuated by steric hindrance.

Polyisobutylene (Vistanex, Oppanol, and Butyl Rubber)

Brill and Halle [20] obtained a fiber pattern from this substance upon stretching it. Fuller [48, 49] reports the occurrence of a very strong pattern, indicating high orientation and macromolecular "crystallinity." He is of the opinion that of the four structural possibilities in the polymerization of isobutylene the most likely one would be that of head-to-tail addition:



The configuration of the chain itself can be considered a helix, whereby the methyl groups complete one revolution (around the chain) within the distance of one fiber period. Destructive hydrogenation of this material [108] yields only paraffinic hydrocarbons, indicating the probability of long aliphatic chains without bridging.

Sebrell reports a similar fiber pattern for Butyl rubber.[186]

Organic Polysulfides (Thiokol Group)

Fuller [49] found certain of the organic polysulfides to be "crystalline" even in the unstretched condition, becoming oriented to a high degree upon elongation. He was able to calculate the fiber periods and recognized a structure of long-chain molecules without bridging between them. His ideas conform very well indeed to the picture of their structure as postulated by Patrick [100] from his chemical studies on Thiokols. Patrick described the tetrasulfide group of Thiokols as long-chain molecules containing, for each tetrasulfide group, two sulfur atoms in the chain, the other two being joined to them. Fuller corroborates this, assuming the configuration to be a ring formed by the four sulfur atoms and the two adjacent CH_2 groups (Fig. 16). For the disulfides in the Thiokol group, the fiber period was calculated to be about twice as long as for the tetrasulfide, indicating a rotation of 180° for every second unit. Sebrell and Dinsmore [184, 185] did not find any fiber diagrams when stretching "commercial, vulcanized Thiokol stock."

Electron Microscope*

The application of electron microscopy to a systematic investigation of the structure of rubber is of quite recent date,[63] although electron micrographs of various elastomers have been previously published.[6, 153, 166]

A special technique to make suitable fiber specimens was worked out by spreading a thin film of rubber in an organic solvent on a water surface and allowing the solvent to evaporate. The film is then picked up with a 200-mesh screen, whereafter it breaks up into fibers ranging in width from several microns down to about 100 Å.

* See paper by A. F. Prebus in Volume V, of this series, page 152 et seq.; also paper by James Hillier and V. Zworykin in this volume.

A very pronounced difference in the structure of the fibers formed from the different rubbers is evident. Fig. 17a shows those obtained from natural rubber (Hevea), Fig. 17b those from neoprene GN, and Fig. 17c those from Buna S. So

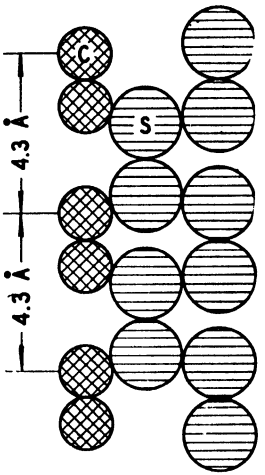


FIGURE 16. Chain configuration of Polyethylene tetrasulfide [C. S. Fuller, *Rub. Chem. Tech.*, **14**, 337 (1941)].

far it is assumed that the globular zones correspond to the sol fraction of the rubber, and the thin cross-linked threads to the gel fraction. The fact that up until now it has not been possible to obtain any films from Buna S which will readily break up into small fibers can be best explained by the assumption that considerable cross-linkage between short polymer chains is prevalent. This would conform to the processing and physical properties of the copolymer. Although the results so far reported have already demonstrated that the electron microscope must be considered as a new tool in the experimental study of the structure of natural and synthetic rubbers, it is still too early to draw any final conclusions as to the extent of its applicability in this field.

SOME COLLOID CHEMICAL ASPECTS

Only when the history of the present world conflict is compiled will one be able to grasp fully the importance which chemical research and development played therein. In the chapter dealing with the application of chemistry to the war efforts of the combatants, the story of synthetic rubber and particularly its gigantic development in the United States will be found to be one of the most fascinating if not the most prominent achievement.

When we once again are able to study with leisure the scientific contributions which were made and published in this field just before and during this war, we shall find—as the bibliography appended to this chapter already shows—a tremendous number of publications pertaining largely to purely theoretical considerations. These publications are mostly concerned with the thermodynamics and kinetics of polymerization reactions and with strictly mathematical treatments of elasticity which are largely based on purely theoretical assumptions * as to the molecular structure of natural rubber and rubber-like synthetic polymers. It cannot be denied that there still exists considerable disagreement between proponents of one or the other theory, and that even the actual experimental data frequently used as basis for these theoretical deductions do not always agree.

* The dangers of such treatment are pointed out in the first paper in Vol. V of this series. Traces of impurities may produce structural changes and override mathematics that ignores them. J. A.

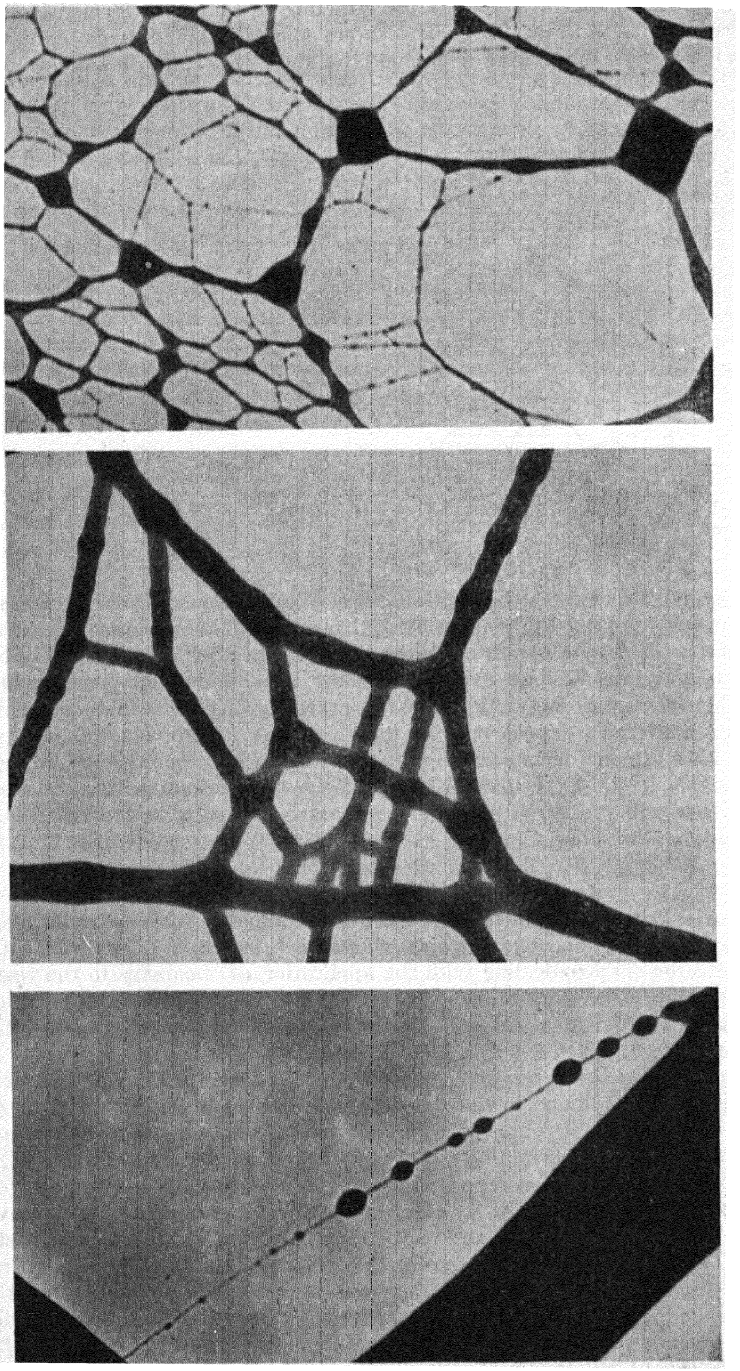


FIGURE 17. Electron micrographs. Top: Hevea rubber = X30,000; Center: Neoprene GN = X26,000; Bottom: Buna S = X24,000.

This should not be too surprising if one bears in mind that many of the reactions involved are extremely complex. Furthermore, most of them fall in one way or the other into the realm of phenomena characteristic only of matter present in the colloidal state. Colloidal systems, however, do not always follow the rigid laws established for matter present either in the liquid, solid or gaseous state. Although there can be no doubt that all the contributions so far offered are of value along the road of broadening our understanding, it certainly would be a mistake to overemphasize them, at least as they do not as yet offer more generally applicable principles.[1, 24, 28, 42, 57, 58, 59, 110, 124, 125, 136, 137, 164, 204, 207, 219] The main reason for this point of view is to be found in the fact that these methods of approach can take only well defined chemical reactions into consideration and do not really permit consideration of effects caused by the presence of often negligible amounts of matter not directly related to the reaction. Even changes in the construction of parts of the equipment which, from a mathematical and engineering point of view might seem of secondary importance, can affect the mechanism of such reactions very pronouncedly.

However, there exist ample indications that more light could be shed on the mechanism of the reactions as well as on the differences in the properties of the polymers formed, if some of the fundamental postulates of colloid chemistry would find somewhat more attention. This should not give the impression that the colloid chemist wants to claim the entire field as a part of colloidal research; but what is meant is that the use and application of some reactions characteristic of the colloidal state of matter, if adapted to this new development, might materially help in arriving at a more general understanding of the reactions and aiding in the development of a truly synthetic rubber.

A few examples may aid in better explaining this point of view. When discussing the production of polybutadiene by the Russian methods, it was emphasized that the properties of the polymer depend to a large extent on the amount of catalyst present. Since, in the rod method, the monomer can come in contact with only the surface of the sodium coat, it is clearly evident that it is the available catalytic surface which plays an important part. It has also been found that intermediary adsorption compounds between sodium and butadiene are formed. It is these compounds which then most probably desorb from the surface and act as nuclei for polymerization. This also explains how so far unreacted sodium becomes exposed for further reaction.

In the case of the vapor-phase method, the sodium particles dispersed in the organic solvent gel [31] already act as individual nuclei for polymerization.

In as yet unpublished work, butadiene was polymerized in the liquid state by distributing therein sodium which had been predispersed in an organic solvent. This permitted a careful visual study of the progress of the polymerization reaction with varying amounts of sodium. It could be clearly demonstrated that the reaction starts at the very surface of the dispersed catalyst particle and progresses radially therefrom. If the amount of catalyst did not exceed 0.2 per cent in weight of the monomer, the reaction was slow and resulted in a polymer of extreme toughness, as far as its processing properties are concerned. If the amount of catalyst was increased to about 0.4 per cent, the reaction yielded a polymer which, from the rubber technologist's point of view, exhibited excellent workability. However, if the concentration of catalyst was further increased to about 0.9 per cent, an extremely soft, molasses-like polymer results.

These differences in reactivity of the monomer and properties of the polymer strike an interesting resemblance to P. P. von Weimarn's law of precipitation,[220] if combined with F. Haber's theory of rate of aggregation and orientation.[60]

In the case of a low catalyst concentration comparable to dilute solutions in von Weimarn's law, the tendency will be to form long-chain polymers which may be, and probably are, branched. The resulting polymer, therefore, will be largely of the gel type. This is because only a few nuclei are formed, and the reaction is primarily

along the lines of chain growth. (See page 395). In the extreme case of high catalyst concentration, the great number of nuclei consume the surrounding monomer so rapidly that the sudden decrease of available monomer minimizes the chances for long-chain growth. This corresponds to the amorphous precipitates of von Weimarn. If medium concentrations of catalyst are used, the formation of long as well as short-chain polymers results. As far as natural rubber is concerned, work of quite recent date clearly indicates that it is the proportion of these two types of polymers (sol and gel) which is responsible for many of its outstanding properties.

When synthetic rubbers are produced by emulsion polymerization they pass, as previously described, through a stage comparable to natural rubber latex. Therefore, emulsion polymerization has permitted us to produce synthetic rubber latices which are now being used in increasing quantities in a great number of applications for which natural rubber latex has so far been utilized.

The technology of natural rubber latex is based to a great extent on the application of colloidal phenomena, and therefore it seems logical that the use of synthetic rubber latices must follow similar lines. So far, largely due to existing secrecy regulations, very little work has been published on this subject, but at least attention can be drawn to a few basic phenomena.

It is well known that natural rubber latex consists of a polydisperse suspension of the rubber hydrocarbon in a watery medium, the particle sizes ranging from about 3μ well down into colloidal dimensions. It has also been ascertained that the shape of the latex particles differs, depending on the species of the plant from which the latex has been obtained. Latex from *Hevea brasiliensis* is characterized by pear- or egg-shaped particles.[67] The reason for this shape is most probably due to the way the globule is formed in the plant. Although it is well known in colloid chemistry that polydisperse spherical particles have the tendency to align in pearl string formation,[75, 208] it is felt that deductions which assume that these non-spherical particles are only the result of such alignment,[130] are unjustified. They have not been based on experiments carried out with fresh latex, and therefore the observed alignment is most probably largely due to a reduced ζ-potential of the particles. Besides this, such a theory would not be able to explain the fact that the most characteristic shape of a latex particle in a Hevea tree is hereditary to its offspring.[66]

Since synthetic latices are obtained from an emulsion, it is logical to assume that the particles would be of spherical shape. The emulsions being produced under controlled conditions furthermore explains why the synthetic latex particles are practically monodisperse. Since the emulsions are produced by strong agitation, the particle size is noticeably smaller than that of the natural product (diameters 0.5-0.2 micron). There is no doubt that the difference in particle size must have a pronounced effect on the mechanism of polymerization and the properties of the polymer. Thus far we have not been able to obtain a really conclusive answer to the question how the plant produces rubber, but we have ample evidence that the degree of polymerization of the hydrocarbon or that of a condensation of sugars (see page 392) is not uniform even in the individual latex particles.[67] There is clear evidence that the highest degree of polymerization is to be found in the surface layer. It is also known that rubber obtained from latices containing the hydrocarbon dispersed therein in extreme fineness is of a very high degree of polymerization, whereas rubbers obtained from latices containing large particles generally are of a low degree.

So far it has not been possible to obtain synthetic latices exhibiting particles larger than those mentioned, nor has it been possible thus far to obtain particles which in themselves are not of uniform degree of polymerization. Since one must assume that polymerization in an emulsion starts at the interface, it is to be expected that the rate of the reaction will be faster and its progress more complete with decreasing particle size. This has been ingeniously demonstrated to be the case by Williams and Walker [224] in their studies on the polymerization of chloroprene.

Unfortunately no more work seems to have been published in this line, although this first attempt to investigate polymerization reactions has given quite a wealth of information, notwithstanding the fact that considerations based entirely on reaction kinetics do not agree with the concept of Williams and Walker.

From these observations and considering what has already been discussed in regard to sol and gel rubber, one may conclude that if the particle size of the monomer could be increased when the emulsion is made or at least during polymerization; a latex and finally a synthetic rubber could be produced, which would approach natural rubber in its properties more than has yet been the case for the now available synthetics.

Since the particles of synthetic rubber latices (Buna S, Buna N and neoprene) are negatively charged, they can be coagulated just like natural rubber latex by the hydrogen ion of acids or the cations of electrolytes when dissociated in solution. However, the pronouncedly smaller particle size, the greater uniformity in particle-size distribution, and the far more powerful emulsifying, dispersing, and protective agents used in their production compared to those present in nature's product, result in a higher ζ-potential on the particles. Thus it is necessary to use either greater concentration of coagulants or cations of a higher valency to obtain satisfactory coagulation.

The smaller particle size and the greater interface of the dispersion resulting therefrom also call for the addition of higher concentrations of such chemicals as wetting agents, which tend to be adsorbed on the surface of the latex particle, if a given reduction in surface tension of the latex is to be achieved.

The small average particle size, the fact that the dispersion is fairly monodisperse and the use of powerful stabilizers explain the low viscosity of synthetic latices as compared with that of natural latex at a given concentration. This difference is of advantage where the latex is to be used for impregnation and the like, but is a serious disadvantage if the rubber dispersed in the latex is to be deposited as a coherent film by dipping or spreading, followed by coagulation or simple drying. Synthetic rubber latices are especially sensitive to drying conditions, and too high a temperature or excessive currents of air will cause the formation of surface skins, which prevent further evaporation from the inside of the film, resulting in blister formation. Due to the very low wet strength of films made from synthetic rubber latex, such distortions cause shrinkage and cracking to a far more pronounced degree than ever experienced with Hevea rubber latex. This low wet strength, as well as the comparatively low tensile strength of uncured pure gum films, is most probably due to the presence of the emulsifying agents and to the high degree of polymerization at the surface of the individual particles, which prevents complete coherence. These drawbacks can be overcome to some extent by the incorporation of appropriate fillers, as for example, colloidal clays, by a careful control of viscosity and drying conditions, and by proper adjustment of the electrocratic condition * of the system, but so far it has not been possible to eliminate them entirely.

One more problem of special interest, both from an economic and a technological standpoint, is the possibility of producing synthetic rubber latices of high concentration. If it were possible to obtain satisfactory polymerization when using emulsions of high concentrations, one would materially contribute to the economy of the production of synthetic rubber. So far, however, several attempts along this line have not yet been too successful. Therefore, the industry using synthetic rubber latices would have to revert to the methods it started out with, when using natural rubber latex before methods of concentration became known. It is therefore understandable that many attempts have been made to apply the methods worked out for the concentration of natural rubber latex to synthetic rubber latices. Rubber latex has been concentrated by evaporation [67] after the addition of protective colloids, by centrifuging [67]

* Electric charge produced by ions, etc.

and by creaming [67] after the addition of strong hydrophilic colloids. The small particle size of synthetic rubber latices would call for even faster centrifuges than had to be used for a satisfactory concentration of natural rubber latex. The use of the standard latex separators has, therefore, not been too successful so far, unless the latex particles are first subjected to controlled agglomeration. However, concentration by evaporation and particularly by creaming has been successful, so that now synthetic rubber latices of concentrations up to 60 per cent are available and are finding increasing application in a great number of fields for which natural rubber latex was previously used.

The progress made during the last few years in the field of synthetic rubber is unparalleled in the history of chemistry. So is the number of publications and patents published on this subject in many languages. This does not refer only to scientific contributions. The development, particularly in the United States, is in itself a monument to progressive technology.*

It was the intention of the authors to convey to the reader only a general survey of the theoretical and practical aspects of these comparatively recent developments of synthetic rubbers. No claim as to completeness of information is made. A great amount of work has been reported in this new branch of science and industry, but only the highlights have been touched upon here. It would constitute a full-time job merely to keep currently abreast of this information, even if one could disregard the difficulties some individuals might have with foreign languages and the undeniable fact that no single library is in possession of all publications pertinent to this field. Periodically or currently issued abstract services are invaluable under such conditions.

The authors, therefore, would consider the bibliography incomplete without at least making references to those abstract compilations to which they have frequently resorted.

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Besides these, periodicals such as the *India Rubber World*, the *Rubber Age* (N. Y.), and the *India Rubber Journal* (London) have at frequent intervals also offered literature compilations.

Charts comparing the special properties of the different synthetic rubbers in specific compounds have been prepared by Schade [182] as well as by Sebrell and Dinsmore; [184] these can be used with advantage for quick reference.

* For a detailed survey of this development see: *Special Report of Office of Rubber Director on the Synthetic Rubber Program*, Plant Investment and Production Costs, dated August 31, 1944.

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See Appendix I for addendum to this article.

The Comparative Behavior of Carbon Black in the Reinforcement of Natural and Synthetic Rubbers

H. A. BRAENDLE

Research Laboratories, Columbian Carbon Co.

The mechanism of the behavior of carbon black and other pigments in natural rubber has intrigued investigators for years, particularly since the unique position of carbon black in the field of rubber reinforcement was noted. One of the earliest of those who investigated this problem was Wiegand,[32] who showed a correlation between apparent surface of the pigment and total energy of resilience of the pigmented rubber mix. North [19, 20] agreed with these findings, as did Spear.[26] Pigment surface determinations had not reached a point where more than an estimate of the specific surface of carbon black was possible. North and Spear devised elaborate surface configurations for carbon black to explain its superior performance. In 1925, Cranor [10] presented a comparative study of carbon blacks at 5, 10, 20 and 50 volume loadings. In discussing the different blacks at the 20-volume loading, which approximated the then common tread ratio, he stated: "The inherent softness of thermatomic compounds, distinguishing them so sharply from those produced by the standard carbon blacks, is strikingly illustrated. . . . In the case of lampblack we find rigidity sufficient to produce firm pneumatic tire treads and to account for its value in solid tires, but also note a lack of ultimate tensile, elongation and energy. . . ." He was thus aware of differences or peculiarities among carbon blacks and referred to three different types, namely, impingement, thermatomic and lampblack.

In 1926 Wiegand,[33] in discussing the stiffening of pigments and fillers in rubber, pointed out that the shape of a pigment particle, as distinguished from its subdivision, might be an important factor in its stiffening action. Thus he showed that the incorporation of ground fibers into a pure gum mix gave a remarkable stiffening action to the early part of the curve as long as the fibers were able to stand the strain. He pointed out further that lampblack, although inferior to carbon black in proof resilience and tensile strength, shows greater stiffening action. He suggested that this might possibly be due to the shape of its particle.

In a similar vein Spear and Moore [27] in 1928 began to differentiate between different carbon types and set up the following classification.

Table 1

	Stiffness or Modulus	Tensile	Elongation
Class I Channel Black	high	high	moderate
Class II L.B.'s & like	high	moderate	low
Class III Thermatomic	low	moderate	moderate
Class IV New type	low	high	exceptionally high

They describe Class I or channel blacks as "unequalled as reinforcing pigments in the manufacture of tread stocks for use on pneumatic tyres." Their Class II carbon, namely, lampblack and the like, they characterize by high stiffness or modulus, moderate tensile and low elongation. Their Classes III and IV were alike in that they produced low stiffness or modulus, differing between themselves in ten-

sile and elongation development. Also in 1928, Blake[1] approached the problem of carbon surface via stearic acid adsorption in mono-layers. He was obliged to assume a particle size diameter for carbon black and ran into considerable difficulty explaining discrepancies between theory and fact. Lunn[17] investigated pigment reinforcement by an approach in which he considered the contribution of the pigment alone and came to the conclusion that the energy contribution of carbon black was outstanding and unique.

In 1929 Parkinson[21] differentiated between types of black. He showed four distinct types of carbon black as in general use, namely, (1) gas black, to which he ascribed a particle size of 50-60 mμ according to Barnard, and 15-200 mμ according to Grenquist; (2) acetylene black, which he stated to be intermediate in size between gas black and lampblack; (3) lampblack, with a particle size in the region of 0.3 to 0.6 μ; and (4) thermatomic black, with a particle diameter of the order of one micron. He made several interesting deductions.

"So far as present knowledge is concerned, there is no proof that the reinforcing effect of chemically inert compounding ingredients depends on factors other than those which can be attributed to particle size, shape and degree and extent of dispersion of the particles." He also found that "The hardness curves on the other hand appear to show little relation to particle size within the range of the three blacks; if anything, acetylene black gives a harder mix."

The irregular behavior of acetylene carbon was thus recognized by Parkinson, just as Cranor had found the rigidity of lampblack to be worthy of comment as differentiating it from the thermatomic carbon and standard carbon blacks.

Shepard, Street and Park,[25] summed up the question of rubber reinforcement with the following:

"The Effect of Particle Size. It has been pointed out that data are lacking which make it possible to determine whether fineness of division alone produces reinforcement. This problem is one of the most difficult; but if solved, it would throw great light on the whole question of reinforcement. It should be possible to prepare powders of identical particle size with widely different surface characteristics."

The general recognition of the need for a method of classifying blacks according to particle size was evidenced in the approach to the problem by Fielding.[13] Thus he says: "The precise grading of carbon black has been a problem to rubber manufacturers for years."

Despite the work of Gehman and Morris[15] of the same laboratory on the determination of particle size of fine pigments including carbon blacks, Fielding was led to state that "Particle size measurements unfortunately are not available. However, over the broad range of black from Thermax to Superspectra, low rebound, toughness of uncured stock, and blackness all mean fine particle size." He finally used rebound, plasticity, nigrometer rating and bound rubber as his criteria for grading rubber quality carbon blacks according to particle size. For a group of six such carbon blacks, his net conclusions of these means of separating them are summarized in the following table.

Test	Total Spread (A)	Av. Deviation from Mean (B)	Ratio A/2B
Rebound	20	±0.6	17
Plasticity	30	±3.0	5
Nigrometer	11	±0.8	7
Bound Rubber	46	±1.9	12

Therefore, of these four tests, rebound seems to give the clearest separation."

Unfortunately this merely gives relative rating, not translatable directly to specific surface or diameter of the pigment or filler.

In 1940[6] the first particle size and surface area determinations by direct measurement on a commercial carbon black became available through the use of the electron

microscope. This required a sharp upward revision of the earlier estimates of specific surface from around two million square inches per cubic inch to about five million. Effects which have been ascribed earlier to the assumption of burr or feather-like surface configurations can now be attributed to fineness of subdivision alone.

Also in 1940 Parkinson [22] investigated the effect of particle size on rubber reinforcement. Using a highly refined sedimentation technique, he arrived at a particle size for rubber channel black which checked closely with the electron microscope determination given above. In his further discussion he was, however, content with pointing out an agreement in order of blacks as determined by sedimentation values and by rubber properties. The sedimentation curves for the carbons other than Micronex given by Parkinson are not capable of use for a size determination such as he arrived at with Micronex, since the same precautions for getting rid of residual agglomerates were not included in these latter studies. He did, however, find that lampblack and acetylene carbon were anomalous in their behavior and concluded that these anomalies "may be related to differences either of particle shape or nature of surface, or both."

In 1941 Wiegand [36] resumed his investigation of the effect of particle size of pigment fillers on the carbon reinforcement of rubber. For the first time there were available particle size and specific surface determinations by direct measurement of a series of colloidal carbons which have been used in rubber. It therefore became possible to plot color, tinctorial strength, liquid absorption, rubber absorption and other physical properties of carbons in raw and vulcanized natural rubber on a quantitative basis; namely, specific surface expressed as acres per pound of carbon.

In 1920 Wiegand [32] had stated that "these effects run parallel with the specific surfaces developed by the various pigment phases."

With direct quantitative measurements of carbon blacks, too fine for resolution by the light microscope, it was now possible for Wiegand [36] to state that "surface is in general the dominating influence, subject however to important and sometimes controlling anomalies."

Electron photomicrographs indicated the presence of chain and network structures in the case of acetylene carbon and lampblack. This configuration made possible the resolution of anomalous behaviors which were consistent in colloidal and rubber properties and suggested three broad types of carbon behavior in rubber.

"(I) Carbon-Rubber Complexes (Reinforced Rubber) are formed. (Examples: S. R. Carbons, Stat-ex and Carbon Blacks).

(II) Carbon-Carbon Complexes or networks are formed in addition to (I). Examples, Acetylene and Lampblacks.

(III) Carbons are inert; neither (I) nor (II) occurs. Examples: Thermal Carbons."

These relationships are brought together in Table 2 taken from the above reference.

This was discussed in greater detail in a release [7] by Columbian Carbon Company Laboratories in September, 1942.

In 1943 Parkinson [28] also continued his earlier investigations of the effect of carbon black particle size on the properties of Hevea. In his discussion of the physical properties of vulcanizates, Parkinson used different methods of presenting data, sometimes plotting on a basis of specific surface and again on a basis of total surface. In discussing tensile strength, he stated:

"The highest values of tensile irrespective of carbon concentration are plotted against particle diameter and specific surface in Fig. 2 [reproduced herewith as Fig. 1]. The points, with the exception of those representing lamp and Shawinigan blacks, lie on reasonably smooth curves with peaks about the position occupied by the rubber grade channel blacks. The anomalous position of lamp and acetylene black is discussed later."

Table 2. Classification of Rubber Carbons

Type Carbons	Action in Rubber	Rubber Compounding Properties	Tinctorial Properties	Colloidal Properties
I Carbon Black Stat-ex Semi-R. Carbons	Form Reinforcing "Carbon-Rubber" Complexes	Normal reinforcement extent of which governed by specific surface of carbon.	Normal trend. Strength rising to maximum. Color rising continuously. Reinforce "active" vehicles in proportion to specific surface.	Density, sed. volumes, oil and H_2O absorption and bound rubber essentially normal, *i.e.*, follow surface values.
II Acetylene Black Lampblack	Form both "Carbon-Rubber" (C-R) and "Carbon-Carbon" (C-C) Complexes	Energy and tensile low due to C-C complexes interfering with C-R complexes Raw plasticity and loading capacity low, also Modulus and hardness high, due to additive effect of C-C and C-R complexes. Electrical anisotropy and conductivity high.	Strength low (acetylene) Color normal Always form matte or dull surfaces in inks and paints Surface of torn rubber duller than Types I and III	Density low. Sed. volume high. Liquid absorptions high due to carbon-carbon network.
III Fine Thermal Coarse Thermal	Inactive—form no complexes	Primary action dilution, but tensile strength improved by fine thermal carbon via plastic film mechanism.	Strength and color normal for particle size. Inactive to all vehicles.	Density high. Sed. volume low. Liquid absorptions low. Bound rubber low. Carbon surface inactive.

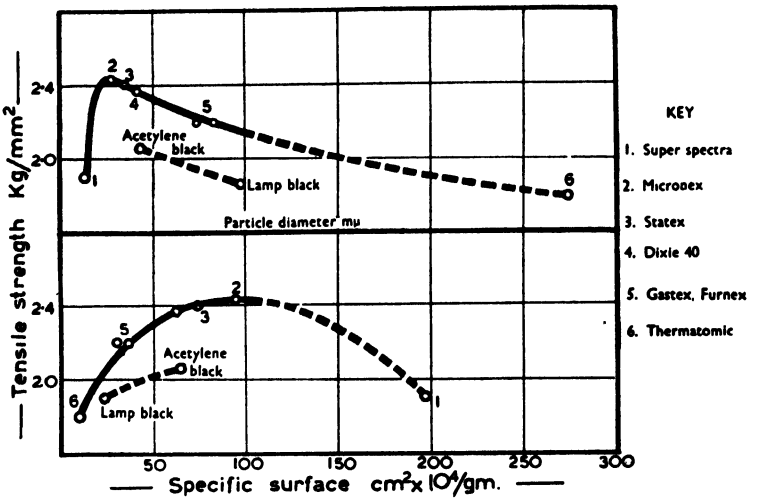

FIGURE 1. The highest values of tensile irrespective of carbon concentration are plotted against particle diameter and specific surface.

Parkinson did not give the loadings corresponding to maximum tensile development for the various carbons. However, using data of Columbian Carbon Company Laboratories [7] and plotting these not against specific surface for the carbon but total surface (specific surface times loading) giving maximum tensile (see Fig. 2) it is

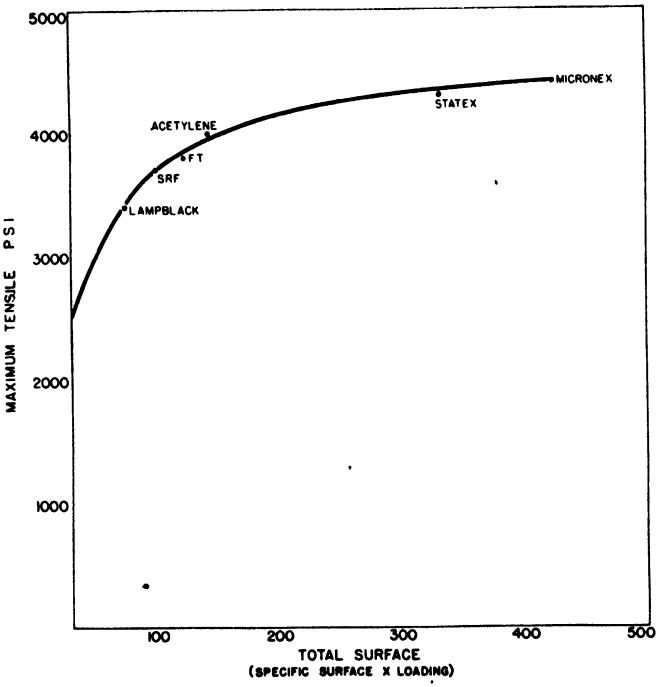

FIGURE 2. Maximum tensile *vs* total surface.

seen that all the carbons lie on a smooth curve. The two structure carbons, lamp and acetylene black, on this basis fall directly in line. This Fig. 2 is to be compared with Parkinson's Fig. 18 (reproduced as Fig. 3), in which he has plotted abrasion loss against total surface. In a summation, Parkinson stated that: "Of the above properties (tensile, tear, stiffness, hardness, resilience and abrasion resistance) one only, abrasion resistance, can be regarded as a criterion of reinforcement."

In view of the similarity of trend in Figs. 2 and 3, it is thought that, had Parkinson plotted tensile strength against total surface as he did abrasion loss, he might have found tensile strength to be a reinforcement criterion at least as good and certainly more easily determinable than abrasion loss.

In discussing Rebound vs. Specific Surface of Carbon, Parkinson shows "an approximately straight line relation" at the 45-part loading. At the 65-part loading he shows a Resilience-Specific Surface curve with a point of inflection similar to that

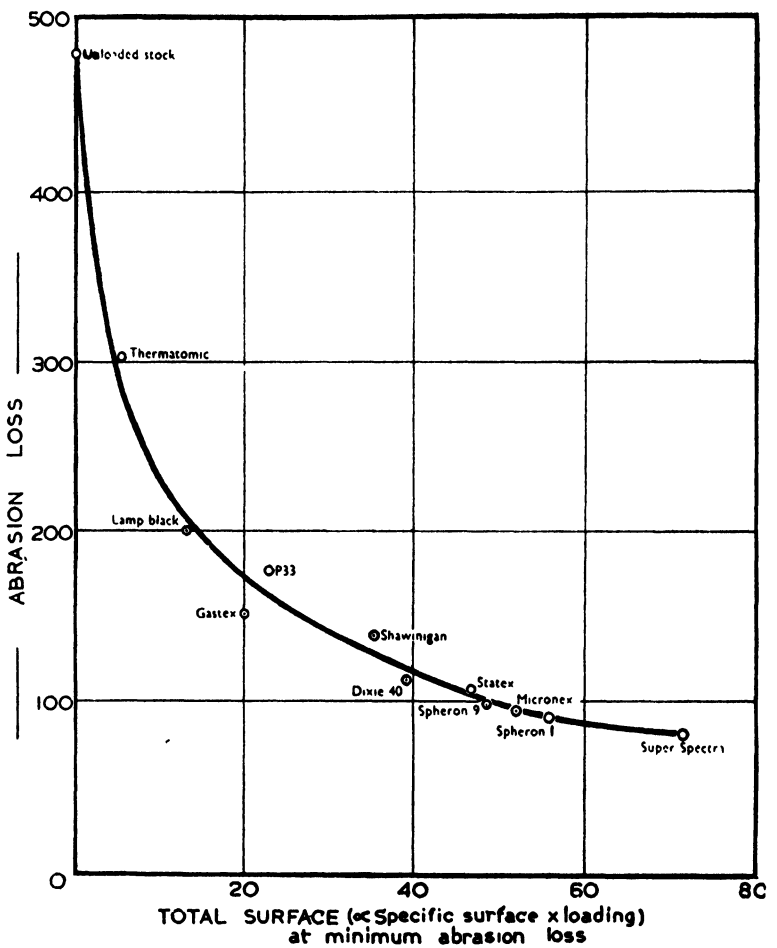

FIGURE 3. Relationship between abrasion loss and the total surface area developed between rubber and carbon, assuming complete dispersion at the concentration giving maximum abrasion resistance. Total surface area is the product of specific surface and carbon loading.

mentioned by Wiegand and Ladd,[37] and reproduced herewith as Fig. 4. If, however, Parkinson's data for the 45- and 65-part loadings are plotted on identical scales, as in Fig. 5, the existence of a point of inflection in the 8-acre region or the 75×10^4 cm^2 per gram region is confirmed for all these loadings, *i.e.*, in the region 10 acres to 8

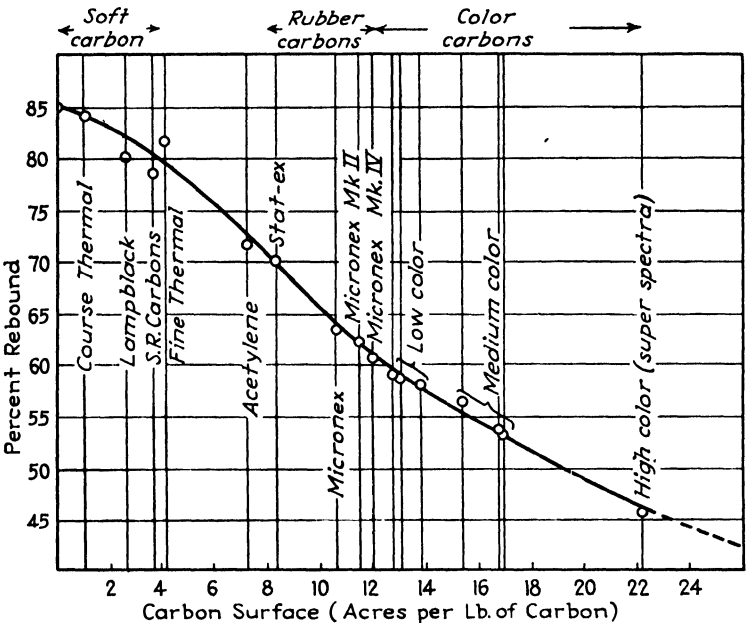

FIGURE 4. Rebound resilience and carbon surface.

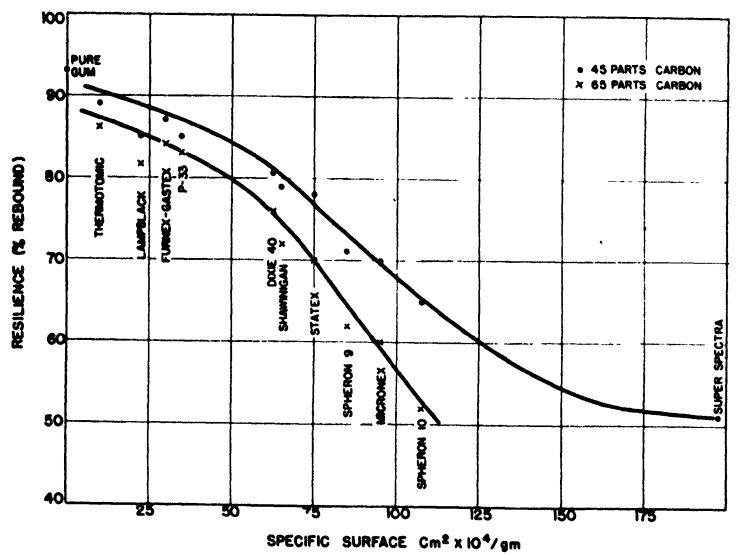

FIGURE 5. Resilience (per cent rebound) *vs* specific surface.

acres, a reduction in particle size pays extra dividends in resilience without exacting the normal penalty in lack of reinforcement.

The Three Building Stones of Carbon Quality

The development of the electron microscope and its application to the physical evaluation of carbon black, coming as it did with the rise in importance of synthetic rubber, greatly facilitated the adaptation of colloidal carbons to the reinforcement of the synthetics, since it provided a common quantitative basis for comparison of carbon effects. It also made possible a more significant interpretation of the effect of the chemical nature of the carbon surface (its pH). Likewise it became possible to differentiate between the effects of particle size and of inherent carbon network structure of blacks, thus explaining the irrationality of behavior of certain types of carbon blacks. Thus there have gradually evolved three basic properties of the carbon blacks themselves which in various combinations afford an understanding of the behavior of carbon, or alternatively, make possible the development of new or special carbons for specific purposes. These three basic properties, viz., specific surface, pH and structure, have come to be known as the three building stones of carbon quality.

pH. This property, described in 1937,[84] evaluates the chemical character of the carbon surface. It assumes greater importance than its actual variation from carbon to carbon or its extreme deviation from neutrality would seem to warrant because it is associated with, and its effects are multiplied by, the extreme surface development of colloidal carbons. Generally it may be said that its primary function in rubbers is to serve as a clue to purity and also to affect rate of vulcanization.

In Hevea, Wiegand and Synder[85] concluded as follows:

"1. Experiments with rubber-sulfur mixings showed that colloidal carbons accelerated vulcanization instead, as generally stated in the literature, of retarding. The fact that this acceleration was found to be independent of the pH value of the carbon suggests that the carbon rubber reinforcement 'reaction' and (physical) vulcanization may be related phenomena.

"2. When colloidal carbon is used, as in tyre treads, in conjunction with other accelerators, disturbances occur due to the selective adsorption properties of the carbon colloid. These disturbances, which are greatest with basic organic accelerators, less with acidic organic accelerators, and least with inorganic accelerators such as litharge, have led to the description of colloidal carbons as quick or slow vulcanizing.

"3. The best guide to this 'rate of vulcanization' characteristic of rubber carbons is their pH value.

"4. Adsorption data are given for cobalt, manganese, lead, and zinc soaps, and vary widely for different colloidal carbons. This variation as to the zinc requirements was confirmed by a rubber compounding series. Thus each carbon, depending on its pH and particle size, presents an individual problem in adsorptive requirements, involving fatty acid, zinc oxide, and accelerator, which should be adjusted in this order.

"5. For use with basic accelerators (*e.g.*, D.P.G.) colloidal carbons of maximum surface (which involves high fatty acid additions with resultant interference with the accelerator) or carbons with low pH (which requires high soluble zinc and, therefore, high fatty acid) are not recommended. Low pH carbons tend to disturb the alkalinity essential to best results, and to adsorb the accelerator.

"6. With acid accelerators (*e.g.*, mercaptobenzothiazole), the finer colloidal carbons of moderate to low pH may safely be used. The higher fatty acid dosage (soluble zinc) which these carbons require, can be freely supplied since it does not deactivate the accelerator.

"7. For use with litharge, the widest range of colloidal carbons is permissible,

extending even to the finest particle, high colour carbons of pH 3, provided fatty acid (and, therefore, soluble lead) is present in amount sufficient for the pH and surface requirements in each case."

In Buna S the relative effect of the carbon black *per se* and the pH of its surface on the curing rate are reversed in order of importance. Using a base compound of Buna S 100, zinc oxide 5, stearic acid 2, medium Pine tar 1, coal tar (Bardol) 1.5, sulfur 2, Captax 1.5, the surface and pH properties and their times to best (hand-picked) cure are given in Table 3.

Table 3. Optimum Cures

Carbon	Surface (acres/lb)	pH	Optimum Cure @ 287° F for Carbon Loadings indicated 30%	40%	50%	60%	75%
Micronex W-6	10.3	4.9	—	80′	80′	65′	—
L.P.	8.6	3.8	100′	90′	80′	—	—
Stat-ex	8.4	9.5	—	75′	60′	50′	45′
G-263	7.8	10.0	90′	60′	55′	50′	45′
G-42	7.3	10.3	75′	75′	60′	60′	55′
L.B.D.D.	6.0	3.0	100′	100′	90′	—	—
Furnex	3.7	8.8	90′	90′	85′	75′	70′
L.B.V.	2.6	3.9	100′	90′	90′	75′	65′

The conclusions from this study follow:

(1) High pH fine carbons (Stat-ex, G-263, G-42) cured faster than low pH fine carbons (Micronex, L.P.), as in rubber.
(2) High pH coarse carbons (*e.g.*, Furnex) cured faster than low pH coarse carbons (L.B.V. and L.B.D.D.), as in rubber.
(3) High pH coarse carbons (Furnex) cured slower than low pH fine carbons (Micronex, L.P.) reversing the behavior in rubber.
(4) Increasing carbon dosage accelerated cure for all carbons.
(5) Under dosages (30 per cent), even of fine carbons, did not produce good cures. This is the reverse of behavior in natural rubber.
(6) At the higher loadings fine carbons cured faster than coarse carbons.
(7) Snappy cures obtained with excessive loadings of coarse carbons showed very poor tear.

A further study of this question of the relative importance of the extent and pH of carbon surface was published by Columbian Laboratories [8] in which the base compound was as follows:

Buna S (GR-S)	100
Carbon	as noted
Zinc oxide	5
Stearic acid *	2
Coal-tar type softener **	5
Sulfur	2
Mercaptobenzothiazole	1.5

* Stearex beads
** Bardol

The carbons employed are given in Table 4.

Table 4

Black	Surface Area (acres/lb of carbon)	pH
Furnex	3.5	9.2
Furnex Mk. II	4.6	9.2
Stat-ex 42	7.2	10.3
Stat-ex 263	7.8	10.0
Stat-ex B	8.0	10.0
Stat-ex A	8.4	9.5
Micronex W-6	10.3	4.9
Micronex Mk. II	11.5	4.1

The question of best or optimum cure selection in order to put the comparison of carbons or other ingredients on a valid basis is not one on which unanimity of practice or opinion has been reached. The Columbian Laboratories selected best cures by a hand test, defining same as the earliest cure of reasonable snap with substantially unimpaired tear.

"Curing was at 293° F and the "Best" cures are listed below.

Carbon	Best Cure for Carbon Loading of 10%	20%	30%	40%	50%	75%
Std. Furnex	—	—	45′	40′	40′	35′
Furnex Mk. II	—	—	40′	35′	35′	30′
Stat-ex 42	40′	35′	35′	30′	30′	25′
Stat-ex 263	40′	40′	30′	30′	25′	20′
Stat-ex B	40′	35′	35′	30′	30′	25′
Stat-ex A	45′	40′	40′	40′	35′	35′
Micronex W-6	45′	45′	45′	45′	40′	35′
Micronex Mk. II	70′	70′	60′	55′	50′	45′

"Maximum tensile, which in natural rubbers finds favor as a cure criterion for comparing carbon blacks for example, is difficult to use in Buna S since for small loadings and coarse carbons the 'tensile-time of cure' curves are very flat and at times irregular. A comparison of the two methods of cure selection as applied to the present study is given in the table below.

"For a series of carbons the position of the 'Best' Hand-Selected Cures relative to the Maximum Tensile Cure are set forth in the table below. Earlier, At or Later Cures are indicated by E, A and L, respectively.

Black	Carbon Surface (acres/lb of carbon)	Carbon Loading 10%	20%	30%	40%	50%	75%
Furnex	3.5	—	—	L	L	L	L
Furnex Mk. II	4.6	—	—	E	L	L	E
Stat-ex 42	7.2	—	L	L	L	L	E
Stat-ex 263	7.8	L	L	L	A	A	E
Stat-ex B	8.0	L	L	L	L	A	E
Stat-ex A	8.4	L	L	E	A	E	E
Micronex W-6	10.3	L	L	E	E	E	E
Micronex Mk. II	11.5	L	L	A	E	E	E

"From the foregoing it is seen that for coarse carbons at all loadings and for small loadings of even the finer carbons maximum tensile occurs before snap develops, *i.e.*, while the rubber is still dead or logy. To get a lively cure it is necessary to overcure for tensile. When adequate loadings and/or fine carbons are employed, good snap develops before tensile has reached its maximum.

"Considerations of aftercure in service, particularly of rubbers as hot running as Buna S, dictate a technical cure well short * of the green tensile maximum. Such a cure, combining good snap, maintained tear and rising tensile, can be obtained only through adequate carbon surface addition.

Carbon Essential to Buna S Cure

"In Figure 6 the position of the best hand-picked cure relative to the maximum tensile cure is plotted against total carbon surface addition expressed as acres of carbon surface per 100 lbs of Buna S, *i.e.*, specific surface × carbon loading.

"Carbon surface additions which produce snappy cures before maximum tensile is reached lie above the median line while those compounds which develop snappy cure only at the cost of falling tensile lie below this median line. All of the carbon grades and loadings of the previous table have been included.

"A trend line has been drawn through the points which indicates that a minimum of 350 to 400 acres of carbon per 100 lbs. of Buna S is required to assure that snappy

* This rule may require modification in special cases such as tire carcasses.

cures are not obtained at the cost of falling tensile. Surface additions less than this are regarded as carbon starvation. The two points in the upper left quadrant are high pH carbons which have consequently developed early snap despite rather low carbon surface.

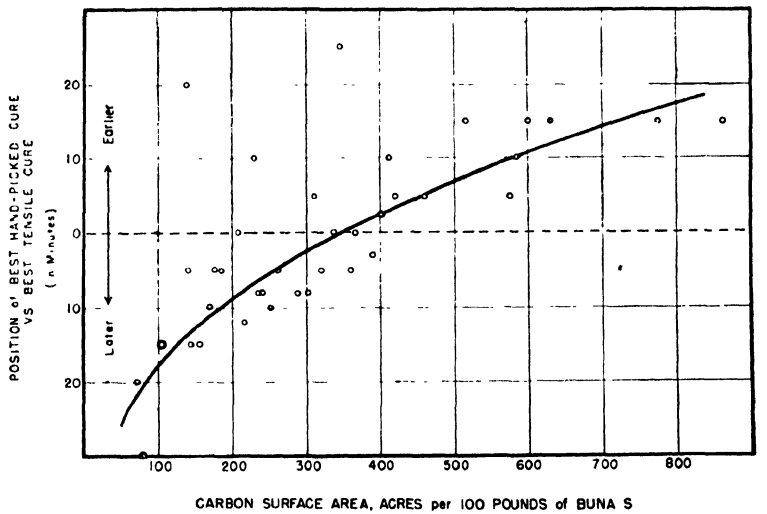

FIGURE 6. Carbon surface requirements for Buna S vulcanization.

"This would appear to rule out all low hysteresis Buna S compounds of good quality and curing behavior. A solution to the dilemma which offers promise is the use of adequate carbon to avoid starvation as outlined above and the softening and cooling of the stock to specification with appropriate softeners."

The *carbon effect* [2] in the vulcanization of Buna S is confirmed by the above data, and the authors state that "Carbon reinforcement is an integral component of Buna S vulcanization."

Garvey and Freese [14] did not disclose their method of cure selection, but in a bulletin on "Carbon Black in GR-S," issued by the War Production Board, covering an extension of the Garvey and Freese studies, the method of cure selection is disclosed. The base compound employed was

Synthetic rubber	100.00
Zinc oxide	5.00
Paraflux	10.00
Age-Rite H.P.	1.00
Sulfur	2.00
Santocure	1.75
Black	Variable

Selected Cure for Tensile Properties

"One of the line graphs plots modulus or stress at 300 per cent elongation against time of cure for each loading. These modulus-time of cure curves show the relative curing rates of the different compounds, and also serve for selecting one time of cure for each compound for use in plotting the tensile properties (modulus, tensile and elongation) against loading.

"This selected curing time is that at which a sharp change occurs in the modulus-cure curve; or in other words it is the point at which the curve begins to have a constant slope. This is the best method the authors have found for selecting comparable states of cure for all stocks.

"For group MT these selected curing times are 45 minutes for each loading. For the other seven groups the selected cures vary with the loading, but they lie in the range 30-45 minutes. For groups SRF and FT the selected cures shorten somewhat with increased loading, whereas for groups MPC, EPC, RF-A, RF-B and LB they lengthen somewhat with increased loading. The balance between the pH and the adsorptive properties of the blacks seems to govern the effect of loading on the selected curing time."

Here it will be noted that pH again assumes importance comparable to its effect on the cure of Hevea. This is due to the type of acceleration. Santocure breaking down to an organic alkali and mercapto at the onset of cure is thus sensitive to the pH of its surroundings.

In neoprene [9] it has been found that the pH of carbon blacks, through the whole range of 4 to 10, and with carbons ranging in particle size from 1 to 12 acres per pound, has no effect on the rate of cure with the conventional magnesia-zinc oxide curing set-up. Where, however, vulcanizates were prepared from simple neoprene-carbon mixtures at 40 parts by weight addition of black on the polymer, the following results obtained.

Table 5

	Area (acre/lb)	pH	Cure @ 287° F	L-300 (psi)	Tens. (psi)	%E	Shore Hard. 30"
Control (No Carbon)			30′	75	1300	920	48
Lampblack	2.6	3.5	50′	1450	2000	460	62
Furnex	3.5	9.8	20′	950	2075	590	55
Stat-ex A	8.4	9.8	20′	1550	2625	485	62
E.P.C.	10.0	5.0	40′	1675	2400	440	64
Peerless	10.6	2.8	60′	1600	2750	500	63
Hi-Tear Mic.	11.0	7.0	40′	1525	2650	590	64
Calcined Mic.	11.0	9.0	40′	1650	2675	485	67

Under these conditions, carbon grade does have an effect on rate of cure. pH is now operative, decreasing pH tending to retard cure.

In Butyl rubber the present author has found that for sulfur-vulcanized polymer the pH of the carbon has an effect on curing rate, high pH carbon curing faster than low pH. In general, carbon concentration has little or no effect.

Turner, Haworth, Smith and Zapp,[31] in discussing curing rates of carbon reinforced Butyl compounds, stated as follows:

"Cure Rate. As to the effect of black type and concentration on cure rate, it is evident that the channel type requires the longest time to reach optimum tensile. As would be expected, this is also generally true with respect to modulus. The concentration of any type behaves about the same throughout the concentration range. With respect to curing characteristics, the reinforcing furnace black gives results which would be expected from this type."

Thus it is apparent that Turner *et al.* also found that the low pH of the channel type carbons was responsible for slower curing rate in comparison with the higher pH of the reinforcing furnace carbon.

In a 1943 release on Perbunan Compounding by the Stanco Distributors [28] a comprehensive study of carbon and non-carbon pigments at 10 to 80 volume concentrations was presented. The base formulation was

Perbunan	100
Zinc oxide	5
Stearic acid	1
Sulfur	1.5
Altax	qs

Accelerator concentrations were adjusted to produce optimum tensiles within the curing range studied. In Table 6 are given the percentages of Altax and the minutes

Table 6. Per Cent Altax and Time to Cure of Maximum Tensile

Vol. Load.	Channel % Altax	Channel Min. of Cure to Max. Tens.	SRF % Altax	SRF Min. of Cure to Max. Tens.	F.T. % Altax	F.T. Min. of Cure to Max. Tens.
10	1	60	0.5	15	0.5	15
20	1	30	0.5	60	0.5	30
30	1	60	1	120	0.75	30
40	1	30	1	120	1	60
60	1.25	60	1	120	1	15
80	—	—	1	15	1	30

Vol. Load.	M.T. % Altax	M.T. Min. of Cure to Max. Tens.	Zinc Oxide (Kadox Black Label) % Altax	Zinc Oxide (Kadox Black Label) Min. of Cure to Max. Tens.
10	0.5	15	1	15
20	0.5	15	1	60
30	0.75	30	1.25	30
40	1	15	1.25	30
60	1	30	1.25	60
80	1	60	—	—

to maximum tensile from these data. From the curing times shown, it can be said that increased pigmentation does retard cure even though not consistnetly so, since it was found necessary to increase acceleration with pigmentation. Among the carbon blacks it would seem that the high pH carbons, namely, SRF and the thermals, were faster-curing than the lower pH or channel carbons. To offset this, however, it must be noted that zinc oxide required as much (or more) accelerator per volume of pigment as did channel black. The effect of pH, if present at all, is less than with Buna S (GR-S) or Butyl, and certainly much less than with natural rubber.

Cohan and Steinberg[4, 5] have discussed various criteria for the rate of cure. Their preferred measure of rate of cure is in essence the per cent of maximum tensile developed (by the compound being tested) at a fixed time of cure on the under side which gives about 60 per cent of maximum tensile for a reference compound of similar character. In natural rubber this criterion consistently showed the high pH carbons (thermal and semi-reinforcing) to be faster-curing than the channel carbons as is well recognized. In GR-S it likewise showed the high pH carbons to be faster-curing. This criterion, desirable as it is because of its elimination of the personal equation, failed to recognize the carbon effect in the cure of GR-S. This carbon effect, first discussed by Bostrum *et al.*,[2] has been confirmed in these laboratories and is also supported by the fact that the coarser carbons, namely SRF and larger, as well as the non-carbon pigments require more sulfur for the development of a good vulcanizate with GR-S than do the fully reinforcing or channel carbons. In GR-I the criteria discussed by Cohan *et al.* again indicate faster cure with the high pH carbon.

In Thiokol, pH of carbon black is again definitely to be reckoned with, although not from the standpoint of cure. Early publications and trade releases on Thiokol[29] deprecated the use of channel carbons in this synthetic. The reference cited stated: "Channel blacks are difficult to disperse and retard cure. Therefore, for general compounding purposes, they are not recommended." Laurence and Perrine[16] also object to channel blacks on the grounds of their effect on cure, stating: "Channel blacks, on the other hand, have a decided retarding effect on cure and result in logy vulcanizates. Tensiles do not reach values which might be expected if usual differences in reinforcing characteristics between channel and SRF blacks are considered." Laurence and Perrine's data of the same reference do not substantiate this statement. Table 1 from their paper, reproduced herewith as Table 7, shows, for example, that hard-processing channel black with a pH of 3.95 shows a declining tensile beyond the

Table 7. Comparison of Blacks in Thiokol FA (70-Part Loading)

Type Black	Cure Min. @ 298° F	300% Modulus	Tensile	Elongation	Durometer	Tear	pH
Hard-processing Channel	30	95	110	590	65	51	3.95
	50	90	105	630	63	47	
	70	80	85	580	61	45	
Medium-processing Channel	30	580	1000	550	75	174	4.15
	50	840	1250	470	76	233	
	70	1020	1385	420	77	306	
Easy-processing Channel	30	575	955	590	76	161	4.77
	50	855	1250	470	77	283	
	70	1000	1350	420	78	315	
Fine Furnace	30	1175	1535	460	75	355	8.74
	50	1595	1760	370	78	368	
	70	——	1825	270	80	311	
High-modulus Furnace	30	1255	1445	370	75	322	——
	50	——	1525	290	77	341	
	70	——	1490	250	77	295	
Semi-reinforcing Furnace	30	915	1100	470	75	298	8.98
	50	1235	1305	370	78	312	
	70	——	1385	280	81	198	

30 minutes' cure. Again, both medium and easy processing channel carbons show almost as rapid a set-up in tensile strength as does semi-reinforcing carbon or even fine furnace carbon with their higher pH values of 8 to 9, all four still showing rising tensiles at the 70 minutes cure. The fine furnace carbon, however, of the type sometimes referred to as an 8-acre carbon, developed the highest tensile of the entire series, indicating that something other than cure disturbances was responsible for the failure of the channel carbons to yield their expected reinforcement. The base compound used by Laurence and Perrine was:

Thiokol	100
Zinc oxide	10
Stearic acid	0.5
Benzothiazyl disulfide	0.4
Diphenylguanidine	0.1

They stated: "It should be possible to accelerate the cure of channel black-Thiokol FA stocks. . . . The Guanidines (DPG, DOTG) were found to increase the curing rate of both types of black to the point where satisfactory vulcanizates were obtained." Thus they showed that by increasing the organic alkali to 0.5 with either MPC or HPC carbon it was possible to secure greatly enhanced tensile values.

The true cause of this unsatisfactory behavior of the channel carbons is probably to be found in literature as released by Thiokol Corp.,[30] where it is stated: "The DPG-Tuads plasticizer combination is of value; the former gives rapid initial softening, the latter, while slower to act, maintains plasticity after the DPG has been partially neutralized by some of the compounding ingredients. In this way the batch is kept soft and cool."

In similar vein, another release by the Thiokol Corp.[29] states as follows: "Thiokol Type F is plasticized with Altax. Very little is required. . . . The softening action of Altax is extremely slow on the mill. . . . When used in combination with DPG, the softening is much faster. Since DPG by itself exerts very little softening, it seems that its function is primarily that of activating the Altax softening. . . . The amount of DPG shown is sufficient for activating the Altax, and it is not recommended that this amount be varied."

Observations of mixed stocks made with channel carbons compared with those formulated with high pH carbons, such as semi-reinforcing or the fine furnace carbon of the Laurence and Perrine paper, show the channel carbons to produce rough stocks

with the carbon poorly dispersed. Further evidence of this effect of the guanidine on Thiokol-carbon stocks is also given in the Laurence and Perrine paper where they show that by raising the DPG concentration to a half or more per cent, or by using DOTG in like amount, greatly enhanced tensile values may be developed. The truth probably is that the acid channel carbons remove by absorption the almost homeopathic proportion of diphenylguanidine, and whether this alkali be regarded as the primary softening agent or the activating agent for the dibenzothiazyl disulfide, the result is the same, namely, a poorly dispersed mix in which the channel carbon cannot do itself justice.

In Table 8 are shown studies by Columbian Carbon Company Research Labora-

Table 8. Physical Properties of Carbons at 50 p.b.w. on Thiokol N

Black	Surface (acres/lb)	pH	Cure @ 287° F	Modulus L-300 (psi)	Tensile @ Break (psi)	Elongation @ Break (%)	Shore Hardness Final 80° F
I. At Fixed Cure: 40′ @ 298° F							
Furnex	3.7	9.2	40′	950	1050	390	69
Statex	8.4	10.0	40′	1040	1250	400	69
Micronex W-6	10.0	4.7	40′	875	1140	440	68
Ultramicronex Mark II	12.0	8.0	40′	1125	1250	375	70
II. At "Best" Cure (as Defined Above)							
Furnex	3.7	9.2	30′	825	975	430	68
Statex	8.4	10.0	30′	900	1200	420	68
Micronex W 6	10.0	4.7	40′	875	1140	440	68
Ultramicronex Mark II	12.0	8.0	30′	950	1225	420	71

tories confirming this point of view, and using Thiokol Type N in the same base formulation as employed by Laurence and Perrine. Comparisons are made at both fixed cure (40 min. at 298° F) and at "best" cure, defined as the cure showing the best tensile and modulus without material loss of hand tear resistance. At fixed cure (40 min.), the advantage of the high pH carbons is apparent, with Furnex (SRF) showing up remarkably well for its particle size rating. When, however, comparisons are made at comparable rather than fixed cures, a truer picture is presented. The primary function of high pH is to enhance quality due to non-interference with the dispersing action of the diphenylguanidine, with a secondary effect on curing rate as claimed by Laurence and Perrine. Support of this view is given in a recent release by the Ministry of Supply[18] where plasticizers are discussed as follows: "Thiokols A and AZ are plasticized with a mixture of diphenylguanidine (DPG) and tetramethylthiuramdisulfide (TMT). Either accelerator alone is capable of plasticising, though diphenylguanidine is the more powerful. Basic materials generally have a plasticising action, and it is on this property that the behaviour of diphenylguanidine depends. It follows that any acidic material, which will neutralize the diphenylguanidine, will counteract its action, and this is found to be the case. Zinc oxide, which forms a complex with diphenylguanidine, will also neutralize it. The action of diphenylguanidine is considerably reduced by adsorption on carbon blacks, particularly channel blacks."

The effect of pH of carbon in the various rubbers is summarized in Table 9.

Carbon Surface and Structure

As stated above the application of the electron microscope to the determination of carbon particle size[30, 7] made possible a rationalization of the varied effects of carbons in natural rubber and other non-rubber media. In 1943 at the instigation of the Office of the Rubber Director a uniform nomenclature[3] for rubber grade carbons was set up. From these two releases the following table has been prepared for convenience in tracing the effect of carbons in the various rubbers.

Table 9. Effect of Carbon pH on Rubber

Rubber	Effect of Carbon pH
Hevea	Acid carbons retard and alkaline carbons accelerate the cure of organically accelerated natural rubber.
GR-S—Buna S	Increasing pH shares with increasing carbon surface in promoting vulcanization of mercapto accelerated GR-S. Where activated mercapto is used, pH has the greater accelerating effect.
Neoprene GN—GR-M	No effect on Magnesia-zinc cured Neoprene. Straight Neoprene-carbon vulcanization responds to increasing pH.
Butyl 1.45	Increasing carbon pH accelerates the cure of sulfur vulcanized Butyl rubber. The effect is a moderate one so that increased loading of carbon has little or no further effect on cure.
Perbunan—Buna N	High pH carbons like the Thermals and SRF cure faster than the acid channel carbons. However, increased loading of either type progressively retards cure.
Thiokol	Little effect on cure. However, acid carbons adsorb the organic alkalies necessary for dispersion of pigments, and development of their reinforcing power is hampered by acid pH.

Due allowance has been made for some variations in carbon particle size for a given grade from different suppliers and for the experimental error of the technique of specific surface determinations. Rounded or typical values have therefore been assigned the standard grades. Fine thermal carbon was originally shown as having a surface area of 4.1 acres per lb.[36, 7] More recent surface determinations on current offerings of this carbon show it to have a specific surface of 2.5 acres per lb.

Name	Symbol	Specific Surface (acres/lb)
Hard-processing Channel	HPC	12
Medium-processing Channel	MPC	11
Easy-processing Channel	EPC	10
Conductive Furnace	CF	8.0
Fine Furnace	FF	7.5
High-modulus Furnace	HMF	6
Semi-reinforcing Furnace	SRF	3.5
Fine Thermal	FT	2.5
Medium Thermal	MT	1.0

A comparison of the behavior of carbons in the various rubbers has been attempted in terms of the specific surface of the carbons. Three properties only, tensile, modulus and rebound resilience, have been included for this broad comparison For the references cited the carbons identifiable through the published trade names corresponding to the uniform nomenclature system were assigned specific surface values as shown above. Intermediate carbons were interpolated between these typical acreages by using the individual authors' own size or surface values. The data have been treated in two ways. First the contributions of the separate authors have been shown in individual graphs thus facilitating the recognition of anomalous behaviors of certain types of carbons. Secondly, the broad normal trends of the three properties as revealed by these individual contributions are brought together to facilitate comparison of the effect of carbon on the different rubbers. Tread type loadings of carbon were used throughout.

Natural Rubber

In Figure 7 four separate sets of data have been brought together to a common scale. Two sets by Columbian Carbon Company have been included, one having been published[7] and the second being a more comprehensive set including a high modulus furnace (HMF) carbon. The data by Drogin[11] gave no modulus values at 300 per cent elongation. However, the modulus values at 400 per cent elongation (L-400) are useful for the demonstration of anomalous behavior. Data from a trade

release by Phillips Petroleum Company [24] were included since they cover a high modulus furnace carbon and a fine thermal carbon.

The general upward trend of tensile strength with increasing carbon surface persists through all four sets of data. Lampblack, HMF carbon and acetylene carbon, the type II carbons of Table 2 or the "structure carbons" consistently fail to develop the tensile strength to be expected from their surface development. It is also ap-

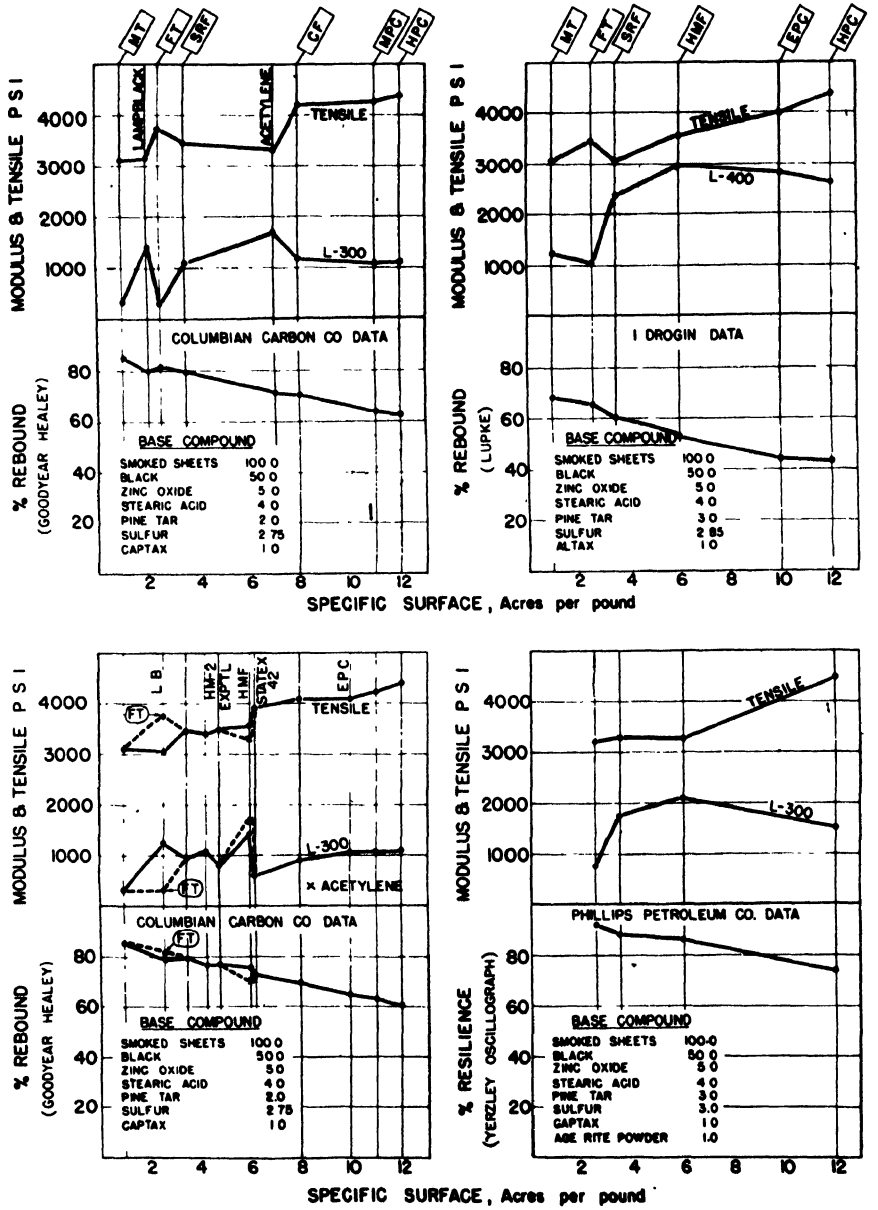

FIGURE 7. Effect of carbon surface and structure in natural rubber.

parent that the CF carbon at eight acres does better than expected. This carbon enjoys an advantage over the channel carbons because of the better curing behavior associated with its high pH.

The trend in modulus with carbon surface is more difficult to discern because of the controlling influence of structural anomalies. As summarized in Table 2, certain carbons, notably semi-reinforcing furnace, Stat-ex or CF carbon and channel rubber carbons fit a smooth curve based on specific surface for a wide variety of tinctorial colloidal and rubber properties. These have therefore been designated as normal carbons for the purpose of this comparison. On this basis modulus at 300 per cent elongation (L-300) of the 50 p.b.w. carbon loadings is relatively unaffected by specific surface.. The trend of L-400, as shown by Drogin's data, is not flat but suggests a maximum at or below ten acre carbon. However, all the data are consistent in showing the thermal carbons, both fine and medium, as having a modulus much below this norm and the "structure carbons," *viz.*, lampblack, acetylene and the newer high modulus furnace carbons, to be stiffer or higher in modulus than the norm.

The general downward trend of rebound or resilience with increasing carbon surface is apparent. The existence of a point of inflection at about the 8-acre region as shown in Figs. 4 and 5 is obscured through the choice of a fixed rebound scale sufficiently compressed to cover all the rubbers of the present review. The failure of structure carbons to develop their expected rebound is however apparent even on this scale.

GR-S (Buna S)

In Fig. 8, six separate sets of data have been brought together. In these, carbon surface is the primary variable but it will be noted that there is also considerable variation in both quantity and kind of softener and accelerator employed. Sulfur ratios have also varied from 1.5 to 2.25. Any deductions as to carbon performance common to all these base compound variants may therefore be regarded as significant. The third set of Columbian Carbon Company data has already been published.[8] In preparing the summary of the Garvey and Freese data, use was made of the exhaustive and comprehensive study prepared for the Office of the Rubber Director a very condensed form of which was published.[14] The data by Drogin and Phillips Petroleum Company were from the same references used for the natural rubber review.

Because of the low gum strength of this polymer the carbon reinforcing effect is much more pronounced than with natural rubber and there is a sharper increase in tensile with carbon surface. In fact, it may be said that carbon surface dominates the tensile development picture in this polymer. There is, on the whole, an indication that finer than regular rubber grade carbons could be used to advantage to develop superior tensiles. One basic defect of GR-S, however, stands in the way of the use of these finer carbons, namely, its hypersensitivity to high temperature processing, which high temperatures are almost unavoidable with the finest rubber carbons.

The anomalous modulus behavior of the "structure carbons" and of the thermal carbons so prominently displayed in natural rubber is still present but to a lesser degree since there is a distinct upward trend in modulus with increasing carbon surface, a fact which may be associated with the carbon effect in the vulcanization of GR-S. As pointed out earlier, carbon surface additions to GR-S of less than about 350 acres per 100 lbs of GR-S result in carbon starvation, and it is to be noted that the upward trend of modulus with carbon surface tends to flatten out at about the 8-acre region, that is at about 400 acres of surface per 100 lbs of GR-S. The modulus data by Drogin at the 400 per cent elongation (L-400) appear to be at variance with the trend shown by the other five references in that he shows SRF carbon to have a

higher modulus than his HMF carbon. Elsewhere [11] in his paper Drogin showed a succession of loadings of typical carbons in which data for modulus at 300 per cent elongation are presented. A comparison at the 50-part loading used in Fig. 8 is not possible since in this second set of comparisons Drogin has shown loadings of 55 parts and 70 parts of K-40, his HMF carbon, and 60 and 65 parts of K-20, his SRF carbon. Interpolating for the 60 part loading of HMF carbon a modulus value, at 300 per cent elongation, of 1980 lbs is indicated, as compared with a modulus of 985 lbs on this same 60-part loading shown for the SRF carbon. Broadly, therefore, the findings of Drogin are in agreement with those of the other references. Carbons which were below normal in modulus in natural rubber also carry their low modulus characteristics into GR-S.

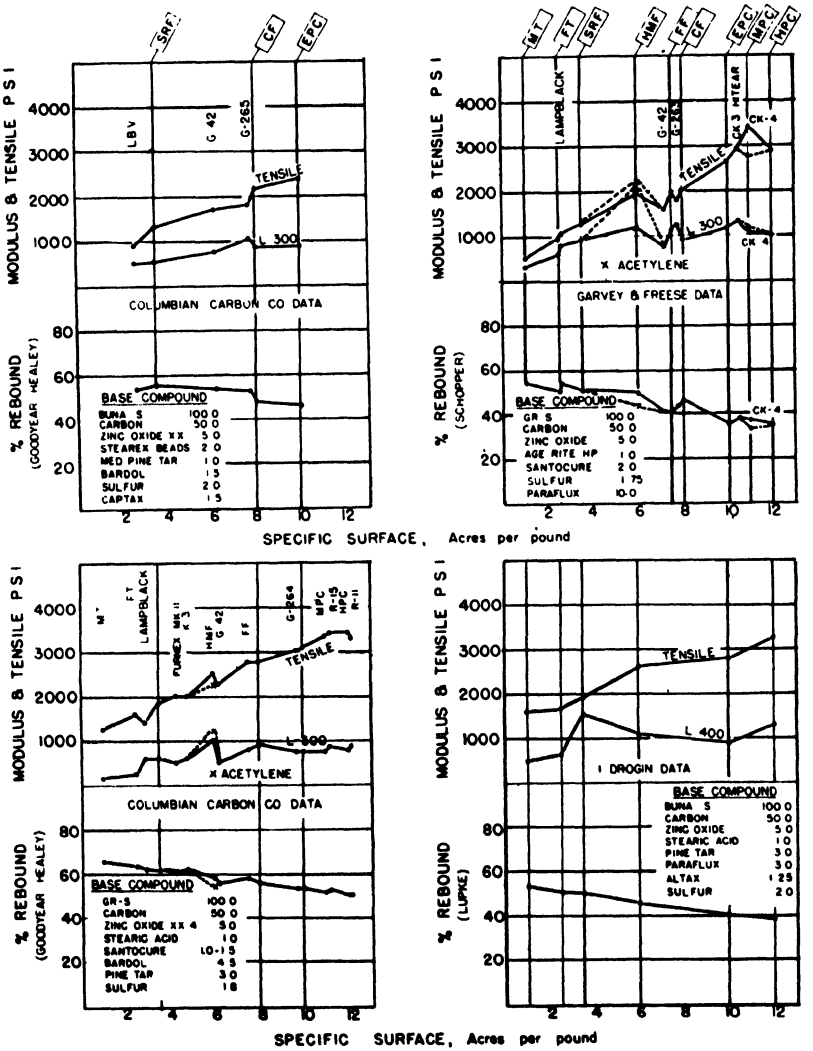

FIGURE 8a and b. Effect of carbon surface and structure in GR-S (Buna S).

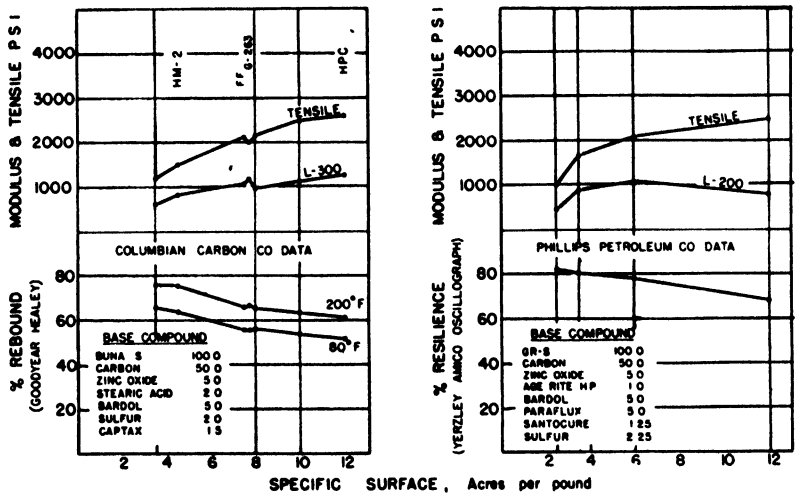

FIGURE 8c. Effect of carbon surface and structure in GR-S (Buna S).

There is a suggestion that both the "structure carbons" and the thermal carbons show better than expected resilience with one exception, acetylene carbon, which to date represents the maximum of structure development so far encountered. It lies below the norm in resilience in both Columbian and Garvey and Freese evaluations.

Neoprene GN

In Fig. 9 are shown two series of data by Columbian Carbon Company [9] and by duPont.[12] The carbon loading employed was 27½ volumes or the equivalent of 50 parts by weight in natural and GR-S. The general upward trend of tensile is almost as striking as with GR-S and arises from the fact that the coarser carbons at any loading depress the tensile of Neoprene GN whereas only carbons having a specific surface in excess of about 7 acres increase the tensile strength of Neoprene GN. The over-all trend of modulus with carbon surface is not unlike that of GR-S rising rather sharply up to about 8 acres and then tending to increase at a slower rate. The relative softness of the thermal or low modulus carbons is striking and explains their wide acceptance for the improvement of the oil resistance of neoprene stocks by their dilution with larger loadings of the thermal carbons than is possible with other types.

Butyl Rubber GR-I

In Fig. 10, four sets of data have been brought together. These include data by Turner *et al.*,[31] Cohan *et al.*,[5] Drogin,[11] and some unpublished data by Columbian Carbon Company Research Laboratories. The general trend of tensile with surface is upward. In the Cohan data, the carbon shown on the HMF acreage line is actually Shawinigan carbon. It gave a tensile below the norm indicating a considerable shortening of the rubber by this carbon in which structure is so highly developed.

Modulus trends are, on the whole, very flat. The thermal carbons again show a stiffening action below the norm and, in view of the low modulus characteristics of the polymer itself, these carbons seem to be contraindicated where service requirements involve toughness. Room-temperature rebound seems to be completely dominated by the loginess or deadness of the polymer itself. However, at elevated temperatures, increasing carbon surface lowers rebound of GR-I as it does that of other rubbers.

Buna N (Perbunan).

Two sources of data (Fig. 11) were available, namely Drogin [11] and a trade release by Stanco Distributors.[28] Buna N is capable of greater reinforcement with carbons in the 4 to 6 acre region than is Buna S, even though both have about the same pure gum strength. The unsatisfactory performance of the thermal carbons for tensile development is even more pronounced in the acrylonitrile copolymer than in the styrene copolymer of butadiene.

The modulus trend for carbons regarded as having normal structure characteristics is substantially flat, with a possible indication of downward trend with increasing carbon surface. Other studies, not detailed here, indicated that this may be due to breakdown of the base polymer with the progressive milling required to incorporate and disperse to a satisfactory degree the finer or high surface carbons. The very low modulus characteristics of the thermal carbons suggest them as equally attractive in Perbunan or Buna N for the enhancement by dilution of the oil-resistant properties of this polymer, as found to be the case with neoprene. The single curve on rebound suggests that the thermal carbons pay a dividend in resilience over expectancy from their surface development.

Thiokol

Only very broad generalizations can be made on the effect of carbon surface in Thiokol because of the inability to locate data which were rigidly comparable. Thus the data (Fig. 12) by Laurence and Perrine [16] have employed 70 parts by weight of carbon black on Thiokol FA. Ministry of Supply [18] give data on 40 part by weight loadings on GR-P type N. Columbian Carbon Company data are at 50 part by weight loadings, also on GR-P type N.

With the exception of the Laurence and Perrine data there is a discernible increase in tensile with increasing particle surface. The serious fall-off in the Laurence and Perrine data for channel carbons is due to the adsorption of the DPG

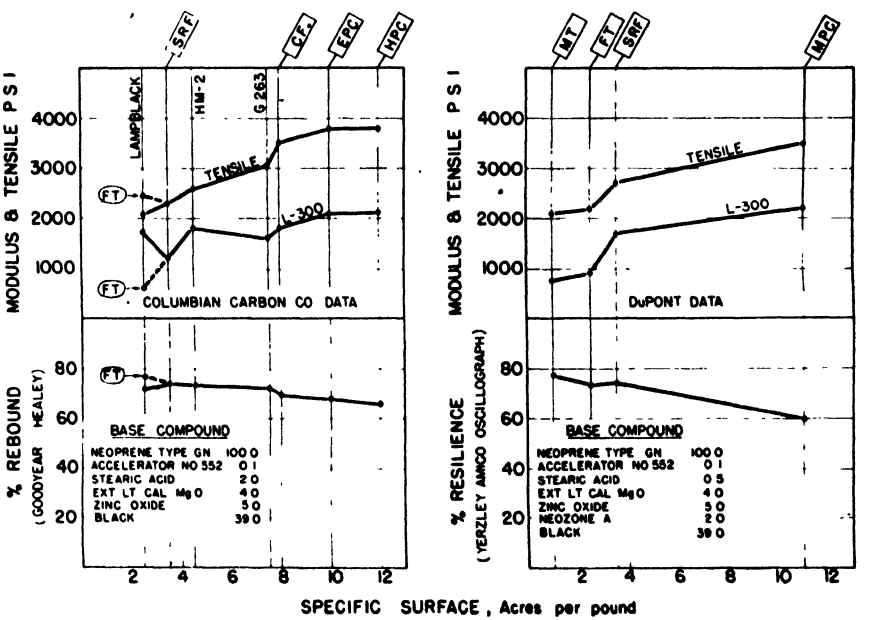

FIGURE 9. Effect of carbon surface and structure in Neoprene GN.

from the mix by the high loading of channel carbons with acid pH. This can be compensated for by an increase in guanidine ratio, as shown by the circled points where 0.5 per cent guanidine was used with MPC and 1.0 per cent was used with HPC, bringing the tensiles into line with those shown by Ministry of Supply and by Columbian where smaller black ratios were used and where, in the case of Columbian data, the 12-acre carbon was an Ultra-Micronex of raised pH.

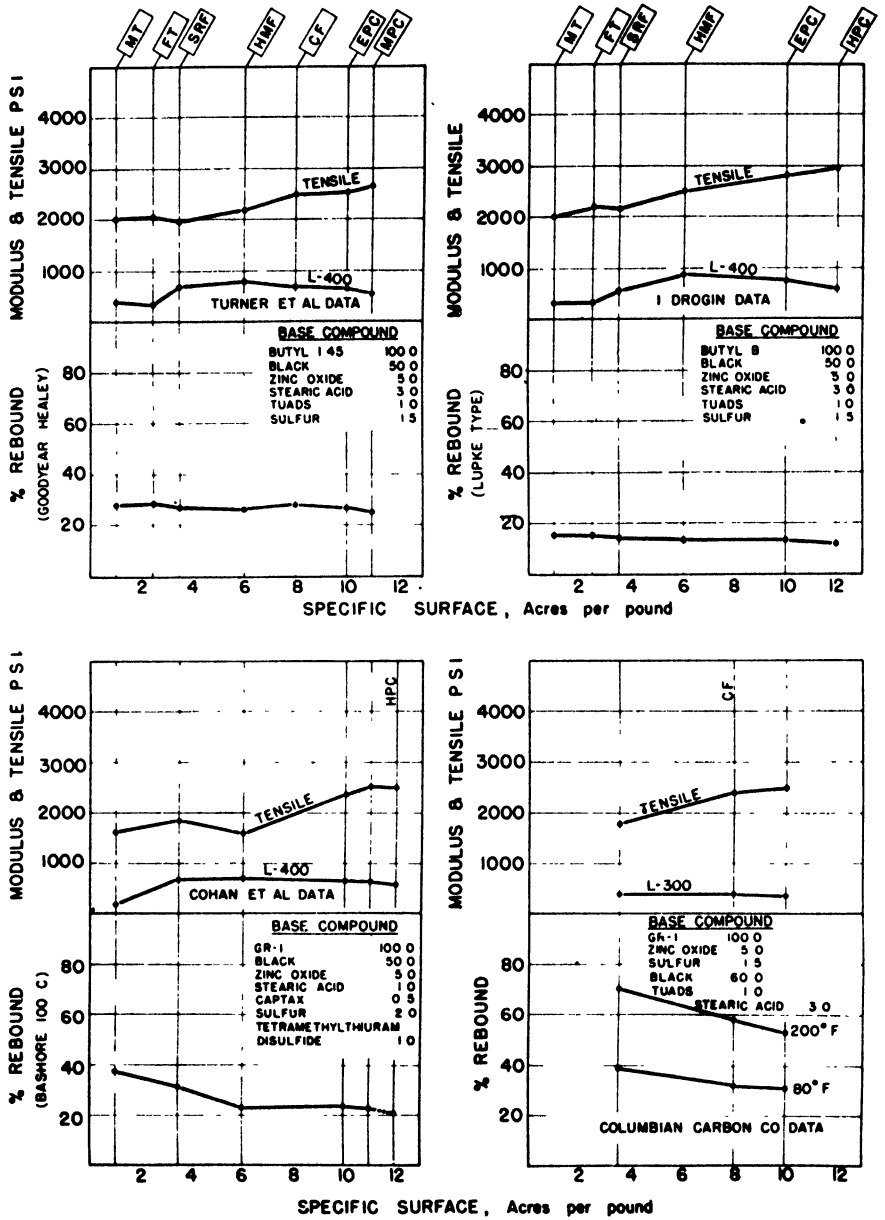

FIGURE 10. Effect of carbon surface and structure in Butyl GR-1

The modulus trends with carbon surface are also slightly upward, the downward trend suggested by the Laurence and Perrine data being due to inadequate guanidine ratios with their high loading of channel carbons. In short, the failure of the fine

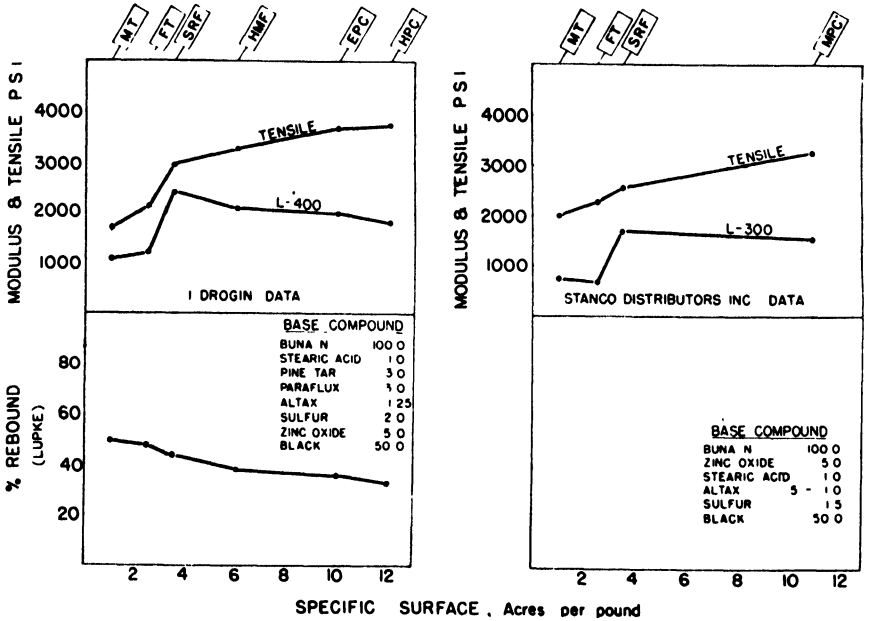

FIGURE 11. Effect of carbon surface and structure in Buna N.

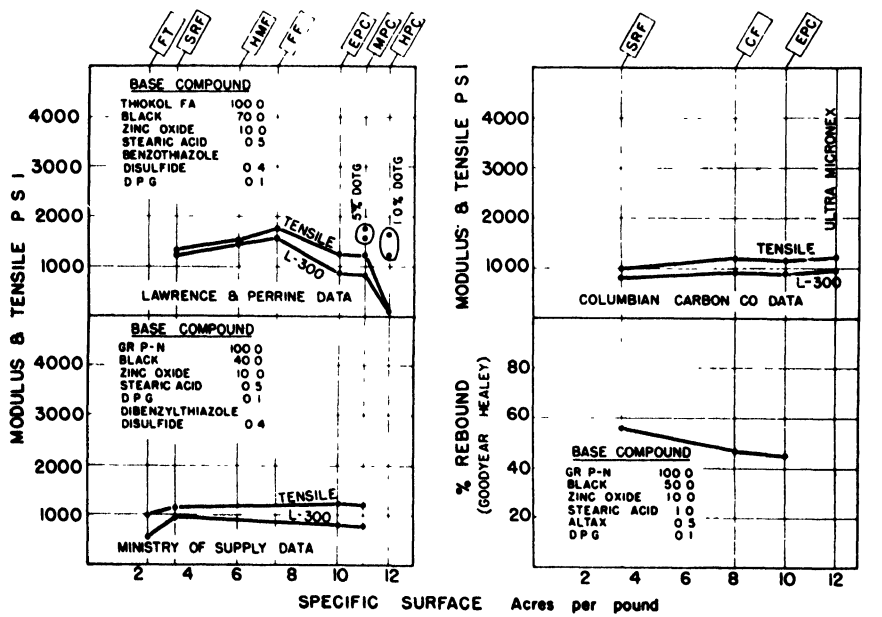

FIGURE 12. Effect of carbon surface and structure in Thiokol.

carbons in this series to produce better rubbers than the coarser grades is due to spoilage of the compound by inadequate allowance for adsorption of guanidine. Again, as in all other rubbers, the trend of rebound with increasing surface is downward.

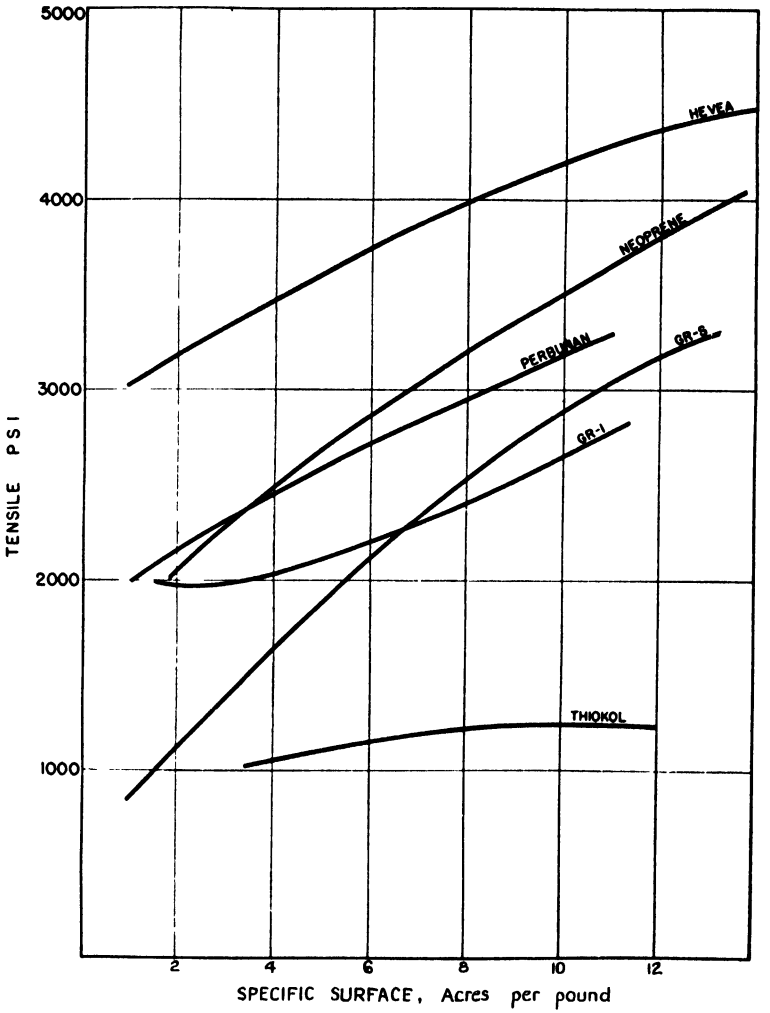

FIGURE 13. Trends in tensile *vs* specific surface for natural and synthetic rubbers.

Comparison of Rubbers

Tensile. In Fig. 13, the basic trend lines of tensile with carbon surface for the six rubbers have been assembled. Anomalies due to structural differences of carbons have been ignored. Superiority of the natural polymer is evident. Despite its good pure gum strength, neoprene turns in a rather poor performance with coarse carbons, but responds well to carbon surface beyond about 7 acres and, with fully reinforcing channel carbons, comes closer to the natural rubber than is ordinarily possible with the other synthetics. The dependence of GR-S on carbon surface for its adequate

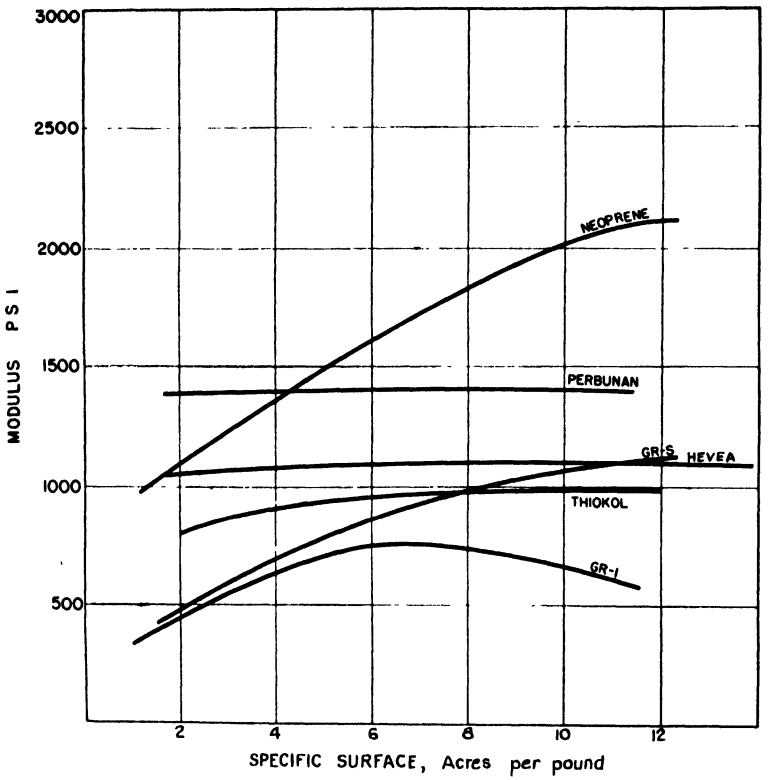

FIGURE 14. Trends in modulus *vs* specific surface for natural and synthetic rubbers.

reinforcement represents one of the horns of the rubber compounders' dilemma, since full reinforcement entails increase in hysteresis of a polymer which is already logier than the natural rubber.

Buna N, as pointed out above, responds better to the coarser carbons than does GR-S. The published data indicate that both Buna N and GR-S tend towards the same tensile development at about 14 acres with normal processing technique. GR-I, because of its better pure gum tensile, has a distinct advantage over GR-S with coarse carbons, but its rate of response to carbon surface increase is relatively low and it falls below GR-S in tensile development with the reinforcing carbons of 8 or more acres specific surface. Thiokol shows the lowest tensile development and the least response to carbon surface, but its unique properties amongst rubbers make it applicable for service where a high degree of reinforcement or strength is not needed.

Modulus. Natural rubber occupies an intermediate position in the family of rubber polymers discussed here. Its modulus is relatively insensitive to specific surface change alone. Buna N shows a similar independence from carbon surface but yields a considerably stiffer stock. Neoprene is the most sensitive of all the rubbers to increasing carbon surface, and the avoidance of reinforcing carbons at loadings of more than 20 to 25 volumes for application where oil resistance is the primary reason for its use is self-evident. Thiokol shows some slight response to increasing carbon surface. GR-S, next to neoprene, is the most sensitive to increasing fineness of carbon particles. It reaches natural rubber modulus only with the finer carbons in the channel black range. GR-I, the softest, also is unique in the trend of its modulus

with increasing carbon surface. It would seem that this rubber is most in need of structure carbons whereas structure carbons would seem to be contraindicated for neoprene.

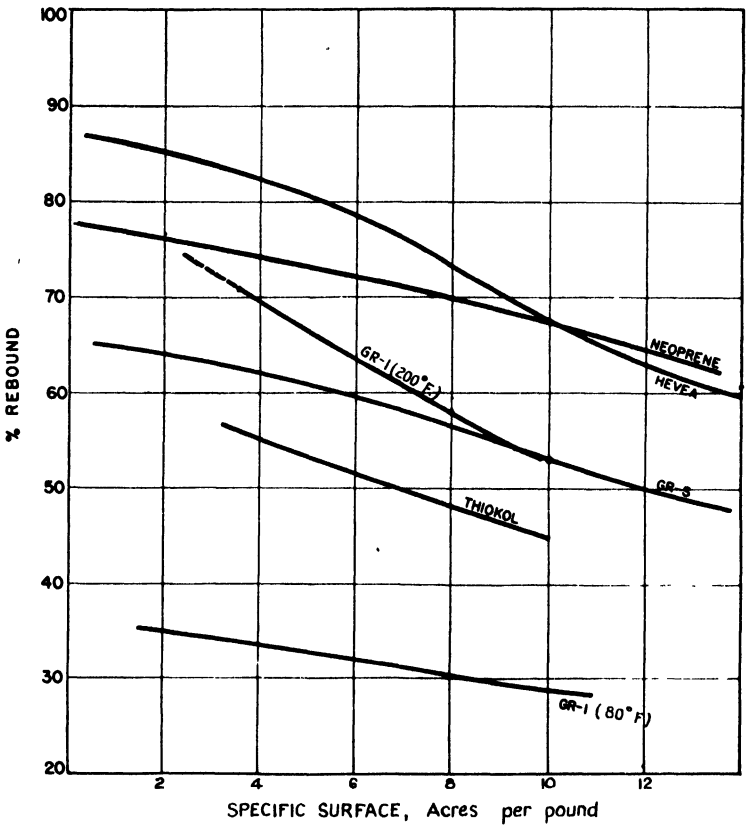

FIGURE 15. Trends in rebound *vs* specific surface for natural and synthetic rubbers.

Rebound. Natural rubber again occupies a leading position, being approximated only by neoprene when both are reinforced with the finer carbons. The curves for neoprene and GR-S run nearly parallel, with neoprene having considerable advantage over GR-S. GR-I has the least resilience at room temperature of the entire group but has probably the highest temperature co-efficient. Thiokol lies intermediate between GR-S and GR-I.

Summary

(1) The behavior of carbons in synthetic rubbers as well as in the natural product is a function of the three building stones of carbon quality: pH, surface and structure.
(2) pH is the least consistent in its action with the different rubbers.
(3) Increase of pH speeds the cure of organically accelerated compounds of Hevea, the Bunas and Butyl but has no effect in neoprene and Thiokol.
(4) Low pH carbons require special compounding in Thiokol because of their adsorption of the small amounts of organic alkali used as dispersing agents.
(5) Carbon surface is the dominating factor in tensile development of all rubbers.

For neoprene there is a critical value (about 8 acres per lb), below which carbons depress tensile strength.

(6) In Hevea, Perbunan and Thiokol, specific surface of carbons plays a minor role in the development of modulus. In GR-S and neoprene, it is as important for modulus as for tensile.

(7) Rebound of all rubbers is depressed by increasing carbon surface.

(8) Increasing specific surface of carbon as well as increasing pH accelerates the cure of GR-S, substantiating the "carbon effect" in the vulcanization of this polymer. In Perbunan, increasing total surface of any carbon grade or even of any pigment filler retards cure.

(9) Carbon structure, the most recently recognized of the three building stones, is the most consistent in its effect on all rubbers. Carbons which are below the norm (as defined) in modulus in natural rubber are also low in modulus in the synthetics. Likewise, the structure carbons develop more modulus in all rubbers than their surface expectancy indicates.

(10) For neoprene, which by its extreme flocculating action on all pigments develops the highest modulus of all the rubbers, structure carbons would seem to be contraindicated except for special uses.

(11) For GR-I with its phenomenally low modulus, carbon structure offers a means of correcting this defect.

(12) Because of the dependence of GR-S on specific surface of carbons for the development of modulus, structure added to the coarser and hence cooler running carbons can help to make up their deficiency in modulus in this rubber compared with Hevea.

(13) The recognition of the role of carbon structure in rubber has given the rubber compounder a new "ingredient" to add to his compounds for the correction of polymer defects or the accomplishment of special effects. It has given the carbon manufacturer another means of tailor making blacks to the specific requirements of polymers and their applications.

Acknowledgement

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Colloidal Graphite

RAYMOND SZYMANOWITZ

Technical Director, Acheson Colloids Corp., Port Huron, Mich.

Colloidal graphite, introduced by Acheson[3] in 1906, was for many years thereafter utilized primarily as a lubricant. Available originally in only mineral oil and distilled water, its employment in the form of the oleosol was confined to those cases where conditions made desirable the use of an adjunct to oil; as the hydrosol, it found service in thread-cutting operations, as a protection for the dies used in fabricating tungsten and, to a limited extent, as a steam cylinder lubricant.

Continued research, however, has made possible the preparation of stable dispersions of graphite in a wide range of media, typical of which are carbon tetrachloride, kerosene, mineral spirits, glycerol, castor oil and phenol-formaldehyde varnish. With the extension of the list of vehicles for colloidal graphite have come many new uses, the more important of which will be discussed in this paper.

Properties of Graphite

Graphite is a dark gray, lustrous, crystalline mineral possessing great unctuosity. It occurs in nature in a variety of forms which are known commercially under such classifications as (a) flake graphite, (b) plumbago or vein graphite and (c) amorphous graphite or "black lead." It should be pointed out that all graphite is crystalline and that even the so-called "amorphous" modification shows microcrystallinity under x-ray examination.

Synthetic or electric-furnace graphite, first produced commercially by Acheson[1] in 1896, is likewise crystalline. Its production can be rigidly controlled, resulting in a uniform product having a high degree of purity.

The graphite allotrope of carbon has a specific gravity of 2.1 to 2.3, depending upon its source. In addition to its greasy feel, it is unusually soft, having a hardness of less than 1 on Moh's scale. It is opaque, has a low coefficient of expansion and is a relatively good conductor of heat and electricity.

Graphite is strongly resistant to the action of acids and alkalies and does not combine with oxygen at temperatures below 600°. In the absence of oxygen or oxidizing influences, it is capable of enduring temperatures above 3500°, after which it undergoes sublimation.

An Important Solid Lubricant

Although graphite has long been employed as a solid lubricant, the reasons for its ability to reduce friction were not uncovered until the x-ray diffraction experiments of such workers as Debye and Scherrer,[81] Hull,[74] Bernal,[17] and others[64, 107] revealed the structure of the graphite crystal. This is made up of carbon atoms arranged in sheets which are parallel to and equidistant from one another. Each sheet or plane might be represented as a hexagonal network wherein carbon atoms are situated at the points or corners of the hexagons, which in alternate planes are directly above one another. Those in adjacent planes are so arranged that lines pro-

jected through the hexagon centers of one plane pass through atoms in the planes immediately above and below (See Figure 1).

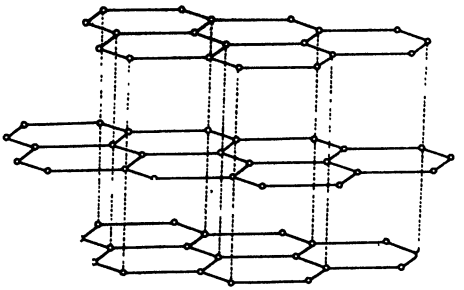

FIGURE 1. Graphite crystallizes in the hexagonal system. Data obtained by means of x-ray diffraction indicate that the length of the hexagon side is 1.42 Å., while the height of the hexagonal prism is 6.70 Å. The distance between atoms in adjacent basal planes is 3.35 Å.

In each of the planes the carbon atoms are in close proximity and exhibit pronounced affinity for one another; but the attraction between the planes, because of the degree to which they are isolated, is exceedingly slight. This distribution of forces makes easy the sliding or separation of the planes, thus accounting for the unusual lubricating qualities of graphite.

The separation of the carbon sheets comprising a graphite crystal is accomplished whenever a line is drawn with a lead pencil. A particle of graphite smeared across a sheet of paper with the tip of a finger produces a thin film of crystals with their slip planes parallel to the surface. If enough graphite is used or if the same path is traversed repeatedly, the surface of the paper becomes smooth and takes on a polish by virtue of the graphite filling in the pores and depressions. When employed as a dry lubricant on mechanical devices, graphite performs a similar function.

The surfaces of bearings, shafts, guides, etc., although carefully machined, are in reality surprisingly rough, showing up under a microscope as a multitude of projections and depressions. When rubbing contact takes place, there is a tendency for the projections of one member to shear off the peaks of the other. However, if powdered graphite is injected between such surfaces, it acts as a smoothing agent by filling in the "valleys." This method of leveling eliminates the projections, which are the primary cause of wear and friction. Furthermore, since the crystals of the solid lubricant are weak in cohesive properties, they—rather than the strongly coherent metallic surfaces—suffer abrasion when bearing and shaft are brought together.

Despite the advantages of dry graphite as a lubricant, its use in powder form is restricted because of the difficulty of application. It is true that small quantities are blown into locks, guns and hinges or rubbed onto wood bearings, piano actions and the like; but in most cases graphite, to be effective, must be used with a fluid carrier.

Greases, because of their consistency, are excellent vehicles for graphite. Ranging from highly viscous liquids to semi-solids, this type of lubricant discourages the separation of any incorporated powdered material. Greases, unfortunately, are of value only when it is necessary to maintain thick protective films on gears or bearings where the motion is slow or intermittent and the loads heavy. Early attempts were also made to use pulverized graphite with oils. These, for the most part, were unsuccessful because the difference between the specific gravities of graphite and petroleum oil resulted in the prompt settling of the solid lubricant. Individuals who

had the temerity to try such mixtures in circulating systems usually had to contend with bearing failures due to clogging of the lubricant feed lines.

Colloidalization of Graphite

In 1901, while endeavoring to determine the suitability of electric-furnace graphite for crucible manufacture, Acheson carried on extensive experiments with clay binders. During the course of this work he discovered that when domestic clays were pugged with substances rich in tannin, the resulting product showed a marked increase in plasticity and tensile strength. Later investigations revealed that many of the clay particles so treated remained suspended in water. In 1906, when Acheson repeated these experiments using graphite instead of clay, he observed that some of the graphite also remained suspended. Acheson described this process as "deflocculation." [2] Subsequently Jerome Alexander examined under the ultramicroscope a specimen of the suspended graphite and recognized it as being colloidal.*

In the course of Acheson's experiments he made trials with a great number of vegetable extracts, employing such materials as straw, nutgalls, tea leaves, sumac, hemlock bark and oak bark. Although these materials varied in efficiency, they all served as protective colloids, yielding stable aqueous dispersions.

Graphite hydrosol, like other hydrophobic colloids, cannot be dried and subsequently redispersed in the same or another medium because flocculation takes place during desiccation. To overcome this difficulty Acheson developed a process [4] whereby transference of graphite could be made directly from water to oil.† Since the pioneer work of Acheson in this field a number of patents have been issued throughout the world covering other processes for rendering graphite colloidal.

Karplus [82] developed a commercial method for producing colloidal graphite, using strong oxidizing agents, preferably sulfuric acid and potassium permanganate, with or without the addition of chromic acid. Although the method is similar to Brodie's [24] process for converting graphite into graphitic acid, this end-product, as well as oxides of carbon and soluble oxidation products related to mellitic acid, may be avoided or kept at a minimum by controlling such factors as temperature and particle size of the graphite under treatment. The graphite, which is peptized by this procedure, is subsequently washed free of acid and stabilized with suitable protective colloids.

When graphitic acid is heated gently, it decomposes with great violence into what has been termed pyrographitic oxide—a black, amorphous residue, which bears a strong physical resemblance to graphite. Although the exact composition of this material has been disputed, it is considered to be pure graphite [127] (Brodie's graphite).

Plauson [114] resorted to a colloid mill, using as protectors fatty acids of high molecular weight, or their esters, ethers or ketones. If the graphite is subjected to a very prolonged treatment in this device, a colloid is said to result. Pigache [113] has been granted a patent covering the colloidalization of graphite by attrition in the presence of gelatin.

Ducas [86] formed dispersions of graphite in oil by a grinding action, employing as a protector what he termed natural colloids, particularly petroleum bodies rich in tar. To stabilize aqueous dispersions he chose certain gums and tannates.

* In reporting an address of Dr. E. G. Acheson in London, Nov. 6th, 1911, the *Journal of the Society of Chemical Industry* stated [30, 1426 (1911)]: "Measurements of the deflocculated particles by Mr. J. Alexander were referred to. The particles were found to be in a true colloidal state, being in rapid motion, and their average size in linear dimensions was estimated by Mr. Alexander at 75 millimicrons." See also paper by E. G. Acheson beginning on page 547 of Vol. III of this series.

† Referring to his products as "dag" (initials for "deflocculated Acheson graphite") Acheson employed the trade-marks "Aquadag" and "Oildag" for the hydrosol and oleosol, respectively.

Bartell [18] succeeded in producing stable suspensions of colloidal graphite in strongly organophilic water-insoluble liquids like gasoline, kerosene, carbon tetrachloride, benzene, etc., by mixing powdered graphite with a disintegrating agent and kneading the mass in a suitable type of mixer. After several hours an oil having a colloid-stabilizing effect is added to the worked product. The resulting paste is then thinned with the organic liquid which is to serve as the final carrier.

Lubrication with Colloidal Graphite

When graphite is colloidally dispersed in water or carbon tetrachloride and applied to solids by brushing, dipping or spraying, a tenacious film of graphite remains upon evaporation of the vehicle. At elevated temperatures a similar condition results when kerosene or light lubricating oil serves as the dispersion medium.[6] The film remaining functions as a dry lubricant, the original colloidal property having been utilized to facilitate application and adhesion.*

An examination of the lubricating properties of such films reveals that the static coefficient of friction on metallic substrates lies in the vicinity of 0.16. Fogg and Hunwicks [51] obtained a value of 0.125, using steel against a graphoid layer which had been freed of oil through the use of solvents. These figures are considerably lower than that obtained with clean metals which, in the case of steel on steel, was found to be 0.58.

The measurements of Hughes and Whittingham [73] show that the kinetic coefficient of friction of mild steel on graphited steel is 0.09. If the graphite film is first polished with a soft cloth to orient the crystallites so that their cleavage planes lie parallel to the surface, the kinetic coefficient of friction drops to 0.065. Under similar test conditions, the kinetic coefficient of friction of mild steel on mild steel is 0.35. In commenting on their findings, these investigators point out that "the results show that on steel, graphite is able to reduce the coefficient of friction to a lower value than any film investigated up to the present apart from 'oily' lubricants."

Dispersions of colloidal graphite in liquids having good penetrating qualities make possible the conductance of the solid lubricant to friction surfaces that are difficult of access. In instances where bearings are remote and operate at high temperatures, colloidal graphite is doubly advantageous.

Kiln-car bearings, baking and enameling oven chains, glass-molding machinery and the hand tools such as turnpins, pincers and cones used by glass workers for firing tumblers and forming necks, lips, stems and tips on miscellaneous glassware,[134] represent but a few of the devices on which graphite films are valuable. Another type of mechanism requiring a lubricant which will not lose viscosity, distill off or decompose is that contained in high-intensity searchlights, motion-picture projectors and special lighting equipment which embodies the use of an electric arc.[118]

During the period when Acheson was developing colloidal graphite, the General Electric Company was endeavoring to produce ductile tungsten and molybdenum.[46] According to Fink,[47] then engaged on the project, the hot-drawing of metals through diamond dies was an art which had not been practiced up to that time. Many difficulties were encountered, especially die wear and wire breakage. The latter troubles were attributed to the failure to obtain a material that would both lubricate and adhere to wire being drawn at red heat. Fink, while attending a lecture at which Acheson described the properties of his graphite hydrosol, obtained a sample and, upon subjecting it to tests at Schenectady, found it to be the solution of the die-lubricant problem. Graphite hydrosol has since been regarded as indispensable in the drawing of tungsten and molybdenum.

* Adhesion is aided by the fine particle size of the graphite and the binding properties of the protective colloid.

Concerning Colloidal-Graphited Oils

Whether one chooses the dry films deposited from colloidal graphite suspensions or ordinary graphite in powder form, the mechanics of lubrication is fundamentally the same. However, when oils containing colloidal graphite are employed for lubricating purposes, the graphite performs in a radically different manner.

The chief advantage of colloidal-graphited oils lies in their ability to form graphoid surfaces * on mechanical parts which are subjected to friction. Such surfaces play a dual role. Not only do they tend to satisfy the surface energy of the metal or other material to which they have become tenaciously adsorbed, but also, because of the low interfacial tension which exists between graphite and petroleum oils, graphoid surfaces discourage oil-film rupture.

Mabery,[92] after conducting a comprehensive series of tests which showed oils containing colloidal graphite to be more effective than oil alone, was the first to suggest that an adsorbed film of graphite was responsible for the improvement. He, incidentally, was also the first to coin the term "graphoid."

Since Mabery's early work, a great number of tests, both in the laboratory and in the field, have been carried out. For the most part, these show that colloidal-graphited oils bring about a lowering of friction, although the amount of reduction varies rather widely with the apparatus employed and the procedure followed. Typical data have been published by Saytzeff,[121] Koethen,[86] Walger and Schneider,[141] Boutaric and Amiot,[21] Walger and Schroeter,[142] and Fogg and Hunwicks.[51]

Like Mabery, other investigators [103, 128] have found that graphoid surfaces, in addition to effecting a reduction in friction, make possible the continuous operation of test bearings without injury for many hours after the oil supply has been discontinued, the time varying with the conditions of the test.

Inasmuch as the size of a colloidal graphite particle is many times less than the thickness of the average oil film existing under "full film" lubrication, boundary conditions are necessary for colloidal graphite to display its maximum effectiveness.

Existence of Graphoid Surfaces Established

During the period between 1913 and 1934 much material appeared in the literature on the formation, maintenance and effect of graphoid surfaces. It was not until the latter year that Jenkins,[78] through the use of the electron-diffraction camera, produced the first tangible evidence that graphoid surfaces really existed.

The principles underlying this method † of examination depend upon the fact that, when a single stream of electrons is made to impinge on a surface, the atoms comprising that surface cause the electrons to be diffracted into a number of beams. The manner in which scattering occurs is controlled by the arrangement of the surface atoms. The paths taken by the scattered electrons are recorded photographically to yield what is known as an electron-diffraction pattern. Because electrons, unlike x-rays, are poor in penetrating power, they are ideal for surface explorations, not only giving information as to the identity of atoms but revealing their orientation as well.[44]

In 1935, Finch, Quarrell and Wilman [44] examined thin graphite layers formed by the evaporation of graphite hydrosol and, like Jenkins, whose work was with the oleosol, confirmed that the graphite crystals were highly oriented with the cleavage slip plane parallel to the support.

Electron-diffraction methods also explain the reason why bearings which have been lubricated with colloidal-graphited oil are able to run without injury for relatively long periods after the oil supply has been discontinued. Finch and Whitmore [45] showed that during the formation of the Beilby layer [15, 43] the graphite is

* Although usage has made "graphoid" the accepted term, "graphitoid" is more accurate.
† See paper by L. H. Germer in Vol. V of this series.

kneaded into the plastic metal, thus becoming entrapped in the amorphous surface of the bearings.

The effect produced might be compared to that obtained during the running-in of the cylinders of internal combustion engines, which are made of cast iron rich in free graphite. During the initial operation of an engine the occluded graphite is brought to the surface and spread thereon by the rubbing action of the pistons. Unfortunately, under these conditions, the supply of graphite is limited unless fresh pores are opened through wear. The addition of colloidal graphite to "break-in" oils makes up for the graphite deficiency of cast iron and also provides added protection under the boundary conditions which are so prevalent during the running-in of new engines.

In 1937, Trillat,[187] while making x-ray diffraction studies in connection with lubrication phenomena, found that a metallic surface which had been in contact with graphite oleosol for approximately a month yielded a pattern characteristic of graphite. This observation, in addition to verifying the results previously obtained in England with the electron-diffraction camera, proved that graphite could be directly adsorbed by metals without mechanical aid.

It is well to refer to the work of Pavelka and Wischin [110] at this time, since they, too, not only succeeded in establishing graphoid surfaces by simple adsorption but are responsible for the creation of another method for the detection of such a surface. Their technique embodies the measurement of the difference in surface tension of metallic pieces toward oil before and after the formation of a graphoid surface. These workers also found that, by lowering the viscosity of the oleosol with suitable diluents, adsorption could be hastened.

Matthews and Wolf,[95] working at the Imperial College of Science and Technology (London), proved the presence of adsorbed graphite by microchemical analysis. Two shafts, made of the same low-carbon steel, were run in, one with plain oil and the second with oil containing colloidal graphite. After the test pieces were repeatedly cleaned with solvents, thin cuts of the order of $\frac{1}{1000}$ of an inch were taken off the surface and also, for comparison purposes, a similar cut was taken from the surface of a piece of metal which had not been treated. The three samples of shavings were then analyzed for carbon content. By employing two distinct procedures—one involving direct combustion and another based on the combustion of the insoluble residue after the metal had been dissolved and filtered—it was found that the specimen which had undergone treatment with colloidal graphite showed the highest carbon content.

For some years a controversy had existed as to the precise manner in which graphoid surfaces were formed. Acheson [2] leaned toward the adsorption theory, while Karplus [83] believed that, as the clearances between the friction planes were reduced, their projections acted as an ultra-filter and entrapped the graphite particles. Falz,[41] also sympathetic to the mechanical view, looked upon the formation of a graphoid surface as a result of a combination of pressure and rotation in the absence of full-film conditions. Now, through electron-diffraction analysis, there has been disclosed still another method whereby colloidal graphite effects a physical union with metal—that of becoming a part of the Beilby layer during running-in. It is reasonable to suppose that graphite may become affixed to metals by any or all of the methods cited.

Function of the Graphoid Surface

When they extend from surface atoms, the cohesive forces which hold the constituent particles of solids in close union are instrumental in promoting friction. These secondary valence forces, while creating a stray field estimated at only 3 Å. deep, are sufficiently powerful to bring about seizure or welding between clean surfaces.[7]

The work of the Hardys [61, 62] demonstrates that the efficacy of a lubricant is con-

trolled in a large measure by the degree to which it is capable of lowering this type of energy. An oxidized sheet of copper exhibits a lower static coefficient of friction than one that is highly polished. The film of oxide performs as a lubricant by lowering the surface energy of the copper.[60]

Wells and Southcombe [147] found that the addition of a small amount of fatty acid to a mineral oil produced an improved lubricant. The "oiliness" of such a mixture was believed to be due to chemical affinity between the bearing and fatty acid.[83] Parallel views have been offered by other investigators [9, 112] in an attempt to explain the low friction values obtained with rape, olive and sperm oils.

X-ray diffraction studies indicate, however, that fatty acids exert their beneficial effect primarily by the manner in which they are oriented on friction surfaces. It has been found that these long-chain molecules support themselves either vertically or at an angle (depending on their length) with their carboxyl group adjacent to the surface. In this position the polar end interacts with the secondary valence forces of the bearing, thus reducing its energy.[136]

Surface energy is likewise lowered by colloidal-graphited lubricants, as indicated by the tenacity with which graphoid films adhere to metals. Unlike most adsorbed substances, which merely discourage adhesion between solids, graphite because of its lamellar structure, also promotes tangential slippage.

Graphoid surfaces, since they are markedly oleophilic, provide a strong link between bearings and fluid lubricants. Bachmann and Brieger,[11] in a series of measurements of heats of wetting, ascertained that the affinity between graphite and oil is seven to ten times that existing between copper and oil.

Trillat,[187] in studying oilspread, found that metals which had acquired a graphoid surface showed a pronounced affinity for polar bodies.

Boutaric and Amiot,[21] investigating the influence of graphite on the adherence of oil to metals, also discovered that after a graphoid layer has been established, the adhesion of a monomolecular film of oil is substantially increased. In the course of their studies these workers, like Trillat, Pavelka and Wischin, found that a graphoid surface did not form at once but required varying lengths of time, dependent upon several influences—particularly pressure. These observations have been confirmed in industry where the effects of colloidal-graphited lubricants are not immediately evident, manifesting their benefits only after a period of "conditioning."

Although graphite is not regarded as an extreme-pressure lubricant, it provides protection under circumstances which bring about the failure of plain lubricants. Tests made on the Daimler-Lanchester Worm Gear Testing Machine at the National Physical Laboratory (England) show that straight mineral oils, when subjected to heavy loads, lose their lubricating ability above a certain critical temperature. The addition of colloidal graphite to the oils, it is interesting to note, raises the critical temperature ten to twenty degrees. Under the conditions of these tests J. H. Hyde [76] found that colloidal graphite had the effect of rendering an inferior oil the equivalent of a superior one. Other tests [104] conducted by this laboratory indicate that on devices where the oil supply can be controlled, the addition of graphite will enable the feed of lubricant to be reduced to about one-third of its normal value.

Colloidal graphite, because of its minute particle size, presents a huge surface for its mass. Being tile-like in form and orienting itself in such a manner that it lies flat, adsorbed graphite from colloidal dispersions possesses great covering power. Extensive trials both in the laboratory and field show that 0.2 per cent of colloidal graphite by weight dispersed in a carrier liquid is ample to form and maintain a graphoid surface in a majority of cases.

Colloidal-Graphited Lubricants in Industry

Although colloidal-graphited lubricants may be used interchangeably with plain oils for a great number of applications, it is not always economically feasible to do

so—nor is it necessary where full-film conditions may be maintained without difficulty. Accordingly, colloidal graphite is generally employed for special or unusual applications where its peculiar properties may be utilized to best advantage.[132]

Mention has already been made of the use of colloidal-graphited lubricants for running-in new engines. Inasmuch as thin-film lubrication frequently predominates during the early stages of initial operation, colloidal graphite is often added to assembly and break-in oils. This practice prevents scoring of the cylinders, reduces wear and yields surfaces which, upon examination with a profilograph, are shown to be structurally better than those which have been conditioned without graphite.[122]

The use of colloidal graphite for the lubrication of Diesel and gasoline engines need not be confined to the run-in period. This supplementary lubricant, when steadily used in the crankcase oil, safeguards the cylinders of internal combustion engines, which, under the reciprocating motion of the pistons, are subject to considerable wear. Formation of a graphoid surface on the cylinder walls provides an effective barrier against metallic friction. The need for this means of protection is greatest at the top of the piston stroke where the thermal conditions are such that dry friction frequently occurs.[69]

It has been a common practice among engineers to add flake graphite to the cylinder oil used in lubricating steam engines which show a tendency to "groan" upon starting or when running under heavy loads. The substitution of colloidal graphite for the flake variety offers some advantages. Its fine particle size permits less solid lubricant to be used; there is little danger of clogging mechanical lubricators; and because of the formation of graphoid surfaces, oil feeds may be substantially reduced. A reduction in the quantity of oil passing to the cylinders not only lowers cost but also the amount of oil that is likely to be carried into the boilers.

Colloidal graphite in water may be used in place of the oleosol for the lubrication of engines operating on saturated steam. The hydrosol is especially advantageous in process work, where it is important that the condensate be kept free of oil.[151]

Another class of lubricant for which colloidal graphite is eminently suited is that designed for reaching remote friction areas by penetration. Spring or spray oils fall in this category. In order that an oil may penetrate capillaries effectively, it must display low interfacial tension and be non-viscous. Since a low-viscosity oil of the kind used in penetrating mixtures is usually poor in load-sustaining properties, a solid lubricant such as graphite is a necessary complement.

Colloidal graphite dispersed in a mixture of glycerol and water forms the base for an effective and non-injurious lubricant for the numerous rubber parts used in the automotive industry.[150] Such a composition is vastly superior to water alone. The glycerol discourages freezing of the mixture and, because of its hygroscopicity, retards evaporation. The graphite constituent reaches remote parts by penetration and compensates for the lubricating deficiency of the other components.

Mechanisms which (a) must function without failure, (b) are frequently neglected and (c) have no provision for the admission of lubricants, constitute a large field for colloidal graphite. This group embodies such devices as fire-alarm boxes, automatic telephone equipment, news tickers, household devices, radio sets, clock mechanisms, locks, etc. In many instances the lubricant is applied only by the manufacturer during assembly or by the serviceman. There are, of course, many highly specialized uses for compositions containing colloidal graphite, but the principles involved are similar to those covered in the applications already cited.

Parting Compounds

The chemical inactivity of graphite, coupled with its lubricating qualities, makes it a valuable aid in separating such objects as a casting from a mold, a gasket from

a manifold, a lamp base from a socket, etc. A material so employed, called a parting compound, is applicable to a great number of articles in a wide variety of fields.

In practice it is customary to coat one of the pieces with graphite, using for the purpose a colloidal dispersion in a suitable liquid. The choice of vehicle is governed by the temperature to which the objects are to be subjected and the speed with which evaporation is required to take place.

Probably the simplest example of the use of graphite as a parting compound is in connection with the manufacture of corrugated board of the kind from which packing cases and cartons are fabricated. The adhesive most widely employed in this work is sodium silicate. Difficulties ensue when this preparation accumulates on the working surface of the assembly machine. Furthermore, its removal is troublesome, especially when dry. It has been discovered that the films which result when the machine parts are painted with graphite hydrosol act as an effective parting compound, facilitating removal of the silicate adhesive.[90]

In the glass industry, graphite is often applied to molds to prevent adhesion of the glass to the cast iron of which these molds are usually made.[94, 184] Unless a mold presents a surface for which glass has no affinity, there is a tendency for the ware being formed to become corrugated because of repeated, momentary clinging—resulting in what is known in the trade as "washboards." Graphite, when employed to discourage this condition, is frequently referred to as a "mold lubricant." * Actually it is a parting compound, since its prime purpose is to eliminate sticking. Its ability to lubricate the molten glass is also a valuable property but, in this case, a secondary one. In applying graphite to very hot parts, like bottle molds or the screw pegs used for threading glass insulators, light spindle oil or kerosene is a satisfactory carrier. An aqueous dispersion may also be used to form graphite veneers on glass-working devices; but in order to obtain strongly adherent films, treatment must be carried on at temperatures below the boiling point of water.

Coatings formed with colloidal graphite dispersions are likewise used in the field of metal casting. A parting compound of this character is necessary on chillers to facilitate their removal from castings. The molds and cores of gravity and pressure die-casting machines require similar preparation, as do the shaping dies employed in forging operations.

Another method of metal casting is that carried on by the printing trade in the manufacture of stereotypes. In this class of work the mold is a "flong" or matrix composed of heavy paper or other fibrous material. In addition to such essential properties as uniform thickness, flexibility, elasticity and adequate tensile strength to withstand the rigors of the casting box, a matrix must have a smooth surface that is capable of registering very fine detail. Furthermore, the surface of a matrix must be heat-resisting, possess no attraction for molten type metal and be sufficiently durable to show no appreciable loss of definition after repeated use.

Several formulas for matrix coating compositions containing colloidal graphite have been patented. These involve the admixture of graphite with materials like resins,[111] potato starch [148] and sodium silicate.[131] Constituents of the type mentioned are designed to serve as binders and to impart stiffness or rigidity to the molded flong.

Colloidal graphite is an effective parting compound for threads of flanges, plugs, bolts and studs.[26] Parts which have been treated with graphite prior to assembly may be readily disassembled without galling or other injury.

It is sometimes difficult to remove from sockets incandescent lamp bases and fuse plugs which have been exposed to corrosive influences, such as chemical fumes and salt air. The tenacious coatings formed with colloidal graphite in carbon tetra-

* Since a parting compound in many cases also acts as a lubricant, it is sometimes difficult to differentiate between parting compounds and lubricants. The criterion in making this distinction is whether the graphite is reducing friction or preventing adhesion.

chloride or in water constitute a parting compound which is electrically conductive as well as chemically inert.[118]

Electrical Uses for Graphite Films

Use is made of graphite films in many electrical devices ranging from miniature incandescent lamps to massive generators. In certain applications these films are employed only for their ability to conduct an electric current. In other instances several properties of graphite come into play with equal importance. Surface layers formed with graphite hydrosol not only have the basic characteristics of graphite itself but, when properly applied, are opaque, show little photoelectric effect, have a low coefficient of expansion, are good adsorbers of gas and—although a gray rather than a "black body"—are efficacious in promoting the absorption and radiation of thermal energy.

If graphite hydrosol is applied to a glass, porcelain or resinous base so as to yield a thin film,[80, 79] or if the graphite dispersion is first mixed with a non-conductive binder like water glass,[80] the resulting coating will be resistant to the passage of an electric current. This principle is utilized in the manufacture of variable and fixed resistors of the type represented by tone controls, volume controls and grid leaks.

Where it is desired to produce high ohmic units, graphite, colloidally dispersed in phenol-formaldehyde varnish, gives very satisfactory, non-hygroscopic coatings.

In the making of variable resistors where a taper is necessary, the simplest procedure is to apply to the base material colloidal graphite suspensions of different concentrations, either by spraying or brushing, to give the required resistance curve. An ingenious method [115] of producing variable resistors consists of electrophoretically coating stainless steel plates with graphite from aqueous colloidal suspensions. The thickness of the coating so formed is made to vary gradually by slowly increasing the depth of immersion of the plate and simultaneously reducing the plating time. By this technique the coating is thickest at the bottom and is graduated without boundaries, becoming uniformly thinner as the top of the plate is approached. After the coating has been dried, the plate is placed in contact with paper strips impregnated with an uncured phenol condensation product. Upon the application of heat and pressure, a quantitative transfer of the graphite from the steel plate to the paper strips takes place. Such a strip, when mounted on a suitable base, forms a tapered resistance unit of a variety sometimes used for controlling the tone and speaker volume of broadcast receivers.

The conductivity of a layer or film of graphite varies with the proximity of the particles of which it is composed. If a coating has been subjected to pressure or if the individual particles have been oriented by buffing, it becomes a better conductor than one which has not undergone such treatment. Coatings processed for maximum conductivity may be successfully employed for numerous diversified applications including the electroplating of such non-metallic materials as glass, wax, plaster of paris, etc.

Jones and Flanzer [81] have electroplated graphite films with nickel to produce a grid leak having improved electrical characteristics. Normally, graphite has a negative temperature coefficient. By superimposing a nickel coating on the graphite, the temperature coefficient of the unit can be made less negative, zero or even positive.

Graphite films * having good conductivity are used rather broadly as electrostatic shields, special electrodes, guard rings and contacts in various kinds of electrical apparatus.[12, 40, 53, 65, 88, 105, 106, 116, 128, 139, 146]

* A coating formed by the direct application of colloidal graphite dispersions is usually referred to as a "graphite" film, layer, etc. "Graphoid" surfaces are those which have been formed through adsorption or any mechanical working that may have prevailed during the operation of a machine lubricated with colloidal graphite.

Representative uses of these films follow: Electrical musical instruments are particularly sensitive to stray alternating electrostatic fields. In the case of a piano, if the interior of the cabinet is painted with an aqueous suspension of colloidal graphite and the resulting coating grounded, this type of difficulty is eliminated.[96, 98]

Church and Daynes[28] have found that the films formed with graphite hydrosol serve as convenient electrodes in testing ebonite, soft rubber and similar materials for insulating qualities. An electrode of this composition is easy to apply, has clearly marked boundaries, adheres well and, being chemically inert, does not become altered upon exposure to air or by contact with acidic surface films. These electrodes are recommended by the British Standards Institution for power-factor tests involving ebonite.[28]

In a unidirectional current-carrying device of the type invented by Grondahl,[56, 57] it is important that the rather rough crystalline cuprous oxide surface, upon which the rectification of alternating current depends, make intimate permanent contact with adjacent discs or plates. An aqueous colloidal graphite dispersion, when applied by spraying, produces a leveling effect by filling in the cavities between the crystals. In some instances the graphite coating is rendered more conductive by subsequent treatment with colloidal metals.[125]

Another use for films formed with aqueous dispersions of colloidal graphite is involved in the manufacture of glass suspension-type insulators. When these articles are assembled, a molten alloy is employed to attach and hold rigid certain metal components. The alloy used in this class of work, when in the fluid state, tends to wet glass, resulting in its adhering to the dielectric upon cooling. It is essential that movement between these parts take place under the stress and temperature changes to which this type of insulator is subjected in outdoor service. To accomplish freedom of motion the glass portions that come into contact with the molten metal are coated with graphite, which functions as a parting compound and a lubricant.[31]

Oil proved unsatisfactory for this application because of its tendency to volatilize during the pouring of the alloy. Furthermore, the rupture of the oil film under high-tension currents promoted electrical failures. When a dry conducting lubricant in the form of graphite was substituted for oil, electrical as well as mechanical troubles were prevented. Graphite coatings also find usefulness in porcelain insulators where they likewise perform as a lubricant.[10]

Corona difficulties inside high-voltage alternators are eliminated by painting with graphite hydrosol the insulating covering of armature conductors that lie within the slots of the magnetic core. The high-resistance coating, which results upon evaporation of the water carrier, is grounded at many points to the iron laminations of the slots. A coating of this character has ample conductivity to maintain the ground potential of the laminations, and yet possesses a resistance sufficiently high to limit the induced currents to a very small value. With the current of the order of one milliampere, the potential gradients in the minute air gaps within the armature slots are not of a magnitude necessary to produce corona.[71]

The belts used to drive industrial machinery often become heavily charged with static electricity. This condition, particularly prevalent in winter when both the temperature and humidity are low, is a hazardous one—especially where dust or inflammable gases are present. The conducting films formed with either aqueous or carbon tetrachloride dispersions of graphite dissipate these charges as they are generated by the friction between air and the belt, the flexing of the belt and its slippage on the pulley.

Electronic Applications Varied

In the field of electronics, graphite coatings are found in many kinds of vacuum tubes. Deposited on either the glass or metal portions of such devices, they are used in receiving and transmitting tubes to retard the emission of secondary or

undesired primary electrons, as ray-focusing anodes in cathode-ray tubes and as shields in amplifiers of the "Pliotron" * type. Graphite films are also employed to adsorb residual gases, render glass opaque and reduce light reflection.

The spectral reflection factor [129] of matte graphite films in the visible region, as obtained with a modified † Hardy spectrophotometer, is shown in Figure 2. When

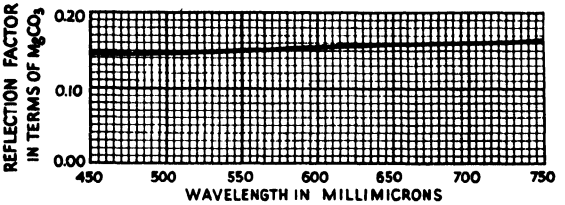

FIGURE 2

a matte graphite coating is buffed, it assumes a high polish and its reflection factor increases somewhat as depicted in Figure 3. The reflection factor of both polished

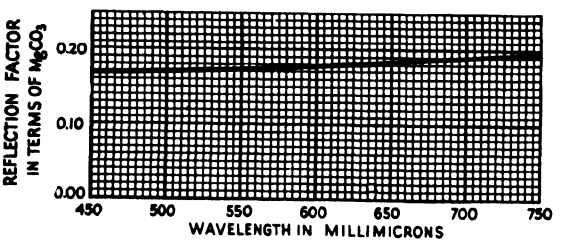

FIGURE 3

and matte graphite films in the photographic and near infrared regions is indicated in Figure 4.

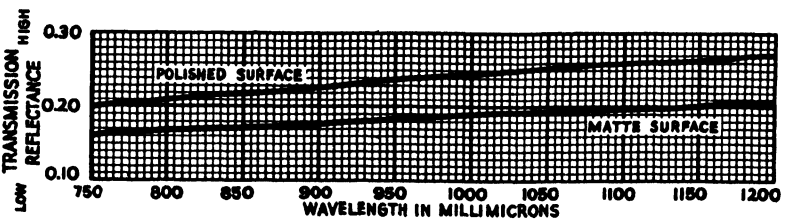

FIGURE 4

When colloidal graphite is required in vacuum-tube manufacture, the hydrosol is generally chosen. This is a thixotropic product having a solids content of from 18 to 22 per cent, depending upon its source. Except for certain special applications, the material is diluted with distilled water before use. The degree of dilution varies over a wide range and is governed by the manner in which the solution is to be employed.

* "Pliotron" is the trade name for voltage-measuring tubes having three or more electrodes as manufactured by the General Electric Company.

† Designed to record wave lengths from 355 to 1200 μ. For details see "Construction of Monochromator Cams for Recording Spectrophotometers" by J. M. Mason, *Rev. Sci. Instruments*, 14, 287-93 (1943).

Metallic objects, such as grids, plates and electron guns, are usually heated in an oven to a temperature slightly above 100°. They are then sprayed with a very dilute dispersion, whereupon the water evaporates to leave a lusterless deposit of graphite which acts as an effective thermal radiator.

Metals may also be graphited by plunging them, while hot, into diluted hydrosol. The extent of heating and the dilution ratio are variables which must necessarily be altered with the mass of the object undergoing treatment and the thickness of coating desired. Metals graphited by dipping should be withdrawn from the solution while their temperature is still above the boiling point of water.

It is possible to impart graphite layers to metals by simple brushing. Satisfactory results are sometimes difficult to achieve, however, especially where highly polished surfaces are involved. Although wetting can be effected by the use of soaps or other polar compounds, the presence of such foreign substances is usually objectionable.

It has been found that metallic surfaces, even though polished to a mirror finish, may, if chemically clean, be wetted by graphite hydrosol at room temperature. Metals which have not been specially cleansed require heating. Practice has revealed that water containing a relatively high percentage of graphite wets reasonably well when the surfaces are warm, while solutions having a low graphite content require a hot surface. Investigation of the temperature range in terms of solids concentration shows that a straight-line relationship exists between the concentration of hydrosol and the minimum temperature at which it will wet what might be called "normally clean" * surfaces. Satisfactory coatings are not obtained when the solids content is less than 3 per cent by weight or when such a dispersion is applied to a surface whose temperature is less than 97°. A hydrosol having 11 per cent solids wets without difficulty at 40°.[185] ✓

When forming graphite films on glass, a colloidal solution containing between 5 and 10 per cent of solids is necessary. In the case of tube envelopes, application may be made with a long-handled brush as the piece is being mechanically rotated. Better results are obtained by filling the object with solution and then permitting the latter to drain out slowly. This is accomplished commercially, in making cathode-ray tubes, by mounting the glass envelope vertically and forcing the graphite solution to the required level with air under pressure.[146] In the absence of compressed air the coating operation can be performed by means of an aspirator bottle filled with the solution and arranged to permit the flow of liquid into the vessel. When the bottle is lowered, the direction of the flow is reversed, and the solution—except that adhering to the wall of the envelope—is recovered. In each of these devices a vent is provided for the passage of air to and from the vessel being treated.

Coatings formed by any of these methods are dried by the circulation of warm air and then baked under vacuum at temperatures up to 450° to bring about carbonization of the protective colloid and to drive off volatile decomposition products therefrom.

The graphite film deposited on the interior wall of the envelopes of cathode-ray tubes extends from the edges of the fluorescent screen to a point in the neck adjacent to the electron gun. The purpose of this coating is to function as a ray-focusing anode. Originally this anode was composed of silver which had been precipitated from an ammoniacal tartrate solution. Such a coating, however, was difficult to prepare, was not adherent to all types of glass and, furthermore, was a good reflector of light, which resulted in a marked decrease in contrast unless the normal ray intensity was maintained at an undesirably high value. Zworykin and Batchelor minimized the reflection problem by applying colloidal graphite over the silver.[154] Since the electron gun also reflected light, it, too, was similarly blackened with graphite.

* As opposed to chemically clean surfaces.

It was later discovered that the employment of fairly concentrated suspensions of graphite hydrosol produced coatings which were sufficiently conductive to make unnecessary the preliminary treatment of the envelope with silver.[145]

Graphite is easy to apply, has a low coefficient of expansion and contributes to contrast by making the glass opaque and reducing internal reflection.[89] Graphite also exhibits "getter" properties which aid in maintaining the high vacuum necessary in these tubes.

In addition to the use of graphite on the walls and metallic electron guns of cathode-ray tubes, non-metallic electrodes consisting of mica discs carrying graphite films have been improvised. These electrodes are alleged to possess advantages over the conventional ones fabricated from metal in that they are not warped by heat treatment, give structural stability with low weight, contain no magnetizable material and have a resistance value great enough to prevent the setting-up of eddy currents.[72]

Graphite coatings on mica also find utility in television transmitting tubes wherein they make up a part of the target or mosaic electrode. In this capacity, use is made of the electrical-conducting and light-absorbing qualities of graphite.[68]

External coatings of graphite may be used on vacuum tubes requiring electrostatic shielding. A typical instance is an especially sensitive tube like the FP-54 "Pliotron," which acquires surface charges during handling that tend to leak off through the control grid circuit and thus appreciably increase the grid current. To avoid this condition it has been found advantageous to apply a film of graphite to the outside of the bulb to within an inch of the control grid connection. If this shield is then connected to a source of potential equal to that of the grid, dissipation of the charges on the bulb takes place.[58]

The envelopes of vacuum tubes of special design frequently bear either an internal or external film of graphite. Examples of this application follow: As wall electrodes in glow discharge tubes used for the regulation of voltage,[128] for the reduction of starting potentials of luminous gaseous discharge lamps,[93] and for miscellaneous purposes in experimental cells[124] and tubes.[105]

Graphite films have also been successfully employed in the form of an annular band on the interior walls of the converter and output tubes used in radio broadcast receivers. The purpose of this coating is to intercept stray electrons from the cathode which would normally bombard the envelope of the tube and drive from the glass objectionable secondary electrons. Being a poor emitter of secondary electrons, the graphite band contributes to tube efficiency by keeping the number of such particles at a minimum.

The chief use of colloidal graphite as a retardant of undesired emissions is its application—usually by the spraying of an aqueous dispersion—to the plates and grids of radio receiving and transmitting tubes.* [91, 102] If the grid of a tube carries a negative charge, thus preventing it from receiving electrons from the cathode, it is capable of emitting electrons by thermionic emission, when it is heated to a high temperature. Electrons may also be the result of a photoelectric effect brought about by the light from the filament or from x-rays produced in the tube and generated by the impact of electrons upon the anode or plate. In power tubes, if the grid is used at positive potential with respect to the cathode, the primary electrons striking the grid can promote secondary emission.

The dark color of graphite is instrumental in discouraging primary emission, since a dull gray to black body radiates heat more readily than a polished metal surface. A grid that has been treated with graphite will, therefore, dissipate heat

* Representative tube types in which graphite hydrosol is used on grids or plates to increase radiation or reduce secondary-electron emission are: (for receiving) power amplifier triode, triple grid power amplifier, beam power amplifier, pentagrid converter, pentagrid mixer amplifier and rectifier-doublers; (for transmitting) power amplifier pentode, RF power amplifier pentode, beam power amplifier and screen grid RF power amplifier.

more effectively and thus show less tendency to emit electrons thermionically. Undesired thermionic emissions may be minimized by roughening the parts to be carbonized. This may be achieved by acid etching, oxidizing or sand blasting the surfaces. While graphite surfaces do not radiate as effectively as those of carbon black, they are, nevertheless, adequate for the large variety of tubes previously cited. The emissive power of a number of typical grid and plates surfaces is set forth in Table 1.[133]

Inasmuch as graphite also shows little photoelectric effect and is remarkably stable under electron bombardment, it constitutes an excellent coating material for metals subjected to the impact of primary particles.

Paradoxically, graphite which is used to retard secondary emission is also valuable in devices, such as electron multipliers, whose prime function is to generate secondary electrons. An efficient secondary emission electrode consists of a base coated with a conductive layer of graphite carrying a film of adsorbed cesium, which is subsequently oxidized.[25]

The peculiar affinity which graphite has for cesium is utilized in the manufacture of several other kinds of vacuum devices. The phenomenon of graphite films adsorbing alkali metals at room temperature and surrendering them upon slight heating finds application, for example, in half-wave rectifiers. When the tube is placed in operation, the heat from the filament liberates the alkali and provides metal vapor in the space between the electrodes. When the tube is cooled, the cesium is re-adsorbed by the graphite. It is stated that even if alkali metal has become affixed to the glass envelope, the metal gradually vaporizes at room temperature and is ultimately taken up by the graphite layer. A similar combination of cesium and graphite may likewise be employed in certain three-element discharge devices.[27]

In the manufacture of photoelectric cells the inclusion of a metallic plate coated with graphite makes unnecessary the usual practice of baking the cell at high temperatures to remove excess alkali metal. The graphite-treated member accomplishes this by adsorption.[90]

Photocells of the alkali-metal type translate light energy into electrical energy. Phototubes employing selenium and tellurium, on the other hand, do not directly convert radiant energy into electricity but, when placed in a circuit, control current flow in keeping with the degree to which the tube is illuminated. This is made possible by the fact that the electrical resistance of selenium decreases as the intensity of the light falling upon it increases. In this latter type of cell graphite may be used as an electrode.[100, 101]

The advantage of graphite over other electrode materials lies in its inability to combine with selenium to form a selenide. Since the electrical conductivity of selenides is greater than that of illuminated selenium and inasmuch as the selenide formation is usually progressive, the sensitivity of the cell to light decreases with time. Counter electrodes, too, may be formed with colloidal graphite. An ultra-thin film applied to the selenium surface greatly increases the sensitivity of the cell to both visible and ultraviolet light.[126]

Miscellaneous Electrical and Allied Uses

Highly concentrated suspensions of colloidal graphite in water, wherein the solids content is upwards of 20 per cent, are obtainable in paste form. Material of this consistency is useful for cementing carbon filaments to the lead-in wires of therapeutical and infrared lamps. Upon evaporation of the water the graphite coalesces to form a strong, electrically conductive bond.

A dispersion of graphite in phenol-formaldehyde resin, when applied as a film or coating to the inside surface of the container can of electrolytic condensers, gives a non-metallic, conductive cathode structure which is non-porous, inert, unbreakable and insoluble.[18]

Table 1. Emissive Power of Specimens in Terms of Watts per Sq Cm
(By Interpolation)

	Temperature °F									
	150	200	250	300	350	400	450	500	550	600
Plain nickel	.003	.005	.007	.010	.014	.018	.022	.027	.033	.038
Plain N.P.C.R.S.*	.003	.006	.010	.015	.022	.029	.038	.048	.058	.071
N.P.C.R.S. acid etched	.003	.007	.012	.018	.026	.034	.046	.059	.073	.089
N.P.C.R.S. sand blasted	.007	.013	.022	.033	.047	.064	.082	.105	.130	.160
Oxidized nickel	.004	.010	.018	.031	.047	.068	.094	.125	.162	.208
Nickel with polished graphite coating	.008	.016	.028	.044	.066	.090	.121	.159	.200	.245
N.P.C.R.S. with matte graphite coating	.007	.016	.028	.044	.066	.093	.125	.165	.210	.260
Oxidized nickel graphite coated	.008	.017	.031	.048	.072	.097	.130	.170	.215	.265
Nickel with matte graphite coating	.009	.019	.033	.051	.075	.102	.135	.176	.220	.270
N.P.C.R.S. with polished graphite coating	.009	.018	.032	.049	.073	.100	.132	.172	.218	.270
N.P.C.R.S. acid etched and graphite coated	.012	.023	.039	.053	.081	.110	.143	.183	.223	.275
N.P.C.R.S. sand blasted and graphite coated	.009	.019	.033	.050	.076	.104	.139	.184	.228	.282
N.P.C.R.S. acid etched and strip carbonized	.008	.018	.032	.051	.078	.108	.145	.194	.245	.310
Oxidized nickel batch carbonized	.013	.027	.049	.076	.114	.156	.210	.275	.346	.430
N.P.C.R.S. sand blasted and strip carbonized	.015	.031	.054	.083	.122	.166	.220	.286	.360	.445

* Nickel plated cold rolled steel.

In electric condensers, lacquer dispersions of colloidal graphite are applied to the dielectric to form a semi-conducting layer which is designed to increase the resistance of the condenser to punctures during electronic surges.[19]

Colloidal graphite is a sufficiently good absorber of radiation to be used for blackening the receivers of thermopiles.[49] Evidence has been collected which indicates that its absorption coefficient is somewhat less than that of lampblack in the visible and near infrared regions but greater than lampblack for long infrared rays around 100μ.[50]

In the study of vibration stresses involving aircraft propellers, locomotive driving rods, etc., a resistance strip, which is electrically sensitive to strain, is made by painting graphite hydrosol on a bond paper base between tinfoil contacts. Briefly, the technique is to attach the strip directly to the stressed part by means of shellac. A graphite strip so mounted is thus strained with the surface. Any change in length of the strip under these conditions results in a change in its electrical resistance. Such a unit can be made a part of an electric circuit which enables one to view on the screen of a cathode-ray tube a wave having a frequency the same as the stress alternations and an amplitude proportional to the stress.[75]

Mention has already been made of the gas-adsorbing properties of films formed with graphite hydrosol in connection with cathode-ray tubes. Graphite also performs as a "getter" in small incandescent lamps and electron discharge devices.[85]

Lamb and Ohl [87] made a study of the adsorption of gases by graphite to determine whether this phenomenon took place only on the external surfaces of the crystals or whether the gas molecules also penetrated the interstices between the basal planes of the carbon atoms in the crystal lattice. Careful measurements made with graphites having different atomic spacings (very finely divided Acheson graphite, Brodie's graphite [24] and the pseudomorphs obtained when the silicon in silicon carbide is volatilized) and gases varying considerably in molecule size (hydrogen, carbon dioxide and difluorodichloromethane) indicate that when graphite takes up gases, the adsorption is confined to the exterior of the crystal.

It is quite likely that the "getter" properties of films formed with aqueous dispersions of graphite are partly due to the presence of elemental carbon resulting from the destruction of the protective colloid during the baking or bombardment treatment generally given vacuum tubes in the course of their manufacture.

Graphite Particles Electrophoretically Mobile

Colloidal graphite, like other colloids, undergoes migration when acted upon by an external electromotive force. In graphite oleosol the particles are charged positively and, therefore, migrate to the cathode; in the hydrosol the particles, being negatively charged, travel to the anode. The commercial utilization of this principle has already been mentioned in the case of variable resistors.[115] The same process has been followed for graphiting the anodes and grids of vacuum tubes.[102]

In investigating the feasibility of producing a self-lubricating bearing metal electrolytically, Fink and Prince [48] successfully co-deposited a mixture of copper and graphite from an acid copper sulfate solution. Graphite hydrosol, when electrolyzed alone, gave a deposit on the anode, as one would expect. However, its addition to acid copper sulfate and subsequent stabilization with gelatin caused the graphite to migrate with the copper ion to the cathode where co-deposition took place. The resulting product was rich in graphite showing, upon analysis, a content of 16 per cent by weight or 42 per cent by volume.

Graphite Dispersions as Impregnating Media

Co-deposition is but one of the procedures by which colloidal graphite can be incorporated with other substances. Intimate mixtures can be formed, for example, by dispersing graphite and a second colloid of like charge in a common vehicle and

co-precipitating them with an electrolyte. When the colloid carries a charge opposite to that of the graphite, flocculation and subsequent precipitation result without the use of an electrolyte. Graphite can also be incorporated with porous bodies by impregnation.

To date the forming of uniform graphite mixtures by co-precipitation has had limited application. Patents involving this technique have, nevertheless, been granted for making a conductive wax[58] and for forming homogeneous mixtures with rubber.[5] Graphite dispersions, however, when employed as impregnating media, are used commercially to treat a variety of materials and objects[117] for the purpose of imparting lubricating qualities, rendering them electrically conductive and for pigmenting.

Among the articles which are graphite-treated to give them lubricity are fibrous packing materials of the kind used in the stuffing boxes of engines and machines,[89] bushings and bearings having a porous structure,[149] and grinding wheels.[63] In the case of abrasive wheels used for grinding and cutting, graphite is sometimes employed to reduce frictional heat in place of greases, waxes or resins, which, if unevenly distributed within a wheel, may seriously affect its dynamic balance at high speeds. Dilute aqueous suspensions of graphite have a relatively low viscosity and are, therefore, easy to inject. When the excess solution is drained from the pores of the wheel and the residual water evaporated by baking, a thin, even deposit of graphite remains to provide lubrication as new surfaces are exposed in the course of grinding.

Graphite is also used for making abrasive wheels conductive, so that they may be made a part of an electric circuit to control automatically or bring about changes in grinding operations.[67]

The impregnation of porous bushings, bearings, grinding wheels and like objects may be carried on by forcing the graphite dispersion in under pressure or by the centrifugal method developed by W. A. Hyde.[77]

In recent years a new technique has been introduced for reducing excessive wear during the running-in of pistons, piston rings, camshafts, valve tappets and similar moving parts. This consists in establishing by chemical or electrolytic means porous granular surface coatings, which are non-metallic * in nature and high in oil-retaining qualities. Such coatings, being a compound of the base metal, are strongly adherent. Although the durability of these surface preparations is limited, they furnish an adequate supply of oil during the critical period when scuffing and scoring are most likely to take place.[54]

Aluminum articles, if made the anode and subjected to a low voltage current in a sulfuric acid bath having a specific gravity between 1.5 and 1.7, take on a hard, porous coating made up of a combination of Al_2O_3, SO_3 and H_2O.[16] Iron and steel parts are chemically treated by immersion in a hot phosphoric bath, which forms on their exteriors a mixture of iron and manganese phosphates.[55]

Both types of coatings are often impregnated with colloidal graphite to improve their lubricating and wear-resisting qualities.[54, 140, 152]

Bearings, bushings, cams, washers, etc., made from laminated plastic materials possess a lower coefficient of friction if graphite is a component. This solid lubricant may be colloidally introduced with the impregnating resin or by first treating the fabric filler with graphite dispersed in either water or a volatile carrier.

The successful impregnation of cloth fabrics and other fibrous materials, such as paper, felt, woven glass and asbestos,† depends upon the degree of wetting of the

* Metallic films, applied either by spraying or electrodeposition, are also used in a similar capacity. Graphite, however, plays no part in this type of coating.

† The possibility of a lyophobic colloid, such as graphite, actually penetrating fibers is quite remote. What most likely happens is that the dispersion forms adsorbed graphite films on the exterior of the individual fibers making up the capillaries.

solid by the liquid,[14] absence of electrolytes, capillary size, nature of the electric charge on the material being impregnated [52] and lack of fillers which may be capable of acting as ultrafilters.

Heating of the fabric is frequently beneficial, since such treatment tends to expel occluded air and moisture and often dissipates static charges. Fillers or weighting substances should be removed by washing or, if of a starch base, with a suitable enzyme.

Clutch facings, brake linings [8, 66] and similar elements are sometimes impregnated with colloidal graphite. Despite the fact that these are friction devices, the presence of a small amount of lubricant discourages momentary seizing, which is usually manifested by squealing or "chattering."

The elimination of corona in high-voltage alternators, by employing graphite hydrosol as a paint on the exterior of the insulating covering of the armature conductors, has already been discussed. Corona elimination can also be accomplished by impregnating the final layer of insulation with colloidal graphite before the covering is applied to the windings.[158]

Colloidal graphite may be incorporated with fabrics made of cellulose acetate to give a gray color which is non-fading as well as fast to washing and rubbing. The use of graphite makes possible an economy in vat dyeing by yielding shades which are deeper than those normally obtained per unit of dyestuff. The graphite may be introduced directly into the spinning solution or by impregnating the finished fabric.[22, 87, 108]

Because of the difficulty of removing colloidal graphite from fabrics, it has become rather common practice both here and abroad to prepare, with either the hydrosol or the oleosol, soiling standards for measuring the detergent efficiency of soaps.[70, 109]

Graphite may also be incorporated with paper to render it electrically conductive, to make it more opaque, or purely as a coloring agent. Paper which has been impregnated with colloidal graphite has various uses in the electrical industry.

In the manufacture of bible paper, a small amount of graphite hydrosol added to the pulp gives increased opacity without imparting any appreciable tint to the finished stock. When incorporating graphite with paper, addition is usually made in the beater. In order to fix the graphite to the fibers, use is made of an electrolyte.

Useful Aid in Experimental Biology

Workers engaged in experimental biology occasionally inject dispersions of colloidal graphite intravenously in place of other particulate material, such as India ink, methylene blue, etc.

Drinker and Churchill,[35] after conducting investigations on the suitability of colloidal graphite as an injection fluid, concluded that a preparation of this kind, stabilized with cherry gum, does not readily agglutinate when mixed with blood and is otherwise well adapted for perfusion experiments.

In studying the passage of particulate matter from the blood circulation to the lymphatics, Field and Drinker [42] preferred graphite to India ink because of the slowness of graphite agglutinization in the blood and the lack of affinity exhibited by it for the vessel walls.

To determine if a partial blockage of the phagocytic activity of the reticuloendothelial system of the rabbit had any effect on the period an animal would survive after complete obstruction in the distal portion of the ilium, Wangensteen and Cooke [144] employed daily intravenous injections of colloidal graphite as the blocking medium.

Menkin [97] has used graphite as a foreign body in the blood stream in his studies on inflammation.*

* See Menkin's paper on Inflammation in Vol. V of this series. J. A.

A rather unusual use for graphite oleosol was published by Hacker.[59] In determining the extent to which oil penetrates the breathing tubes of mosquito larvae, this worker found suspensions of lampblack and of carmine in kerosene deficient because the suspended particles filtered out at the spiracle or tube entry. When a colloidal dispersion of graphite in oil was adopted, separation of the graphite from its carrier did not occur, thus making easily visible the distribution of the black suspensoid within the tubes.

Further Uses for Colloidal Graphite

An attempt has been made in this paper to group or classify the numerous uses for graphite dispersions. However, with a material capable of adoption in such a wide variety of fields there are many applications which cannot readily be assembled under one heading.

A typical example is the employment of colloidal-graphited cutting fluids used during the machining of metals.[82] A cutting fluid functions not only as a lubricant but also as a coolant. In certain machining operations the fluid may perform chiefly as a coolant with lubrication playing a minor part; in other instances the reverse is true. Experiments carried on by Boston, Gilbert and Kraus [20] showed that colloidal graphite, when added to a cutting oil, permitted an increase in cutting speed and gave at the same time improved tool life and superior finish. Graphited cutting oils, for the most part, are opaque, which limits their utility to operations that do not require constant inspection during the machining.

Another application which falls outside the groupings previously cited involves the addition of colloidal graphite to steam boilers to prevent the formation of scale. The minute graphite particles serve as nuclei for the crystals, which would otherwise be deposited on the boiler tubes and walls. When the graphite with its adsorbed salts eventually precipitates, a slime is formed which, in addition to being a good conductor of heat, is easily removable.[88]

Graphite may be colloidally dispersed in boiler feed water to give stable, nonfrothing suspensions when protected by a material such as waste sulfite liquor. It is claimed that a preparation of this character not only prevents the accumulation of new scale but also is effective in loosening old deposits.[84]

A second process based upon the adsorption ability of colloidal graphite is that used for the recovery of paints, lacquers and enamels from the atmosphere and walls of the chambers in which these coating preparations are applied. Aqueous sprays and water curtains containing colloidal graphite are successful in bringing about the adsorption, coagulation and precipitation of the excess surface-finishing materials which escape the object being treated. By the use of solvents and centrifuging, recovery of the coating constituents is accomplished.[120]

In certain special applications it is advantageous to employ surface coatings of graphite which are highly durable and able to resist abrasion, heat, water and corrosive influences. They can be prepared by incorporating a small amount of gelatin with the graphite hydrosol and subjecting the films formed therewith to the action of formaldehyde. An alternate procedure is to expose to either artificial or natural light surface layers resulting from a mixture of graphite hydrosol, gelatin and potassium bichromate.[130]

Even in photography graphite hydrosol finds utility. When brushed on negatives it forms thin, flexible coatings, which are useful for the masking or blanking out of sections to be omitted in printing. Most photographic opaques, in order to be impervious to light, must be applied in reasonably heavy layers. Thick coatings are objectionable, especially on film stock, since they tend to chip upon being flexed. Thin opaque layers of oriented graphite which have been brushed or sprayed on photographic film can be bent double without cracking or peeling. Furthermore, if desired, graphite films may be easily removed with water.

The technical applications described herein represent only a cross-section of the many fields in which colloidal graphite dispersions are being employed in industry today. The literature is rich in parallel and supplementary uses for this material.

In addition to the efforts being spent to extend the usefulness of colloidal graphite in the various branches of applied science, research work of a purely academic nature is also occupying the attention of numerous investigators. Much has already been done on such scholarly projects as the effect of x-radiation on the electrokinetic potential of colloidal graphite,[29] the relationship between diamagnetic susceptibility and particle size,[119] and the effect of crystal structure on its diamagnetic qualities.[188] These, like many similar researches before them, may some day be translated into practical applications of considerable importance.

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Principles and Practice of Soil Stabilization

HANS F. WINTERKORN

Department of Civil Engineering, Princeton University, Princeton, New Jersey

Soil stabilization is the collective term for any physical, chemical or other method employed to improve certain properties of a specific soil to make it serve better as a foundation or construction material. The different uses of soil pose different requirements of strength and water resistance. It is a vastly different matter to stabilize the slope of a cut or fill against erosion, than to stabilize a soil to carry successfully a B-29 plane. The relativity of strength is nowhere better described than in Holmes' "The Deacon's Masterpiece, or The Wonderful One-Hoss Shay."

Consequently, the term "soil stabilization" possesses a definite meaning only if properly specified. While stabilization has been employed successfully for improving deep foundation soils and for decreasing the permeability of earth dams and reservoir bottoms, as well as for slope protection against erosion, its main application has been in the field of highway and airport engineering. In this field, soils are exposed not only to mechanical stresses incidental to their usage, but also to the dynamic effects of local climate. Consequently, soil stabilization involves more than a mere increase in compressive strength or shear resistance or the improvement of any other physical property of a soil; it involves the supplying of a defense mechanism against the continuously acting dynamic forces connected with the exposure of the respective soil body to daily and seasonal moisture and temperature changes and to microbial activity, which all tend toward lowering its mechanical stability.

Proper solution of the various problems in soil stabilization involve:

(1) A knowledge of the mechanical properties of the soil under consideration by actual measurement with recognized methods; this requires at least a qualitative understanding of how the measured properties are functions of the size composition, mineralogical and (or) chemical character, surface chemical factors, and structural arrangement of the soil constituents;
(2) A knowledge of the climatic and other dynamic forces to which the soil system under consideration is exposed and of the reaction of the latter to these forces;
(3) A thorough and broad knowledge of physics and chemistry especially as related to surface and colloidal reactions, to select the proper treatment after diagnosis has been made on the basis of the items named in the two preceding paragraphs.

One who desires to improve the properties of a soil finds himself in much the same situation as a practicing physician. There exist striking analogies between the sources they have to draw on, the creative imagination by which piece-meal data are built into working concepts, and their integration by practical experience.

Sources of Soil Knowledge

Soil knowledge has developed from many different sources, such as agriculture, engineering, pottery, geology, mineralogy, chemistry, physics, and other related sciences, professions, and arts; the available information is spread throughout the respective literature, and has not yet been brought together in one single place. For

the presentation of that part of the available information which is of special interest in soil stabilization, the scheme of contemplating the different structural levels of soil systems has been selected. This scheme was first formulated by Jerome Alexander.*

In the highest order of structure, soil is a part of the earth surface which to the geologist and engineer may be just unconsolidated rock, but to the pedologist represents soil proper in the upper layers and soil parent material in the lower. Both soil and parent material, in the pedologic sense, represent systems formed and given definite characteristics by climate, vegetation, topography, time, and parent rock. Such systems are truly colloidal or surface-chemical if these terms are used interchangeably and if they denote systems in which surface reactions far outweigh volume reactions. The systems usually possess one gas, one liquid and several solid phases arranged in definite patterns; the latter may be recognized by visual inspection and are employed in the classification of the soil systems. The properties of such systems vary little in horizontal directions but vary greatly in the vertical direction, where elutriation and accumulation zones are formed which are called horizons; the horizons; make up the profile.

For soils, as for any other group of items, a classification is an important tool. Soils as natural systems, in the sense indicated above, have been classified especially through the endeavors of Marbut.[1] Because of the importance of this classification for soil stabilizing purposes, its bases are given on the following pages in a condensed form.

Soil Classification of the U. S. Soil Survey, Department of Agriculture †

I. SOIL TYPE

A. *Soil Series Name*

The specific name of a Soil Series is usually a geographic term indicating the location where the series was first recognized or described. The determination of the Soil Series is based upon the following soil characteristics.

1. Soil Forming Material
   - a. Rocks
     - (1) Igneous
     - (2) Sedimentary
     - (3) Metamorphic
   - b. Unconsolidated Materials
     - (1) Gravels
     - (2) Sands
     - (3) Clays
2. Mode of Formation
   - a. Residual
   - b. Water
   - c. Wind
   - d. Ice
3. Topographic Position
   - a. Rugged to Depressed
4. Natural Drainage
   - a. Excessive to Poor
5. Profile
   - a. Heavy and Light Layers
   - b. Thickness
   - c. Structure
   - d. Color
   - e. Chemical Composition
   - f. Hard Pans
   - g. Bed Rock

* See tables in the first papers of Vol. I (1926) and Vol. II (1928) of this series. Also "Colloid Chemistry," D. Van Nostrand Co., 2nd ed. 1924 and subsequent editions.

† This treatment follows an outline prepared by Dr. Linwood L. Lee of the United States Soil Conservation Service, which he prepared for a lecture given in the frame of a War Time Training Course given this Spring (1944) under the direction of the author at Camden, New Jersey.

All soils in which the above described characteristics are identical are classified in the same Soil Series.

B. *Soil Class Name* (Texture)

The Soil Class designates the texture (relative lightness or heaviness) of the soil. It is dependent upon the relative proportions of the various sized particles which a soil contains.

1. Soil Particles—Soil Separates

Name	*Size*
a. Gravel	> 2.0 mm
b. Coarse Sand	2.0 – 0.2 mm
c. Fine Sand	0.2 – 0.02 mm
d. Silt	0.02 – 0.002 mm
e. Clay	0.002 – 0 mm
f. Colloids	< 0.001 mm

2. Soil Classes
   a. Coarse Sand
   b. Sand
   c. Fine Sand
   d. Very Fine Sand
   e. Loamy Coarse Sand
   f. Loamy Sand
   g. Loamy Fine Sand
   h. Loamy Very Fine Sand
   i. Coarse Sandy Loam
   j. Sandy Loam
   k. Fine Sandy Loam
   l. Very Fine Sandy Loam
   m. Loam
   n. Silt Loam
   o. Sandy Clay Loam
   p. Silty Clay Loam
   q. Clay Loam
   r. Sandy Clay
   s. Silty Clay
   t. Clay

If a soil contains considerable gravel, shale or stone the term gravelly, shaly or stony is added to designate the soil type.

A very helpful device for the textural classification of soils is the triangular chart given in Figure 1.

Like the pedologist, the foundation engineer is interested in the properties of a soil system as a whole, though mainly with the deeper layers. For this reason he is interested in field tests and in laboratory tests made on samples which are in as undisturbed a condition as possible. For this purpose he has developed an excellent set of techniques, not only for the sampling but also for the testing of the samples for those properties that are of special interest to him. The latter are: compressibility, consolidation behavior, permeability, and shear resistance of the soil as encountered and used by him in the field. Since he in most cases must use the soil in its natural condition with little chance of improving it by stabilization methods, he is mostly interested in what the soil properties actually are, not so much in why they are as found. His greatest contribution to soil science lies in the working out and standardization of soil mechanical test methods.

The next lower order of soil structure is that of mechanically disturbed soils. Soils in this condition are used in farming, highway engineering, construction of earth dams, earth floors, pond bottoms, and similar structures. In this disturbed condition, the macro-structure of the system has been destroyed; however, practically all the finer particles are aggregated with each other and with larger particles to secondary units or secondary structural elements. This is especially obvious in good agricultural soils. This aggregation is of greatest importance in agriculture and engineering where it determines, to a considerable degree, the ease of working of the soil and its suitability for different agricultural and engineering purposes. The particular secondary structure of a certain soil depends upon its mechanical composition, the

type and amount of clay, the type and amount of organic matter, the salt content, and the type and amount of exchangeable ions in the clay. The mechanism of aggregation is obviously a colloidal phenomenon.

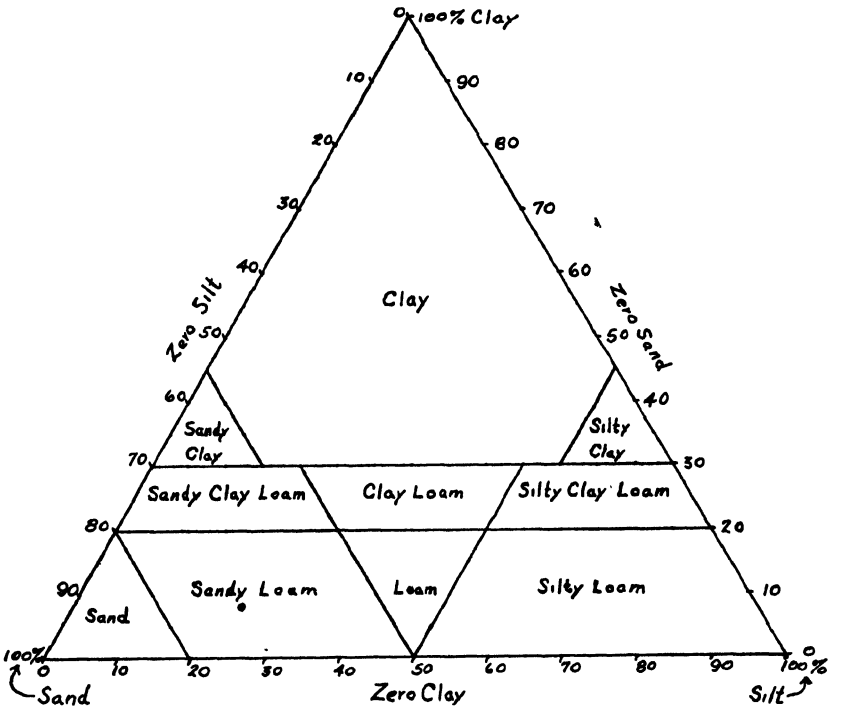


FIGURE 1

The physical properties which are usually determined of soils in this disturbed state are: the consistency properties such as plastic and liquid limits (Atterberg), the shrinkage limit, the field moisture equivalent, the centrifuge moisture equivalent, and others; also by soil mechanical tests, the compressibility, the shear resistance, and the permeability. The correlation of these engineering properties with surface chemical phenomena has been furthered mainly by the work of Winterkorn and his school.[2]

The next lower order of structure is concerned with the mineralogical and crystallographic properties of the solid soil constituents. Within recent years improved x-ray techniques and the electron microscope have opened the field of clay mineralogy.* These new tools have verified experimentally previously made assumptions on size and shape of clay particles and have revealed the crystallographic structures of a number of important clay minerals. This knowledge permits the picturing of the electronic structure of the mineral surface which together with our knowledge of the properties of the H_2O dipole and of the behavior of ions in an electric field promises to lead to a better understanding of the structure of water films on clay minerals than is available at the present time. A great contribution toward the solution of this problem had been made previously by Ducleaux,[3] who developed formulae for the equilibrium conditions between the electrostatic attraction and the kinetic fugacity of the ionic atmosphere surrounding a charged spherical colloidal particle. Winter-

* See paper by E. A. Hauser and D. S. le Beau in this volume. J. A.

korn [4] expanded this concept to cover flat particles with uniform as well as non-uniform charges. This led to the recognition of two types of swelling in soils, one of which is connected with a significant amount of energy, the other representing a type of free interstitial water between the hydrated particle surface and the hydrated ions. By means of this concept the swelling behavior of the different clay minerals has become a logical consequence of well established physical laws.

Soil Stability

Stability in an engineering sense denotes the maintenance of a reasonably high bearing power connected with constancy of volume and shape. The bearing power of a soil is a function of its resistance to shear. It was found early that the shear resistance for soils consisting only of relatively large sized material such as sand and gravel was a direct function of the normal pressure on the shear plane:

Shear resistance = normal pressure × coefficient of friction.

With moist clay soils the shear resistance was found to be either independent of the normal pressure or to be a complex function of the latter depending upon the experimental conditions. This property was called cohesion, and was found to be dependent on the presence of moisture films around the clay particles. These give rise to:

(1) Apparent cohesion due to the water-air interfacial tension of water wedges between soil particles, vanishing with the obliteration of the interfaces (most easily observed in sandy and silty soils);
(2) True cohesion by means of chains of oriented dipoles connecting positive charges on one particle with negative ones on the next. These chains shorten with moisture loss due to elevated temperatures or compression;
(3) A combination of apparent and true cohesion, this being the most common case.

Since the cohesion of a soil is functionally connected with the thickness and structure of the moisture films around its constituent particles, a change of the structure of these films by changing the electric surface field of the soil particles is bound to result in a change of the cohesion of the soil. The easiest way of changing these fields is by substitution of different ions for those present in the natural soil. The effect of such ionic substitution on the engineering properties of soils has been shown especially by Winterkorn and his co-workers.[2]

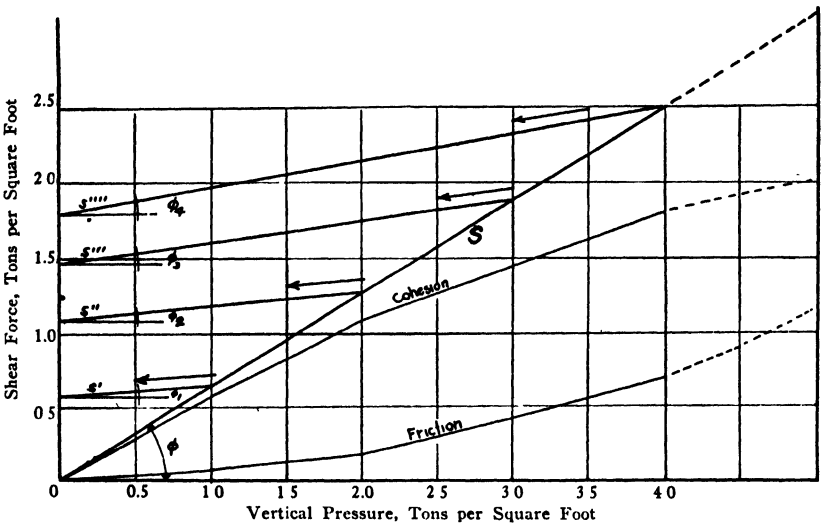
For intermediate soil types, possessing both frictional and cohesive properties the engineer usually employs the formula:

Shear resistance = cohesion + normal pressure × coefficient of friction.

This equation represents a very dangerous half truth, and what successful use has been made of it is due more to a judicious choice of the factors of safety than to any merit of the formula.

Graph 1 gives a typical plot of shear resistance data obtained on a cohesive soil. S represents the virgin curve on which the shear resistance is plotted as a function of the vertical pressure after the soil has reached equilibrium with the latter. At the origin the soil possesses a moisture content equal to its liquid limit, at the higher pressures the moisture content is that which the soil can hold against the obtaining pressure; ϕ is the angle of friction as obtained if only the virgin curve is considered. If soil samples are first permitted to come to an equilibrium with the pressures indicated by the abscissae of the points in which the curves s', s'', s''', s'''', join the virgin curve, and then tested for shear resistance at lower normal pressures, the curves s', s'', etc., are obtained. Their intercept with the ordinate expresses the cohesion of the system, while the angle of friction has been reduced from ϕ to ϕ_1, ϕ_2, etc., respectively. Which is now the correct angle of friction and the correct value of cohesion to be employed? This question is extremely important for the stability of earth dams and similar structures.

From the data expressed in the above named curves, curves for the change of cohesion and of the angle of friction can be obtained as functions of the preconsolidation pressure. Obviously, the cohesion increases with increasing preconsolidation pressure, approaching a constant value. The coefficient of friction increases to a constant value, approaching at very high preconsolidation pressures that of the virgin data. This result, which might be surprising to the formalistically minded, is the only rational one if the film properties of the component particles are considered. If two particles, connected by chains of ions and dipoles approach each other, their attraction increases up to a certain point at which the respective parts of their films are



GRAPH 1. Friction and cohesion as functions of consolidation load. Separation and extrapolation of friction and cohesion data indicate that both cohesion and the angle of friction increase with increasing pressure to a certain limit, whence they continue as constants. (Derived from typical shear test curve for cohesive soils. Hogentogler, "Engr. Prop. of Soils," p. 214.)

so strongly held that they resist greater thinning. Further compression may even result in rapidly rising repulsive forces. This explains the behavior of the cohesion component of the shear resistance—pressure relationship. The coefficient of friction also increases with increasing closeness of the solid particles. At large moisture contents and great separation of the solid particles from each other (*e.g.*, at the liquid limit) the shear resistance involves only the relatively small friction of water molecules which are almost free from restraining surface forces. At increasing closeness of the particles the plane of shear will go successively through plastic and semisolid water films—this condition being caused by the attraction and orienting forces originating at the particle surfaces—until the mineral surfaces or the solidified water layers of the particles touch each other. From this point on the coefficient of friction is practically constant. It is this latter value which the engineer seems to have in mind when using the term friction. Fundamentally there exists no difference between the friction in a cohesionless and a cohesive soil respectively; the great practical difference lies in the fact that in the case of coarse material, possessing only a small amount of water in the film state, equilibrium between normal pressure and friction is obtained almost instantaneously. In the case of clay soils possessing a large specific surface and, under normal conditions, a large amount of film water, equilibrium is

reached only very slowly between the normal pressure and the thickness of the water film. The latter, of course, governs the coefficient of friction.

The Destructive Action of Climate [5]

It is well recognized by the highway engineer that climatic agents are responsible to a great extent for the destruction of our highways. However, very little is known concerning the actual mechanism of destruction. Thus, while water is known as the chief enemy of highway pavements and highway bases, cases are on record of road and airport bases continuously saturated with water which have stood up well, while roads through deserts have failed because of water action even though the distance from the water table was rather great and precipitation negligible. It is for such reasons that the highway engineer recognizes on one hand the importance of climate, but on the other hand feels rather at a loss to put his finger on just what happens. The present approach attempts to give some general concepts concerning the mechanisms of climatic action on soils.

The general effect of climate is to loosen a soil system and to lower its shear resistance. In loosening up such a system, climate must weaken and overcome the cohesion of the system, or, in the case of a cohesionless material, it must overcome the confining pressure and the force of gravity. One of the problems involved in the destructive action of climate on a cohesive system is illustrated simply by the phenomena occurring if a clay clod is immersed in water. If the clod is moist it may be found to resist indefinitely the action of water. However, if dried out and then immersed in water, it will probably slake in a few minutes. Repeated wetting and drying is often used in the laboratory to break down large clods of very cohesive clay which are extremely difficult to break down by mechanical means. In conformance with this illustration the central thesis of the present treatment is as follows.

The destructive action of climate on highway structures is not so much a function of the average moisture and temperature level, but rather of the moisture and temperature fluctuations occurring in the structures as a result of climatic influences. Of course, the average temperature and moisture levels cannot be entirely disregarded. According to van't Hoff's rule, the speed of a slow chemical reaction is doubled by an increase in temperature of 10°; also, the presence of a certain minimum amount of moisture is often the *sine qua non* of a reaction. Consequently, the average temperature and moisture levels influence especially the speed and location of the equilibrium in the case of chemical reactions which may be involved in the deteriorating process. Evidence for the correctness of the thesis formulated above, and indications of the working mechanism of climatic forces are treated below.

The Mechanism of Water Attack on Dry Cohesive Systems [6]

The entrance of water into any porous system is due to the affinity of the water for the internal surface of the system concerned. If this affinity is not present no entrance will take place, irrespective of the surface tension of the liquid. This is illustrated by the entrance of water into a glass capillary, on one hand, with resulting capillary rise, and the resistance of mercury to enter a glass capillary for which it has no affinity. If the affinity between the liquid and the capillary wall is greater than the affinity of one molecule of the liquid for another, then the adsorbed film of the liquid may carry along a liquid column to a height which is determined by the surface tension of the liquid, *i.e.*, by its molecular attractive forces. This basic importance of the affinity of the liquid for the surface of the solid must be kept in mind for the proper understanding of all capillary phenomena.

As previously indicated, the results of exposure of a soil to water depend upon the moisture content of the soil, *i.e.*, the extent to which the water affinity has already been satisfied. In general, two main factors appear to govern the consequences of the water attack. These are the driving force or the affinity of the internal soil surface

for water, and the cohesive forces holding the system together. The relative magnitudes of these forces determine the general reaction picture. On the other hand, the speed with which the particular reaction occurs depends to a great extent on the permeability of the soil system, and upon the ease with which free and adsorbed gases may escape from the pore space. If this escape is prevented, a type of failure may occur which possesses great similarity to an explosion, although of course not liberating so high an amount of energy as is usually associated with this term. The concept that the driving force is the affinity of the internal surface for water, makes it easy to understand why certain moist cohesive systems may be exposed to free water for any length of time without observable change. It is obvious that the affinity for water is satisfied in such systems, and that no driving force for the water attack is left. Depending upon the type of soil considered, its location, and possible confinement, water attack may result in erosion, in mud flows, in slides, or in a general loosening up of the soil.[6] In the latter case, the total amount of loosening up depends on the number of wetting and drying cycles the system has undergone. This loosening up, though less dramatic than, for instance, a mud flow, may result in a very severe decrease of the stability of a sub-grade soil, and may lead to a road failure in the case of flexible pavements or of rigid pavements which do not possess sufficient thickness and beam strength to distribute the applied load over a large enough area, or to bridge over weak spots.

So far, an attempt has been made to treat the effects of moisture, independent of the effect of temperature variations. It is obvious that such a separation does not exist in nature, where moisture changes usually go hand in hand with temperature changes. This results in a greater complexity of the observed phenomena than has been indicated. An additional important item, perhaps the key for the understanding of the outstanding riddles, lies in the complexity of water as a material. This complexity is especially apparent if the water is contained in porous systems possessing hydrophilic internal surfaces.

The Condition of Water in Porous Systems [7]

Water is a peculiar substance. It is liquid at normal temperatures while similar compounds with higher molecular weight, *e.g.*, H_2S and H_2Te are gaseous in the same temperature range; while in the liquid state, water gives x-ray patterns which are indicative of crystalline, *i.e.*, solid materials. The melting point of normal liquids increases with increasing pressure, while that of water decreases first with increasing pressure, and behaves "normally" only at relatively high pressures. The underlying reason for all these phenomena is the architecture and the dipole character of the water molecule. These permit it to associate easily and with considerable energy with molecules of its own kind. Qualitatively, one might say that water behaves normally only when the externally applied pressure outweighs considerably the intermolecular attraction. The complexity of water behavior is indicated by the graph in Figure 2 which represents a simplified picture of the findings of Tammann [8] and of Bridgman,* respectively. This figure gives five different modifications of solid water stable at different temperatures and pressures, four of them having corresponding liquid modifications at temperatures above the solid-liquid curve. The figure is rendered even more complex by the existence of hysteresis phenomena and of submodifications such as Ice I′, III′, etc.

There is considerable evidence that large attraction pressures exist on the surfaces of mineral materials. While these pressures are probably largely of an electrostatic nature, and as such possible of solution by molecular theoretical analysis, a different approach appears to be more directly useful. The way for such an approach was shown by Tammann in explaining the relationship between surface tension and

* See paper by P. W. Bridgman in Vol. V of this series; also paper by I. Traube in Vol. I. J. A.

compressibility of water; for this he employed the concept that internal pressures may be assumed to produce the same type of results as external pressures.

Employment of this concept on the condition of water in porous systems necessitates a knowledge, or at least an estimate, of the attraction pressures involved. Freundlich [9] calculated from experimental data by Gurwitsch that fuller's earth adsorbed 183 volume per cent of methyl alcohol with an average pressure of from 20,000 to 25,000 atmospheres. There exists sufficient evidence that water is usually more strongly adsorbed on mineral surfaces than is methyl alcohol. The phase diagram shows that the melting point of water at a pressure of 25,000 atmospheres is considerably above 50°.

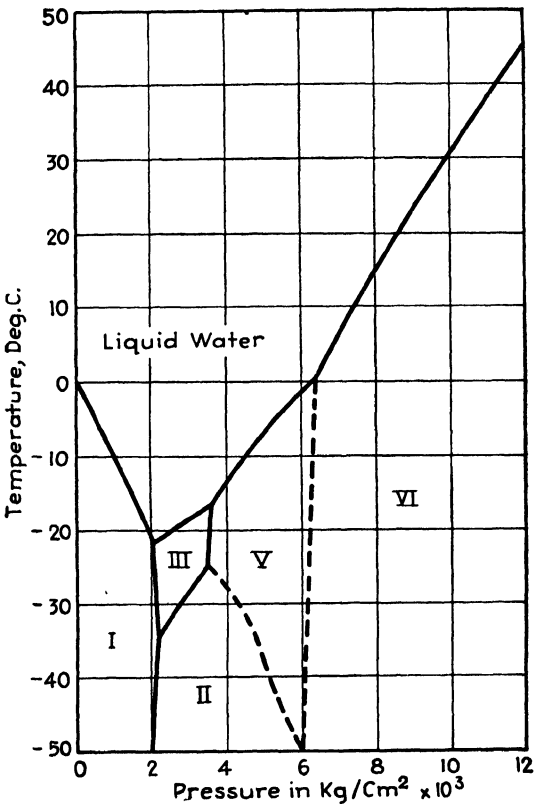


FIGURE 2

The conclusion which must be drawn from this evidence is that in a moist porous system practically every temperature change results in the change of some water from the solid to the liquid, or from the liquid to the solid condition with accompanying expansion or contraction. At pressures below 2,050 atmospheres and temperatures between 0° and −22°, expansion occurs upon solidification. This continuous change of state with corresponding change in volume cannot help but exert a general loosening effect on the system. This loosening-up has so far been recognized only for the expansion in connection with the formation of Ice I; recognition of its existence over the entire temperature scale should be helpful in throwing light on a number of phenomena which hitherto have been a mystery to most.

Porous construction materials such as concrete, soil-cement, soil-aggregate, and others often are tested for durability by permitting them to absorb water with subsequent exposure to freezing. The normally adopted freezing temperature is −10° F, which is slightly below the lowest freezing point of the expansive Ice I. This point is well chosen, since the maximum freezing pressure exists at this point, *i.e.*, 2,050 atmospheres. Some investigators, ignorant of the theoretical importance of this point, have tried to obtain more severe freezing effects by cooling to still lower temperatures. They were surprised to find that this resulted in a smaller destructive action; this phenomenon, of course, is easily accounted for by shrinkage of the ice at decreasing temperatures resulting in a relief of the expansion pressures set up in the freezing of Ice I.

In the attempted freezing of some moist but well compacted clay-gravel mixtures, it was found that they do not expand, but shrink upon cooling to −10° F. The obvious explanation for this phenomenon is that the water contained in the system was under such great adsorption pressures that it fell out of the domain of the expansive Ice I. Well documented examples of this type are available by the score. Detailed treatment of them is omitted, since the main purpose of this discussion is to point out the availability and usefulness of the concept employed. Its further specific application must be left to those who can make use of this tool.

This new tool helps to explain why a road in the Imperial Valley failed by water accumulation in the sub-grade despite the fact that the adjoining soil was dry and the ground water table a considerable distance away; it also helps to understand why inundation with a foot of water did not hurt the Omaha municipal airport, the clay-gravel base of which is normally saturated with water. The principle involved in these phenomena is identical with that employed in the "aerial" wells of the Greek city of Theodosia two thousand years ago. These aerial wells consisted of pyramidal aggregations of calcareous rock fragments erected on the heights overlooking the city where they were exposed to cold and water-laden night winds. The ruins of these structures, which were 30 x 20 x 10 meters, can still be seen. They represented a city water supply furnishing an estimated daily quantity of 15,000 gallons for drinking and irrigation. Similar aerial wells have been built in modern times in southern France. The working of an aerial well and the mechanism of water condensation in soil are described somewhat as follows by Chaptal [10] a French authority on the subject:

"At low temperatures water is adsorbed on the surface of the soil (or mineral) particles and held there by surface tension; thus the particles are surrounded by a thin liquid film. With rise in temperature the surface tension decreases. Since the force of gravity remains constant the film tends to thicken at the lower position of the mineral particle at the expense of the other parts. When this water accumulation on the lower part is sufficiently large, a drop detaches itself, which, protected from immediate evaporation by the particle above takes the form of either capillary or free water depending upon the condition of the soil. Thus, the adsorbed moisture becomes available to plants and represents an actual moisture gain to the earth. When the temperature falls, the liberated drop is not available to thicken the adsorbed water film; instead, a new quantity of atmospheric water vapor is captured and fixed at the surface of the soil particles. This theory is confirmed by the fact that in the 'aerial well,' all other conditions being equal, maximum water release is observed during the hottest days."

Chaptal's theory is, in general, correct; it can be improved by reference to some data obtained by Baver and Winterkorn.[11] The latter showed that at a constant water pressure of 30 mm Hg, the water adsorption by Putnam clay decreased from 25 per cent (on the basis of the dry weight of the clay) at 30° to less than 12 per cent at 40°, that of bentonite from 33 to less than 14 per cent, and that of Davidson clay from 21 to less than 4 per cent, for the same temperature change. While adsorption data were not obtained for temperatures lower than 30°, the trend of the moisture-temperature curves indicates that the difference in adsorption power between 20° and 30°

would be even greater than that between 30° and 40°. Therefore, a considerable part of the moisture adsorbed and strongly held at lower temperatures becomes free water at elevated temperatures. This free water can then be released in accordance with Chaptal's theory.

From the evidence available the following conditions appear to be conducive to good water collection:

(1) Sufficient aeration to permit the passage of a large volume of air through the collector; however, the aeration should not be too violent, since this causes evaporation losses;
(2) Low temperature of the collector to permit maximum water adsorption from either hot or cold humid air;
(3) Sufficient temperature variation in the collector to change adsorbed into free water which descends under the influence of gravity;
(4) A great difference in the water holding capacity of the mineral surfaces at the different temperatures obtaining in the structure;
(5) The type of construction and material employed should favor nocturnal radiation and impede heating up during day time.

It is evident that these conditions are present to a greater or lesser extent in highway fills and sub-grades. Black pavements, warming up rapidly in day time, and cooling rapidly at night may add the finishing touches to make these systems good water collectors. For these reasons, the principles involved in aerial wells deserve consideration by the highway engineer. The immediate cause for such detrimental water accumulation is fluctuation of temperature.

Frost Heaving and Formation of Ice Lenses

A very important mechanism of climatic damage to soil structures is that involved in frost heaving as a result of the formation of ice lenses.

The forces responsible for the formation of adsorbed water films are also responsible for the movement of water in soils, independent of the direction of the force of gravity. This movement is generally explained (or better, left unexplained) by reference to capillarity as a result of surface tension; but the fact that water rises in a glass capillary in which mercury is depressed shows clearly that the moving force is the affinity of the walls for water. The establishment of a meniscus in capillaries is only a secondary phenomenon. The so-called capillary rise in a system will come to an end when the energy of adsorption on the walls just balances the frictional resistance and the weight of the water sheet or column. From this it evolves, as Vageler [12] has emphasized, that with decreasing diameter of a tube a maximum capillary rise will be reached; after this, a decrease will follow because of the increased frictional resistance in the adsorbed water film. This holds also true for the speed of capillary rise; contrary to the usual conception that greatest speed of capillary rise is obtained in the widest capillaries, good practical evidence exists that, at least in sands, maximum speed of capillary rise exists at intermediate pore sizes.[18] This is obvious from a consideration of the energies involved in capillary rise:

(1) The kinetic energy of the moving water column is $\frac{mv^2}{2}$, m being proportional to $r^2 \pi \cdot h$; this energy must be furnished by the product of the attraction energy per unit surface of the capillary and the wetted area of the capillary. Setting these two energies equal to each other, and simplifying, one obtains $v = k\sqrt{\frac{1}{r}}$. This means that the speed of capillary rise in relatively large pores (compared with which the adsorbed water films are negligible) increases as a function of decreasing radius of the capillary. However, as the thickness of strongly adsorbed water films becomes of the

same order of magnitude as the radius of the capillary, a decrease in speed of rise takes place because of the different physical properties of water in the film phase.[7]

A very important consequence of the movement of capillary water in soils is the formation of large ice lenses resulting in frost heaving, and in frost boils, or mud pools, after thawing. In this phenomenon the following factors play a role.

(1) The presence of a water reservoir either as ground water or as pore water saturating the soil body.
(2) The speed of penetration of the cold front into the soil.
(3) The mechanics and dynamics of the water movement to the zone of freezing. The latter are functions of:
   (a) The total attractive force—thermodynamically expressed by the difference in vapor pressure of the water in the reservoir from that of the capillary water at the elevation of the freezing zone, the latter pressure being equal to that of the forming ice lens.
   (b) The physical condition of the pore water under the influence of the surface forces originating on the solid pore walls, and the frictional and gravitational resistance to movement of the pore water to the freezing zone.
   (c) Crystallo-chemical considerations especially the ease of nuclei formation for ice crystals.

The speed and the amplitude of the cold wave penetrating into the soil are functions of the temperature conditions at the surface, and of the original temperature, heat capacity and heat conductivity of the soil. The chances for the formation of detrimental ice lenses at a certain depth depends on the speed of water moving thereto and on the distance of the water reservoir. In a transcendental way lens formation is closely related to the formation of Liesegang rings, *i.e.*, it is a type of rhythmic flocculation with the temperature taking the place of the flocculating agent.

The crystallization of ice in layers without inclusion of the soil particles is also a crystallo-chemical phenomeon. Uniform freezing of a soil without layer formation is comparable to the inclusion of sand in lime spar and gypsum; ice lens formation is comparable to the crystallization as pure minerals of gypsum, aragonite, and marcasite in clay soils. There can be no reasonable doubt that the type of crystallization of ice in soil depends on the type and amount of internal soil surface. This means that the frost heave problem has many colloid-chemical aspects and can be solved satisfactorily only by paying proper attention to the latter.

There are of course quite a number of other factors to be considered in the analysis of an actual case of frost heaving, such as the influence of repeated freezing and thawing periods which tends to aggregate the primary smaller lenses into secondary larger structures. Though much work has been done on frost heaving, especially by such pioneers as Taber,[14] Beskow,[15] and others,[16] its complexity makes it still one of the great and very incompletely understood problems in highway and airport engineering.

As previously stated, the purpose of this treatment was to show that the destructive action of climate on highway pavements and bases is not so much a function of the average moisture and temperature level, but rather of the moisture and temperature fluctuations occurring in the respective structures. The better the action mechanisms of climate are understood the greater is the chance for the development of stabilization methods which prevent or counteract the destructive forces involved.

Different Methods of Soil Stabilization

According to the previous discussions, internal friction in the engineering sense is a property of coarse grain sizes, such as sand, gravel, and rock, while cohesion is due to the combined action of clay and colloidal particles and their water films. Friction thus defined is practically independent of the moisture content, while cohesion is practically governed by the latter. Purely frictional material, such as dry sand, has

no stability unless it is under a confining pressure. Purely cohesive material may have extremely high strength when dry and practically none when wet. These facts indicate the main lines of endeavor in soil stabilization:

(1) Supplying of cohesion to purely frictional soils;
(2) Supplying of friction to cohesive soils;
(3) Waterproofing of cohesive soils.

In addition, stabilization should provide a defense mechanism against the loosening forces of climate.

Classification of Stabilization Methods [17]

Several attempts have been made to classify soil stabilization methods from both engineering and scientific points of view. Such attempts are interesting and valuable, since they usually involve a close scrutiny of the most important phases of the different methods. So far, however, none of the available classifications has been generally accepted. The major difficulty involved is that there exists in practice, no scientifically pure type of stabilization; mechanical, physical, physico- and colloid-chemical, and chemical phenomena are encountered in every field method employed. The usage evolving at the present time indicates the type of mixture or admixture involved in a stabilized soil system such as: clay-aggregate, soil-bitumen, soil-cement, etc. No attempt of classification of the different practical methods is made at this place; however, it has seemed desirable to list different items which singly or combined are of importance in the different stabilization methods as used at the present time.

(1) Mechanical: manipulation and compaction of cohesive soils at their optimum liquid content to greatest density obtainable with available equipment, and vibration for densification of non-cohesive soils;
(2) Physical: establishment of proper gradation of coarse and fine soil constituents, *e.g.*, clay-gravel and sand-clay systems;
(3) Physico-Chemical and Colloid-Chemical: change of soil properties by surface-chemical effects, inorganic and organic cements, etc.

As previously stated, every practical stabilization method may involve any one, two, or all three of the above-named principles. The following specific treatment is given under the generally accepted engineering names: granular stabilization, soil-bitumen, soil-cement, etc.

Stabilization by Densification

This comprises the densification of soils to increase their frictional and cohesive stability, and to decrease the pore volume and its accessibility to water.

With purely frictional material such as gravel and sand, densification is usually obtained by application of mechanical impact forces often applied in a certain rhythm (vibration). Because of its lubrication effect, water is often employed in this type of densification. The amount of water used is not critical because of the small amount of mineral surface available per unit volume of soil material. Excess of water will easily drain off.

Densification of cohesive soils is governed by their water content and by the compactive effort. In densification the soil particles must be moved over one another. In a dry, pulverized, cohesive soil this movement is resisted by the friction between the soil particles; also densification is resisted by the adsorbed air films, which show considerable elasticity. In extreme cases these air films may impart to the soil flow properties similar to those of liquids.* In very wet condition the soil

* This is strikingly shown by carbon blacks, many of which flow like water because of adsorbed air. J. A.

particles are kept apart by the adsorbed water films. There exists an intermediate condition where the soil particles possess water films of such thickness and of such consistency of the outermost layer that they are easily moved over each other under the applied compaction forces. This is the optimum moisture content for the compactive effort employed and results in the maximum density obtainable by the latter. For greater compactive effort the optimum moisture content moves toward smaller values. It is to the great merit of Proctor to have demonstrated to the engineer the basic principles involved in the compaction of cohesive soils, and to have worked out a laboratory method in which the compactive effort of the then available field compaction equipment was duplicated.[18] This procedure permitted laboratory determination of the optimum moisture content and of the maximum density obtainable in the field, the values obtained forming the basis for construction specifications. Recent developments in compaction machinery have made it necessary to modify the original Proctor procedure without, however, encroaching on the established fundamental principles. Compaction tests based on these principles have been standardized by several national organizations and are available in specification form.[19]

The optimum moisture content for a particular compactive effort is, of course, a function of the specific surface of a soil system and of its chemical and physical character. This has been demonstrated especially by the work of Winterkorn and his school.[2] Graph 2 shows typical Proctor curves for soils of different texture and consequently different amounts and types of specific surface. Table 1 gives the

Table 1. The Size Composition of Soils, The Optimum Moisture Content and Maximum Density of Which Are Given in Graph II

Soil Symbol	Texture		
	Sand	Silt	Clay
B	67	11	22
E	50	32	18
G	30	56	14
L	55	28	17
M	45	30	25
N	33	27	40
P	77	12	11
U	39	41	20
V	34	21	45

mechanical composition of these soils. Graph 3 shows Proctor curves for different modifications of Putnam clay, the modifications having been made by substitution of specific cations for those adsorbed on the internal surface of the natural soil. While the amount of internal surface present in the different modifications is thus the same, the structure of the adsorbed water films is different because of the difference in the ionic atmosphere surrounding the solid soil constituents.

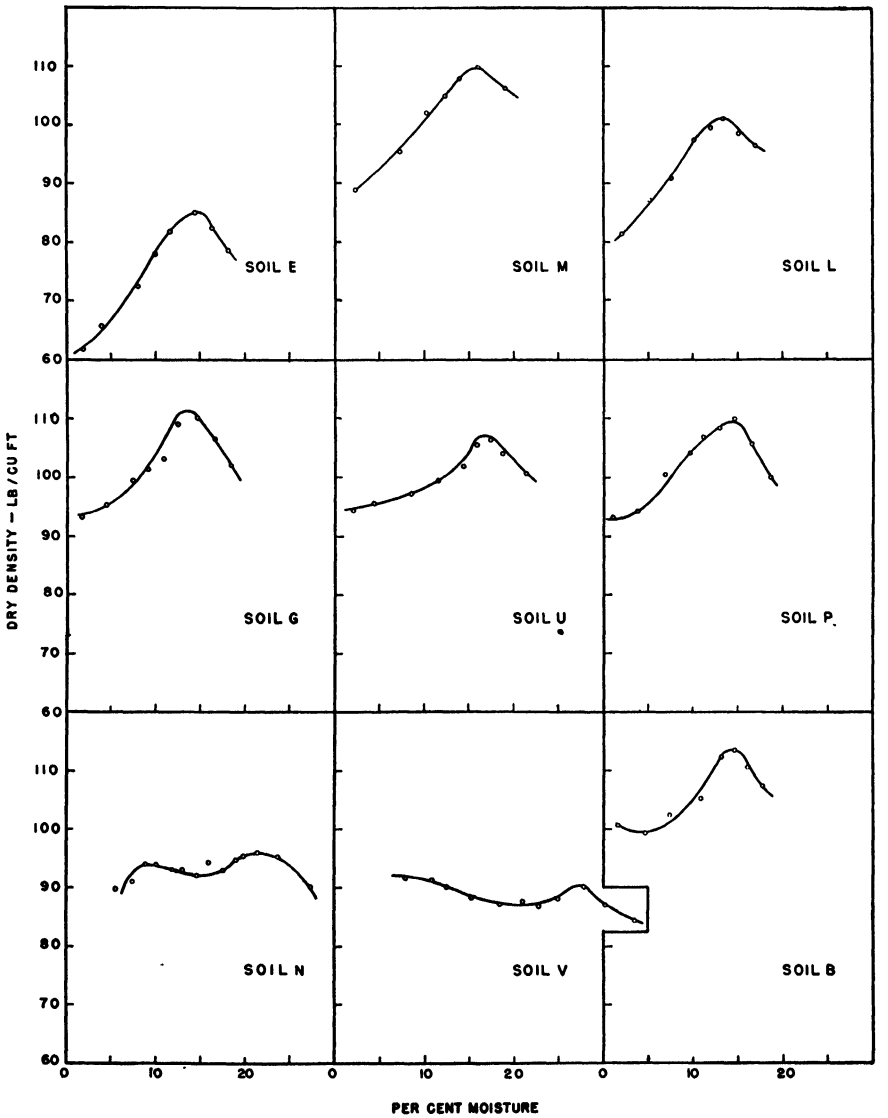
The compaction principles demonstrated by Proctor are employed in the construction of earth dams, fills, and levees, in the preparation of shallow foundations for buildings and highways, and in combination with all other types of soil stabilization. The work of Proctor may be judged as one of the most important contributions to soil engineering. It may be of interest, and it is of physical significance, that the optimum moisture content of a specific soil as determined by the original Proctor method is usually close to its plastic limit. The latter represents that moisture content, at which a cohesive soil may just be rolled out by slight pressure of the hand into threads ⅛″ in diameter without crumbling.

Granular Soil Stabilization: Clay-Gravel, Sand-Clay [20]

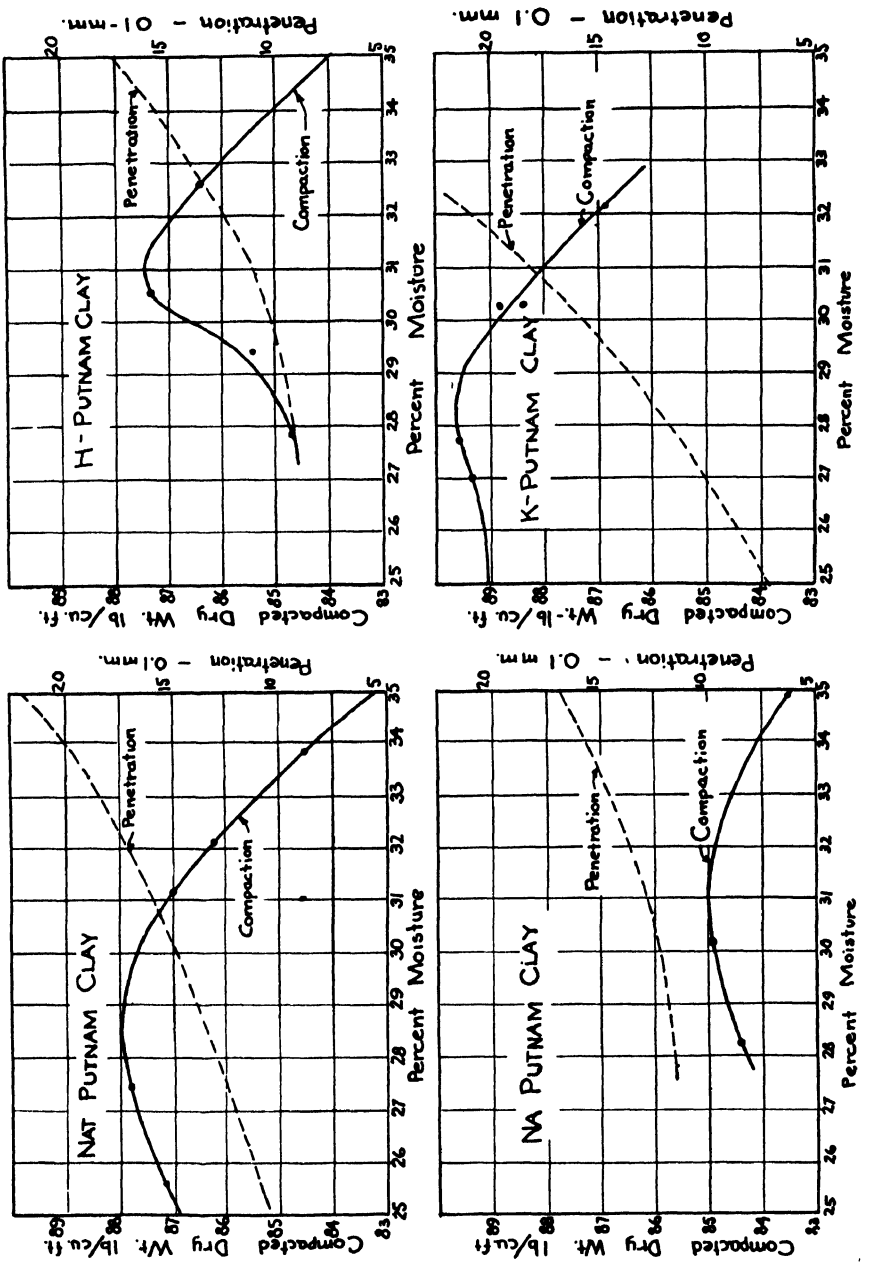
This type of stabilization is based mainly on physical phenomena. Stability under both wet and dry conditions is sought by proper blending of cohesive soils with granular aggregate, whereby the latter may range from the size of sand to that of large gravel. The fine and coarse portions of the blend may both be of natural origin

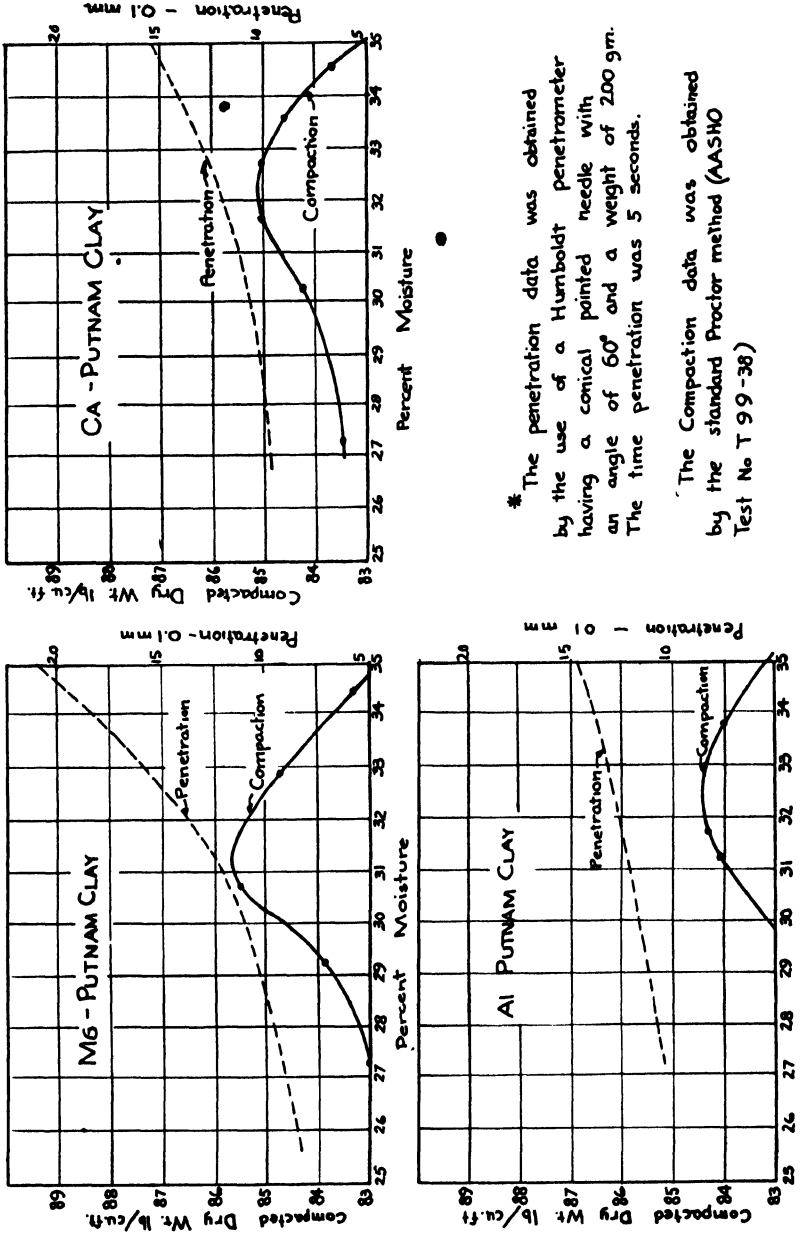
and thus represent soil material, or one of the components of the system may be an artificially prepared material such as crushed rock, slag, mining chat (tailings), screenings, rock flour, etc.

It is easy to see that the optimum gradation of a soil material would change with the purpose and location for which this material is intended. The gradation is, of course, also limited by the maximum particle size to be used. Table 2 gives typical gradation specifications as recommended by the American Society for Testing Materials (A. S. T. M.). Differentiation is made between the composition of the surface course and of the base course. The surface course requires more soil binder and needs greater cohesion in order to resist the abrasive effect of traffic. The base course



GRAPH 2. Results of the Proctor compaction tests.


H-PUTNAM CLAY
K-PUTNAM CLAY
NAT PUTNAM CLAY
NA PUTNAM CLAY
Penetration
Compaction
Penetration — 0.1 mm.
Compacted Dry Wt. lb/cu. ft.
Percent Moisture



GRAPH 3. Proctor compaction and penetration curves * for natural and homoionic putnam soils.

Table 2. Tentative Specifications

Materials For Stabilized Base Course

Type A

Sieve	Percentage Passing
1-in	100
No. 10 (2000-micron)	65 to 100
The material passing the No. 10 sieve shall conform to the following requirements:	
No. 10 (2000-micron)	100
No. 20 (840-micron)	55 to 90
No. 40 (420-micron)	35 to 70
No. 200 (74-micron)	8 to 25 [a]

Type B

Sieve	Percentage Passing B-1 1-in max size	Percentage Passing B-2 2-in max size
2-in		100
1½-in		70 to 100
1-in	100	55 to 85
¾-in	70 to 100	50 to 80
⅜-in	50 to 80	40 to 70
No. 4 (4760-micron)	35 to 65	30 to 60
No. 10 (2000-micron)	25 to 50	20 to 50
No. 40 (420-micron)	15 to 30	10 to 30
No. 200 (740-micron)	5 to 15 [a]	5 to 15 [a]

Type C

Sieve	Percentage Passing
¾-in	100
No. 4 (4760-micron)	70 to 100
No. 10 (2000-micron)	35 to 80
No. 40 (420-micron)	25 to 50
No. 200 (74-micron)	8 to 25 [a]

[a] The %-age passing the No. 200 sieve shall be not more than ⅔ of that passing the No. 40 sieve.

Materials For Stabilized Surface Course

Type A

Sieve	Percentage Passing
1-in	100
No. 10 (2000-micron)	65 to 100
The material passing the No. 10 sieve shall conform to the following requirements:	
No. 10 (2000-micron)	100
No. 20 (840-micron)	55 to 90
No. 40 (420-micron)	35 to 70
No. 200 (74-micron)	8 to 25 [a]

Type B

Sieve	Percentage Passing
1-in	100
¾-in	85 to 100
⅜-in	65 to 100
No. 4 (4760-micron)	55 to 85
No. 10 (2000-micron)	40 to 70
No. 40 (420-micron)	25 to 45
No. 200 (74-micron)	10 to 25 [a]

Type C

Sieve	Percentage Passing
¾-in	100
No. 4 (4760-micron)	70 to 100
No. 10 (2000-micron)	35 to 80
No. 40 (420-micron)	25 to 50
No. 200 (74-micron)	8 to 25 [a]

[a] The %-age passing the No 200 sieve shall be not more than ⅜ of that passing the No. 40 sieve.

should possess as low a water affinity and, consequently, as low a clay content as feasible, in order that swelling and softening of the base course may be kept within permissible limits. The permissible amount and activity of the clay in such a system is expressed indirectly by the limitation of the plastic index of the material passing the No. 40 sieve. It is obvious that specifications as given by the A. S. T. M., the Public Roads Administration (P. R. A.) and other federal, state, and industrial agencies give only general limitations, but that for each purpose and each specific location, an optimum exists, which has to be found by trial and error. Unfortunately, this fact is finding only slow recognition. For the reasons indicated, theory and practice of physical soil stabilization should be correlated with and should be based on all available experience of soil usage.

A proper way to approach the problem of proper gradation for a particular purpose is to analyze what makes a soil especially adapted for this purpose. This type of approach is also basic for a "use classification" of soils. Fortunately, two such classifications have been available for some time, *viz.*, the system of the P. R. A. (see Table 3), and that proposed by Professor Casagrande (see Table 4). Recently the Civil Aeronautics Administration (C. A. A.) has brought forth a third classification, which seems to be closely related to that of the P. R. A. The special merit of the C. A. A. classification appears to be the recognition of the climatic factors; this, however, is still rudimentary.

Most experience in subgrade soil behavior and in soil stabilization has been correlated with the P. R. A. classification, whereby the obvious inadequacies of the latter were taken care of by simultaneous use of the pedological classification of Marbut.* The Casagrande system avoids some of the pitfalls of the P. R. A. scheme; it is more positive in its implications, and, for this reason, it has been adopted by the Army Engineers, for whose purposes it serves well. However, this scheme neglects to supply the information usually supplied by the pedologic system, which is normally used in conjunction with the P. R. A. classification. The positiveness of Casagrande's system, which is its main advantage for use by the Army Engineers, probably represents a drawback from the point of view that it may give an erroneous impression of much greater soil knowledge than is really possessed by the engineer. Thus it may actually impede the acquisition by the engineer of important pedological knowledge.

The proposed soil gradations and the classification schemes make it appear that all that is required for the soil engineer is to get the right gradation of the soil material and the right plasticity index for the binder portion which is that material which passes the No. 40 sieve. It is well known that the action of a soil binder depends not only on its own intrinsic properties but also upon the properties of the material, in this case the aggregate, which it is supposed to bind. It was shown by Hubbard [21] thirty years ago that the type of filler employed in water-bound macadam played a great role as far as the stability of the pavement is concerned. Also, every road builder is acquainted with the better adhesion of podsolic clay to limestone and other basic rock, as compared with its adhesion to quartz and other acidic minerals. The reasons for these phenomena are obvious on the basis of the electrostatic theory of soil cohesion. In the design of any clay-aggregate mixture it must be kept in mind that:

(1) An addition of fine materials to larger aggregates does not just fill the available pore space, but the fines are also adsorbed on the surface of the larger particles, thereby increasing the total volume. The thicker this film, the more the behavior of the wet system will approach that of wet soil fines. Therefore, only such an amount of fines should be incorporated in the structure as will not appreciably separate the coarse particles from one another.

* Good examples of this are the procedures employed especially by the State Highway Departments of Michigan, Missouri, and Indiana, respectively.

(2) Soil with a high plastic index (plate shaped clay particles, large base exchange capacity, relatively uniform electrostatic character) will improve the dry and wet cohesion of the system, if the aggregate is of an opposite electrostatic character or if there exists a chance for hydrogen linkage. Otherwise, a high plastic index may indicate detrimental volume change and loss of stability when wet. Governing factors of what the effect of exposure to moisture will be, are the relative dryness and

Table 3. Summary of Soil Characteristics and Classification
(Public Roads, Febr. 1942)

Group	A-1	A-2		A-3
		Friable	Plastic	
General stability properties.	Highly stable at all times.	Stable when dry; may ravel.	Good stable material.	Ideal support when confined.
Physical constants:				
Internal friction	High	High	High	High
Cohesion	do	Low	do	None
Shrinkage	Not detrimental	Not significant	Detrimental when poorly graded	Not significant
Expansion	None	None	Some	Slight
Capillarity	do	do	do	do
Elasticity	do	do	do	None
Textural classification:				
General Grading	Uniformly graded; coarse-fine excellent binder.	Poor grading; poor binder.	Poor grading; inferior binder.	Coarse material only; no binder.
Approximate limits:				
Sand..per cent	70-85	55-80	55-80	75-100
Silt....do	10-20	0-45	0-45	[1]
Clay...do	5-10	0-45	0-45	[1]
Physical characteristics:				
Liquid limit	14-35 [2]	35 (maximum).	35 (maximum)	NP [3]
Plasticity index	4 9 [2]	NP-3 [3]	3-15	NP [3]
Fld. moisture equivalent	Not essential	Not essential.	Not essential	Not essential.
Centrifuge moisture equivalent	15 (maximum).	12-25.	25 (maximum)	12 (maximum).
Shrinkage limit	14-20	15-25	25 (maximum)	Not essential.
Shrinkage ratio	1.7-1.9	1.7-1.9	1.7-1.9	do
Volume change	0-10	0-6	0-16	None
Lineal shrinkage	0-3	0-2	0-4	do
Compaction characteristics:				
Maximum dry weight, lbs per cu ft	130 (minimum).	120-130	120-130	120-130
Opt. moisture, %-age of dry weight (approximate)	9	9-12.	9-12	9-12
Maximum field compaction required, percentage of maximum dry weight, lbs per cu foot	90	90	90	90
Rating for fills 50 ft or less in height	Excellent	Good	Good	Good
Rating for fills more than 50 ft in height	Good	Good to fair.	Good to fair	Good to fair
Required total thickness for subbase, base and surfacing, inches	0-6	0-6	2-8	0-6

[1] Percentage passing No. 200 sieve, 0-10.
[2] When used as a base course for thin flexible surfaces the plasticity index and liquid limit should not exceed 6 and 25, respectively.
[3] NP—nonplastic.

the water attraction potential of the soil, the permeability of the soil, and the time of exposure to water (See: Mechanism of Water Attack on Dry Cohesive Systems).

(3) If a graded structure is used as a road base, the frictional stability caused by confining effect of surface course, combined with a surface-tension cohesion due to normal moisture content, is usually sufficient without required recourse to clay-furnished cohesion. For base courses, the plastic index of the binder should, therefore, be low or even zero.

(4) For surface courses small amounts of clay with a large plastic index, furnishing marked electrostatic cohesion, and preferably with a large ratio of osmotic to

A-4	A-5	A-6	A-7	A-8
Satisfactory when dry; loss of stability when wet or by frost action.	Difficult to compact; stability doubtful.	Good stability when properly compacted.	Good stability when properly compacted.	Incapable of support
Variable	Variable	Low	Low	Low.
....do	Low	High	High	do.
....do	Variable	Detrimental	Detrimental	Detrimental.
....do	High	High	....do	do.
Detrimental	....do	....do	High	do.
Variable	Detrimental	None	....do	do.
Fine sand cohesionless silt and friable clay.	Micaceous and diatomaceous.	Deflocculated cohesive clays.	Drainable flocculated clays.	Peat and muck.
55 (maximum)	55 (maximum)	55 (maximum)	55 (maximum)	55 (maximum).
High	Medium	Medium	Medium	Not significant
Low	Low	30 (minimum)	30 (minimum)	do.
20-40	35 (minimum)	35 (minimum)	35 (minimum)	35-400.
0-15	0-60	18 (minimum)	12 (minimum)	0-60.
30 (maximum)	30-120	50 (maximum)	30-100	30-400.
Not essential	Not essential	Not essential	Not essential	Not essential.
20-30	30-120	6-14	10-30	30-120.
1.5-1.7	0.7-1.5	1.7-2.0	1.7-2.0	0.3-1.4.
0-16	0-16	17 (minimum)	17 (minimum)	4-200.
0-4	0-4	5 (minimum)	5 (minimum)	1-30.
110-120	80-100	80-110	80-110	90 (maximum)
12-17	22-30	17-28	17-28	
95	100	100	100	Waste.
Good to poor	Poor to very poor.	Fair to poor	Fair to poor	Unsatisfactory.
Fair to poor	Very poor	Very poor	Very poor	do.
9-18	9-24	12-24	12-24	

Table 4. Casagrande Soil Classification for Airfield Projects[1]

1		2	3	4		5	6	7
Major Divisions		Soil Groups & Typical Names	Suggested Group Symbols	General Identification		Observations and Tests Relating to Material in Place	Principal Classification Tests (on Disturbed Samples)	Value as Foundation When Not Subject to Frost Action
				Dry Strength	Other Pertinent Exams.			
COARSE GRAINED SOILS	Gravel and Gravelly Soils	Well Graded Gravel & Gravel-Sand Mixtures, Little or No Fines	GW	None	Gradation, Grain Shape	Dry Unit Weight or Void Ratio,	Mechanical Analysis	Excellent
		Well Graded Gravel-Sand-Clay Mixtures, Excellent Binder	GC	Medium to High	Gradation, Grain Shape, Binder Exam. Wet & Dry	Degree of Compaction,	Mechanical Analysis Liquid & Plastic Limits on Binder	Excellent
		Poorly Graded Gravel & Gravel-Sand Mixtures, Little or No Fines	GP	None	Gradation, Grain Shape	Cementation, Durability of Grains	Mechanical Analysis	Good to Excellent
		Gravel with Fines, Very Silty Gravel, Clayey Gravel, Poorly Graded Gravel-Sand-Clay Mixtures	GF	Very Slight to High	Gradation, Grain Shape Binder Exam. Wet & Dry	Stratification & Drainage Characteristics,	Mechanical Analysis, Liquid & Plastic Limits on Binder if Applicable	Good to Excellent
	Sands and Sandy Soils	Well Graded Sands & Gravelly Sands, Little or No Fines	SW	None	Gradation, Grain Shape	Ground Water Conditions,	Mechanical Analysis	Excellent to Good
		Well Graded Sand-Clay Mixtures, Excellent Binder	SC	Medium to High	Gradation, Grain Shape, Binder Exam. Wet & Dry	Traffic Tests,	Mechanical Analysis, Liquid & Plastic Limits on Binder	Excellent to Good
		Poorly Graded Sands, Little or No Fines	SP	None	Gradation, Grain Shape	Large Scale Load Tests	Mechanical Analysis	Fair to Good
		Sand with Fines, Very Silty Sands, Clayey Sands, Poorly Graded Sand-Clay Mixtures	SF	Very Slight to High	Gradation, Grain Shape, Binder Exam. Wet & Dry	California Bearing Tests	Mechanical Analysis, Liquid & Plastic Limits on Binder if Applicable	Fair to Good
FINE GRAINED SOILS Containing Little or No Coarse Grained Material	Fine Grained Soils Having Low to Medium Compressibility	Silts (Inorganic) & Very Fine Sands, Mo, Rock Flour, Silty or Clayey Fine Sands with Slight Plasticity	ML	Very Slight to Medium	Examination Wet (Shaking Test & Plasticity)	Dry Unit Weight, Water Content & Void Ratio,	Mechanical Analysis, Liquid & Plastic Limits if Applicable	Fair to Poor
		Clays (Inorganic) of Low to Medium Plasticity, Sandy Clays, Silty Clays, Lean Clays	CL	Medium to High	Examination in Plastic Range	Consistency—Undisturbed & Remolded	Liquid & Plastic Limits	Fair to Poor
		Organic Silts & Organic Silt-Clays of Low Plasticity	OL	Slight to Medium	Examination in Plastic Range—Odor	Stratification, Root Holes, Fissures Etc, Drainage & Ground Water Conditions, Traffic Tests,	Liquid & Plastic Limits From Natural Condition & After Oven Drying	Poor
	Fine Grained Soils Having High Compressibility	Micaceous or Diatomaceous Fine Sandy & Silty Soils, Elastic Silts	MH	Very Slight to Medium	Examination Wet (Shaking Test & Plasticity)	Large Scale Load Tests, California Bearing Tests or Compression Tests	Mechanical Analysis, Liquid & Plastic Limits if Applicable	Poor
		Clays (Inorganic) of High Plasticity, Fat Clays	CH	High	Examination in Plastic Range		Liquid & Plastic Limits	Poor to Very Poor
		Organic Clays of Medium to High Plasticity	OH	High	Examination in Plastic Range—Odor		Liquid & Plastic Limits From Natural Condition & After Oven Drying	Very Poor
Fibrous Organic Soils with Very High Compressibility		Peat and Other Highly Organic Swamp Soils	Pt	Readily Identified		Consistency, Texture	and Natural Water Content	Extremely Poor

[1] ENGINEERING MANUAL, Chapter XX, Part II, Exhibit 1 (U S ENGINEER DEPARTMENT)

Major Divisions		8 Value as Wearing Surface for Stage or Emergency Construct. With Dust Palliative	8 Value as Wearing Surface for Stage or Emergency Construct. With Bit. Surface Treatment	9 Potential Frost Action	10 Shrinkage, Expansion, Elasticity	11 Drainage Characteristics	12 Compaction Characteristics and Equipment	13 * Solids at Opt. Compaction Lb per Cu Ft Void Ratio, e	14 Cal. Bearing Ratio for Compacted & Soaked Specimen	15 Comparable Groups in Public Roads Classification
COARSE GRAINED SOILS	Gravel	Fair to Poor	Excellent	None to Very Slight	Almost None	Excellent	Excellent, Tractor	>125 e<0.35	>50	A-3
	and	Excellent	Excellent	Medium	Very Slight	Practically Impervious	Excellent, Tamping Roller	>130 e<0.30	>40	A-1
	Gravelly	Poor	Poor to Fair	None to Very Slight	Almost None	Excellent	Good, Tractor	>115 e<0.45	25-60	A-3
	Soils	Poor to Good	Fair to Good	Slight to Medium	Almost None to Slight	Fair to Practically Impervious	Good, Close Control Essential, Rubber Tired Roller, Tractor	>120 e<0.40	>20	A-2
	Sands	Poor	Good	None to Very Slight	Almost None	Excellent	Excellent, Tractor	>120 e<0.40	20-60	A-3
	and	Excellent	Excellent	Medium	Very Slight	Practically Impervious	Excellent, Tamping Roller	>125 e<0.35	20-60	A-1
	Sandy	Poor	Poor	None to Very Slight	Almost None	Excellent	Good, Tractor	>100 e<0.70	10-30	A-3
	Soils	Poor to Good	Poor to Good	Slight to High	Almost None to Medium	Fair to Practically Impervious	Good, Close Control Essential, Rubber Tired Roller, Tractor	>105 e<0 60	8-30	A-2
FINE GRAINED SOILS Containing Little or No Coarse Grained Material	Fine Grained Soils Having Low to Medium Compressibility	Poor		Medium to Very High	Slight to Medium	Fair to Poor	Good to Poor, Close Control Essential, Rubber Tired Roller	>100 e<0.70	6-25	A-4 A-6 A-7
		Poor		Medium to High	Medium	Practically Impervious	Fair to Good, Tamping Roller	>100 e<0.70	4-15	A-4 A-6 A-7
		Very Poor		Medium to High	Medium to High	Poor	Fair to Poor, Tamping Roller	>90 e<0.90	3-8	A-4 A-7
	Fine Grained Soils Having High Compressibility	Very Poor		Medium to Very High	High	Fair to Poor	Poor to Very Poor	>100 e<0.70	<7	A-5
		Very Poor		Medium	High	Practically Impervious	Fair to Poor, Tamping Roller	>90 e<0.90	<6	A-6 A-7
		Useless		Medium	High	Practically Impervious	Poor to Very Poor	<100 e>0.70	<4	A-7 A-8
Fibrous Organic Soils with Very High Compressibility		Useless		Slight	Very High	Fair to Poor	Compaction Not Practical			A-8

* These weights apply only to soils having specific gravities from 2.65 to 2.75.
Values in columns 7 and 8 are for guidance only.
Values in column 7 are not for base courses *directly* under wearing surface.

hydration swelling,[4] is most appropriate. In dry weather, the electrostatic attraction increases the stability of the road, while in wet weather the osmotic swelling closes the pores making the soil impervious to water, without possessing enough energy to push the soil system apart.

These considerations indicate that there is no such thing as a pure type of stabilization. As closely as one may define physical stabilization, one still encounters physico-chemical and chemical effects. Such effects are still more obvious if solutions of salts such as NaCl, $CaCl_2$, sea water, or others, are added to the soil mixture for the purpose of attracting or retaining moisture during the dry season and thus preventing dusting and raveling. While calcium chloride, because of its hygroscopic nature, is known in free condition to attract water from the atmosphere, it is impossible to predict entirely what it will do if part of a soil system. A portion of it may remain in the soil solution as calcium and chloride ions; the calcium ions may undergo exchange reactions with the colloidal soil complexes, etc. It was observed by Winterkorn in Missouri in 1932 that calcium chloride treated sections of an experimental road looked and behaved "wetter" than adjoining untreated sections; however, analysis showed that the sections without calcium chloride actually contained more moisture.

Admixture of sodium chloride with a soil to enhance water retention, exerts usually the additional effect of dispersing the clay material, leading to greater compacted densities and decreasing the permeability of the treated systems.

Soil-Bitumen [22]

The best known examples of stabilization methods in which physico-chemical phenomena play a more or less determinant role, are those in which bitumen is employed as a waterproofing or cementing agent. Soil-bituminous systems have found their greatest use in the construction of road bases and surfaces; some use has also been made in low cost housing and in water-proofed adobe construction for exposition buildings.

If a soil is of the cohesive type, it possesses satisfactory bearing capacity at low moisture contents. In such a soil, bitumen is incorporated as a waterproofing agent to maintain a low moisture content and an adequate bearing capacity. If a soil is of the non-cohesive, granular type, bitumen is incorporated to act as a binding or cementing medium.

Depending upon the mechanical composition of the available soil material and the function of the bitumen incorporated, there are four types of bituminous soil stabilization in common use today:

(1) Soil-bitumen proper, a waterproofed cohesive soil system;
(2) Sand-bitumen, a system in which loose beach, dune, or other sand of similar character is cemented together by bituminous material;
(3) Waterproofed mechanical stabilization in which the soil material possesses good gradation from coarse to fine constituents, meeting certain high potential density requirements, and is waterproofed by uniform distribution of small amounts of bitumen;
(4) Oiled earth, in which the surface of an earth road is made water resistant by the application of slow or medium curing road oils.

The term "soil," as used in this paper, comprises: bank gravel, bank sand, beach and dune sand, agricultural soils ranging from those of predominantly sandy texture to colloidal clays, and mixtures and combinations of these materials.

Similarity in gradation of two soil materials indicates a certain similarity in their general behavior; however, the gradation as determined by sieving and sedimentation does not give any information concerning such important properties as hardness and

angularity of the coarse fractions, or shape and mineralogical and chemical composition of the finer fractions. Hardness and angularity are important for mechanical stability if gravel and sand particles predominate, while the shape and the mineralogical and chemical composition of the clay particles determine the water affinity and the swelling properties of fine-grained soils.

The bituminous materials employed are of two general types; asphalts and tars. The specific grades used for soil-bituminous roads are of liquid consistency at normal temperatures and include: road oils (SC-2, SC-3), medium curing cutbacks (MC-2, MC-3), rapid curing cutbacks (RC-1, RC-2, RC-3), slow-setting emulsified asphalts, and tars (RT-3 to RT-6).

Soil-Bitumen Proper

The term "soil-bitumen" is usually applied to cohesive soils which have been waterproofed by means of a bituminous admixture. The amount of bitumen required to obtain a certain degree of waterproofing depends upon the water affinity of the soil and the type of bitumen; it averages between five and seven per cent on the basis of the dry weight of the soil. In general, water affinity and bitumen requirements increase with increasing clay content. Presence of a considerable amount of sand and (or) gravel decreases the bitumen requirements and increases the general mechanical stability of the system. The advantages of a well graded soil are therefore obvious. Most suitable to this type of stabilization are soils with compositions falling within the following grain-size limits:

(1) Maximum size; not greater than approximately one-third the compacted thickness, or the same size as the thickness of a compacted lift if the latter is a fraction of the thickness of the base.
(2) Passing No. 4 sieve; more than 50 per cent.
(3) Passing No. 40 sieve; 35 to 100 per cent.
(4) Passing No. 200 sieve; not more than 50 nor less than 10 per cent.

The soil fraction passing the No. 40 sieve should preferably have a liquid limit smaller than forty and a plasticity index smaller than eighteen.

If the size composition of a soil varies greatly from the above limits, one must judge whether the desired action of the bitumen is to effect waterproofing or to supply cohesion. If it is a matter of waterproofing, the bitumen requirement increases generally with increasing clay and colloid content; however, soils of like clay content may require different amounts of bitumen, depending upon the water affinity of the clay, which in turn is a function of mineralogical and chemical factors. Concerning the latter, the following statements are made on the basis of fundamental research work and of a considerable amount of field experience.[28]

(1) The higher the amount of silica contained in the clay minerals, the greater are the bitumen requirements for satisfactory stabilization. Highly siliceous clay minerals are of the montmorillonite, illite, and related types; low-silica clay minerals are of the kaolinite type.

(2) The higher the amount of iron and aluminum compounds in the clay minerals, the smaller is the amount of bitumen required for satisfactory stabilization; this, of course, is a consequence of the facts stated in the preceding paragraph.

(3) The higher the valences of the exchangeable cations in the clay, *i.e.*, Na, K, Ca, Al and others, the easier can bituminous stabilization be achieved.

(4) The effect of organic soil constituents depends upon the conditions under which the organic material was formed and accumulated. Acid organic matter from leached forest and river bottom soils appears to be definitely detrimental, while neutral and basic organic matter from arid and semi-arid regions does not seem to possess a detrimental effect, other than that produced at times by the presence of monovalent ions.

(5) Among the monovalent ions, sodium appears always to be detrimental, while potassium may be either detrimental or beneficial.

Sand-Bitumen

Sand-bitumen designates a beach, dune, or other sand, the particles of which are cemented together by means of bitumen. The amount of bitumen required depends upon the gradation of the sand, and generally ranges between four and ten per cent, on the basis of the dry weight of the sand.

Sand

Since sand-bitumen is a well established type of construction, definite recommendations can be made. The sand employed must have reasonable inherent stability. Testing for this stability is done either by means of the Florida Bearing Value method or by the Asphalt Institute method (Construction Specification RM-3 for Sand-Asphalt). These stability requirements are usually fulfilled if the sand contains up to twelve per cent of −200 mesh material or up to ten per cent of clay.

Sands which fail to meet the specified strength requirements may be brought up to specification by a suitable admixture. Frequently, non-cohesive filler is found in the vicinity, and the cost of providing a suitable admixture is low. Sometimes it is desirable to add one per cent of Portland cement to aid in overcoming hydrophilic properties of the sand. This cement admixture also accelerates drying in the base, especially if bitumen emulsions are employed. Of special importance in this type of stabilization is the adhesiveness of the bitumen to the sand.[24]

Bitumen

The bituminous materials commonly used are cutback asphalts (RC-1, RC-2, and RC-3), coal tar (RT-6, RT-7, RT-8), or emulsified asphalt (fine aggregate mixing grade meeting the specifications for this type of construction). The quantity of bitumen employed ranges from 0.3 to 1.3 gallons per square yard per inch thickness. The exact proportions are specified on the basis of laboratory tests correlated with field experience.

Waterproofed Mechanical Stabilization *

As the name indicates, systems in this classification consist of soil materials approaching the gradation required for mechanical stabilization in which the soil binder is waterproofed by addition of small amounts (one to three per cent) of bitumen.

For mechanically stabilized mixtures of the coarse aggregate type, *i.e.*, made from gravel, sand, and clay binder, the grading of the finished mix should be as follows:

	Range (%)	Ideal (%)
Passing 1-inch square screen	100	100
Passing No. 4 sieve	50 to 75	70
Passing No. 10 sieve	35 to 60	50
Passing No. 40 sieve	20 to 35	27
Passing No. 100 sieve	13 to 23	18
Passing No. 200 sieve	10 to 16	13

For mechanically stabilized mixtures, of the fine aggregate type, *i.e.*, containing no particles larger than No. 4 sieve, the grading of the finished mix should be as follows:

	Range (%)	Ideal (%)
Passing 1-inch square screen		100
Passing No. 4 sieve	80 to 100	100
Passing No. 10 sieve	65 to 100	85
Passing No. 40 sieve	35 to 65	52
Passing No. 100 sieve	25 to 45	35
Passing No. 200 sieve	20 to 35	25

* This treatment follows very closely the work of McLeod[25] who deserves complete credit for the development of this type of stabilization.

A finished mixture having a grading which tends to vary from the minimum specified for passing one sieve to the maximum specified for passing the next coarser sieve, should not be tolerated. The bituminous material should be distributed throughout the stabilized soil as a waterproofing agent, all particles of aggregate and clay binder being uniformly coated.

When the finished mixture is of the coarse aggregate type, it should contain from one to two (specify) per cent of RC-1 liquid asphalt, and when of the fine aggregate type, it should contain from two to three (specify) per cent of RC-1 liquid asphalt, homogeneously distributed throughout the stabilized mixture as a waterproofing material. All particles of aggregate and clay binder must be coated uniformly with this liquid asphalt.

The moisture content of the finished stabilized mixture should be between 5.5 and 6.5 per cent for the coarse aggregate type, and between 7.0 and 9.0 per cent for the fine aggregate type in order to facilitate later rolling operations on the highway or runway.

Waterproofed mechanically stabilized base courses, or other soil-bitumen base courses, should not be used:

(1) Where rainfall is so high and regular that the periods of dry weather are of insufficient duration to lower the moisture content of the base course to the three to four per cent required for developing reasonable bearing capacity without causing construction delays.

(2) Where it would be in perpetual contact with free water (because the water table is near the elevation of the grade line, etc.) which would keep it saturated and therefore weak.

(3) Where the subgrade is not firm and properly designed. It will fail like any other base course under this condition.

(4) Unless adequate field laboratory control is provided over every phase of construction, to insure proper proportioning of the ingredients at the mixing plant, thorough mixing, and ample control of the density obtained during rolling operations.

Construction Procedures

To give the desired service, soil-bitumen must not only contain the right amount of bitumen, but it must also be properly mixed and compacted. To insure proper mixing no large clay clods are permitted, and it is usually specified that at least 85 per cent of aggregated soil fines must pass the No. 4 mesh sieve. In practice the loosening up of the soil and the pulverization of the clay is usually performed by means of plows, scarifiers, Killefer discs, and similar equipment. The mixing is done either by blading and discing, or by traveling or stationary plants.

In the case of slow-curing bituminous material and bituminous emulsions, water is often added to the mixture. In this case the sum of the water and bitumen should not exceed the pore volume of the mixture after compaction. Compaction is done either by means of loaded trucks and multiple-wheel pneumatic tire rollers, in layers of approximately two inch compacted thickness, or by means of sheep-foot rollers, in layers of six inch compacted thickness. Flat rollers are employed for the final smoothing of the surface. In the case of a cohesive subgrade, the latter should be primed with about one third of a gallon per square yard of cutback asphalt, or tar.

Wearing Surfaces

With the exception of certain sand-bitumen types, soil-bituminous mixtures are usually too friable to serve as wearing courses. They tend to wear rapidly under the scuffing of traffic, to develop an uneven surface and eventually "potholes." They should, therefore, be covered with a wearing surface very soon after construction.

The type and thickness of surfacing required for stabilized bases naturally varies

according to the anticipated volume of traffic. On relatively light traffic areas, such as auxiliary runways and light traffic roads, a very satisfactory surfacing has been found to consist of a penetrating prime followed by an application of high viscosity emulsified asphalt, RC-cutback, hot penetration asphalt, or tar. Usually four-tenths to one-half a gallon per square yard is adequate; the bitumen is covered with clean stone chips up to one-half inch in size. Where the base has a tendency to flex under the action of traffic, a thicker wearing surface is required. It should preferably consist of two or three inches of cold-mixed or hot-mixed bituminous concrete of standard design. Open, porous penetration armor-coats, or thin penetration pavements are definitely undesirable, because they are nonsealing and in wet weather become filled with free water which cannot escape readily to the subgrade due to the moisture underneath. This reservoir of water on top of the stabilized base finally produces some surface softening which, in time, results in damage to thin macadam surfacings. If a bituminous macadam wearing surface is provided, it should be well sealed to prevent entrance of surface water.

Maintenance of Soil-Bituminous Roads

If local defects in the soil-bitumen should occur, it is best to remove the defective portion as completely as possible, and to replace it with a soil-bitumen mixture of desired composition and quality.

A significant feature of soil-bituminous mixes is the adaptability to being disturbed and recompacted without material effect on the original properties of the base. It is sometimes necessary to correct soft subgrade spots by aeration, drainage installations or removal of objectionable material overlooked during construction. In such cases, the base material is recovered and recompacted on the corrected subgrade. Where areas rich in bitumen or lacking bitumen develop in the base itself, the condition can be corrected readily by remixing with additional soil material in the first case and with additional bitumen in the other.

The surface course, or wearing course, covering the base is frequently only a thin seal coat of stone or gravel chips. This course has to be replaced periodically. In preparing the worn surface for sealing, a honing disc (Killefer) has proved to be a valuable piece of maintenance equipment.

Oiled Earth [26]

Oiled earth describes the road surface produced by simple surface application of liquid bituminous materials. This method has been originally applied as dust palliative measure, but investigations, especially in the mid-western states, have proved it a very economical construction procedure for tertiary and secondary roads, when comparison is made with untreated and unsurfaced type earth roads. The amount of liquid bitumen employed is usually about one gallon per square yard. This is spread in most cases in two or three applications, the temperature of application being about 160° F. With silty soils, the depth of penetration is usually about one-half to three-quarters of an inch. With heavy soils, it is often less, while it is greater with sandy soils. Oiling should not be done on dusty and crusted earth surfaces; rather the soil should be slightly moist for best results.

Very good results have been obtained with this type of treatment especially in loess soils. The surface of oiled earth roads has the disadvantage of slipperiness in wet weather. However, blotter treatments involving the use of sand or pea gravel have been employed successfully for combatting this deficiency.

"Potholes" are a frequent and typical development associated with oiled earth roads. When reworking becomes necessary, the honing disc, mentioned earlier, may be used in smoothing up old surfaces preparatory to re-oiling. The oil requirement for such retreatments is usually one quart per square yard. Since uncured mixtures are not suitable for patching, patch material consisting of soil mixed with oil, cured

and stockpiled at intervals along the road, should be provided. A little experience in trimming, moistening, backfilling and tamping will develop a technique for making a satisfactory patch on this type of surface.

While considerable experience has been gained on soil-bitumen during the last fifteen years, it must be realized that the whole field of soil stabilization is still in a state of development. For this reason special attention should be given every new job in order that not only all available knowledge be used in design and construction, but that every project may also contribute new knowledge to the art.

Soil-Cement [27]

Laboratory research and field work have demonstrated that systems may be prepared by proper combinations of natural soil and Portland cement, which give adequate and economic service as highway and airport bases. The quality of such systems depends on the characteristics of the soil, the amount of Portland cement and the amount of water employed, and upon the density achieved by compaction. Different soils require different amounts of cement and water to produce the desired engineering properties. The latter are tested by standard methods, and the systems to be acceptable must meet certain minimum requirements. The Proctor method is used for density control. The test methods employed, and which have been approved by the American Society for Testing Materials are:

(1) "Tentative Method of Test for Moisture-Density Relations of Soil-Cement Mixtures" A. S. T. M. Designation: D 558-40 T.
(2) "Tentative Method of Wetting-and-Drying Test of Compacted Soil-Cement Mixtures" A. S. T. M. Designation: D 559-40 T.
(3) "Tentative Method of Freezing and Thawing Test of Compacted Soil-Cement Mixtures" A. S. T. M. Designation: D 560-40 T.

The freeze-thaw test involves exposure of the specimens in moist condition to 12 cycles of cooling to −10° F and thawing at room temperature, with brushing of the specimens by means of a standardized stiff wire brush after each cycle, to remove loosened material from the surface.

The wet-dry test involves 12 cycles of drying at 150° F and rewetting, with brushing after each cycle.

The permitted maximum loss of dry material by brushing after twelve cycles of wetting and drying or freezing and thawing (the most severe test being used as an indicator) are for:

(1) Sandy Soils (P. R. A. Class. A-2 and A-3) less than 14 per cent.
(2) Loamy Soils (P. R. A. Class. A-4 and A-5) less than 10 per cent.
(3) Clay Soils (P. R. A. Class. A-6 and A-7) less than 7 per cent.

These tests simulate climatic forces, and are, therefore, more appropriate and more severe than the simple water exposure tests which are employed in other types of stabilization.

Supplementary tests which furnish useful information are:

(1) Compressive strength test after seven days curing, if time is not available for the cycle tests (minimum strength 500 lbs/sq in).

(2) Colorimetric organic test to detect materials which may retard proper setting and hardening.

(3) Gradation (there are no particular requirements for this except that: 100 per cent pass the 3″-sieve, 50 per cent pass the No. 4 sieve, and that the type and amount of clay present does not prevent proper pulverization).

Other soil data such as pH, voids ratio, surface area, bulk density and consistency limits, are of little or no direct value to judge the cement requirements.

While the standardization of test and construction-control methods represents a good engineering solution of the problems involved in soil-cement, further practical advance in this field calls for basic colloid-chemical studies of the relationships between soil and Portland cement. Two outstanding practical problems are:

(1) The reduction of the time required by the present testing methods (about 4 weeks):

(2) The possible chemical treatment of "bad acting" soils which require either too large an amount of cement to be economical or which react in an unpredictable way (retarded and flash setting).

It would be desirable if the susceptibility of a soil to stabilization by means of Portland cement could be predicted on the basis of a few simple tests performed on the respective soil, or if the cement requirements could be related to the classification of a soil in one or the other available systems. In an extensive investigation Catton [28] explored the possible connection between cement requirements and soil type according to the Classification of the Public Roads Administration. He found a general trend of increasing cement requirements with increasing clay content of the soil; but this trend was not sufficiently definite, and there were so many exceptions that he came to the conclusion that chemical soil characteristics were likely more important than physical characteristics, such as the gradation and the surface area.

Hicks [29] in North Carolina has made a very valuable contribution in correlating cement requirements with the different pedologic soil types found in his state and with the different horizons of the same soil type. Once the cement requirements for a certain soil type and horizon have been determined by the standard methods, the findings may be applied, wherever this soil type and horizon is encountered in any part of the state or country. This results in the saving of a great deal of testing work, since the soils in the United States have been well identified and mapped by the Division of Soil Survey of the Bureau of Plant Industry (formerly the Bureau of Chemistry and Soils). The pedologic name of a soil identifies qualitatively a complex colloid chemical system, the properties of which can not as yet be satisfactorily expressed by more specific physical and chemical terms. It is like the overall character of a complex human system; once we have had intimate experience with such a character, it is possible to predict certain reactions even without complete understanding of the complex physiological and psychological mechanisms involved.

Winterkorn and co-workers [30] have attacked the outstanding problems in soil-cement from a combined pedologic and colloid-chemical point of view. Data were procured on four clay soils of different pedologic and, therefore, different surface-chemical character, and on a number of their homoionic modifications. The ionic treatment was used to produce definite variations in the chemical and physical characteristics in the four soil types employed.

Standard weathering tests and compression tests were employed to obtain data on the influence of exchangeable cations, physical soil constants, density of the soil-cement systems, and moisture content at the time of compaction.

The results obtained showed that:

(1) Surface-chemical as well as physical factors greatly influence the hardening of clay soils by means of Portland cement.

(2) Ionic treatment of a soil can improve considerably its susceptibility to stabilization.

(3) The difference between the optimum moisture content for compaction and the shrinkage limit of an inorganic clay, appears to be an indicator of its susceptibility to stabilization.

(4) The behavior of a soil-cement system in the wetting and drying cycles depends on the water affinity and the accessibility of its internal surface.

(5) The behavior of a soil-cement system in the freezing and thawing cycles depends upon the permeability of the system and, especially, on the amount of pore space filled with water which is not strongly adsorbed on the internal soil surface.

(6) Increasing density at constant moisture content decreases the accessibility of the internal soil surface and the pore space available for freezing water, with resulting improvement of the weathering resistance of the soil-cement system.

(7) Increasing moisture content at constant density exerts a general beneficial effect. The reason for this may be an increased satisfaction of the water binding ability of both soil and cement, resulting in a lowered differential avidity for water.

(8) The presence of soil organic matter appears to be undesirable, especially if it is of an acid nature.

(9) Compressive strength tests performed on soil-cement systems appear to give a general indication of their quality. However, such tests cannot be considered as reliable if they are not performed at a standardized temperature and on samples which have attained equilibrium conditions with water throughout their entire volume.

(10) From a general point of view the cycle tests, including the brushing of the specimens, appear to be preferable to compressive strength tests, since the former imitate more closely the action of climatic forces and since the surface layer of the specimens may be considered as being more fully exposed to the weathering agents than the interior of the specimens.

(11) It appears feasible to design shorter test procedures for inorganic clay-cement systems based on the relative magnitude of the optimum moisture content and the shrinkage limit of the soils, and upon the permeability and water affinity of the respective soil-cement systems.

Recognition of the importance of chemical factors in soil-cement has already resulted in a very practical method of treating soils containing undesirable organic matter by means of bi- and trivalent metal chlorides. The most economical salt employed for this at the present time is calcium chloride.[31]

Construction Methods

The proper construction of soil-cement involves pulverization of the soil, dry mixing of the soil with the predetermined amount of cement, wet mixing with the predetermined amount of water, and compaction to the predetermined density. Close field control is an absolute necessity. As far as the subgrade is concerned, the same considerations hold which were previously described in the section on soil bitumen. The various methods of design, construction control, and construction of soil-cement have been concisely and authoritatively described in a recent Wartime Bulletin[27] rendering it unnecessary to treat these features here in more detail.

Recent Developments in Soil Stabilization

The importance of soil stabilization for the construction of airdromes all over the world has resulted in a great increase of interest in the above described traditional methods of stabilization; it has also stimulated the search for new stabilizing agents. This search was directed especially toward the discovery of more active agents which would decrease the great bulk of materials to be shipped by rail, water, or plane. The quantities of materials required in soil stabilization are indicated by the following considerations. Of the traditional materials, such as bitumen and Portland cement, 6 to 12 per cent, on the basis of the dry weight of soil, are normally required for stabilization. The average weight of one cubic foot of soil is about 100 lbs. A six-inch base of one runway possessing the dimensions 4000′ × 50′ represents 5000 tons of soil to be treated and 400 tons of Portland cement, or somewhat less of bitumen, as a treating agent. The shipping distances and risks involved in this global war, also the shortage of bottoms, allowed the consideration of materials for stabilization which

were not normally economical during peace time. This permitted unfettered research, with the result that permanently valuable information has been gained, in addition to the direct contributions to the war effort.

A number of inorganic and organic chemicals were investigated by different agencies. Among the former, the possibility of utilizing the reaction of sodium silicate with calcium chloride or with other salts of bi- and trivalent cations attracted a number of investigators. A special incentive was the previously reported good results obtained with this reaction in the stabilization of building foundations and in the treatment of earth dams and similar structures. However, there exists a great difference in the effectiveness of a chemical treatment depending on whether the treated soil is within or outside the zone of daily and seasonal moisture and temperature fluctuations. So far, none of the soil treatments based on the formation of an insoluble silicate, phosphate, borate, or other inorganic salt in the soil has been successful in shallow soil stabilization, within an economical range of materials employed. Winterkorn believes that no formation of an insoluble compound will result in satisfactory soil stabilization for road and airport bases, if such formation involves also the formation of a soluble salt, which may increase the water affinity of the soil system. Thus, in the reaction $2Na_3PO_4 + 3CaCl_2 \rightarrow Ca_3(PO_4)_2 + 6NaCl$ the sodium chloride formed represents a definite liability as far as resistance of the soil sample to wetting and drying is concerned.

The most successful highly active stabilizing agents available at the present time are the outgrowth of work by Winterkorn and his coöperators on activating low priced bituminous materials to make them better soil stabilizing agents.[26] Also, his studies on adhesion promoters between bitumen and mineral particles have been of definite help.[24] The respective agents which are effective in amounts of fractions of one per cent are derivatives of rosins, natural and artificial resins, and of similar natural and synthetic materials. While most of the work involved is of a confidential nature, two reports on such agents have been recently released by the Civil Aeronautics Administration.[82] The divulging of further data must await the completion of this war.

Stabilization by Injections

A general treatise on soil stabilization such as the present must include at least a short mention of injection methods employed for the stabilization and impermeabilization of foundations, levees, and similar structures. It is important to realize that the strength requirements of such systems are much less exacting than those of highway and airport bases; also, because of the bulk or location of the respective soil systems, the dynamic forces of climate are negligible or entirely absent. In addition, injections are employed more often for decreasing the permeability of a soil than for adding strength.

The following materials are usually employed in injection work:

(1) Cement Grout
(2) Cement-Clay Grout } Applicable for pore sizes larger than 0.1 mm

(3) Bituminous Emulsions { Range depending on size and electrical properties of bitumen globules

(4) Inorganic Chemicals: especially reaction products of sodium silicate.
   (a) Sodium silicate and acid or salt solution. The two-solution method by Joosten is applicable only for materials possessing a coefficient of permeability larger than 1000×10^{-4} cm/sec.
   (b) The one-solution method by Rodio employs a specially prepared sodium silicate solution and is applicable for a permeability range of 1 to 10×10^{-4} cm/sec.
   (c) The one-solution Langer-Brunner method employs a silicate solution sensitized by means of acid, with a similar soil permeability range as the Rodio method.

(5) Organic Chemicals: especially artificial resins, and resin forming materials which have recently been introduced in the oil-well cementing industry.

Injection stabilization is a highly technical type of work and should be entrusted only to agencies which have successful experience in this very complicated field. An excellent treatise on the theory and practice of injection has been published by Kollbrunner and Blattner.[88]

Closing Remarks

The purpose of this treatise was to introduce the interested scientist, engineer and educated layman into the theory and practice of soil stabilization. In addition, this work should also be of interest to the expert in soil stabilization, because it treats the phenomena encountered in a more fundamental way than is usually found in the stabilization literature. It is hoped that this treatment will attract qualified scientists and engineers possessed of a pioneering spirit to the vast new frontiers which are open in the field of soil stabilization.

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The Flotation Process

A. M. GAUDIN

Richards Professor of Mineral Dressing, Massachusetts Institute of Technology

Since its introduction for the treatment of low-grade sulfide ores, the flotation process has grown by leaps and bounds. For the concentration of ores and minerals other than coal and iron ores it exceeds in importance all other processes put together; and it bids fair to occupy a large niche for coal cleaning and iron-ore beneficiation in the not too distant future. Its applications have spilled over the boundaries of the mineral industry: the process should rather be regarded as one of the tools available to any one interested in the separation of solids in finely divided form—whether that be for the salvage of pulp from waste paper, the separation of crystals in chemical processes, the purification of rayon-manufacturing liquors, or the separation of germinating from barren seed.

Concentration by flotation is typified by Fig. 1. Three identical charges consisting of granular marmatite (ferruginous ZnS), granular calcite ($CaCO_3$) and water were placed in test tubes and treated as follows. One (the first from the right) was shaken and allowed to settle: the solids are gathered at the bottom without visible segregation. A second was shaken in like manner after receiving suitable, minute additions of potassium ethyl xanthate, terpineol and copper sulfate: the marmatite floated as a black froth at the surface of the water and the calcite sank. The third

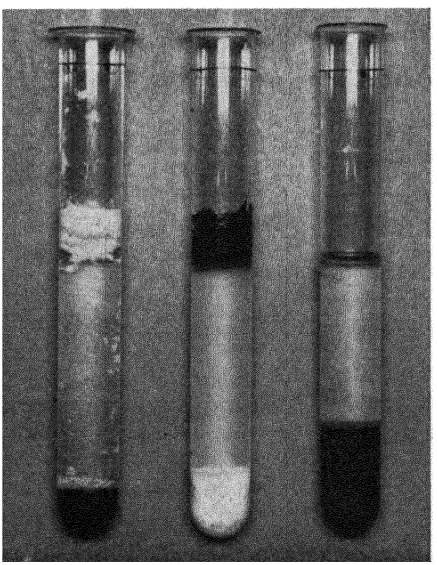


FIGURE 1. Typical behavior of mineral mixtures in flotation.

received additions of sodium oleate, terpineol, and sodium sulfide: the calcite floated as a white froth at the surface of the water and the marmatite sank.

Flotation can be said to be a process for separating particles of finely divided solids from one another and from the water in which they are suspended. But much depends upon the meaning attached to the expression "finely divided." Lest flotation be interpreted as a process depending for its success upon typical colloid phenomena, there are presented in Table 1, for comparative purposes, the size-distributions of a

Table 1. Size distribution (cumulative per cent undersize) of typical pulps subjected to flotation separation (E, F, G) compared with two mineral colloids (A, B), two clays, (C, D), and a pulp prepared for table agglomeration (H) †

Size (microns)	Pulp A	B	C	D	E	F	G	H
4699								99
2327								85
1181						100	100	62
589						99	95	30
295						88	62	3
147				(100)	100	69	23	0
74 *				(99)	93	42	6	
37				(95)	80	27	1	
18.5				87	52	15	(0)	
9.2			100	77	28	10		
4.6			95	54	15	6		
2.3			88	29	(9)	(4)		
1.15			77	13	(5)	(3)		
0.58			63	6	(3)	(2)		
0.29		100	38	1	(2)	(1)		
0.14		92	13	(0)	(0)	(0)		
0.072		35	6					
0.036	100	0	(2)					

A. Finest fraction from Wyoming bentonite (montmorillonite), prepared by Hauser and Reed[14] (their fraction I).
B. Coarsest fraction from Wyoming bentonite, prepared by Hauser and Reed (their fraction VI).
C. No. 90 English Ball clay, from England, supplied by Paper Makers Importing Company, sample H cited in the paper by Norton and Speil[18].
D. No Karb clay from Georgia, supplied by Edgar Bros. Co., sample D cited in the paper by Norton and Speil.
E. A finely ground lead-zinc-iron ore, prepared for flotation.
F. A coarsely ground copper ore, prepared for flotation.
G. A phosphate-flotation plant feed from Florida, deslimed pulp.
H. A phosphate feed for table-agglomeration separation, from Florida.
* Opening of a standard 200-mesh sieve.
† Figures in parentheses are extrapolated; numbers are rounded off to the nearest unit.

number of dispersions. Dispersions A and B are of bentonite, the typical mineral colloid; dispersions C and D, of clays selected for their representativeness, and the others of flotation pulps. A and B are colloids, C and D contain large proportions of colloid, E and F small quantities and G and H, none. Clearly colloid properties are not prerequisite for flotation although colloid phenomena on occasion may play a part, perhaps an important part.

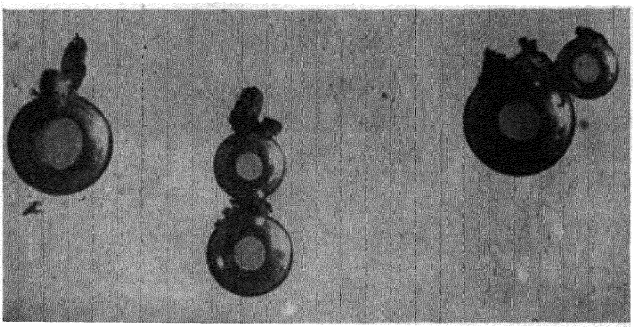
Flotation Varieties

The noun "flotation" has been qualified in the past by hyphenation and by the use of adjectives. Thus we have had oil flotation, bulk flotation, skin flotation, froth flotation, selective flotation, differential flotation, etc., *ad nauseam*. Some of these terms require attention, mostly because of the misconceptions that they have created and are perpetuating. Thus, in respect to oil: with few exceptions, about which more will be said below, there is no oil as such in modern flotation operations. Differential flotation is the same as selective flotation, the adjectives merely indicating that a separa-

tion between difficultly separable companions is accomplished. It may be contrasted to bulk or collective flotation.

In all cases flotation involves the adhesion of certain selected solids to air, together with non-adhesion of some other solids to air. If the process occurs at the free surface of a body of water, skin flotation results. If it occurs within the body of water and the mineralized bubbles are heavier than water, the bubbles cluster in grape-like bunches and sink. These agglomerates can then be separated from non-agglomerated material on a shaking table or other gravity-concentration device.[2] Finally, if the adhesion occurs within the body of water and the mineralized bubbles are lighter than water, the bubbles rise to the surface and cluster, forming a froth.[25] This is the customary form of flotation, or froth flotation.

Fig. 2 shows the manner in which particles stick to air: a portion of the solid is



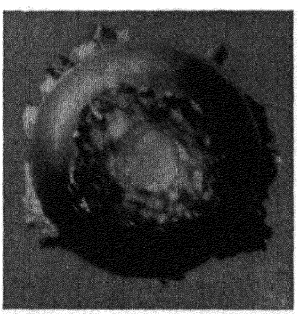


FIGURE 2. a. (above) Galena-gas clusters, 75x. (Courtesy H. Rush Spedden, M.I.T.) b. (left) Partly mineralized air bubble. (Courtesy S. J. Swainson, American Cyanamid Co.)

directly in contact with air, another with water. The line of demarcation or 3-phase boundary preferably passes through those points or edges of the surface of the solid where there is a sudden change in curvature.

Native Flotability

Although not essentially dependent upon colloid phenomena, flotation processes essentially do depend upon the play of interfacial forces. The fundamental fact is the air-adherence of mineral particles of one category, and the lack of air-adherence of those of another category. Where air-adherence occurs the contact angle * may reach 106° (the contact angle for paraffin), or be nil, as for the majority of clean mineral surfaces.

Fig. 3a shows non-adhesion of clean galena to air, and Fig. 3b shows the adhesion of paraffin to air with a contact angle of 106° measured across the water.

* The contact angle is the angle made by the three interfaces at their line of contact; it is measured across the water.

There is a relationship between crystal structure and native floatability—that is, the floatability in the state obtained by usual crushing and grinding methods. The exact nature of this relationship is not wholly settled, but it seems that native floatability is a property of molecular crystals, while ionic, covalent and metallic crystals are fully wetted by water. In a different terminology, it may be said that non-polarity goes with floatability, and polarity with non-floatability.[5]

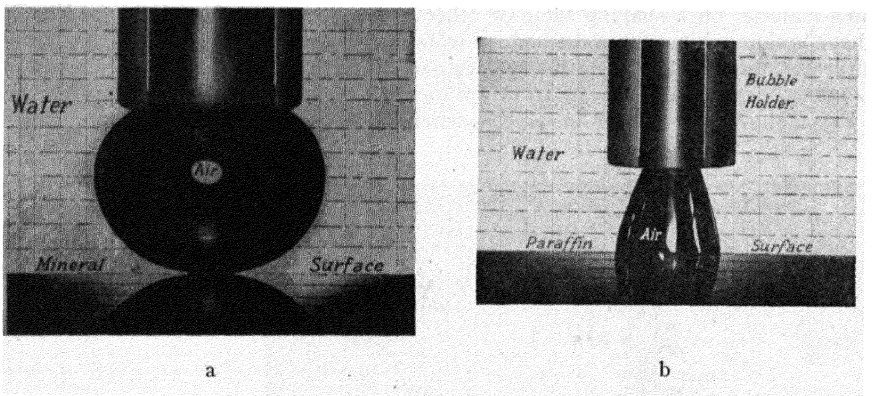


FIGURE 3. Adhesion and nonadhesion of submerged solids to air: a, clean galena (contact angle 0°); b, paraffin (contact angle 106°). (Courtesy Ian W. Wark, "Principles of Flotation," Australian Inst. of Mining and Metallurgy)

Were it impossible for naturally non-floatable solids to acquire floatability by surface change, the flotation process would be limited in application to the extraction of minerals that are naturally floatable. This class now appears to include few minerals beside natural hydrocarbons, graphite, sulfur, and talc.[31, 27] Fortunately, naturally non-floatable minerals acquire floatability by exposure to certain reagents dissolved in water, or in some instances merely by exposure to contaminants present unintentionally in minute quantity. The facility with which this change in behavior occurs is so great in some cases as to have been the cause of many arguments as to native floatability: some minerals pick up greasy constituents from mining operations, milling operations, or even from atmospheric pollution so readily that the greatest care is required to secure them with an uncontaminated surface. Others, on the contrary, require very precisely defined conditions to become air-adherent. Thus glass and salt are made floatable with difficulty, while galena and chalcopyrite are made floatable with great ease.

Control of Character of Solid Surface

Collecting Agents. Agents designed to make the solid floatable (collectable in a froth) are termed "collecting agents." All are organic compounds, and most are water-soluble salts of organic acids or organic bases; for example, sodium ethyl xanthate, sodium oleate, and lauryl amine hydrochloride. However, the corresponding acids or bases can be used likewise. It may be convenient to remember that collecting agents have heteropolar molecules or ions, and that a heteropolar structure is the only one which makes possible the conversion of an unfloatable to a floatable surface.

The collector is abstracted by the collected solid and forms a thin coating on the solid. When the collector is a salt dissolved in water, the active ions (*e.g.*, anions in the case of xanthates) are abstracted to form (a) a more or less complete monoionic layer on the collected solid, (b) reaction-product heaps several to many molecules thick at the surface of the solid.[11]

In exchange the solid gives up to the solution (a) ions adsorbed previously,[6, 29, 28] (b) ions that form part of the lattice of the solid itself.[9, 15] That is, the process of collection consists of two chemical processes operating jointly:

(a) exchange chemosorption

(b) bulk reaction (usually metathesis)

followed by a third process of non-chemical nature:

(c) adhesion to gas.

In some cases these three processes are supplemented by reactions between the solid and the coating involving diffusion in the solid state,[8] or by reactions between the coating and gases dissolved in the water; *e.g.*, oxidation.[13]

Oils. Formerly, oils were used extensively for flotation purposes. It was soon found that all oils did not behave alike, some being useful as froth producers, others to gather the mineral in the froth. The latter, or collecting oils, gave rise to the collecting agents when it was established that collecting quality is not necessarily an attribute of oiliness, *viz.*, high viscosity. So, the use of oils has been decreasing until it now has become restricted to certain specialized systems.

The oils that are now used as such are hydrocarbon oils—precisely those that were regarded as the least valuable in the early days of the art. Although their influence has not been wholly elucidated, it seems that they may perform three related yet distinct functions:

(a) They are useful in the flotation of flaky, highly-floatable minerals, such as graphite and molybdenite. In this case they smear themselves over the surface of the particles, replacing the somewhat air-adhesive mineral surface by the more air-adhesive hydrocarbon surface.

(b) They are useful in the flotation of porous oxide minerals, partly as pore fillers (Fig. 4), and partly as antidotes for the excessive frothing qualities of the collectors used for those minerals.

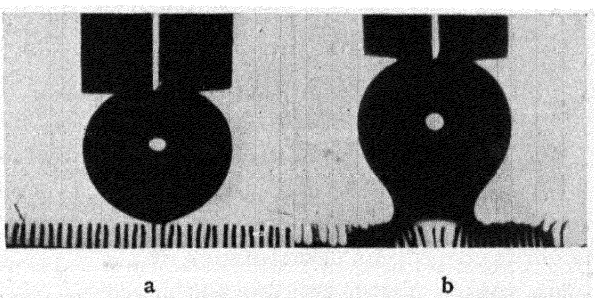


FIGURE 4. Behavior of a porous air-adherent solid with respect to an air bubble. a, Without pore-filling oil; b, With pore-filling oil. (Courtesy Cuban-American Manganese Corp.)

(c) They are useful in the flotation of finely ground pulps (particularly those of crumbly, porous oxide minerals) to agglutinate fine particles to coarser granules. Where the quantity of oil is large, granulation occurs, even to the exclusion of air.

The second and third effects take place on surfaces already conditioned by collectors, and therefore endowed with a hydrocarbon surface.

Activators. Certain other agents (so far invariably inorganic) are useful in making collectors effective in those instances where the collectors alone would be ineffective. These are the activators.*

A typical instance of the need for and the action of activators is provided by the flotation of sphalerite or zinc blende, ZnS.[4, 20] Upon addition of potassium ethyl

* Activators and collectors are sometimes jointly termed "promoters," since their function is to promote the floatability of minerals.

xanthate, other sulfides, *e.g.*, galena (PbS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), become air-adhesive, but zinc blende does not. This can be overcome, however, if sphalerite is first treated with copper sulfate or even with a solution of copper hydroxide. Zinc ions from the mineral surface change place with copper ions, and the copper-covered blende now can abstract xanthate ion from water solution and become air-adhesive.

Another typical instance of activation is that in which an ion adsorbed on the surface of the activated solid is replaced by the activator ion, for example, H^+ by Ba^{++} in the activation of quartz for soap flotation.[10] In this instance the ion evolved is not a participant in the lattice of the solid, while in the other case it is; otherwise the action is the same.

Thus it will be clear that activator coatings are very thin. Where the activator ion is of about the same size as the displaced ion, the coating usually is monoionic, as diffusion in the solid state is slow. But where the activated coating has a very different lattice, as in the activation of lead carbonate by sulfide ion, the coat is so permeable that the reaction proceeds to subsurface ions: a relatively thick, loose, crust is obtained (Fig. 5).

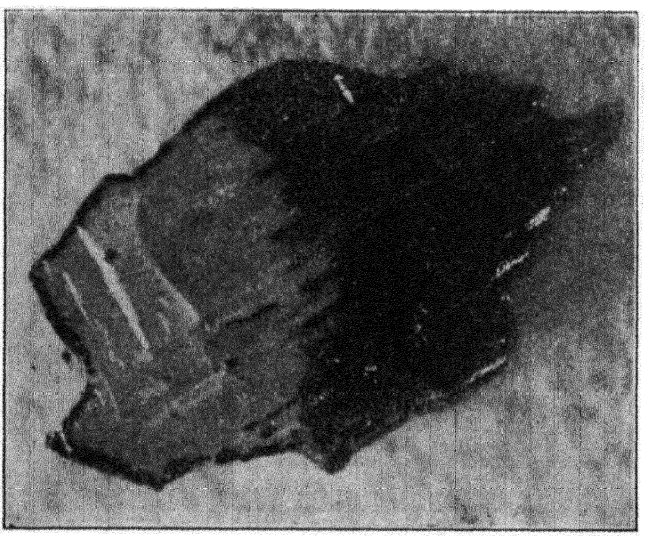


FIGURE 5. Crystalline cerussite partly coated with lead sulphide as a result of reaction with 0.5 per cent solution of sodium sulphide. Reaction time, 30 seconds. The light-colored area was protected by a paraffin coating which was subsequently removed (× 10). (*From "Principles of Mineral Dressing,"* McGraw-Hill Book Co., N. Y.)

Residual Collector or Activator. For both collection and activation some excess of the active ingredient is needed. That is, the concentration in solution of the active ingredient may not be nil, after its work is done, although in some instances it may well be vanishingly small. Thus, collector additions for sulfide ores are in the range of 3 to 30 parts per million parts of water (0.03 to 0.20 lb per ton of ore); of this quantity from 90 per cent upward is usually consumed, leaving a residual concentration of collector generally smaller than 0.5 part per million.

Modifiers. Were collectors and activators alone available, much could no doubt be done by way of collective flotation. Fortunately, however, it is possible to supplement the effectiveness of these agents by that of so-called depressing agents, deactivating agents, pH regulators and by certain protective colloids. These various

agents can be lumped together under the name "modifying agents," since their object is so to modify the relative floatability of different minerals as to make their response to bubbles more unlike. Thus, cyanide ion can be used to prevent pyrite or chalcopyrite from floating, while it allows galena to float; [23, 24] and sulfide ion can be used to prevent galena from floating, while it allows rhodochrosite to float.[7]

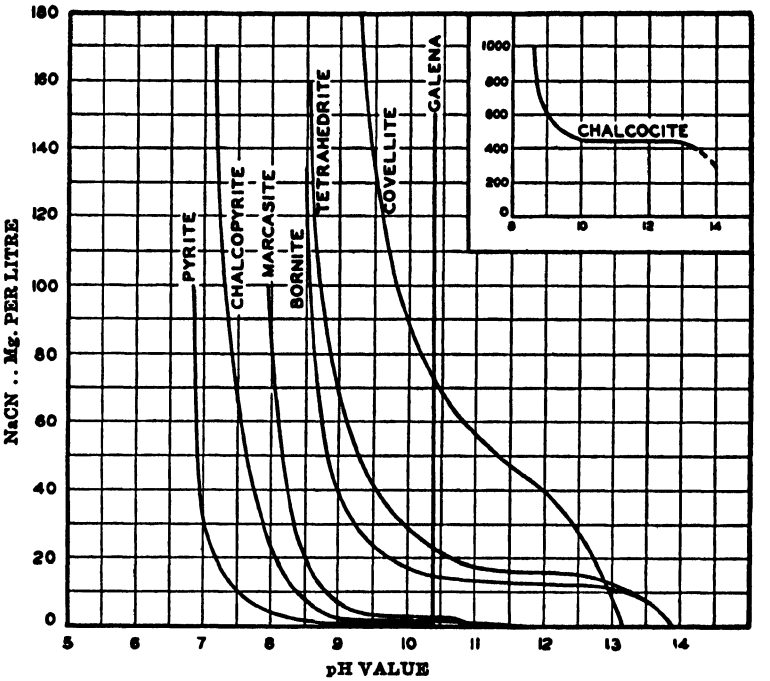


FIGURE 6. Contact curves for several sulphide minerals, determined by the captive-bubble method. (*Reproduced from I. W. Wark, "Principles of Flotation,"* McGraw-Hill Book Co., N. Y.)

Much work has been done to elucidate the mechanism of depressing agents, especially by Wark and Cox * in Australia. They used the method of the captive bubble illustrated by Fig. 3, determining thereby the quantity of agent that delineates adherence to air from non-adherence. Fig. 6, for instance, shows contact curves for eight sulfide minerals, pyrite (FeS_2), chalcopyrite ($CuFeS_2$), marcasite (FeS_2), bornite (Cu_5FeS_4), tetrahedrite (Cu_3SbS_3), covellite (CuS), galena (PbS), and chalcocite (Cu_2S). In the figure each curve denotes the boundary between the conditions for flotation (below the line) and non-flotation (above the line).

Fig. 6 suggests that in the absence of cyanide ion several of the copper minerals should float ahead of galena, provided the pH is kept high enough, while addition of a suitable quantity of cyanide ion (*e.g.*, 20 mg per liter) permits galena to float while pyrite and chalcopyrite are depressed in the pH range of 8 to 10. As a matter of fact, the selective flotation of lead sulfide from iron sulfides or from copper sulfides is based on the judicious use of cyanide ion. In connection with Fig. 6 attention may be drawn to the fact that it records the behavior of the various minerals in respect to

* Their beautiful contribution is contained in two series of articles published by the *American Institute of Mining and Metallurgical Engineers* and in the *Journal of Physical Chemistry*, and summarized in Wark's book "Principles of Flotation." [27]

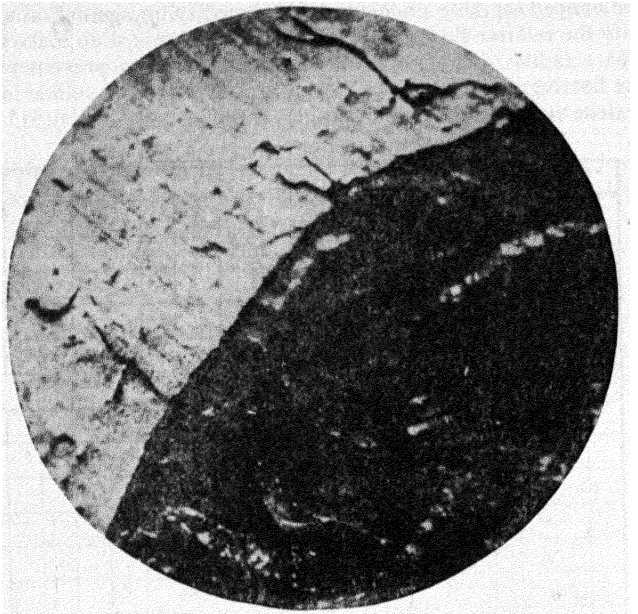


FIGURE 7. Sphalerite coated with copper sulphide by reaction with copper sulphate. One part of the surface as subsequently coated with paraffin, and the specimen was exposed to sodium cyanide; this dissolved the copper sulphide coating where the coating was not protected by paraffin (× 44). (*From "Principles of Mineral Dressing,"* McGraw-Hill Book Co., N. Y.)

two variables: the quantity of cyanide and the pH. Control of the pH has for many years been acknowledged to be one of the most important factors in regulating flotation behavior.

Table 2 shows that the concentration of sodium cyanide required to prevent flotation of a given mineral at various pH values varies a great deal, but that the concentration of cyanide ion is substantially constant. This establishes that the effective controlling agent is the ion (CN^-) not NaCN. Further proof is afforded in the case of depression of chalcopyrite by sodium sulfide (Table 3). In this case the effective agent is hydrosulfide ion, not hydrogen sulfide nor sulfide ion. These facts are of importance as they clearly point to an ionic competition between collector ion and depressing ion for chemosorption at the surface of the minerals.

Depressants compete with the collector for the surface of the mineral, the composition of the resulting adsorbed film being a compromise whose exact composition depends upon the concentrations of the various ions in the pulp and upon the adsorbability of each ion by the surface. Where several solids are present, the reactions involved may be quite complex, one surface acting as a sort of sponge for one kind of ion, and another type of surface for some other kind.

De-activators are those modifiers that undo the work of activators by incorporating the activating ion into a complex ion that is undissociated, practically speaking. They are especially useful if unintentional activation has occurred. For instance, many lead-zinc ores have been so affected by minute quantities of copper ion that it is not possible to obtain a commercially satisfactory separation of galena from sphalerite and pyrite without the use of some cyanide ion. Here the cyanide ion acts not only as a depressant for ZnS and FeS_2, but it also removes the activating coating of copper sulfide on zinc sulfide by dissolving it to form $Cu(CN)_3^{--}$.

Table 2. Influence of Cyanide-ion Concentration on Contact
(Courtesy I. W. Wark and A. B. Cox, *Trans. A. I. M. M. E.*, **112**, (1934)

Chalcocite			Covellite			Bornite		
pH	NaCN Added (mg per liter)	CN^- (mg per liter) Calc	pH	NaCN (mg per liter)	CN^- (mg per liter) Calc.	pH	NaCN (mg per liter)	CN^- (mg per liter) Calc.
8.7	1000	101	9.0	235	40.0	8.5	100	6.9
9.0	600	102	9.5	130	41.2	9.0	37	6.3
9.5	480	152	10.0	88	38.6	10.0	17	7.4
10.0	450	197	11.0	55	28.6	11.0	13	6.8
11.0	440	229	12.0	40	21.2	12.0	13	6.9
12.0	435	230	13.0	(7)	(3.7)	13.0	12	6.4
13.0	430	228						
Mean		177			33.9			6.8

Chalcopyrite			Pyrite		
pH	NaCN (mg per liter)	CN^- (mg per liter) Calc.	pH	NaCN (mg per liter)	CN^- (mg per liter) Calc.
7.2	150	0.49	6.8	100	0.157
7.5	67	0.52	7.0	31	0.077
8.0	21	0.50	7.5	10	0.078
8.5	5.0	0.34	8.0	3.5	0.083
9.0	2.0	0.34	8.5	(1.5)	(0.103)
10.0	(1)	(0.44)	9.0	(<1)	(<.17)
11.0	(<1)	(<0.52)	10.0	(<1)	(<.4)
		0.44			0.10

Table 3. Concentration of Sulfide Ion, Hydrosulfide Ion and Hydrogen Sulfide in Solution Containing Just Sufficient Total Sulfide to Prevent Contact at a Chalcopyrite Surface. (Courtesy I. W. Wark, "Principles of Flotation," McGraw-Hill Book Co.)

pH Value	Total Sulfide as $Na_2S \cdot 9H_2O$ (mg per liter)	H_2S (mg per liter)	HS^- (mg per liter)	S^{--} (mg per liter)
5.0	150	21	0.21	4×10^{-11}
5.5	52	7.2	0.22	1.4×10^{-10}
6.0	21	2.7	0.25	6×10^{-10}
6.5	8	0.8	0.27	1.7×10^{-9}
7.0	4	0.3	0.28	5.2×10^{-9}
8.0	3	0.04	0.37	7.8×10^{-9}
9.0	3	0.004	0.41	7.8×10^{-7}
10.0	2.5	0.00035	0.34	6.5×10^{-6}
11.0	2.5	0.000035	0.34	6.5×10^{-5}

Fig. 7 shows a sphalerite surface coated with copper sulfide by treatment with copper sulfate and subsequently treated with sodium cyanide for dissolution of the coating over part of the surface. The copper sulfide coating was made visible by extreme intensification of usual flotation conditions.

The quantity of pH regulators and depressants required is often large compared to the quantity of collector or activator used. This is because these agents are not utilized primarily at the mineral surface, but as control substances in the solution. Thus their final concentration in the solution is more important than the total quantity abstracted by the mineral.

Fig. 8 summarizes schematically the surface conditions which it is desired to ob-

tain simultaneously on solids that are to be separated. Such results are obtained by the joint use of collectors, activators, and modifiers.

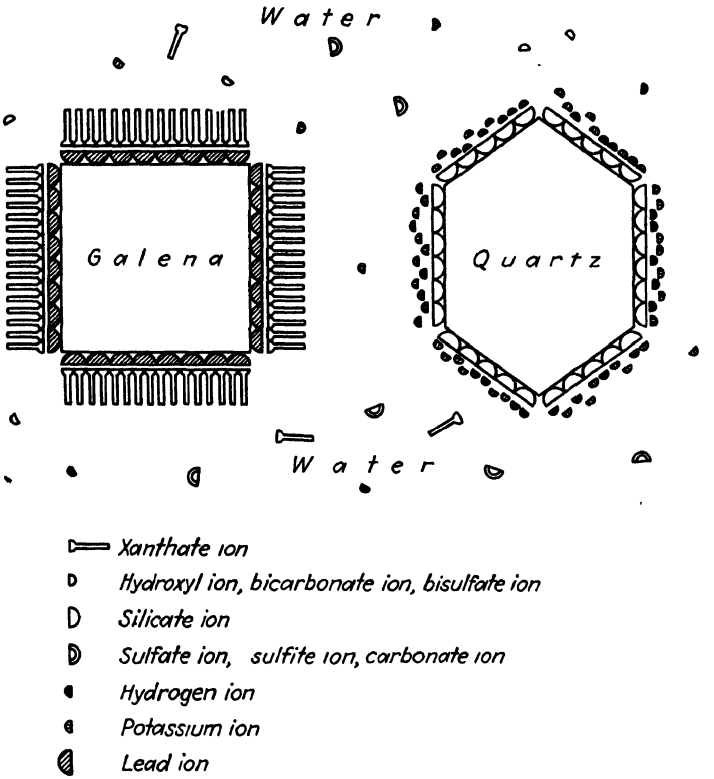


FIGURE 8. Conventionalized representation of two particles, one of PbS and the other of SiO_2 in a dilute solution of potassium xanthate. The sulfate, sulfite, carbonate, bicarbonate, and bisulfate ions came from the surface of the PbS on which they were adsorbed prior to immersion in the xanthate bath. (From "Principles of Mineral Dressing," McGraw-Hill Book Co., Inc.)

Mechanics of Solid-Gas Adhesion

The mechanism whereby a particle suitably coated by a collector becomes airborne has been the subject of considerable debate. The weight of the evidence [5] is that the process is one involving collision between air bubbles and particles, and growth of the mineralized bubbles by repetition of this process as well as by coagulation of partly mineralized bubbles. That is, adhesion to gas involves (a) a probability of collision and (b) a probability of adhesion. The probability of collision is a function of the concentration of the particles, the concentration of the bubbles, the shape of the particles, the size and type of motions (viscous flow or eddying flow) of the particles and bubbles, and the concentration of inert particles. The probability of adhesion is a function of the relative inertias of the bubbles and particles, the surface energies of solid-gas and solid-liquid interfaces, and the shape of the surface. In addition, the probability of rupture of solid-gas attachment must be considered.

The nature of these probabilities indicates that floatability, or at least the *rate of flotation* is a function of particle size.

An analytic study of the rate of flotation has recently been made.[22] It shows that

problems involving the rate of flotation are complex, but that some hope for their solution can be held if a kinetic approach is chosen. For example, the kinetic approach has already made clear why flotation is better suited for the separation of granular solids than for that of colloids. It has also indicated what role selective flocculation of very fine particles plays in accelerating the recovery of the floated solid.[12] Fig. 9 gives some idea of the variation in the quality of the separation in a

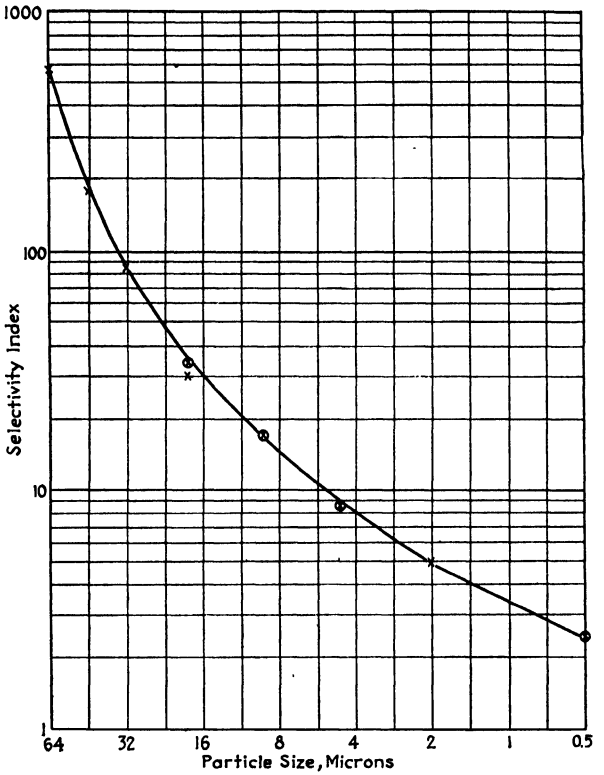


FIGURE 9. Variation in selectivity index, with the size of the particles in the separation of galena from chalcopyrite; two tests. (J. J. Brunner, Montana School of Mines, M.Sc. Thesis)

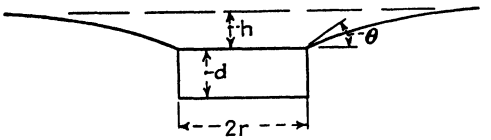
case where the solids consisted of free particles only. In this diagram the ordinate is the selectivity index, a pure number that equals unity where there is no separation and infinity for a perfect separation.* The effect of particle size on selection and on rate of flotation should be carefully segregated from the effect on selection of inadequate liberation of attached solids. That effect is discussed below.

There is a maximum floatable size, as might be realized from a consideration of the forces acting at the line of attachment of a particle to a bubble (Fig. 10). These forces are the vertical component of the gas-liquid surface tension and the net force exerted by gravity (or a centrifugal field) on the particle. If r denotes the radius of the particle (assumed here to be cylindrical or disc-shaped), d its thickness, h the depth of the dimple, the support of surface tension is

$$2\pi r\sigma \sin\theta$$

* A selectivity index of 5 connotes separation of relatively poor quality; of 10, fair; and of 50, exceptionally good.

FIGURE 10. a. Attachment of a particle to an air bubble. Photograph after del Giudice.



b., Sketch of above.

where σ is the surface tension and θ the angle to the horizontal made by the surface of water at the line of contact. The maximum value of θ is, of course, the contact angle θ_{max}. The disrupting force of gravity is

$$\pi r^2 d\Delta g - \pi r^2 (d + h)g$$

where Δ is the specific gravity of the solid and g the acceleration of gravity.

Equating these forces, it is possible with the help of numerical values for h to estimate the relationship of θ to the other variables. Typical results are presented in Table 4.

Table 4. Contact Angle Sufficient for Support of Galena Discs (Diameter = Thickness) of Various Sizes Against Gravity and Against a Centrifugal Force 100 Times Gravity (From "Principles of Mineral Dressing," McGraw-Hill Book Co.)

Diameter (microns)	Minimum angle required against g	Minimum contact angle required against 100 g
2,290	90°	Impossible
500	3°8′	Impossible
200 (65-mesh)	0°30′	61°
100 (150-mesh)	0°7′30″	12°40′
50	0°1′52″	3°8′
20	0°0′18″	0°30′
10	0°0′4″	0°7′30″

The rather involved effects of size of particle on flotation may be summarized as follows:

(1) The rate of flotation decreases with size.

(2) The selection between particles of unlike character decreases with size.

(3) Flocculation of very fine particles more or less counterbalances effect (1).

(4) There is a maximum size above which solid-gas attachment is ruptured by the action of gravity and/or centrifugal forces.

Frothers. For froth flotation it is necessary to generate many bubbles. These bubbles must be fine if a given volume of gas is to have a fair carrying capacity; the latter is, of course, proportional to the extent of the gas-liquid interface, which becomes lined with particles one deep, rather than to the volume of gas; as a result one of the requirements for froth flotation is the generation of many fine bubbles. The size of bubbles depends upon the composition of the liquid. It is well known that bubbles in pure water are large, but that so-called surface-active organic compounds per-

mit fine bubbles to survive. Actually, the addition of as little as five parts of terpineol or xylenol per million parts of water changes radically the appearance of water in which air is being blown. This quantity is vastly less than that required to form a saturated solution; it is of the order of magnitude that corresponds to a surface tension depression of one dyne per centimeter. Such substances as terpineol and xylenol are the frothing agents. Quantities needed usually range from 0.02 to 0.5 lb per ton of ore; that is, from 2 to 50 parts per million of water. Much of this quantity of reagent is lost by evaporation and a substantial part of the remainder goes off with (and perhaps on) the mineral in the froth, leaving a residuum in the tailing pulp that may often be as low as a small fraction of one part per million.

Addition of a frother makes for fine bubbles because the gas-liquid interface then has the property of elasticity.[5] Within limits, the more frother added the greater is the elasticity of the froth, and the greater its permanence. The desired quantity is the least quantity that will permit the bubbles to be removed from the flotation tank, as such a limited quantity will permit very rapid collapse of the froth after this removal. A too permanent froth is harmful to retreatment operation and to dewatering of the froth products.

Choice of Conditions for Operation

Size Preparation Prior to Flotation. The effect of particle size on the probability of successful particle-bubble attachment has already been discussed; broadly speaking, the coarser the mineral, the greater the probability of attachment per unit time. This already favors the flotation of the coarsest grades. In addition, fine particles are often more extensively contaminated because they do not have so young a surface, and because they are more likely to have arisen from the crumbly or readily-sliming portions of an ore. This adds to the difficulty of treating them. Again, fine particles of non-floatable nature may be caused to overflow by the agitation inherent in any flotation operation, thus polluting the float with particles that do not belong there.

Against all these advantages it must be observed that fine particles are more likely to be pure than coarse ones—that is, to consist of one mineral only. Flotation will sort locked particles from each other, but it cannot do this as well as it will sort free particles. Thus, it should be clear that for each case there is an optimum size at which favorable freeing is counterbalanced by the increased cost of securing increased fineness and the increased metallurgical objections to excessive fineness.

Increasing the liberation is one of the principal objectives of the now-common middling regrinding step. The step consists in dividing the pulp in three parts, a concentrate, a tailing, and a middling; this last product contains the bulk of the locked particles, together with some free particles. Regrinding of the middling applies the additional grinding to material containing the major part of the particles that need it. Fig. 11 is a typical example of what may be obtained by such a retreatment. In this case the regrind increased the overall liberation of the principal valuable mineral (bornite) from about 45 per cent to about 75 per cent.

Flotation Conditions. Successful operation requires many things besides proper selection of ore fineness. Among the required factors may be listed the following:

(1) Selection of reagents such that even wide fluctuation in character or in quantity of ore will make but small changes in results.

(2) Selection of machines and of layout such that a sudden shut-down will not cause grievous delays in starting; such delays are largely due to sanding of machines, and can be very costly.

(3) Design of plant and assignment of staff duties such that accurate data can be obtained and records kept of the quantity and grade of the feed and of the products obtained. Automatic samplers that cannot be tampered with, employment of a competent plant metallurgist, and a liberal allowance for controlling and testing equipment are sound investments even for fairly small plants.

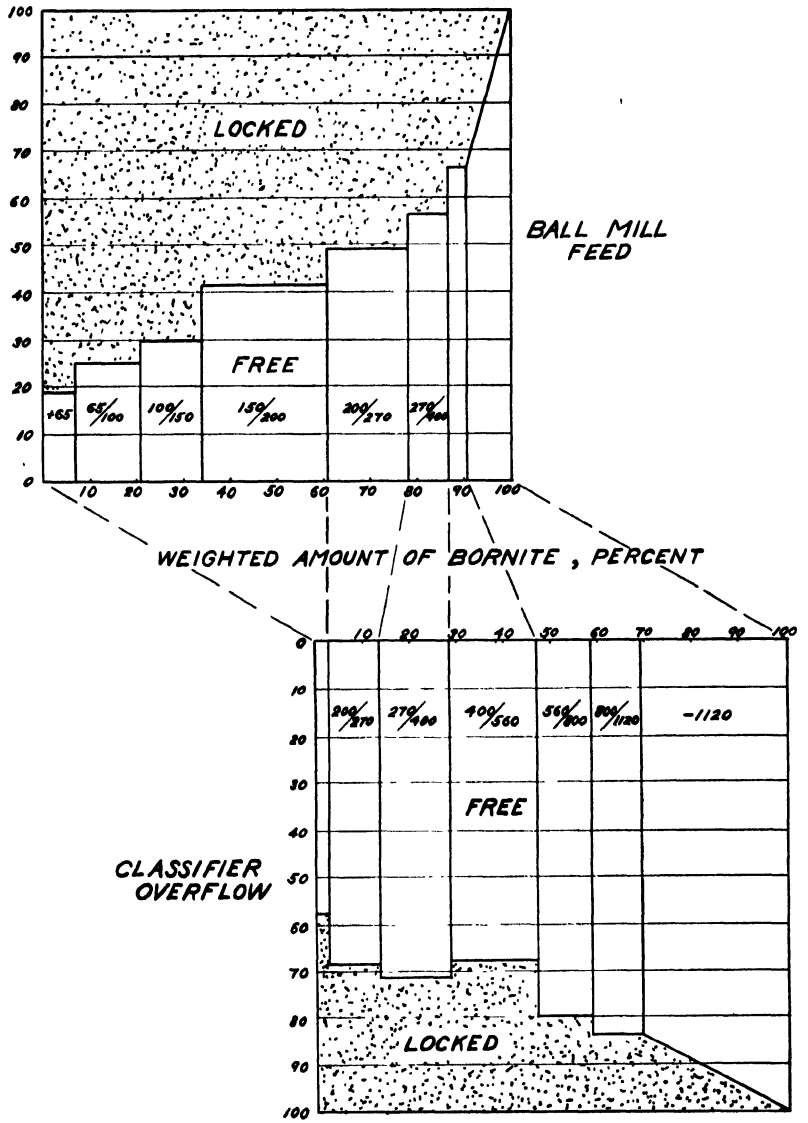


FIGURE 11. Degree of liberation of bornite in regrind feed and reground product from pilot-mill operation, Anaconda mill. (R. L. Moncrief, Montana School of Mines, M.Sc. Thesis)

(4) Design of plant in such a way as to even out fluctuations in grade and quantity, so as to permit wherever possible the independent operation of one out of several units in parallel, and so as not to "hobnail" a given machine to the grief of another.

A typical flowsheet is presented in Fig. 12.

Details of flowsheets and machines, as well as descriptions of typical and special operations are outside the scope of this introduction. For information on those phases of the flotation art, the reader is referred to specialized texts.[5, 6, 19, 26]

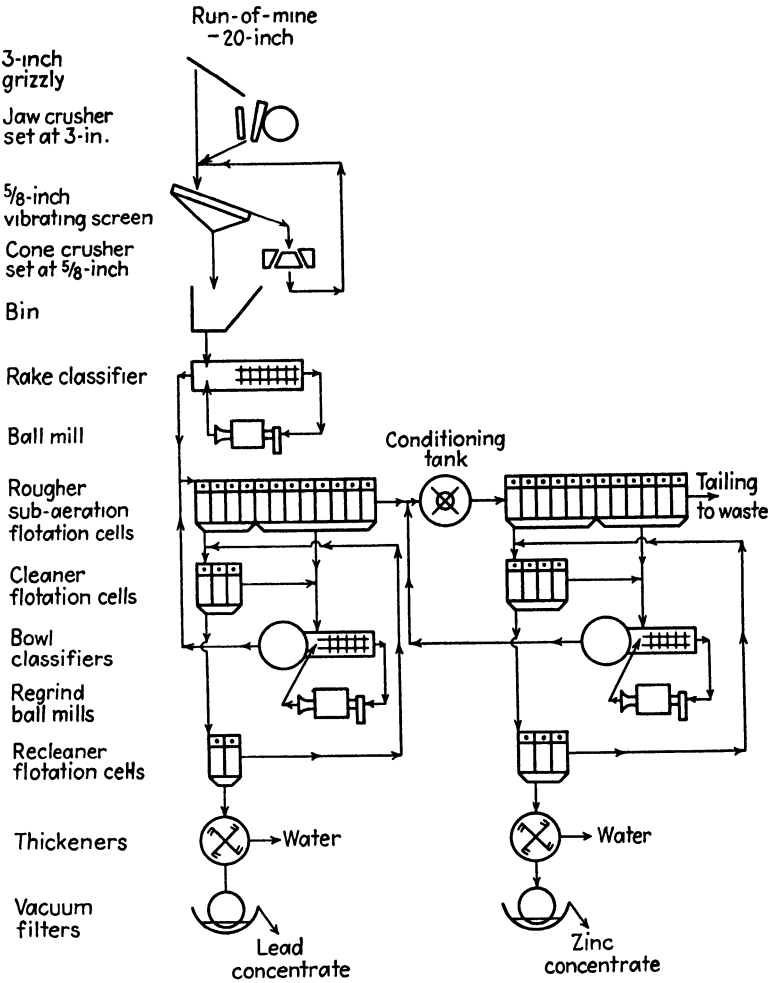


FIGURE 12. Typical flowsheet for the flotation concentration of a complex lead-zinc ore. (From "Principles of Mineral Dressing," McGraw-Hill Book Co., Inc.)

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Colloidal Features of Drilling Fluids

DELMAR H. LARSEN

There are two principal methods of drilling bore holes for oil and gas wells: the cable tool—sometimes known as "churn" or "standard"—method, and the rotary method. In cable-tool drilling, with which this paper is not directly concerned, a heavy cylindrical metal drill bit is alternately raised several feet and let fall by means of an attached cable extending to the surface. The drilling operation, usually carried on with a variable quantity of water in the hole, is suspended from time to time as cuttings accumulate and are removed by a bailer lowered for the purpose.

During the last four decades this simple but effective method (the Chinese several centuries ago were able to churn-drill to depths exceeding 1500 feet [98]) has been increasingly supplanted by so-called rotary drilling, which is better adapted to the increased depths to which wells are now being drilled in search of oil. In rotary drilling, a bit, which may be of the fish-tail type or the roller type, is rotated at the end of a "string" of coupled drill pipe which extends to the surface. The drill pipe, which is generally considerably smaller in diameter than the hole being bored, is hollow, and serves to conduct a drilling fluid, or "drilling mud," down to the bottom of the hole, where it passes out through holes in the bit and thence upward through the annular space between the drill pipe and the wall of the hole to the surface, where it is recirculated by means of pumps.

The drill pipe, and with it the bit, are rotated by means of a length of hollow square pipe attached to the upper end of the drill pipe. The section of square pipe passes through a rotating table fitted with a square hole, so that while the drill pipe is rotated it is also free to move vertically as the bit progresses. The mud fluid is pumped in at the top of the section of square pipe through a swivel joint, at which point the entire drill pipe assembly is suspended by a block and tackle assembly extending to the top of the derrick. Rotating speeds of from one to several hundred revolutions per minute are commonly used, while pump pressures from a few hundred to two or three thousand pounds per square inch are generally applied, the volume of mud pumped commonly amounting to several hundred gallons per minute.

From time to time sections of hole drilled are cased off with casing pipe, cemented exteriorly at the bottom and extending to the surface, drilling then being continued with a smaller-diameter bit. In order that too narrow a hole may not result before the desired depth is reached, casing is set only when necessary, as for example when water-bearing sands must be shut off from lower-lying oil-bearing sands, or when a long section of exposed open hole gives trouble by sloughing and caving, or when production is desired simultaneously from different oil-bearing formations.

Functions of Drilling Mud

The primary function of drilling mud is to transport bit cuttings to the surface. At the same time the mud exerts a hydrostatic pressure on exposed fluid-bearing formations greater than the formation pressure, so that entry of these fluids, such as oil, gas, and water, into the hole is prevented. Also, the circulating fluid cools and in a measure lubricates the bit, assists in keeping the walls of the hole in place, inhibits caving, heaving, and sloughing by the pressure exerted, buoys drill pipe and

casing, aids the bit in penetrating the formation by hydraulic action, and finally marks the occurrence of oil-, gas-, or salt-water-bearing formations by bringing "shows" therefrom to the surface.

The mud can perform all of these functions only if it possesses a variety of special characteristics which at first sight may seem to be mutually exclusive. For example, the mud must be dense enough to provide adequate hydrostatic pressure, but at the same time must be fluid enough to be readily pumpable. It must be somewhat thixotropic in order that cuttings may be suspended in the bore hole if circulation is stopped, as otherwise they would settle down and pack off the drill pipe; but the yield point of the mud under agitation must be sufficiently low to enable the cuttings to drop out and gas to be released when the mud flows horizontally in the ditches at the surface. Nevertheless, this last property must not be so low in value that the mud cannot lift cuttings under conditions of reduced upward flow, such as may occur in an enlarged portion of the hole, so that at such a point the accumulated cuttings [40, 99] pack off the drill pipe. When the mud is filtered against a porous formation, the superior hydrostatic pressure drives the liquid phase of the mud into the formation, and the solids remain as a filter cake on the walls of the hole. The filter cake so formed by the mud must be of extremely low permeability, not only so that water may thus be kept from penetrating porous formations (where it often leads to caving, sloughing, or swelling, or in the case of oil-bearing formations to reduced oil permeability) but so that further rapid increase of the filter cake may be prevented, which would then reduce the effective diameter of the hole and again hinder the withdrawal of drill pipe.

Moreover, these properties must be retained in spite of deep bottom-hole temperatures (which make chemical deflocculation difficult, as discussed below), drilled-up colloidal material such as plastic shales (which necessitates either its removal or the dilution of the entire mud system), flocculating substances encountered during drilling (such as salt, salt water, or anhydrite), and many other difficult extremes of environment. It is scarcely to be wondered at that the unique problems occurring in drilling mud technology have attracted the attention of many colloid chemists, physicists, and chemical engineers.

General Composition of Drilling Fluids

Drilling muds may be conveniently classified according to whether they have as a fluid base (1) water, or (2) a non-aqueous liquid. While perhaps 95 per cent of all drilling muds now used throughout the world consist of a simple mixture of water, clay, and occasionally a weighting material, the much less frequently used "non-aqueous" drilling fluids are of nearly equal interest from a colloidal point of view, and are discussed in detail at the end of this paper. These comprise oil, oil and water emulsions, oil admixed with other substances (yielding filter-cake impermeability, thixotropy, and density), and proposed drilling fluids such as molten sulfur and heavy organic liquids, such as acetylene tetrabromide and the like.

The usual composition of the ordinary drilling mud, however, is as follows:

98 to 65 per cent by volume of water. (Fresh or sea water may have been used, and the aqueous phase may be more or less saturated with sodium chloride and occasionally with anhydrite or gypsum in certain areas).

2 to 30 per cent by volume of clay. (The lower figure for highly swelling clays such as montmorillonite, the upper for the least plastic, least colloidal of the surface clays used as admixtures.)

0 to 35 per cent by volume of weighting material. (Usually this is −325 mesh barytes, but occasionally hematite or celestite is used.)

0 to 10 per cent by volume of substances arising from the drilling operations, such as sand, shale and other rock cuttings and gas.

The proportions of these ingredients are varied according to the current requirements of density, filter-cake permeability, and rheological properties.

Consideration of the specific clay minerals present in drilling muds is beyond the scope of this paper. The attention of those interested in this subject, however, is called to reviews by Hobson,[45] Marshall,[68] Kerr,[54] Grim,[33, 34] and Hauser.[38] Reference should also be made to a series of papers by Hauser [37] and co-workers chiefly concerned with bentonite suspensions.

Rheology of Drilling Muds

Drilling muds are generally non-Newtonian fluids. They possess an apparent viscosity which decreases with increasing rate of shear, and moreover are often markedly thixotropic, the initial yield point increasing with time upon cessation of agitation, or, somewhat differently put, the apparent viscosity at any given rate of shear being lowered by agitation at higher rates of shear just prior to test.

The terms (which follow petroleum engineering usage) used throughout this section may be defined as follows: "gel strength," "shear strength," or "yield point" are used synonymously and refer to the stress necessary to initiate shear in a non-Newtonian fluid. All three of these terms are commonly (in this art) prefaced by the word "initial" when the property in question is determined in a thixotropic mud immediately after great agitation. This property is measured in terms of stress at the wall, *i.e.*, in units of force per unit area. It should not be inferred that such a property, of unique value, is susceptible of unique determination in all muds; there are both practical and theoretical complications involved in its determination, even in non-thixotropic muds; the reader is referred to Houwink [47] and to Scott-Blair.[82, 88]

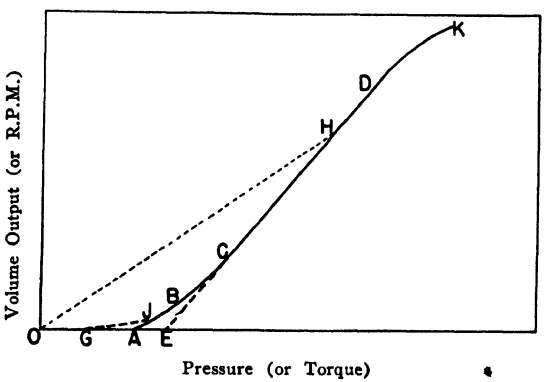


FIGURE 1

Fig. 1 illustrates a portion of an idealized stress-strain curve for a non-Newtonian but non-thixotropic mud. Abscissas are pressure (for a capillary viscometer) or torque (for a rotating cylinder viscometer); while ordinates are volume output (for a capillary viscometer) or rate of revolution (for a rotating-cylinder viscometer). While the wall stress, in terms of force per unit area, at the wall where shearing initially takes place is a linear function of pressure and torque for the respective types of viscometers, the average rate of shear is not a linear function of volume output or rate of revolution (except for the case of a Newtonian fluid), for the reason that in those portions of the viscometer where the shearing stress is less than the shear strength of the fluid, no shear takes place at all, such portions accordingly moving or rotating as a solid plug or annulus. The term "stress-strain" is thus used in its broader sense.

In a negligibly thixotropic mud, possessing little tendency toward syneresis, *ABCD* may be taken as a normal stress-strain curve. In accordance with the foregoing, the point *A* is the "initial" yield point, or "initial" gel strength, or "initial" shear strength. The slope of the straight line portion of the curve, *CD*, will be known as the mobility; the intercept of *CD* on the stress axis, *E*, as the yield value; and the reciprocal of the slope of the line drawn through the origin and any point *H* on the stress-strain curve as the apparent viscosity at the rate of shear corresponding to *H*. In accordance with a development of the Bingham equation for plastic flow given not only by Bingham but later elaborated by Buckingham [12] and Reiner,[76] and applied to drilling muds by Evans and Reid,[22] the distance *OA* is, in the absence of complicating factors, ¾ of the distance *OE*, for the case of a tube of circular cross-section.

There is no such constant relation for rotating-cylinder viscometers. In muds in which syneresis occurs, and especially in highly thixotropic fluids, there may be an exaggerated initial "lubricated plug" flow, shear taking place only at wall surfaces, giving rise to a linear portion of the curve *GJ* instead of *AJ*, which may result in the observed yield point in a capillary viscometer being less than ¾ of the yield value. Other complications due to thixotropy are discussed below. In the portion *JB* the shear gradually spreads from the wall presenting the greatest shearing stress across to the other wall of the viscometer; this behavior leads to the phrase "apparent rate of shear," since in this region part of the annulus of fluid is in shear, and part moves as a solid. As the straight-line portion of the curve is exceeded, the region of turbulent flow is entered.

A drilling mud possessing only Newtonian viscosity, even upon standing, is generally undesirable. Any particle denser than the fluid, and greater than colloidal size, will eventually settle in such a fluid, regardless of the magnitude of its viscosity. Thus, weighting material will drop out in the ditch and pits and, together with sand and cuttings, will settle in the hole when circulation is stopped, packing off or "freezing" the drilling string, as mentioned above. A mud in which the yield point increases to a substantial value upon standing is satisfactory even though it approaches a Newtonian fluid under agitation, for plug flow will tend to occur in the annular space in the bore-hole where the mud is flowing upward because of the relatively quiescent conditions, especially in enlarged portions of the hole, so that cuttings will be carried from the hole even though the upward velocity of the mud is low. As a matter of fact, a mud of large yield point under agitation is not desirable, as it necessitates the use of special equipment, such as vibrating screens, in order to remove sand and cuttings, and tends to retain gas, since bubbles thereof cannot rise to the surface.

The quantitative determination of the rheological properties of drilling muds is by no means simple, as is evidenced by the fact that each investigator in the field has made an almost individual approach to the problem. A non-Newtonian but non-thixotropic suspension can be fairly well characterized rheologically by a determination of rate of shear as a function of shearing stress, since the former should be a single-valued function of the latter. Such a determination is indicated in Fig. 1. In the case of a thixotropic fluid, however, time enters as an additional variable, in that as shearing stresses are suddenly changed from one value to another, unique values of rates of shear are not obtained, but rather values which vary with time (generally approaching an equilibrium value for any given rate of shear). A strictly complete rheological characterization of a thixotropic fluid would accordingly be extraordinarily involved and difficult of attainment, for such a complete set of data for a given fluid should enable one to calculate, for example, the rate of attainment of equilibrium shearing stress when the shearing rate for the fluid is suddenly changed from any given value to any other given value. An exact quantitative prediction of rates and magnitudes of changes in mobility and yield point during changes in degree and type

of turbulence should also be properly obtainable therefrom. Manifestly, this is not easy (one recalls Jerome Alexander's note on page 21 of Volume I of this series); but the point is somewhat elaborated upon here in view of the occasional tacit disregard of the importance of the part played by thixotropy in the rheological behavior of drilling fluids.

In selecting the type of rheological data to be obtained for a given drilling fluid in order that useful results may be obtained from a practicable and reasonable amount of experimentation, it appears that one may largely disregard all rates of change of apparent viscosity (except as (3) below may be considered such), and confine oneself to the following three sets of data: (1) shearing stress necessary to produce a number of rates of shear from nearly zero to a high value, each datum being obtained as nearly as possible instantaneously after agitation of the (thixotropic) fluid at very high rates of shear; (2) shearing stress necessary to produce a number of rates of shear from nearly zero to a high value, each datum representing an equilibrium value obtained upon indefinitely continuing shear at a constant rate; (3) the rate of change of shear strength upon standing quiescent, following agitation at very high rates of shear. (1) and (2) should be carried out with such an apparatus that the rate of shear does not vary from point to point in the apparatus, as is unfortunately the case with capillary viscometers; (3) is often difficult in practice because of the tendency for syneresis to occur in many drilling fluids. Hence measurements made with, for example, a concentric cylinder or a capillary viscometer upon a mud after standing some time are most misleading, movement (of the cylinder in the former or of the plug of fluid in the latter case) being facilitated by lubrication by a film of separated water, often thick enough to be observable by the unaided eye.

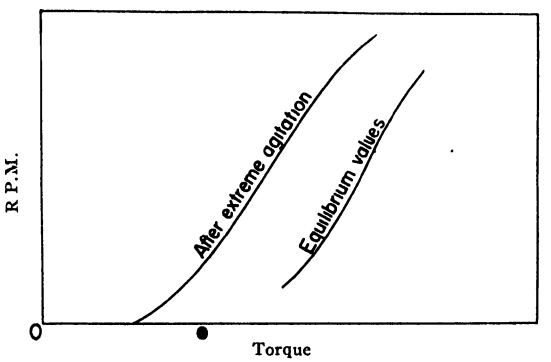


FIGURE 2

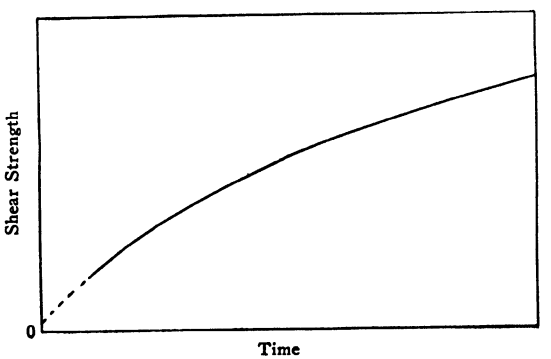


FIGURE 3

Such curves for a hypothetical mud are shown in Figs. 2 and 3. A fairly thixotropic mud is indicated; the two curves of Fig. 2 would of course coincide for a mud of no thixotropy, and the curve of Fig. 3 would be a straight line parallel to the time axis for such a mud. So far as the writer is aware, a set of experimental data corresponding to the hypothetical case described above has so far not been presented in the literature for a single drilling mud or clay suspension, although all three treatments suggested above, together with a great many more, have been applied by different investigators to individual muds. A successful application of von Smoluchowski's [91] treatment of coagulation rate has been applied to data of the type represented by Fig. 3 by Garrison,[26] who derives the following relation between gel strength S_t at time t, the duration of quiescence τ, and the gel strength at infinite time S_∞:

$$S_t = \frac{S_\infty k\tau}{1 + k\tau}.$$

The common use of the Stormer viscometer [86] in drilling fluid rheology deserves mention. This instrument consists of a metal cylinder, open at the bottom, which dips into a cup provided with a central baffle and exterior vanes in the annulus between cylinder and cup, both being coplanar with the axis of rotation. The cylinder is driven at various measured rates by means of a falling weight and gear train. The baffles have the disadvantage of causing turbulence at relatively low rates of rotation, thus introducing an undue dependence of apparent viscosity upon the density of the fluid, even for true fluids of moderate viscosity. However, the baffles allow extreme agitation and thorough mixing of the mud to be achieved by rotating the cylinder very fast with a hand crank, so that measurements of apparent viscosities may be made in an average time of 6 or 8 seconds after extreme shear, as well as fairly satisfactory measurements of "initial" gel strength. The viscometer is also well adapted to determinations of increase of gel strength with time of quiescence. Actual results of determinations on typical muds are shown on Figs. 4 and 5. (Data ob-

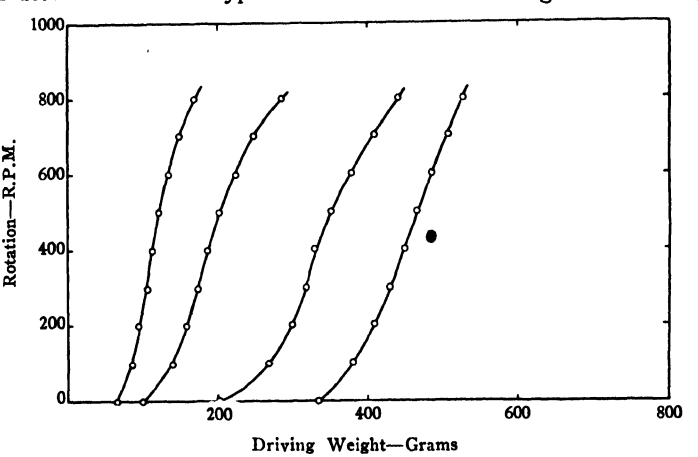


FIGURE 4

tained by Robert J. White.) The revolutions per minute at various loads for the muds of Fig. 4 were determined immediately after extreme agitation; those for Fig. 5 were equilibrium loads at the given rate of shear, as nearly as could be determined with the necessarily interrupted rotation. The datum for the lower extremity of each curve was determined from measurements of load required to give initial movement just after extreme agitation.

The flow of drilling mud under the conditions of turbulence, such as occur in the

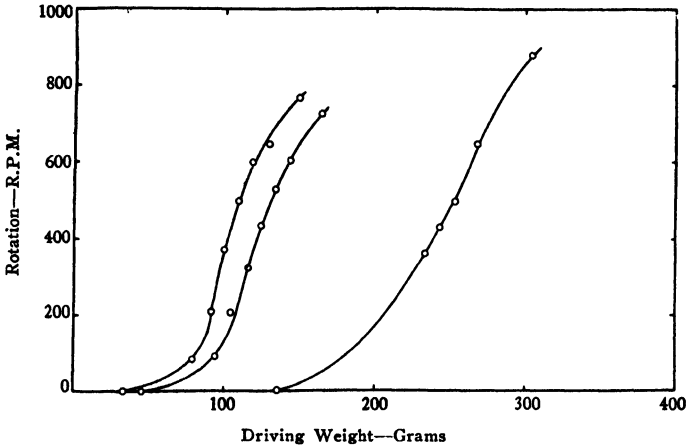


FIGURE 5

drill-pipe and certain other portions of the circulating system—when rates of flow are sufficiently high—has been subjected to less complete analysis than the behavior of muds under conditions of viscous flow. Empirical data for drilling muds and clay suspensions have been published by Herrick,[44] Gregory,[32] and Ambrose and Loomis,[1] and discussed by Moore,[70] Pigott,[75] and Evans and Reid.[22] The last two authors have given a particularly excellent analytical treatment of the turbulent flow of non-Newtonian non-thixotropic fluids. Fig. 6 is redrawn from their work, and illustrates

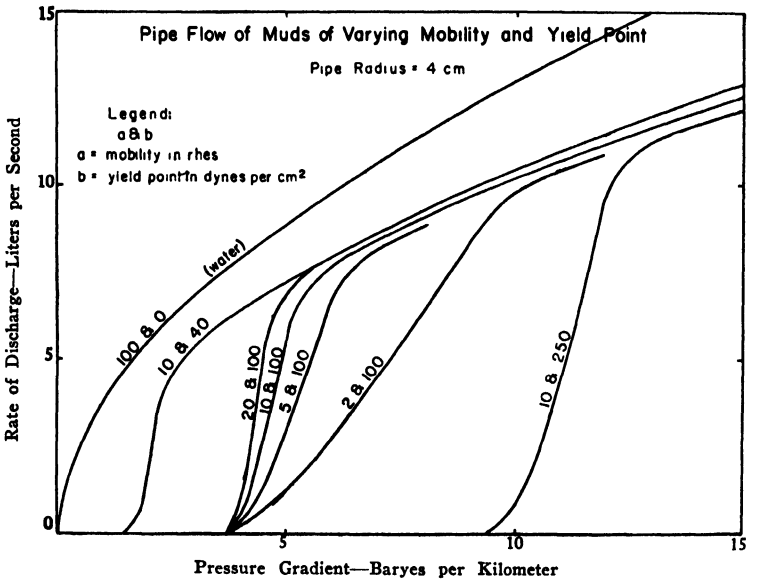


FIGURE 6

the effects produced by differences in yield point and mobility. As one might expect, differences in yield point have relatively little effect in the turbulent region; one might also expect turbulent behavior to be but slightly dependent upon thixotropy, although the latter would probably have a considerable influence in determining the

mean velocity at which turbulence sets in, through its tendency to increase plug flow.

It is of interest to consider that the tendency of flat particles suspended in a liquid undergoing shear is effectively to align themselves with their flat side normal to the shear gradient, *i.e.*, parallel with the direction of flow.* [57, 64, 89] When plug flow occurs after a region of agitation—such as a restriction in the annulus between drill-pipe and casing—is passed, the plug of moving fluid probably sets up with some degree of orientation of clay particles being present, so that the plug is rheologically anisotropic. The rotation of the drill pipe would tend toward orientation of flat particles in the same sense. The net effect of such orientation, aside from its influence on filter-cake properties, may well be to lower the pump pressure necessary to "break circulation" after flow in the circulating system has ceased for a time.

Dilatancy,[78] the opposite phenomenon from thixotropy, probably is an important factor in the sticking of drill pipe which occurs as a result of deposition of cuttings in an enlarged portion of the annulus, in the manner described above. The gradual accumulation of such detritus packs presumably leads to a close-packed arrangement, so that when an attempt is made to withdraw the drill pipe, disturbance of the pack increases its effective volume, thus leading to seizure of the pipe. The beneficial effects of hammering on or jarring the pipe during attempted withdrawal are obvious. The situation is not precisely the same as in the classical examples of dilatancy, such as sand on the wet seashore, or uncooked concentrated starch suspensions stirred in a beaker, where the ratio of liquid volume to solid volume is fixed; but the net effect is the same: the change from close to loose packing results in sharply increased immobility.

Filtration Behavior of Drilling Muds

Generally speaking, the pressure exerted by a column of drilling mud is kept higher, either by mud density or pressure drilling heads or both, than that of the fluid (oil, gas, or water) in a porous formation at any point in the bore hole. Occasionally it is not practicable to maintain such a pressure difference at all points, and many areas exist where, during drilling, isolated strata of low permeability containing gas or salt water under abnormally high pressure are simply allowed to "bleed" into the bore hole. Even in this case, however, the majority of the porous formations traversed by the bore hole have a lower pressure than that of the mud opposite thereto. The result is a filtration of the fluid phase of the mud into the porous formation, leaving the solids behind (together with some fluid) as a filter cake on the wall of the hole.

Much attention has been paid to the permeability of the filter cake so deposited.[18, 51, 55, 59, 95] Naturally, a low permeability leads to a low rate of increase of filter-cake thickness with time, and a correspondingly low rate of loss of filtrate to the opposing formation. The benefits of low filter-cake permeability are chiefly the rather negative ones of freedom from the difficulties otherwise occurring: loss of effective bore-hole diameter; sloughing and caving of formations resulting from filtrate penetration; and damage to oil-bearing sands from filtrate flooding. The last will be discussed later in connection with surface-active agents.

Not only do the filter-cake permeabilities of clays differ widely from clay to clay, but the same clay is capable of giving widely differing permeabilities depending upon the state of aggregation of the particles comprising the filter cake, which in turn is a function of the state of flocculation or deflocculation of the clay. The marked correspondence between filter-cake permeability and sedimentation volume is shown in the data below (compare the data of von Buzágh and Erényi [90] for quartz powder in solutions of various salts):

* That is, the couple tending to rotate the particle is least when the angle between flat side and direction of flow is at a minimum, so that a given particle spends much more time with this angle less than 45° than with it greater, even though it may rotate more or less continuously.

Suspension: 5% Hector (Calif.) Bentonite in Water

Treatment of Suspension	Apparent Viscosity [1]	Water-Solids Ratio in Cake [2]	Filter Cake Permeability [3]	Sedimentation Volume [4]
Partially deflocculated with $(NaPO_3)_6$	15	5.6	0.7	1.6
No treatment	25	6.4	1.2	2.4
Partially flocculated with MgO	115	10.6	8.1	25.

Suspension: 51% Clay #34 (A colloidal, illite-bearing California clay)

Treatment of Suspension	Apparent Viscosity [1]	Water-Solids Ratio in Cake [2]	Filter Cake Permeability [3]	Sedimentation Volume [4]
Partially deflocculated with $(NaPO_3)_6$	65	0.57	1.0	1.40
No treatment	100	0.55	1.2	1.66
Partially flocculated with MgO	*ca.* 300	0.62	2.4	1.82

[1] Stormer viscometer at 600 rpm
[2] Weight ratio; from 30-minute filtration at 100 lbs per sq in
[3] Microdarcys as calculated from 30-minute filtration at 100 lbs per sq in
[4] Cc per gram of clay, as centrifugally sedimented from a 10 to 1 dilution of the clay suspensions in distilled water. Centrifugal field: 85 g

Many drilling muds show an increased gel strength when raised in temperature to perhaps 80 or 90°. If the mud has been previously exposed to agitation and heat, as is the case with mud from a drilling well, this effect, which appears to be a temperature flocculation, is reversible. Generally such a temperature flocculation is accompanied by increased filter-cake permeability and increased sedimentation volume, as one would expect.

Mention should be made of the possibility that the partial orientation which probably occurs in the annulus between drill pipe and bore wall may lead to a lower filter-cake permeability than would be obtained with random orientation. The proposal has been made to enhance this effect by imposing an electrical field parallel to the bore walls, to take advantage of the well-known orientation of clay particles which takes place in such a field.[62]

It is of interest to note that the per cent solids in the filter cake (a somewhat different function was shown in the table above, for readier comparison), for a normal clay suspension to which neither flocculating nor deflocculating agents have been added, is of the same order of magnitude as the per cent solids in the clay-water mass obtained when an excess of water is poured over the dry clay, the latter swelling by imbibition of water without, however, any agitation being applied. For example, aqueous bentonite suspensions (second column) and a Mojave desert dry-lake clay (third column) give filter cakes having the following per cent solids:

	Bentonite	Mojave Desert Dry Lake
	Per Cent	
Free imbibition	14.4	62.0
Filter cake, 100 lbs per sq in	15.0	64.8
" " 500 " " " "	16.1	68.0
" " 1000 " " " "	16.7	69.4

The values in the last three rows were obtained from suspensions of 4.53 and 30.2 per cent respectively, but the filter-cake composition appears to be independent of the concentration of solids in the suspension which is filtered. That the packing volume should be fairly independent of the conditions under which the cake was laid down is perhaps readily understood, but it is at first glance surprising that about the same packing volume should be attained when reached from the opposite direction, *i.e.*, from the dry clay. One would not expect this relationship to hold either for clays which are naturally "flocculated" (*i.e.*, will not disperse when agitated with water) or for clays which exhibit extraordinary self-peptizing powers, such as clays admixed with natural or artificial deflocculating agents, since flocculation, non-

swelling, and large sedimentation volume * are generally concomitants, as are deflocculation, swelling, and small sedimentation volume.

Deflocculation of Drilling Muds

The average clay used for drilling mud, when suspended in moderately pure water, is generally in an incompletely deflocculated state. Clays which are not self-peptizing, such as most calcium clays, are usually avoided by the practical oil-well driller, as such clays are found to settle out when an attempt is made to prepare a drilling fluid from them. The average newly made drilling mud, however, can be deflocculated, and the measure of deflocculation in the ordinary case is the reduction in viscosity caused by the addition of any of several deflocculating agents. Those in common use, or of interest chemically, are:

Type One [4]
- Sodium hydroxide
- Sodium carbonate and bicarbonate
- Sodium silicate
- Sodium oxalate
- Sodium orthophosphates (mono-, di-, and tri-)

Type Two
- Molecularly dehydrated phosphates,[94] such as:
  - Sodium pyrophosphate [94] ($Na_4P_2O_7$ and $Na_2H_2P_2O_7$)
  - Sodium polymetaphosphate $(NaPO_3)_n$
  - Sodium triphosphate [80] ($Na_5P_3O_{10}$)
  - Sodium tetraphosphate [29] ($Na_6P_4O_{13}$)
- Vanadium analogs of the above,[96] such as:
  - Sodium pyrovanadate ($Na_4V_2O_7$)
  - Sodium polymetavanadate $(NaVO_3)_n$
- Thiotetraphosphates,[24, 94] such as:
  - Sodium trithiotetraphosphate ($Na_6P_4O_{10}S_3$)
- Borophosphates,[28, 94, 97] -vanadates, -tungstates, and the like, such as:
  - Sodium borophosphate glass, $[NaBO_3)_x\ (NaPO_3)_y]_n$
- Esters of molecularly dehydrated phosphoric acids.[98]
- Alkali-metal phytates.[58]

Type Three
- Tannin-like substances [4]
  - Tannic acid
  - Quebracho extract
  - Chestnut extract
  - Gallic acid

These agents have been divided into three groups, the justification for which is amply supplied by empirical considerations of effectiveness. The supporting theory is none too well developed at the present time. Generally speaking, deflocculants of the first type are only occasionally effective, and then only over a very short range of concentration, excessive additions rapidly bringing about flocculation. As may be readily seen, they comprise either alkalies or simple compounds which form insoluble calcium and magnesium salts. Naturally, those deflocculants forming highly insoluble calcium salts are effective particularly in cases where flocculation is due to Portland cement or anhydrite contamination.

The deflocculants (where this term is used herein the unique degelling character of the phenomenon of thinning a drilling mud must be kept in mind) in the second group are characterized by effectiveness at much lower concentrations than those in the first group, as well as by much greater ultimate deflocculation. Figures 7 and 8,

* Assuming dispersion of such clays having been effected in spite of the clay's low peptizability, *e.g.*, mechanically.

redrawn from data by Garrison and ten Brink,[27] and by Ford, Loomis, and Fidiam,[28] respectively, illustrate the magnitude of the effects produced.

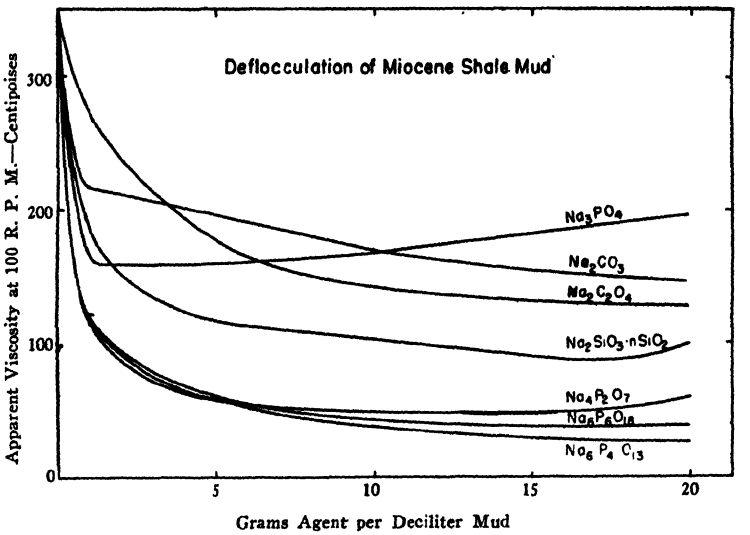


FIGURE 7

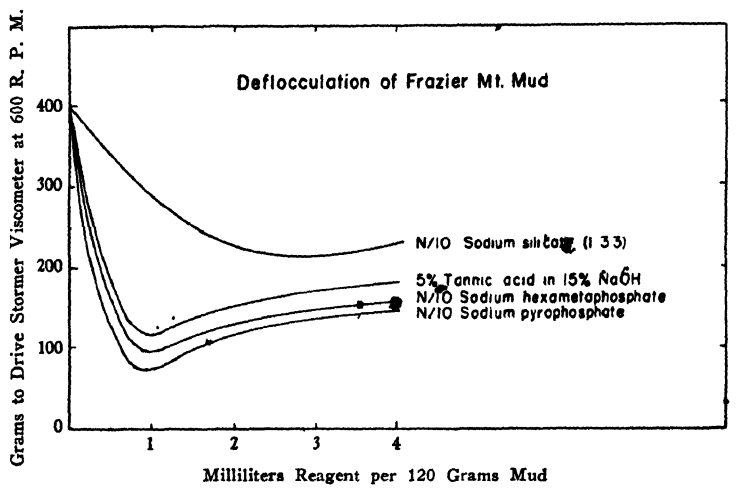


FIGURE 8

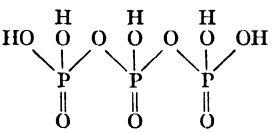
A fair amount of experimental data showing the effects of deflocculants of the second group on those properties of clay suspensions of particular interest to drilling-fluid technologists, such as fluidity, yield point, and rate of gelation, has been published; but no data on the effect on cataphoretic velocity, or even upon swelling, of such deflocculants have so far appeared, to the writer's knowledge. Since no wholly satisfactory theory has appeared, even in a related case where ample experimental data are available, namely the flocculation of clays (see, for example, Mattson's [66] data on the increase of cataphoretic velocity during flocculation of clays by electrolytes, and the discussions by Ostwald,[74]) no explanation for the extraordinary be-

havior of deflocculants of the second group is hazarded here. However, attention should be drawn to the following peculiarities of various of the members of the second and third group of deflocculants, which help one to understand in a general way what the mechanism may be:

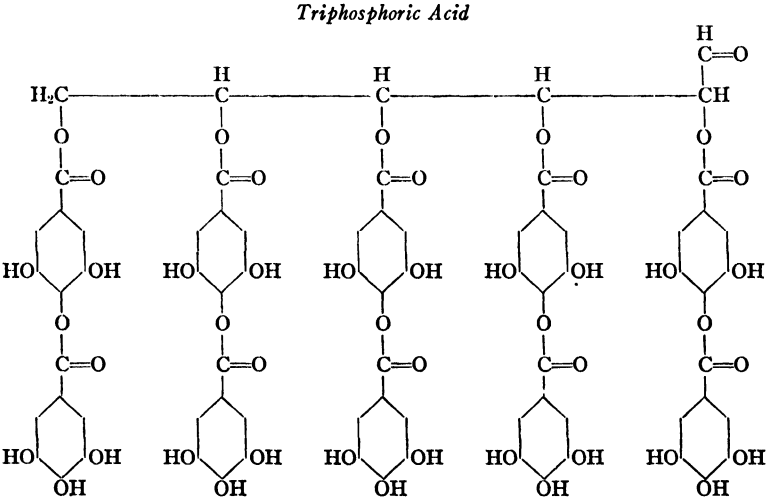
(1) Certain of the phosphates have calcium-sequestering properties. Although sodium pyrophosphate was found to have negligible calcium-binding power by Andress and Wüst,[3] Reitemeyer and Buehrer [77] find it to be equal to sodium hexametaphosphate (so-called; "Graham's salt") in its ability to prevent the precipitation of calcium carbonate from ammoniacal solutions when present in stoichiometrically minute quantities. The latter authors found the vanadium analogs to have no such inhibiting action; although according to the patent specification of Williams [96] the latter compounds rank with the complex phosphates in deflocculant efficiency. (No other experimental data on the vanadates appear to have been published.)

While calcium-sequestering power does not appear to be a necessary prerequisite for powerful clay deflocculant action (compare also the tanstuffs), nevertheless it will certainly enhance any deflocculating power otherwise possessed by a compound, at least to the extent to which such compounds as sodium carbonate and sodium oxalate are effective.

(2) Considering the probable structural configurations of triphosphoric acid and tannic acid, for example:



Triphosphoric Acid



Tannic Acid

one is struck by the fact that these are capable of yielding spatially extensive anions, in which, in the ionized state, the negative charge is rather more uniformly distributed along the extent of the molecule than is the case, for example, in the orthophosphate or carbonate ion (even when the latter are fully ionized, which requires a pH seldom occurring in drilling muds). Ford, Loomis, and Fidiam [25] have in fact considered both the complex phosphates and the tanstuffs as "plating" the clay particles, and have obtained semi-quantitative correlations between the areal extent of complex

phosphate and tannin molecules and the amqunts of the latter necessary to yield maximum deflocculation, which latter may be taken to correspond to equally complete plating of all the clay particles present.

(3) The fact that even the simpler of the molecularly dehydrated phosphates probably yield anions of higher charge than those compounds of the first group, because of the apparently higher dissociation constants of the former, adds to the general picture of a "platable" polyvalent anion. For example, the dissociation constants of pyrophosphoric and orthophosphoric acids are as follows:

$H_4P_2O_7$: $10^{-0.85}$, $10^{-1.96}$, $10^{-6.54}$, $10^{-8.44}$
H_3PO_4: $10^{-1.96}$, $10^{-6.7}$, $10^{-12.4}$

Since most drilling muds possess pH values of from 8.5 to 10, we must deduce from the above that any soluble pyrophosphate present in such a mud will be largely ionized to give $P_2O_7^{----}$ ions, while an orthophosphate will give HPO_4^{--} ions. The general trend is shown further by the fact that $Na_6P_6O_{18}$ and $Na_6P_4O_{13}$ behave as though they were salts of fairly strong acids, giving pH values of about 7 and 8 respectively for their 1 per cent solutions in water. Tanstuffs require a higher mud pH for maximum effectiveness, which is no doubt related to the fact that they are weaker acids than the complex phosphates.

As mentioned above, one refrains from making positive assertions regarding the action of adsorbed polyvalent anions in the deflocculation of clay suspensions because of (1) lack of experimental data regarding both the degree of polyvalency and the degree of adsorption of such anions, and (2) lack of experimental data regarding the electrokinetic behavior of such deflocculants (of the second group) with clay suspensions,* and finally (3) the somewhat confused state of present views on flocculation of clays, in view of the fact that the observed cataphoretic velocity of clay particles often increases instead of decreases during the course of flocculation by added salts. Johnson and Norton [50] have recently given a review of deflocculation theory, although deflocculants of the second group are not extensively considered. Moreover, their work was on non-swelling ceramic clays, which present a quite different picture from swelling drilling mud clays.

In passing, it may be noted that all of the molecularly dehydrated phosphates appear to revert to the ortho form in the course of time when added to a drilling fluid. Naturally, this effect is most pronounced at elevated temperatures, so that in deep wells the tanstuffs (which, incidentally, are probably eventually oxidized, although in this environment generally not at as fast a rate as the complex phosphates rehydrate) are often particularly useful, because of high bottom-hole circulating temperatures.

When added in small amounts to a drilling mud, acidic deflocculants such as tannin or disodium dihydrogen pyrophosphate do not generally need to be neutralized before addition, since the high buffer capacity of the mud, arising in large part from its content of clays of high base-exchange capacity (as is possessed by most moderately and highly colloidal clays used for drilling muds), permits a substantial addition of such materials without a very great change in pH. Higher concentrations, however, particularly of tanstuffs, are usually neutralized with caustic soda, and the solution so obtained is then added to the mud.

Generally speaking, deflocculants are added to a drilling mud (1) to counteract flocculating substances encountered in the course of drilling, such as salt water, anhydrite, and the like; (2) to obtain workable viscosities when mud-making formations such as plastic hydratable shales are being drilled through (mere dilution with water is not always satisfactory, as an embarrassingly large volume of mud may be produced, or, of more importance, the density of the mud will decrease, having been

* Such data would be of interest as shedding some light on the role played by the electroviscous effect before and after deflocculation.

raised by the addition of relatively valuable weighting materials); (3) to enable the addition of more gel-forming colloids such as bentonite; or (4) as a general measure of "conditioning," usually to decrease filter-cake permeability.

Flocculation of Drilling Muds

Flocculation of drilling muds occurs, as mentioned, from contamination with salt, salt water and brines of various compositions, anhydrite, gypsum, and Portland cement. The net result of such flocculation depends upon several factors: (1) the concentration of the flocculating agent, (2) the relative degrees of cohesion-probability increase and of dehydration, and (3) the ratio of the flocculated gel volume to the total volume, which in turn is dependent upon the concentration of the clay.

Small concentrations of Portland cement (perhaps 0.1 per cent), for example, actually have a peptizing effect upon some muds, the consistency decreasing upon its addition. Larger amounts (of the order of magnitude of 0.5 to 1 gram per 100 cc of mud) usually convert a fluid mud into a clabbery, stiff gel which soon exhibits syneresis, but which even upon long standing retains its gel form, a large amount of water being entrapped by the flocculated clay. Small amounts of salt (for example 0.5 gram per 100 cc) have a similar thickening effect upon average muds, which likewise is fairly permanent; but larger amounts (upwards of 5 grams per 100 cc) cause an initial thickening (presumably of the same type caused by calcium ion, which general effect has been well described by Kruyt,[58]) later followed by a precipitation of the clay, with a nearly complete loss of gel properties. The effect is shown in Fig. 9 for a 6 per cent Wyoming bentonite suspension.

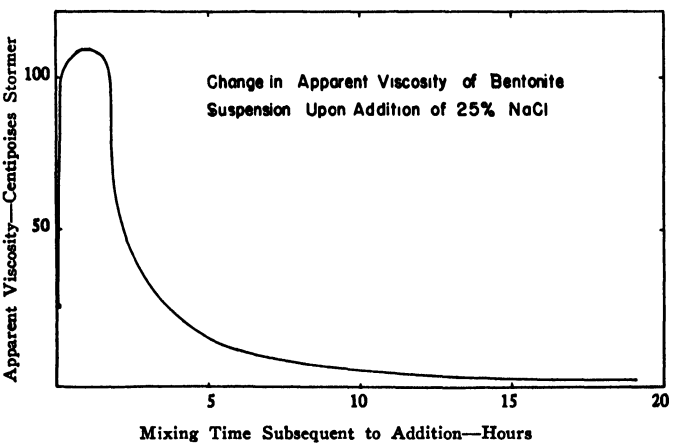


FIGURE 9

The effect of clay concentration upon flocculation behavior is usually noticed only in the laboratory, for most actual drilling muds contain enough gel-forming colloidal clay to give a stiff gel upon the addition of calcium hydroxide, for example. However, if such a mud is first diluted with several parts of water and then flocculated with lime, partial sedimentation takes place before the floc becomes concentrated enough to form a single mass of gel, and the character of the latter is considerably modified.

In certain areas where oil is found it is necessary to drill through many hundreds of feet of rock salt in order to reach the oil-bearing strata. In such cases saturation of an aqueous drilling mud with salt is unavoidable, and all ordinary clays are of scant use in such a mud, as they settle out whenever agitation is ceased, contribute

no gel strength to the fluid, and do not give relatively impervious filter cakes. Emulsoid colloids which are as purely lyocratic as possible are used with considerable success in such muds. Such substances [86] as starch (of course in its gelatinized or emulsoid form); gums, such as arabic, karaya, ghatti, and tragacanth; and seaweeds and seaweed products, such as agar, Irish moss, and sodium alginate, are regularly or occasionally used. Generally speaking, from 0.5 to 1 gram per 100 cc of such additives serves to contribute a filter-cake permeability, even in saturated salt water, as low as is obtainable in fresh water with bentonite.[31]

The interesting discovery was made by Cross [17] that fuller's earth of the Florida-Georgia type (Attapulgus clay, for example) possesses the ability to give the same gelation in salt water that it does in fresh water, although a reasonable amount of mechanical agitation is necessary; indeed, five grams per 100 cc of water will give a suspension of about fifteen centipoises (apparent Stormer) viscosity in either distilled or salt-saturated water. This type of clay is extensively used in rock-salt areas for imparting gel strength to muds, so that cuttings can be transported from the hole. However, the filter cake permeability of this type of clay is very high, whether from a fresh or salt water suspension, quite possibly as a result of its apparently fibrous [11, 65, 78] character, in contrast to the platy character of other clays.

Electrokinetics of Drilling Muds

Electric Logging. In the later stages of drilling the average well, several thousand feet of bore hole will usually be uncased to the bottom, so that filtration of water from the drilling fluid is taking place continuously and simultaneously into all exposed permeable strata, through a filter cake on the sides of the hole. Opposite impermeable strata, such as most shales, chert, some types of limestone, and the like, however, no filtration occurs. In the first case, a difference of potential arises between the drilling fluid (here assumed to be an average clay-water mud) and the interior of the porous stratum from at least two sources: (1) streaming potential across the mud cake, and (2) concentration cell EMF resulting from the usual difference in electrolyte concentration of filtrate and formation water. In the second case, streaming potential naturally does not occur.

During the nineteen-twenties a method of logging bore holes was developed [80] which included, among other measurements, a determination of the potential of the drilling fluid in an open hole with respect to the earth. The measurement is carried out by lowering an electrode on a suitable cable to the bottom of a well and recording the potential as a function of depth, during which time the drill pipe and bit are withdrawn, while the hole is kept full of drilling mud. Such a log of a bore hole gives useful indications of the nature of the strata traversed, which while not always completely definitive may still be used to correlate subsurface geologic structure from well to well in the same area.

Recently an important contributing factor to the total potential so observed has been recognized to be the natural potentials of the rock strata themselves, dissociated from any effects produced by drilling.[20, 21, 72] Additionally, distinctive effects related to concentration-cell potentials have been noted [72, 81] in connection with shales. The result of these later findings has been to diminish the importance ascribed to streaming potential, but there is no doubt that the latter remains an appreciable factor in the total.

The magnitude of the streaming potential is governed *inter alia* by the well-known equation of Helmholtz:

$$E = \frac{\zeta DPR}{4\pi\eta}$$

where E is the streaming potential; ζ is the double layer potential of pore material surface; D is the dielectric constant of the liquid of the double layer; P is the pres-

sure drop across the membrane; R is the resistivity of the fluid; and η is the viscosity of the fluid.

The zeta potential of the filter cakes from most clay-water muds is reasonably high, and although that of the usual porous formation rocks (silica, feldspars, and related acidic rocks) is of at least comparable magnitude, by far the greater part of the pressure drop between mud and porous formation is across the filter cake, because of its far lower permeability. Accordingly, it may be deduced that the greatest contribution to the streaming potential is made by the flow through the mud cake. No particular amount of work seems to have been done, however, on the streaming potentials obtainable with different drilling muds. It would seem that such a study, including particularly the effects of temperature and electrolyte concentration, would be of value.

One aspect of "self-potential" measurements which should be noted is the fact that what is recorded is not the actual natural, streaming and concentration potentials (such as would be obtained if a particular stratum could be isolated) but the EMF remaining after the system has contributed some current to the partial short circuit resulting from the finite conductivity of the drilling mud. Suppose an isolated one-foot stratum of porous sand ideally gave a self-potential of −50 millivolts, and a second isolated one-foot stratum only −25 millivolts. If these two strata are now juxtaposed and connected by a bore hole filled with mud of a certain conductivity, current will flow so that less than 50 and more than 25 millivolts will be actually recorded by the electrode system opposite the two strata respectively. If the conductivity of the mud is increased, not only is the short circuit intensified, but the observed potential is correspondingly lowered (other factors remaining constant). This effect has been recognized since the beginning of the electric logging art; but what seems to have been generally overlooked is the fact that, in order to give an appreciable streaming potential to a mud of finite conductivity, a filter cake must function not simply as an EMF cell but as a current cell; otherwise stated, the filter cake must have a low internal resistance while supplying a finite amount of current under prevailing conditions of filtrate flow. It is to be expected that the filter cakes from different clays will vary widely in "streaming current" productivity; it would appear that extremely low values of cake permeability, probably far lower than have as yet been obtained in practice, might be undesirable from the electric logging standpoint, since if filtrate flow is infinitesimal, the wattage produceable from a given area of such a cake will likewise be infinitesimal. High zeta potentials should naturally be generally desirable.

From the equation given above, it is clear that streaming potential should increase with pressure. This effect has been observed in some cases when pressure has been externally applied to the mud column, but has been found lacking or of only slight magnitude in other cases.[21, 72] This must not be taken as conclusive evidence of the unimportance of streaming potentials in the so called "self-potential" measurements, but rather may result from the compression of the mud cake caused by applied pressure, which results in only slightly more filtrate flow, so that while the theoretical "open circuit" EMF is increased, this is offset by the loss in effectiveness of the filter cake as a source of current. In other words, the applied pressure increases not only the EMF but also the effective internal resistance of the cell.

It should be noted that in the usual case, with filtrate flow into the formation, and mud less saline than formation fluid, both streaming potential and concentration cell EMF are in the same sense, and lead to a negative potential of the bore hole contents with respect to the formation. The magnitude of the potentials encountered is appreciable; average logs show differences between adjacent unlike strata of 25 to 50 millivolts and more, while the overall potential difference between ground and the bore hole several thousand feet down may be as much as 200 millivolts.

Conditioning of Drilling Muds. Electrophoresis has been proposed [41] as a useful aid in reconditioning drilling muds. The art of purifying clay electrophoretically is of course decades old, but the application to drilling muds involves several factors not present in ceramic purification. The general scheme is to rotate a positively charged drum in a trough of clay slurry, scraping off the electrodeposit with fixed blades. In drilling muds, it may be desired to remove some of the gel-forming colloidal material without removing weighting material, a situation which occurs frequently when drilling through plastic, mud-making shales, in which case the drilling mud density is usually kept high in order to inhibit caving. Again, the object may be to perform a desanding operation, especially with muds of thick consistency which are not too well handled by settling ditches or vibrating screens. While electrophoretic velocity is fairly independent of particle size, and grains of non-clay silicates may have migration velocities possibly as high as any clays present, nevertheless concentration by electrophoretic means of a portion of the solids present may enable the remainder of the fluid to become lowered in consistency so that settling of sand will take place satisfactorily. An attempt to do this by simple dilution involves a considerable increase in total volume, and corresponding reduction in density.

Electrophoretic Removal of Filter Cakes. After a well has been drilled and it is desired to produce oil therefrom, a filter cake of clay solids will generally be interposed between the liner (the perforated section of pipe opposite the productive zone) and the oil-bearing formation. In the case of high-pressure reservoirs, the cake is merely pushed off by the inflowing oil; but with low-pressure reservoirs swabbing (the application of a suction to the formation in question by repeatedly pulling a swab upward above the liner) is resorted to. The mud cake, especially if one of high per cent solids content, and therefore tough, occasionally resists even persistent swabbing, and may lower the productivity of the well by failing to be completely removed. The proposal has been made [14] to remove the mud cake electrophoretically by simply lowering an electrode into the liner and applying a positive potential. A variation [49] of the general method comprises substituting a non-conducting liquid, such as alcohol, acetone, or nitrobenzene for the usual well fluid, on the theory that the electrophoretic effect will be enhanced, since, all other factors remaining equal, migration velocity diminishes with increasing fluid conductivity. It would seem a matter for investigation, however, whether the actual migration velocities of mud-cake particles are increased by the substitution of such liquids, as an appreciable diminution, if not in fact a reversal, of the zeta potential, may be thereby effected.

Electrophoretic Deposition of Filter Cakes. The proposal has also been made [42] to assist the natural deposition of filter cakes on the walls of the bore hole by electrophoresis, using an electrode in the well, which may be part of the drill string. This would have the salutary effect of enabling a filter cake to be built up without a corresponding loss of water to the formation.

Surface- and Interfacial-Tension Modifying Agents

Anti-"Gas-Cutting" Agents. The possibility of entrainment of gas in drilling muds has been mentioned. Ordinarily such gas rises to the surface of the mud and is freed therefrom as the mud passes from the flow line through the ditch, and through the screen, if any, into the suction pit; but if (1) the mud possesses a high gel strength, even under agitation, or if (2) there is present in the mud a foam-stabilizing agent, such as starch, gums, soil humus material, or the like, especially in conjunction with a salty mud, the gas will not be freed. Besides the disadvantage which has been mentioned previously, that of increasing the possibility of a blowout of the well, a second feature of a "gas-cut" mud which gives trouble in the difficulty which the pumps may have in operating; a mechanism designed for an incompressible fluid is suddenly called upon to pump a compressible fluid; the piston may reciprocate without operating the valves.

For successful gas removal, the initial gel strength of the mud must be reduced. In fact, one of the first patents [61] to issue for drilling-mud deflocculation contemplated the use of alkaline tannates especially for muds laden with gas bubbles. If it is not possible for the individual bubbles to rise through the mud to the surface, the use of a chemical foam breaker *per se* can scarcely be effective. Reduction in gel strength is usually accomplished by chemical deflocculation, by dilution with water (with addition of weighting material), or by agitation of the mud by allowing it to cascade down a riffle board. Since the ratio of buoyant force to wall stress is greater for large bubbles than for small, it is sometimes effective to pass the mud through a vacuum degasser, in which a steam injector furnishes a pressure of one-third atmosphere or less, absolute.

Even though bubbles can rise to the surface, they may fail to break, being stabilized by the agents mentioned above. One patent [2] uses such water-miscible organic solvents as ethanol, isopropanol, acetone, ethyl acetate, and the like, and ascribes their effectiveness to reduction in surface tension. Such an action can scarcely be the major factor in the behavior of foam breakers, as many foam stabilizers have a like effect, although it is undeniable that exceedingly small bubbles (in which $2T/R$ is comparable with the total pressure) will be enabled to become larger, and hence possibly to rise. Indeed, any foam breaker must lower surface tension in order to be able to concentrate in the interface, where it would appear to have to arrive in order to be effective. Useful at somewhat lower concentrations than the agents just mentioned are such foam breakers as octyl alcohol [7] (2-ethyl hexanol is commercially available), fenchyl alcohol,[7] long-chain fatty acids,[52] such as coconut oil fatty acid, and esters thereof,[58] such as butyl stearate.

The use of volatile or semi-volatile organic compounds as foam breakers is subject to a practical difficulty in the case of deep wells, in that the temperature of the mud flowing from the well is often so high (140 to 160° F is not uncommon) as to cause rapid loss from evaporation. The very tendency of foam breakers to concentrate in the interface, *i.e.*, in the foam, exaggerates their volatility.

Treatment of Oil-Bearing Sands. It has been shown by Bartell [9] and co-workers that most reservoir sands exhibit acute contact angles for water against oil, or as commonly stated, they are selectively wet by water. (A full discussion of selective wetting is given by Bartell in an earlier volume of this series.[10]) This follows from the hydrophilic character of the common silicate rocks, and is apparently the case even where oil has been in contact with the rocks for millions of years. The disposition of oil and water coexisting in a porous sandstone is quite analogous to the case of air and water in soils, the geometry of which has been described by geologists and soil scientists such as Slichter,[84] Haines,[35] and Fisher,[23] except that contact angles are finitely acute instead of zero. In oil reservoirs, the interstitial water (the possibility of the coexistence of which with oil has been realized only in recent years) occupies the regions immediately surrounding the points of contact of adjacent sand grains, and such of the smaller capillaries as its volume relative to that of the water will allow. If oil flowing toward the bore hole sets up a slight pressure gradient across a small doubly corniform capillary containing water (terminated at both ends by an oil-water interface), the water will merely move only so far as is necessary for the difference in curvature of the front and rear interfaces to compensate for the pressure difference. Unless the latter is large enough, the water will continue to block the capillary. However, if the interfacial tension across the oil-water interfaces should be reduced, the necessary pressure difference is likewise reduced, so that the water can then be flushed out and the pore made available for oil flow. The result is that the permeability of a porous formation to oil is dependent upon the amount of interstitial water present, which latter can be progressively removed, and the oil permeability thereby increased, only by (1) increased pressure gradients of flow, or (2) decreased interfacial tension (or increased contact angle).

Consider a flowing well with a given reservoir pressure, and a certain amount of interstitial water originally present in the formation. Since in radial flow the pressure gradient varies inversely as the radial distance from the center of the bore-hole, we may assume that the interstitial water closer than a certain distance r from the bore hole has been partially flushed out, while beyond the distance r the flow pressure gradient is insufficient to dislodge the interstitial water. The permeability of the formation to oil will then be constant beyond r, but will increase as the bore hole is approached closer than r. Aqueous filtrate from a drilling mud close to the bore hole will simply be flushed back into the well; but if filtrate should be forced beyond r, it will remain (only partially just beyond r, more completely as r is exceeded), and the overall permeance of the system to oil flow will be permanently diminished. This example is necessarily greatly idealized, but it illustrates the general case of "water-lock" which commonly occurs when productive formations are drilled into with mud of high filter-cake permeability. It also makes understandable the observed fact that small amounts of filtrate generally do no particular apparent harm to the resulting productivity.

Recently the technique has been developed of giving oil-bearing formations a flushing with a liquid designed to lower oil-water interfacial tension, after drilling is completed but before production is commenced. Two distinctly different types of compounds are used: substances such as the lower aliphatic alcohols, acetone, dioxane, and the like, which have no very marked surface-active properties but which are mutual solvents for oil and water, and may be said to lower interfacial tension by making the whole of the aqueous phase more like the whole of the oil phase; and solutions of highly surface-active materials, such as the newer wetting agents.

Drilling Fluids of Unusual Composition

Sodium Silicate Muds. Those varieties of sodium silicate with more than the stoichiometrically equivalent ratio of SiO_2 to Na_2O (cf. the monograph on water glass in an earlier volume of this series [85]), especially the grade known commercially as "D" brand, find occasional application in drilling muds for drilling through "heaving" shale, and, when used at all in such muds, usually constitute the bulk of the fluid phase. Most clays fail to swell at all in concentrated solutions of electrolytes, and water glass not only presents a high concentration of the latter but also forms highly insoluble precipitates with calcium and magnesium ions, usually found in heaving shales. Accordingly, these neither disperse nor swell in water glass.

An average sodium silicate mud [6] is compounded of two-thirds by volume of sodium silicate solution and one-third saturated salt brine, to which is added sufficient weighting material to give the desired density. It is remarkable that as small a concentration as one per cent of bentonite imparts sufficient gel strength to such a mud to maintain the weighting material in suspension.

Oil-Base Drilling Muds. Drilling fluids made up with oil as a fluid base instead of water are of considerable interest colloidally. They represent an attempt to avoid the difficulties of swelling formations and reduction of oil permeability mentioned in earlier sections. Ordinary fuel oil ("gas oil") is commonly used, to which is added a material (analogous to clay in water-base muds) to impart gel strength and even thixotropy. Typical materials for this purpose are blown asphalt,[18, 68] calcium hydroxide,[69] fluffy magnesium oxide or carbonate,[48] lampblack [43] (cf. printing inks), heavy metal soaps [79] (cf. greases), and alkali-metal soaps.[19, 67]

As flocculation is decreased by low solid-liquid interfacial tension, one naturally turns to oleophilic, rather than hydrophilic substances for use as weighting materials in oil-base muds. Metals such as lead dust or zinc dust, metallic sulfides such as galena or pyrite, certain of the less hydrophilic metallic oxides such as litharge and magnetite, carbonates such as ground limestone, oyster shells, dolomite, and magnesite, and hydrophilic substances coated with carbonaceous matter such as spent re-

finery clay or barytes superficially carbonized,[69] have been proposed and in some cases used to increase the density of oil-base muds.

Oil-soluble deflocculants also have a place in such fluids, reducing gel strength and lessening the tendency for the weighting materials to settle out. (Compare the work of Bartell and Osterhof on paints.[8]) Typical of deflocculants suitable for this purpose are long-chain fatty acids such as oleic acid,[16] nitrogen bases,[87] especially of large radicals, such as cetyl amine, xylidine, and picoline, sulfonates such as obtained in oil refining,[71] sulfated higher alcohols,[88] and similar other oil-soluble heteropolar compounds.

Oil-base drilling fluids are not very frequently used, since the cost per barrel of fluid is quite high. Water encountered during drilling tends to emulsify with the mixture as well as to wet and settle out only feebly oil-wettable additives such as limestone or oyster shells or hydrophilic materials such as barytes or ground silica. Handling the fluid at the well is difficult and possibly dangerous from the standpoint of fire-hazard. Finally, the results obtained as far as the productivity of the well is concerned do not always justify the trouble and cost. However, future developments may increase their general use.

Oil-Water Emulsions

Oil-in-water emulsions have been proposed[89] as drilling fluids, since almost any desired degree of gel strength can be obtained by proper choice and treatment of the emulsion. However, it appears difficult to impart thixotropy to an emulsion, and this property is a prerequisite to really satisfactory drilling muds. It is of interest to note that the simple addition of a small amount of sulfuric acid to ordinary crude oil generally forms a sufficiency of emulsifying agent, so that no other agent need be added. The plastic properties of such emulsions lend themselves to use for the placement of gravel packs.[60]

Sulfur as a Drilling Fluid

Sulfur is a substance whose colloidal behavior is as extraordinary as its ultimate composition is simple. (A recent review is given by Houwink;[46] see also P. P. von Weimarn's section on sulfur in an earlier volume of this series.[92]) Molten sulfur appears to offer interesting possibilities as a drilling fluid,[5] since a high density (1.8) is obtained without the use of weighting agents; upon cooling it solidifies, thereby consolidating loose formations and replacing in part both cement and casing; and high viscosities may be obtained by carrying the temperature up into the region of so-called "anomalous" viscosity.

It has been proposed[15] that the viscosity of molten sulfur drilling fluids, especially in the anomalous region, be lowered by the addition of such compounds as arsenic, phosphorus, and antimony sulfides; zinc, lead, cadmium, bismuth, and alkaline-earth sulfides; naphthalene, anthracene, and phenanthrene; vinyl polymers, and polysulfide elastomers, all of which possess this property. Possibly these substances act as peptizing agents for the only partially mutually soluble $S\lambda$ and $S\mu$. In any case, their use allows heating of the sulfur to a higher temperature than otherwise before pumping it down the well, thus minimizing the possibility of freezing the drilling string by premature cooling of the liquid sulfur.

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Colloidal Factors in the Petroleum Industry

C. E. NABUCO DE ARAUJO, JR.

Rio de Janeiro, Brazil

Although crude petroleum does not possess very pronounced colloidal properties, great care is exercised in drilling operations to prevent the oil sands from becoming wet with the water also present in the deposit, and thus becoming impermeable to the oil. Research workers have been unable to demonstrate the presence of substances in colloidal dispersion, even though fluorescence or bloom seems to be caused in part by colloidal particles invisible in the ultramicroscope. Anomalous viscosity of several crude oils resembles the pronounced changes in viscosity frequently found in certain colloidal solutions which have a tendency to form a gel at low temperatures and a sol at higher ones. The asphaltic solid constituents of petroleum are generally considered as typical examples of colloidal dispersion.

Wolfgang Ostwald [1] considers high-boiling petroleum fractions as iso-colloids, in which the dispersed phase and the dispersion medium possess the same or similar chemical constitution. Dunstan and Thole [2] consider that the blue cone of light displayed by certain lubricating oils is due to the presence of amicrons in the oils. Thus it is more than probable that petroleum and petroleum distillates may contain colloidally dispersed material.

In drilling an oil well one must consider first the producing horizon, since oil is generally dispersed as droplets in water, and secondly, in modern drilling practice, the drilling muds employed. With fine emulsions, the difficulties have been overcome, in several cases, by electrical or chemical methods usually recommended for breaking emulsions.*

Drilling muds involve many applications of colloid chemistry.† Such "muds" flush out the cutting, keep the bit cool, and, in addition to coating the walls, penetrate into and seal up porous strata abutting the hole. The chemical and physical characteristics of the mud are controlled by the drillers. If the pressures are not so great as to require a heavier fluid, oil may be used instead of mud. According to the specific aim in view, bentonite, barytes, and iron oxide are usually used as mud constituents.

The formation of emulsions when the well begins to produce is due partly to underground gas and water and partly to agitation by pumping; steps should be taken to prevent this occurrence and to remove the water from the oil as quickly as possible on reaching the surface. Standard economical dehydration methods must be applied, the choice depending greatly upon the qualitative and quantitative characteristics of the emulsion formed, as well as upon the nature of the component emulsified. The presence of emulsions in crude oil has its disadvantages, since water reduces the calorific value of the oil in direct ratio to the percentage of water present, and the refining becomes not only more expensive but also dangerous because of the formation of foams which, besides making redistillation necessary, become an

* See paper by L. T. Monson and R. W. Stenzel in this volume. J. A.

† See paper by D. H. Larson in this volume. J. A.

imminent fire hazard. The most common method among those recommended for foam inhibition or destruction is addition of a substance which coagulates, or neutralizes, the action of stabilizing colloidal substances.

Chemical methods of dehydrating emulsions are applicable when there is no danger of introducing objectionable foreign substances into the oil. The efficiency of treatment with a chemical depends on the point of introduction of the chemical; the degree and duration of agitation of the system; the kind, amount and strength of the chemical solution; and finally on the temperature of the treatment.

Emulsions causing disturbance may also be formed during the process of refining. In certain processes there exist conditions which are favorable to the formation of emulsions, whereas in other cases continuous emulsification is prevented. Therefore, in order to avoid emulsion formation, it is quite important that *correct methods* be chosen for the refining of petroleum distillates.

When sulfuric acid is used in refining, sulfonic compounds and naphthenic acids formed during the treatment combine with the alkaline solution used for washing, producing soaps which assist emulsion formation. Concentrated alkali is advantageous, since the soap is salted out and does not dissolve; vigorous mixing or stirring during neutralization or wash should be avoided.

Very often emulsion formation is encountered when refining crude oil, and the breaking of these emulsions sometimes involves more trouble than the refining itself.

Generally speaking the refining processes of colloid chemical interest are:

(1) treatment with sulfuric acid;
(2) refining with alkalies;
(3) refining with various solvents or salts;
(4) treatment with various absorbents.

Sulfuric acid was first used for refining vegetable and animal oils,[8] and has been successfully employed in the treatment of various petroleum distillates since the beginning of the petroleum industry, due largely to its efficiency, cheapness and availability. The action of sulfuric acid is very complex and varies with the different distillates to be treated. Sulfuric acid leads to the formation of certain sulfonated substances or to products of polymerization and condensation reactions, and the disposal of the sludge is troublesome. On the other hand, some new solvent methods fail to separate asphalt from oil, possibly because of the colloidal nature of the asphaltic particles and their insolubility. In such cases, precipitating agents are employed for elimination of asphalt. Practically all petroleum distillates must be treated with sulfuric acid, which is more general in its action than solvents; however, solvent refining is recommended for the production of lubricating oils of remarkable qualities.

Alkali treatment can be considered as a second procedure in acid refining. The use of an aqueous alkaline solution produces troublesome emulsions and in some cases does not extract the weaker acidic substances, nor does it decompose or remove the relatively stable sulfuric esters.

Adsorbents constitute generally a good help to refiners in completing the refining process with alkalies. Various earths and minerals have been used and chosen, taking into consideration the material to be adsorbed. The action of adsorbents in petroleum refining is chiefly concerned with decoloration, desulfurization and separation of unsaturated hydrocarbons. Fuller's earth, China clay, alumina, magnesite, iron oxide, bentonite, silica gel, bone ash, bone black, blood charcoal and many other substances have been employed to remove suspended, colloidal and dissolved impurities, such as carbon, resinous and asphaltic substances, especially those rich in combined oxygen and hydrocarbons poor in hydrogen. This increases the chemical stability and neutralizes acid-treated oils without washing and the use of alkaline solutions.

The field for technological applications of colloid chemistry in the petroleum

industry is relatively large. In lubricating greases * for instance, two phases exhibiting colloidal properties may be found. Lubricating greases are composed of a mineral oil suspended in a soap, the first acting as the liquid phase and the latter as the solid gel. Wolfgang Ostwald [4] considered that gels may be formed by changes in the following properties of a colloidal system:

(a) formation of an insoluble precipitate,
(b) the degree of hydration,
(c) the concentration of the gel-former.

Klemgard [5] says: "Greases are ordinarily classified as heat-reversible elastic gels, *i.e.*, the temperature solubility curve for the soap in the oil is a steep one. At low temperatures the soap is relatively insoluble." Other investigators, however, regard lubricating greases as colloidal suspensions or emulsions stabilized with soap.

Petroleum jelly is considered as a purified mixture of semi-solid hydrocarbons, colloidal wax being one of the components. The manufacture of artificial Vaseline comprises the addition of mineral oil to the melted paraffin wax. After cooling the mixture, the paraffin crystallizes in fine needles which account perhaps for some of the characteristic properties of the Vaseline. These needles seem to be of colloidal dimensions, at least in thickness. The Vaseline structure is somewhat like that of a soft gel, like the wiping solder used by plumbers.

The tendency of paraffin wax to crystallize in the shape of fine needles may be regarded as the reason why concentrated solutions of paraffin waxes in benzene, chloroform, etc., gelatinize readily. Although this characteristic does not prove that the paraffin wax particles in these solutions are "amorphous" or in colloidal dispersion, the large number of nuclei formed and the slow rate of crystallization transform the whole mass to a jelly-like gel, which generally is not stable. The high stability of Vaseline may be accounted for by the presence in the dispersing oil of substances which prevent further nucleation, but permit the paraffin crystals to grow. Cosmetic creams are dispersions of mineral oils in aqueous soaps.

Soluble cutting oils, which are emulsions of compounded mineral oils in water, are valuable for the lubrication of cutting tools; they are of the oil-in-water type, containing a large amount of water and a small quantity of oil. However, some of the soluble cutting oils may be considered merely as solutions of soaps, or saponified sulfonated fatty oils. Petroleum sulfonic acids have been suggested as wetting agents in dyeing operations, and their effectiveness in breaking emulsions of the water-in-oil type has been also reported. Petroleum sulfonates present several advantages as wetting agents, and as vehicles for insecticides, mainly in spraying solutions. The emulsifying powers of sulfonates make them useful in polishing compounds, while water-soluble petroleum sulfonates have been recommended as dust fixatives.

Asphalt emulsions † have long been used for coating and making dust-free roads not subjected to heavy traffic. The diluted emulsions are easily spread, and the asphalt left after the evaporation of the water binds the road surface into a coherent layer.

Colloidal suspensions of graphite ‡ in mineral oil are used for lubricating purposes. The graphite is said to improve the qualities of a lubricant by coating the metal surfaces of bearings and by increasing their smoothness and causing the lubricating film to adhere to the surfaces under friction.

Other interesting applications of colloid chemistry in the petroleum industry are colloidal fuel and printing inks. Colloidal fuel § consists of a suspension of powdered

* See paper by C. J. Boner in this volume.
† See paper by F. J. Nellensteyn in Vol. III of this series, and also the Editorial Note following this paper. J. A.
‡ See paper on Colloidal Graphite by R. Szymanowitz in this volume.
§ See paper on Colloidal Fuel by L. W. Bates in Vol. III of this series.

coal in petroleum, the coal dispersion being stabilized by the addition of soaps. Colloidal suspensions of carbon black in mineral oil are used in the manufacture of printing inks for newspapers. The particles of carbon black are very small, and its concentration in these types of inks is generally more than ten per cent.

Among other physical properties influencing the character of a liquid or greasy lubricant are viscosity, capillarity and oiliness, all related to the colloidal structure. The lubricating power * of an oil may be defined as a measure of the internal resistance to motion of a fluid by reason of the forces of cohesion between molecules or molecular groupings. The addition of high molecular weight hydrocarbons to mineral oils refined by modern methods produces high-viscosity oils having the characteristics of colloidal suspensions. The viscosity of the suspension is a function of the concentration of solute and its molecular weight.

Capillarity or surface activity is of remarkable importance for lubricating oils. A satisfactory lubricant must wet the surfaces of the bearings in such a manner that a thin film of oil is forced to move between the two parts under friction. The mechanism of the lubrication process may be regarded as a reduction in interfacial tension. Assuming that the lubricant must penetrate the narrow spaces between journal and bearings, a liquid which does not wet the solid surface cannot be considered as a lubricant. However, the surface tension of petroleum may vary, because petroleum is a solution containing a large number of substances, with a composite surface having surface-active or "polar" molecules. These active substances have a marked influence in decreasing the surface tension with increasing temperature.

Oiliness is considered to be that property of an oil by virtue of which it has a lower coefficient of friction than another of the same viscosity. Several investigators found that active substances present in the oil form oriented layers on the solid surfaces; the hydrophobic group is thus turned toward the solid surface and the hydrophilic methyl group away from it. Langmuir [6] considers that oiliness is dependent on chemical forces called into play between the active part of the oil molecule and the solid surfaces of the bearing, and that it is a function of the chemical constitution of the lubricant. Lubricating oils of high "oiliness" are so penetrating, that films are maintained on journal surfaces even upon long standing.

Much research has recently been done to discover in what way petroleum lubricating oils are improved by addition of fats, fatty acids and their derivatives.

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The Technology of Resolving Petroleum Emulsions

LOUIS T. MONSON
Tretolite Co. of California

AND

RICHARD W. STENZEL
Petroleum Rectifying Co. of California

The Nature of Emulsions

Emulsions are systems in which one liquid is relatively stably distributed or dispersed in the form of droplets in another substantially immiscible liquid. The liquid which occurs as discrete particles is known as the internal, disperse, or discontinuous phase, while the other liquid is known as the dispersing medium, the external, or continuous phase. Although the basic concepts of emulsions seem to have been clearly recognized for a hundred years, the general emphasis has been on the oil-in-water type, rather than on water-in-oil emulsions. The latter type, almost completely ignored until 1910,[1] now has important commercial significance in the field of petroleum production and refining,* in the manufacture of artificial gas (especially oil gas), and in several other minor fields, such as ship ballast water, and the manufacture of asphalt by air-blowing. The oil-in-water type occurs widely as milk, salad dressings, agricultural emulsion sprays, beauty creams, cutting-oil emulsions, asphalt paving emulsions, etc., and to a limited extent in petroleum production.

Pure liquids do not produce stable concentrated emulsions, but form unstable dispersions which may be of the water-in-oil or the oil-in-water type, depending on the phase volume ratios and other factors.[2] When the dispersion is one of extremely small particles, so that the sedimentation rate is very low, and when it is very dilute, so that particle collisions are few, reasonable stability is obtainable with substantially pure liquids. Such systems produce turbid waters and cloudy oils.

Emulsions, on the other hand, are stabilized by small concentrations of a third component, variously referred to as the emulsifying agent, emulsifying colloid, emulsifier, stabilizing agent, etc. Emulsifying agents act broadly in conformity with Bancroft's Rule,[3] which may be expressed as follows: An emulsifying agent which is preferentially soluble or dispersible in or wettable by water will stabilize an oil-in-water emulsion; an emulsifying agent which is preferentially soluble or dispersible in or wettable by oil will produce a water-in-oil emulsion.† Exceptions to this rule have been cited, but in general it fits the facts well. "Water" in this discussion will refer to the aqueous phase and "oil" will refer to the non-aqueous phase, rather than to any pure materials.

The emulsifying agent is obviously an extremely important factor in the forma-

* References to petroleum emulsions will be found in the papers of Dunstan (p. 491), Morrell and Egloff (p. 503), and Gurwitsch (p. 523), in Volume III of the present series. Also see "Emulsions and Foams," by Berkman and Egloff, Reinhold Publishing Corp., New York, 1941.

† In this connection see a paper "On the Physiological Utility of the Fats etc.," by Dr. F. M. Ascherson presented to the Paris Academy of Sciences on Nov. 12, 1838 (Archiv. f. Anatomie, Physiologie, etc., 1840, p. 44. A translation is printed in "The Foundations of Colloid Chemistry," E. Hatschek (E. Benn Ltd., London, 1925). J. A.

tion and stabilization of emulsions. Crude oil emulsions, which are commonly of the water-in-oil type, are stabilized by emulsifying agents which vary with the oil in question. Depending upon the investigator, these have been termed "asphaltic and resinous compounds,"[4] "hydrophobe resinous substances and hydrophobe lime-naphthenate soaps,"[5] "asphaltic materials,"[6,7] etc. In the field of petroleum oil-in-water emulsions, plant sprays and cutting oils frequently employ water-soluble soaps as emulsifying agents.

In general, emulsifying agents are composed of large molecules or colloidal aggregates, which are polar in nature, as a consequence of which they tend to concentrate at liquid interfaces in oriented fashion, and thereby in varying degrees to stabilize such interfaces. The inclusion of small proportions of finely divided inert solids often serves markedly to increase emulsion stability. The details of the oriented adsorbed film theory are beyond the scope of this discussion, but they may be found in various treatises dealing with emulsions.[8] A more recently advanced theory takes into account the many complicating factors encountered in natural and commercial emulsions and thus better illuminates the formerly unaccountable behavior of such systems.[9] It should be particularly noted that the particles of emulsifying agent move more or less rapidly from the body of the continuous phase to the interface, and there form a protecting film, which may even approximate a plastic solid in properties. This results in an "ageing" phenomenon, which is coming to be recognized as of importance in the handling of petroleum emulsions. The particles of dispersed phase generally assume spherical shapes, because of interfacial tension effects, except where close packing produces distortion.[10] In the more stable emulsions, the particles are capable of withstanding appreciable distortion upon contact without rupture of the films and coalescence.

Emulsions have the general properties of being miscible with such liquids as are compatible with the continuous phase of the emulsion, of being more viscous with increasing proportions of disperse phase, and of being less stable at higher temperatures. They do not in general follow Einstein's viscosity law, and viscosity-composition relations need to be empirically determined.[11,12] Since, in general, the two liquids of the emulsion are of different densities, prolonged or centrifugally accelerated sedimentation will usually cause a "creaming" or a "sludging" effect, but only in the case of the relatively unstable emulsions will any appreciable coalescence of the disperse phase occur as the result of such treatment.[13]

Oil-field Emulsions

Practically all oil-field emulsions are of the water-in-oil type, being variously characterized as "wet oil," "cut oil," "roily oil," "bottom settlings," "basic sediment," "B.S.," etc. It is estimated that about 30 per cent of the crude oil being brought to the earth's surface contains appreciable amounts of water in emulsified form. The percentage of such emulsified water is variable, and may be as great as 90 per cent. The pipeline and other transportation companies, as common carriers, have specifications for crude oil which preclude the introduction of oil into their lines or systems if it contains more than a predetermined tolerance of water and sediment. The permissible amount is determined in part by the extent to which the emulsion can be commercially resolved; but in general it is less than 3 per cent, and in most cases is less than 1 per cent.[14] Consequently, crude oil is required to be treated, usually at or near the point of production, to resolve the emulsion and to remove the water thereby separated. Oil must be demulsified because otherwise the water present would cause refining difficulties such as corrosion, coke deposition, and foaming; transportation difficulties, such as pipeline and tank corrosion, increased power consumption and equipment wear because of the increased viscosity and volumes involved; and corresponding adverse effects on the production equipment. Therefore,

a premium is placed on dry oil, each degree of API gravity [15] gained through the elimination of water usually bringing a higher price for the product.

Petroleum oil-in-water type emulsions are rare and usually low in oil content. They are found in certain California and Texas fields, and in a few other areas. The oil content is commonly less than 1 per cent, and the treatment of such emulsions is in many instances associated with oil field waste water disposal projects rather than with oil production. Because of their rarity, they will be dealt with only briefly in this discussion. The water-in-oil type emulsion will always be implied, except when the oil-in-water type is specifically referred to.

In rare instances, a multiple emulsion may be encountered. Such emulsions comprise water-in-oil-in-water or oil-in-water-in-oil, and in some systems are said to become quinque-multiple.[16] When conditions are favorable to the production of the previously mentioned oil-in-water type petroleum emulsions, it would be reasonable to expect to find the dual oil-in-water-in-oil type also present, by the emulsification of some of the oil-in-water emulsion into the accompanying oil. This is sometimes actually the case, and the resolution of water-in-oil emulsions sometimes results in the liberation of an aqueous phase which is itself an oil-in-water emulsion.

Crude oils differ in characteristics, according to their geologic age, their chemical constitution, and their associated impurities. Consequently, crude oil emulsions are stabilized by a variety of materials, depending on their origin. The heavy, black, asphaltic oils (which are frequently associated with waters of fairly low hardness and salinity) emulsify readily with oil field waters, and it is difficult to resolve such emulsions rapidly and completely. The emulsifying agent in such cases is probably broadly to be termed "asphaltic material," although this term is far from definitive, and denotes a highly complex material.[17, 18, 19] In some oils, appreciable percentages of petroleum acids such as naphthenic acids are found, which may promote either type of emulsion, depending on their nature and on the form in which they occur. For example, the anhydrous heavy metal or alkaline-earth salts of the lower-molecular-weight naphthenic acids are emulsifying agents for water-in-oil emulsions, while their alkali salts will stabilize oil-in-water emulsions. The paraffinic oils contain little in the way of emulsifying agents; but the presence of wax in an oil containing asphaltic or other emulsifying agents facilitates the stabilization of emulsions, especially at temperatures below the precipitation point of the wax. Whatever the emulsifying agent, it is definitely associated with the crude oil, because exceptionally stable emulsions may be produced by agitating almost any crude oil with distilled water.

The waters associated with crude oils likewise vary widely in characteristics. Certain Michigan well waters have densities approximating 1.20, and have correspondingly high chloride salinities. Certain Texas well waters have high total hardness as well as extremely high chloride salinity,[20, 21] while certain California well waters are only mildly saline, and often contain less hardness than local drinking water supplies. In general, mineral salts, comprising sodium, calcium, magnesium, chloride, bicarbonate, and sulfate ions, and in fewer cases rarer ions, notably iodide, are found in oil well waters.

Some wells drilled into poorly consolidated shales, sands, or similar formations produce fluids which persistently carry small proportions of solid formation materials. In general, such solids increase the difficulties of resolving the emulsions which occur in such fields. Likewise, the corrosive gases, notably hydrogen sulfide, produced with the fluids in some fields attack the metals in the well and deliver into the fluids being produced small amounts of corrosion products which also increase the stability of the emulsions.

Oil formations commonly contain, in addition to petroleum, varying proportions of water and natural gas. Since the crude oil ordinarily contains enough emulsifying agent to stabilize an emulsion, all that is required to form such emulsion is that the well produce some water at the same time, and that sufficient agitation be present to

accomplish the requisite mixing. Agitation arises from the turbulent flow of the oil and water through pipes and orifices in the well casing, tubing, or surface equipment. Flowing wells, which usually produce their fluids under high pressures and in the presence of much gas, offer turbulent flow conditions extremely favorable to a high degree of emulsification, especially when such wells are controlled by flow devices such as "chokes" or "flow beans," consisting of restricted apertures inserted in the well or flowline. Wells produced by gas- or air-lift are broadly equivalent to high-pressure flowing wells in this respect. Wells in older, more nearly depleted fields, where gas pressures have declined appreciably, do not offer conditions so favorable to the production of emulsions; but the necessary pumping devices in the wells and in transfer equipment frequently cause emulsification, especially if not maintained in good condition.[22] It is doubtful that any appreciable emulsification occurs before the fluids reach the immediate proximity of the well bore.

Resolution of Crude Oil Emulsions

The problem of resolving petroleum emulsions has been attacked in a number of different ways, only two of which are now practised commercially on a large scale. These are embodied in the chemical and the electrical processes of demulsification. (Those oils in which the water coalesces and settles completely merely upon heating are not considered to be emulsions in the sense used in this discussion.) Of the more than four million barrels of crude oil being produced daily in the United States, it is estimated that as much as 30 per cent requires demulsification. Most of this is at present being treated by chemical and electrical dehydration processes. Earlier processes employed centrifugal action, heat and pressure, filtration, etc., but all of these have become obsolete today because of their lower efficiency.

The need for resolving petroleum emulsions arose here in the 1880's, when the oil-producing area was extended westward from Pennsylvania to embrace the black oil of certain Ohio fields. It became of increasing annoyance in the course of expanding oil production in Indiana, Illinois, Kansas, Oklahoma, and Texas. Simultaneously, it arose in the California fields. The early attempts to meet the situation were principally in the direction of supplying large storage facilities to provide extended settling times so that the emulsions could be resolved or at least stratified sufficiently to permit the withdrawal of a supernatant layer of clean oil. Open pits or sumps permitted the sun to contribute some small added temperature and opportunity for water evaporation to the process; and "sunning" was accordingly common. Retorts and stills were employed in some instances, a portion of the oil available being used to fire the apparatus to recover more oil. A period then followed in which centrifugal separation was widely used, some of the installations being very elaborate and costing hundreds of thousands of dollars. With the advent of the chemical and electrical processes, these earlier procedures were gradually superseded, because they were incapable of resolving the emulsions completely into oil and water, but left an accumulation of residual unresolvable "sludges" which had to be discarded or burned.

The chemical approach to the problem was first thoroughly investigated by William S. Barnickel, a pharmaceutical chemist of St. Louis; while Frederick G. Cottrell, then of the University of California, was the first to apply high voltages to petroleum emulsions. The chemical method was first practised in the Mid-Continent and Gulf Coast oil fields; the electrical process was introduced in California. Today, the chemical process has extended its influence until it is in commercial use throughout the United States, as well as in foreign fields such as Mexico, Romania, Russia, and South America. Electric dehydration has also spread to many areas outside of California, especially the Gulf Coast, and foreign areas such as South America, Russia and Egypt.

Chemical Resolution. The field of emulsion resolution is so young that the art has far outstripped the science, and the scientific basis for the effects observed when

demulsifying agents are added to emulsions is not yet too well defined. The whole art has passed from the pioneering or experimental stage to full operating status within the past 25 years. Accordingly, much of the procedure employed in resolving emulsions has been on an empirical basis and has not been thoroughly rationalized.

The first reagent employed by Barnickel was copperas, *i.e.*, ferrous sulfate. This proved of very limited utility. (Inorganic reagents are almost completely obsolete for this use today.) He next discovered the resolving power of common household soap, employed in small proportions; and modifications of this general reagent, such as popular washing powders, have in the past actually been used in large quantities for this purpose. A still later development was the class of "modified fatty acids," of which sulfonated castor oil was the most widely used embodiment. This last class of reagents represented a phenomenal improvement over the simple soaps. (Experiments by one of the authors have shown that in some instances selected commercial sulfonated castor oil reagents are from 10 to more than 40 times as effective as sodium oleate, and in some instances are infinitely better, in that sodium oleate does not produce satisfactory resolution of the emulsion regardless of the amount used.) Each of these classes has been superseded by newer and more efficient complex organic reagents, until the art may be said recently to have entered its fourth and multifarious stage, where no single class of reagents dominates the field.

An enormous number of classes of reagents, practically all of them organic, have been suggested for the purpose of resolving petroleum emulsions, mostly through the medium of letters patent.[23] Some of these, like the earlier ordinary soap reagents, are water-soluble or water-dispersible, while some are oil-soluble or oil-dispersible. Some are apparently not soluble or dispersible in any appreciable concentration in either oily or aqueous materials. Some are anion-active materials, some are cation-active. Inorganic reagents, while very rare today, are still sometimes strikingly effective. Members of each of these classes have found important practical use over a period of time. Therefore, before one can suggest an answer to the question of which class of reagents is the most effective, he must know from what area the particular emulsion referred to was produced, and many other facts, such as the conditions of production, etc. As a consequence, reagent selection is ordinarily accomplished by actual test on a sample of emulsion. The highly specific nature of the chemical reagents used today for resolving petroleum emulsions suggests that the mechanism of the emulsion-resolving process is quite complicated, and will not be explicable by any simple theory.

Because of this variability and the fact that the field is at present in such a rapidly changing and probably transitory condition, no attempt is made here to evaluate any of the newest reagents. To do so might result in attaching a wholly artificial importance to some class which may be really of minor importance and may shortly become obsolete.

Companies manufacturing reagents for this purpose may make as many as several hundred different commercial reagents, and a number of them may be in use in a single oil field at any given time. Obsolescence rates are high, and reagents of one type may be succeeded in a given oil field by reagents of very different composition and properties. All these facts have not simplified the problem of evolving a satisfactory theory to explain observed field results.

Theories of chemical demulsification generally focus on interfacial tension lowering. Also, most of such discussion has in the past minimized or ignored the emulsifying agent. One theory [24] is that emulsion resolution is an intermediate stage in the transition from the water-in-oil to the oil-in-water type, and that careful application, to a water-in-oil emulsion, of a reagent capable of stabilizing oil-in-water emulsions should tend to reverse the former and produce free oil and water at the inversion point. So long as the demulsifying agents employed were water-dispersible and known to stabilize oil-in-water emulsions, this reversal theory was useful. How it

should be modified to meet the condition when substantially water-insoluble materials are involved is not yet clear. DeGroote has written a comprehensive discussion of demulsification theory,[25] to which attention is directed.

Although the specificity of reagents and the variable nature of crude oil emulsions have combined to make the commercial application of such reagents to such emulsions a highly individual problem, the operative steps of practising the process are simple. Emulsion and reagent are thoroughly admixed; then quiescent standing results in separation of the formerly emulsified water. Laboratory and field technique comprise the proper application of the innumerable variations of this procedure. In some cases, batch treatment is employed, although present practise is importantly in favor of continuous operation. In some instances heating is necessary, but in an increasing proportion of cases the reagents are effective enough to resolve the emulsions in the absence of added heat. Special apparatus is required at times, but the tendency in general has been to place on the reagent the obligation of meeting stringent conditions, and to develop improved reagents which would satisfy such requirements. Consequently, the procedure of resolving petroleum emulsions chemically remains a simple process, with little or no special equipment required. Usually, the ordinary production equipment found on the producing property is sufficient to permit satisfactory application of the reagent to the emulsion and to secure separation of the emulsified water. Where additional equipment is required, it is usually standard production equipment, such as tanks, boilers, pumps, pipe, etc.

Originally, the practise was to fill a tank with emulsified oil, introduce the reagent, agitate the mixture by means of gas or air, or even by hand, heat it by means of coils or by circulating through a heater as required, and allow the water to settle. General current practice is to conduct a continuous process, introducing the reagent into the emulsion at the well head or even into the well ("down-the-hole"), heating in the flowline as required, and settling in a tank. The reagent is metered accurately by means of a proportioning pump, which may be driven by any source of motion at the site. Gas- or electrically-driven pumps are usually used when no source of mechanical motion is available. In introducing the reagent down-the-hole, different procedures can be used. Water-dispersible reagents are introduced continuously, in water dispersion, or are occasionally introduced by intermittent injection of the dispersion, the intervals being as great as one week. Flushing the reagent down the well with a small part of the oil being produced is sometimes practised. In some cases, a stream of water is employed to flush down a reagent even though the latter is water-insoluble.[26]

Heating of emulsions to promote resolution and settling has been used from the earliest days, and still is relied on in some areas. However, it is fast becoming a minor adjunct in the chemical resolution process, with emulsions of even the heavier, more viscous crudes frequently responding to chemical action without being raised to a temperature above that at which they are produced. For example, in California one emulsion of a 16° API oil (sp. gr. 0.96 at 60° F) is resolved without the application of heat, merely by injecting the chemical reagent and allowing the mixture to flow to a relatively distant shipping station where the water is separated. In general, the use of heat involves the danger of vaporization loss, which must always be considered, especially with the lighter oils.[27]

Heating may be achieved by the use of direct-fire heaters of various design, boiler heaters, or pipe coils in tanks. The use of low-pressure steam or hot water is preferred to high-pressure steam in such coils. The use of live steam injection or perforated steam coils is usually disastrous, as the steam condensate constitutes additional emulsified water which is often extremely difficult to remove from the oil.

The action of heat is principally to reduce the viscosity of the emulsion, which may be more than four times as viscous as the oil it contains.[11, 12] The viscosity of emulsions varies directly with the proportion of dispersed phase. For any given

dispersed phase content, the viscosity is a function of the degree of dispersion, the more highly dispersed systems being the more viscous. The more viscous petroleum emulsions do not stratify appreciably on prolonged standing, even when the water particles are comparatively large. Reducing the viscosity of the medium increases the settling rate proportionately, in accordance with Stokes' Law, as is well known. The demulsifying reagent, by increasing the particle size, frequently acts strikingly to reduce the viscosity of the emulsion. Some wells can not be produced economically without injecting such a reagent down-the-hole to reduce emulsion viscosity. In other instances, productivity is greatly increased and the lifting equipment required is reduced by applying this procedure.

Equipment which may be employed in practising what is known as "flowline" treatment, the most widely used procedure today, is shown in Fig. 1. This figure

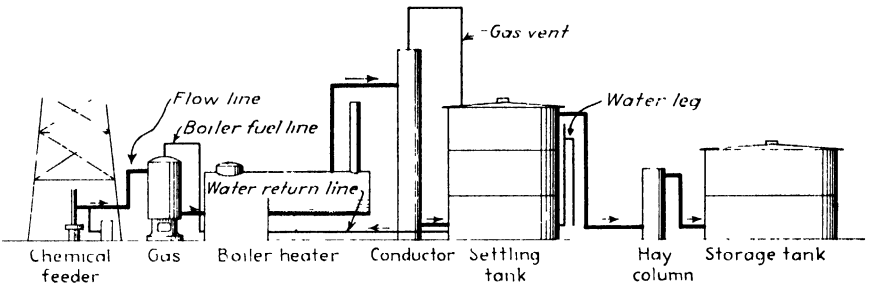

FIGURE 1. Diagram of comprehensive chemical demulsification plant.

is to be regarded solely as illustrative and diagrammatic. Few treating installations include more than two or three of the elements there shown, some comprising simply a reagent injection device and a single tank. Others employ modifications of the items shown. In the figure, the emulsion is mixed with demulsifying reagent as it reaches the surface of the ground; it then passes through the conventional gas separator; flows through a heater of any suitable design; travels thence to a settling tank; passes through an apparatus symbolized by the "hay column" and which is described below; and then goes to storage, ready for shipment. As previously stated, heat is only required in some cases; and the heater is consequently optional. Discarded oil-field boilers capable of withstanding moderate pressures have been reconditioned and used widely for this purpose with good success. Their temperatures are usually controlled automatically by thermostats; and good design calls for a low-level water return line from the subsequently placed settling tank, to prevent damage if some failure or stoppage occurs. The liquids pass to the settling tank through various arrangements, but in general the purpose is to introduce them into the tank in such a manner as not to disturb the contents of the tank. The oil conductor illustrated may be inside or outside the tank and may be of varying design, so long as it conducts the fluids into the settling tank with as little disturbance of the contents as possible. The water in the settling tank is usually maintained at some experimentally determined level, by means of a water overflow or "water leg." The hay column is a relatively rarely employed piece of apparatus. It is used to trap any entrained water particles that have been swept out of the settling tank because of excessive velocity of flow or high viscosity of oil, or other cause. It may be placed ahead of the settling tank, to act as a mixing chamber. In some instances, it may be a substitute for a settling tank. Its name derives from the use of wood shavings or excelsior ("hay") as a packing medium.

Down-the-hole treating is accomplished by the use of similar apparatus, the reagent being injected into the well, usually in the annulus between the casing and the tubing.

The method is valuable at times in reducing viscosity, as already stated, in taking advantage of higher sub-surface temperatures, and in attacking the emulsion at the time of its formation, which is in general conducive to more economical operation.

Batch- or tank-treating usually employs an emulsion storage tank, a transfer pump by means of which the emulsion may be moved to another tank or circulated back to the original one, a reagent injection device, and a heater as required. Mixing is accomplished by the transfer or circulating operation. If a single tank is used it may be fitted with a gas or air line to accomplish agitation. The settling step takes place in the second tank, or in the original tank after circulation is stopped. Heating may be accomplished as before, by a heater in the transfer or circulating line, or by coils in the tanks.

Shea [28] has published a comprehensive presentation of the practical aspects of resolving emulsions chemically. Other authors [29, 30] have considered various operating phases of the problem.

Chemical reagents are finding increasing use in the laboratory testing and analysis of emulsions. They are useful in determining the water content of emulsion samples, in determining "dry gravity" (density of the oil phase of the emulsion), and in determining the salinity of crude oil. To determine the water content of emulsions, the centrifugal method has been adopted as one standard.[31] By the use of a drop or two of demulsifying reagent in the centrifuge tube, along with the sample and the diluent, the emulsion can be completely resolved, so that free water only is precipitated, instead of the emulsion being only partially resolved, as is otherwise usually the case. To determine the dry gravity of the oil in an emulsion sample, resolution of the emulsion is accomplished in a sealed container to conserve the lighter fractions of the oil, and undiluted reagent is added to achieve resolution. A portion of the oil recovered is tested for water content (by centrifuging or by distilling with xylene) to insure that resolution has been complete and the water removed to the extent desired, before the density is determined by standard methods. It is preferable, in each case, to employ the reagent which is in commercial use in the area from which the emulsion comes. The use of demulsifying reagents in the analysis of crude oil for salt has been suggested by Blair.[32]

The cost of resolving petroleum emulsions chemically obviously varies with the nature of the emulsion, the efficiency of the demulsifying reagent, the type of equipment available, and the procedure employed. Overall costs are difficult to determine accurately for many reasons, not the least of which is the variation in accounting systems. In general, the average ratio of reagent to recovered oil is at present about 1 to 10,000. (The volume of oil recovered is the only proper basis for calculating reagent costs, since the oil content of emulsions is so variable.) In some installations, ratios as favorable as 1 to 400,000 have been achieved. A small proportion of especially refractory emulsions, which are required to be treated under unfavorable conditions, may show ratios of reagent to recovered oil of as much as 1 to 4,000 or larger.

Electrical Resolution. The electrical resolution of petroleum emulsions was at first considered to be a very simple process. Particles suspended in a medium of lower dielectric constant (*e.g.*, water particles in oil) are attracted to each other if an electric field, either alternating or direct, of sufficiently high gradient is imposed on the system. The greater the resistivity of the dispersing medium, the greater the electrical stress it should sustain without breakdown and, therefore, the greater the coalescing forces. Since petroleum oils in general have comparatively high resistivities (approximately 10^9 ohm cm), it is apparent that powerful electrical forces could be brought into play to draw the water particles together. Such is actually the case, and in electrically resolvable systems the rate of coalescence of the water upon application of a high-gradient field is truly astonishing. Graphic evidence of the speed of the primary coalescence when an electric field is applied to an emulsion is given

by the photomicrographs of Fig. 2. This is a motion picture made with the high-speed technique of Edgerton.[38] The emulsion, which had a water content of 12 per cent, was placed in a cell between electrodes 1.25 mm apart, and 60-cycle electric current at 600 volts was applied at the instant designated by the arrow. The ruled line on the film is an approximation of the voltage wave recorded separately and simultaneously by an oscillograph, the voltage being maximum at the edges of the film and zero at the middle. Careful inspection reveals that coalescence has already

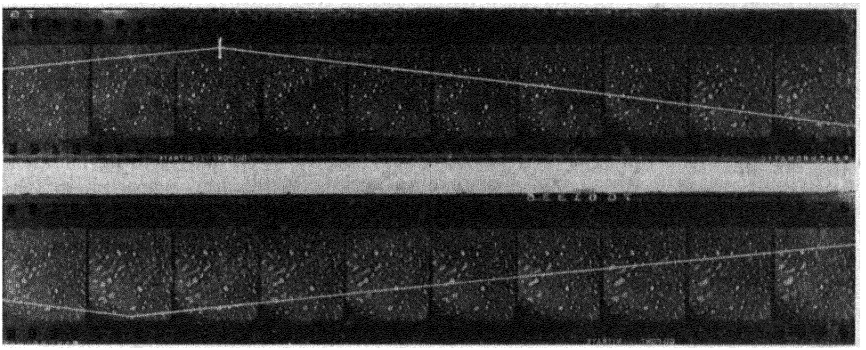

FIGURE 2. High-speed cinematic photomicrograph of electrical demulsification.

begun in the frame immediately following the application of the voltage, and is far advanced in the sixth frame. From the oscillograph record, it can thus be seen that primary coalescence occurs within a fraction of a cycle of the current, *i.e.*, within a few thousandths of a second. Subsequent coalescence is somewhat slower, but proceeds at rates still much greater than could be accomplished by any mechanical methods. The exceedingly rapid action of the electric field accounts for the particular utility of this method of treating emulsions industrially where high flow rates and a minimum of tankage and process time are important economic factors.

In the electrical dehydration art, as in the chemical, it was soon found that an apparatus and flow design suitable for one emulsion might be commercially impracticable for another. As the use of the electrical process was extended, it was found that not all emulsions respond equally readily to the application of the electric field; and many investigations have been made to determine the optimum conditions and most favorable field configurations for most expeditiously and economically separating emulsions into their components.

The previous discussion of the nature of emulsions has already indicated the problems involved in their resolution, and that these problems revolve largely about the character of the emulsifying agents responsible for the relative permanence of the emulsions. It has already been shown that high temperatures alone are usually not sufficient to cause adequate coalescence of the dispersed water particles, and that direct evaporation of the water from an emulsion is most impractical. A study of the conditions essential to most efficient electrical dehydration shows that the electric field functions not only to bring the dispersed water particles rapidly together, but also to modify the interfacial film to such an extent that actual coalescence can occur after the particles have been brought into contact. Such an action by the electric field is readily understandable when it is remembered that the stabilizing materials are always highly polar, and will therefore respond to an imposed field by oscillation or displacement, the magnitudes of which will depend on the character and strength of the field applied. These external forces greatly weaken the interfacial film, so that coalescence between particles becomes possible whenever they come into contact, and the resolution of the emulsion then proceeds apace. That the electric field has a

definite destabilizing effect can be demonstrated in a number of ways, but a very simple one is a comparison between the results obtained on a typical crude oil emulsion by electrical and by centrifugal action. In the latter case, the emulsion particles are tightly compacted and drawn together, but little or no coalescence usually occurs, whereas the electric field can completely resolve the emulsion into its components without leaving any residual sludge.

The emulsifying agents in crude oils sometimes form very rigid films, which appear to have definite phase-transition temperatures that must be exceeded before any coalescence is obtainable. Under such conditions, satisfactory electrical dehydration can be obtained only when this film has first been brought to such temperatures. This critical temperature appears to be lower if the field is applied soon after the emulsion has been made, and advantage of this is often taken in the "flow-line" system of electrical dehydration.

It is frequently possible to add a small proportion of a suitably chosen demulsifying chemical reagent which has a displacing action on the film material, in which case the necessity for increasing the temperature to achieve coalescence by the electric field is reduced or eliminated. The quantities of such reagents employed are always much smaller than would be required to resolve the emulsion by purely chemical means. This indicates that the emulsifying films are only partially destabilized by the chemical reagent and, further, that the reagent renders the emulsion responsive to the electric field.

As in the chemical process, the theoretical explanations have followed rather than preceded the development of the apparatus for the efficient electrical resolution of emulsions. Many configurations have been tested, and there have gradually evolved those which have had the requisite degree of effectiveness and engineering feasibility to provide the greatest commercial advantages.

The details of electrical dehydration installations have often been described in the literature, *e.g.*, by Pettefer,[34] French,[35] Uren,[36] and Shea,[37] and need not be extensively considered here. As the character of the installation must be suited to the particular crude oil to be treated, no single dehydrator or flow system is most efficient on all oils. A diagrammatic flow-sheet of one type of dehydration plant is shown in Fig. 3. In this plant, the principles previously set forth regarding the

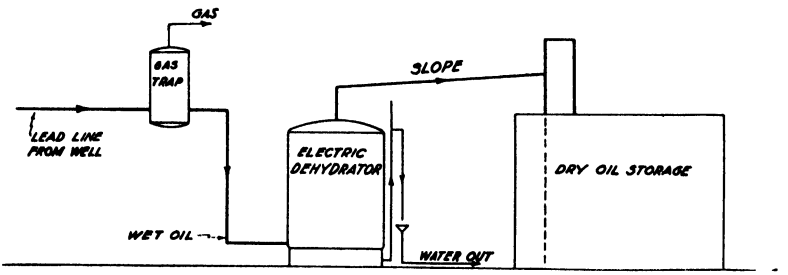

FIGURE 3. Diagrammatic flow-sheet of electrical dehydration plant.

desirability of treating emulsions directly as produced by the well have been utilized. The emulsion from the well flows directly through a gas trap, a heater if necessary, and then to the electric dehydrator. This last is a tank 10 feet in diameter and 12 feet high, bearing the necessary electrodes, insulators, transformers, and other equipment. The emulsion flows through a distributor into a high-tension alternating electric field, the potential of the electrode system being ordinarily 11.5 to 33 kilovolts. As the emulsion enters the field, rapid coalescence of the emulsion particles takes place, the coalesced water masses settling to the bottom of the dehydrator. The dehydrated oil is continuously withdrawn from the top of the dehydrator, while the

separated water is taken out at the bottom. The separation of the phases is so rapid that a tank of the size mentioned will deliver from 500 to 3000 barrels daily of dehydrated oil, the rate depending upon the character of the oil and the operating conditions. The rate of flow attainable is primarily determined by the viscosity of the oil, the gravity differential between the oil and the water, the rate of coalescence (*i.e.*, the relative stability of the emulsion), and the permissible residual water content of the dehydrated oil.

Modern electrical dehydration plants have electrical controls so that the operations can be made entirely automatic, and only periodic inspection is required for maintenance. Among the electrical controls utilized are automatic low-level switches which break the electrical circuits if the tank is not completely full of liquid; automatic water bleeders which maintain a constant water level in the tank, thus withdrawing the water as fast as it settles from the emulsion; and choke coils which prevent overloads on the transformers in case of accidental short circuits, etc.

A typical dehydrator installation is shown in Fig. 4. This is a two-unit dehydration plant operating on the flowline principle. The lines from the individual wells on this property are brought directly to the plant, where the oil is heated and immediately dehydrated. This plant is entirely automatic and needs to be only periodically inspected.

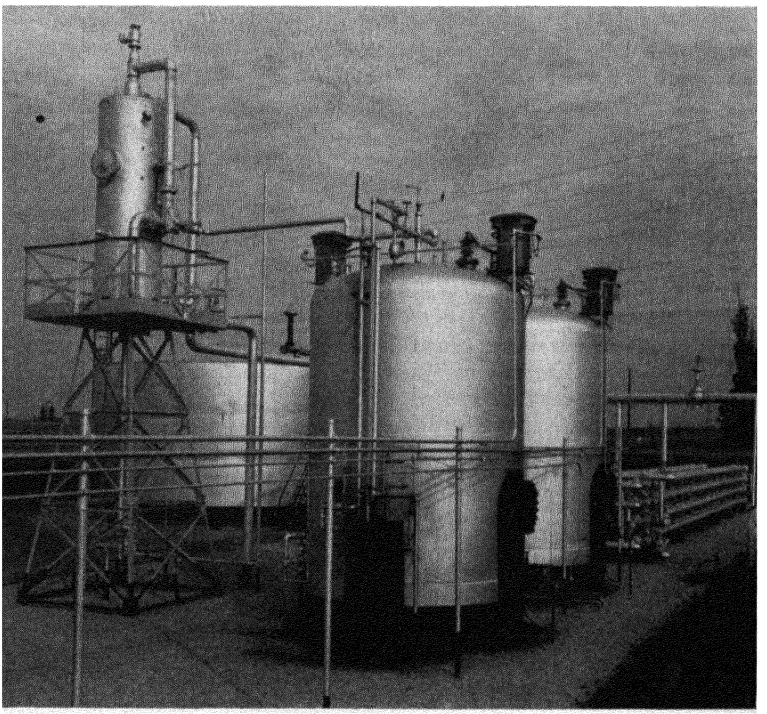

FIGURE 4. Typical electric dehydrator installation.

Another common practice in electrical dehydration is to provide a central multiple-unit plant, which dehydrates all the oil from a large property. This is particularly suitable where the oil from many wells can be brought to a central location, and allows a concentration of equipment which is more economical of labor and apparatus than when the units are widely scattered.

Desalting Crude Petroleum

The dehydration processes described above reduce the water content of crude petroleum to small proportions; but it is generally impossible to reduce it by such methods below a few tenths of one per cent without excessive cost. Consequently, the petroleum oil charged to refinery stills usually contains appreciable amounts of mineral salts, such as sodium, calcium, and magnesium chlorides, bicarbonates, and sulfates. These are usually found in solution in the small residual emulsion particles, although the presence of salt crystals in crude oils has been discussed.[38, 39] In topped crude, of course, any salts present would be expected to be in the solid state. Because of the varying salinity of such residual water, the crude oil charged to the refinery apparatus may contain from a few pounds to thousands of pounds of salts per thousand barrels of oil, the higher values often resulting from the use of inefficient field dehydration methods. In many cases, the water or brine particles are so concentrated in salts that exposure of thin films of the oil to the air will cause rapid crystallization to take place. An elaborate photomicrographic study of the salts present in crude oil has recently been made.[40] Certain of these salts, particularly calcium and magnesium chlorides, are destructive of refinery equipment, by producing corrosive acidic compounds under the high-temperature conditions that prevail. All such salts are becoming of increasing concern to the refiner, because, as refining processes become more complex and refining temperatures are raised higher and higher, the deleterious effects of salts become greater. The literature on the subject to desalting has grown rapidly in recent years.[41]

In all cases, mineral residues in the charging stock tend to deposit somewhere in the system. They deposit in still tubes where they initiate or aggravate coking effects by increasing the plugging rate, and forming flinty coke that is difficult to remove by the usual cleaning-out processes. It was formerly estimated that, if the crude oil charged to the stills contained more than 25 pounds per thousand barrels of "salt," refinery difficulties were to be expected.[42] (The usual method of determining the salt content of crude oils is to extract and analyze for chlorides, and the standard form of expressing results is "pounds per thousand barrels," "ptb.") This maximum figure is generally exceeded, for even California oils which are usually associated with comparatively fresh oil well waters often go to the refinery carrying more than 25 ptb, even when containing only 0.3-0.4 per cent water. Crude oils produced in other sections of the United States reach the refinery having salt contents as high as 2,000 ptb.

Salts and other non-volatile impurities will of course be concentrated in the residua from the distillation and cracking operations, and will adversely affect the properties of those materials. Asphalts containing appreciable amounts of solids are often rejected for use as road materials, and residual fuel oils are likewise made unsuitable by solid impurities because of the tendency of the latter to plug burner nozzles.

When crude oil containing salts is charged to stills or cracking furnaces, there is a certain amount of decomposition of the salts under the elevated temperature conditions encountered, to form hydrochloric acid, which is highly corrosive to the equipment. Corrosion is especially evidenced in the upper sections of fractionating towers and in the condenser sections, where the presence of water vapor and condensed steam aggravate the corrosive action of the hydrochloric acid. The mechanism of this type of hydrolysis of the salts, previously obscure, has recently been elucidated independently by several workers in the field.[43, 44] From analogy with their behavior in aqueous solutions, it was originally thought that, of the salts commonly present in crude oil, magnesium chloride alone would be hydrolyzed sufficiently to evolve appreciable amounts of hydrochloric acid. It has now been shown that the presence of organic acids in crude oil greatly alters this concept, and that, with

many types of crude oils, both calcium and sodium chloride can be additional sources of hydrochloric acid under distillation conditions. Furthermore, there is always some dissolved or dispersed water present in the petroleum materials charged to the furnaces, which will increase the evolution of hydrochloric acid by hydrolytic action. These considerations show that any estimate of the maximum salt content which can be safely tolerated must take into account the variations in the composition of the salts and of the oils in which they occur. This is confirmed by the industrial users of desalting processes, some refiners finding it advantageous to desalt crude oils containing chlorides in amounts as low as 15 ptb, while others with different oils can tolerate considerably more without excessive plugging or corrosion difficulties.

The corrosive action of evolved hydrochloric acid is often combatted by the introduction of ammonia into the fractionating towers; but, even though the addition is carefully controlled to provide the optimum pH conditions under which corrosion will be minimized, the resulting ammonium chloride is still quite corrosive. It also tends to plug the exchangers and condensers through which it flows. Consequently, it is generally found most economical to remove the salts from the crude oil before it enters the distillation and cracking equipment.

Thorough removal of the salts from a crude oil before it is processed will, in addition to alleviating these various deleterious effects, also produce other less tangible but nevertheless important benefits, especially in connection with cracking operations. Among those which have been reported by various refiners are: (1) a decrease in doctor-treating requirements of the gasoline produced; (2) superior color in gasoline and kerosene fractions; (3) an increase in lead susceptibility of the gasoline. The degree to which these improvements are evidenced in the products seems to depend considerably upon the degree of salt removal accomplished.

Refiners have for many years endeavored to reduce the amount of salt in their refining stocks by various modifications of simple settling methods.[45] For example, the crude oil was allowed to flow through large pressure drums, called "salt settlers," where it was heated to about 350° F and where some settling of the salt water particles could take place. In other instances, a little fresh water was added to the oil before it entered the settler, in order to wash out as much of the salt as possible. In the latter case, it was necessary to regulate the degree of dispersion carefully, to avoid carrying some of the added water into the still. The difficulties attendant on securing a synthetic emulsion in which the water particles are sufficiently small to produce desalted oil when the emulsion is resolved, and yet having it sufficiently unstable to be resolved by heat and pressure, are great.

These methods were quite inefficient, and were able to produce only a partial removal of the salt, seldom over 50 per cent. The chemical and electrical methods more recently introduced for the desalting of petroleum oils have found wide use because of their greater efficiency and dependability.

Electrical Desalting. In applying the principle of electrical precipitation to the removal of residual impurities in crude oil, many factors must be considered which are not present in the process of resolving oil-field emulsions. The oil to be treated has initially a low water content and in general has previously been subjected to a dehydration process. The oil usually contains from a few tenths to one per cent of water, carrying the saline impurities. It is necessary to mix carefully with this oil relatively fresh water in such a manner as to provide conditions suitable for the electrical coalescence of the dispersed fresh water particles with the original brine droplets. It has been found that, in order to obtain maximum removal of the brine, some of the fresh water particles should be made very small; in fact, they should approach the size of the original brine droplets. With many oils, such high dispersion results in the formation of emulsions which are relatively stable and which will not separate by gravity even under elevated temperature conditions.

When the emulsions are made coarse, so as to be rapidly and substantially completely resolvable simply by settling, only a small amount of coalescence between brine particles and admixed fresh water results. Because of the accelerated coalescence produced by the action of the electric field, it is possible to utilize relatively intense mixing of the fresh water with the oil and still obtain complete resolution later. The high degree of emulsification produces thorough interdispersion of the brine and fresh water droplets and makes it possible to obtain a high degree of salt removal, since the electric field will cause a proportionate coalescence of the two types of water particles. When the fresh water is properly emulsified with the salty oil, there is at first very little if any coalescence between the brine and the fresh water as a result of the mixing procedure. The two types of particles can be made to co-exist and apparently have no particular tendency to coalesce. This is graphically shown in Fig. 5, where A is a photomicrograph of a salty oil containing about 1 per cent

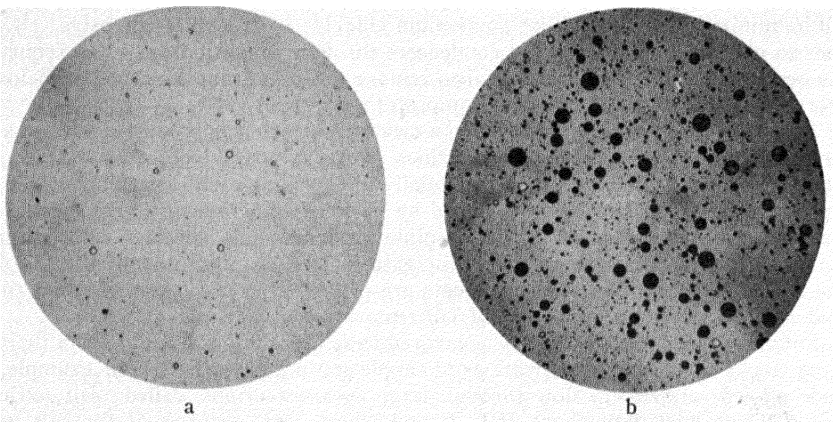

FIGURE 5. Photomicrographs illustrating emulsification in desalting. a, oil to be desalted. b, same oil emulsified with 10 per cent fresh water.

water and B is the same oil into which about 10 per cent of fresh water has been incorporated. The dark-appearing particles in B are those of the added fresh water, while the lighter ones are the original brine particles.

In commercial operation, the electric treaters used for desalting purposes are similar to the dehydrators previously described. They are of standardized dimensions, and their number in a desalting installation depends upon the amount of oil it is desired to process. Fig. 6 is a photograph of a commercial plant processing 16,000-20,000 barrels of oil daily. Since the desalters are generally installed adjacent to the refinery distillation equipment, it is necessary that the usual safety precautions invoked in refineries be observed. Control of the desalting plant is usually entirely automatic, and explosion-proof switches and controls are usually required. The salty oil is ordinarily heated by exchange from the refinery streams, then mixed with the heated fresh water, and the system adequately emulsified before introduction into the desalting unit. The desalted oil is withdrawn from the top of the unit into a surge drum, from which it is pumped directly into the still. It can be seen that the operation of the desalting plant must be entirely dependable to avoid upsetting refinery operations.

While most desalting plants are installed in conjunction with refineries, there are some installations in the oil fields themselves as adjuncts to crude oil stabilization plants. This is a highly satisfactory arrangement for eliminating salt difficulties both at the stabilizing plant and at the refinery.

The extent and effectiveness of the electrical desalting process can be gathered

from the fact that millions of barrels of salty oil were processed monthly during 1944. The oils treated contained originally from 15 to 1500 pounds of salt per thousand barrels, and the oil gravities ranged from 18-45° API (sp gr, 0.80-0.95). Of the salts originally present, from 90 to 98 per cent was removed by the desalting operation, the average salt removal being about 95 per cent.

FIGURE 6. Typical electric desalting plant installation.

Chemical Desalting. The chemical desalting process employs a variety of procedures, all of which are basically identical, in that a synthetic emulsion of salty oil and fresh water is resolved by the aid of a chemical reagent.[46] Excellent results may be achieved with only 2 per cent of added water. In other cases, best results are obtained when 10 per cent or more of water is added. The reagent may be added to the oil, to the water, or to the synthetic emulsion produced from them. In general, it is preferred to add the reagent to the oil, and subsequently to introduce the water. Emulsification may be accomplished in any desired manner, *e.g.*, by means of an emulsifying valve which may be variably loaded. The water is usually separated at an elevated temperature in pressure settling vessels of the type found in most refinery installations. In this way, the heat already added to the oil in the heat exchangers is conserved, and additional storage or settling-tank installations are avoided. The cost of chemical desalting of crude oil is small, the consumption of reagent being usually only about 1/20,000 to 1/75,000 the volume of oil desalted. The quantity of oil being desalted chemically was of the order of millions of barrels a month, in 1944.

Resolution of Miscellaneous Emulsions

Asphalt distillate emulsions are produced when air-blown asphalt is made by the introduction of air and steam into asphaltic petroleum residues. The distillate from this operation comprises large volumes of steam condensate and some proportion of petroleum derivatives, including some solid matter. These materials produce an extremely stable water-in-oil emulsion, usually containing large percentages of water. Such emulsions have been found to be resolvable by both chemical and electrical methods. By introducing demulsifying chemical reagents into the overhead line from the stills, stable emulsions are prevented, so that separated oil and water layers instead of emulsions are formed in the condenser tank. In one instance, the

emulsion had previously been discarded as waste. By adequate chemical treatment, it was possible to utilize the separated oil as fuel, replacing formerly purchased oil.

Gas-tar emulsions are produced, *e.g.*, in the manufacture of city gas, when an oil charge is passed through heated checker-brick, a process used widely in areas not supplied by natural gas. The tars formed are of high density and high viscosity, and frequently contain large proportions of water and some solids such as carbon. These emulsions are encountered in the wash boxes and scrubbers of the gas plant. Suitably dehydrated, the tar has considerable commercial value as road material, etc. To resolve this type of emulsion chemicals have been used in a manner similar to that employed in resolving crude-oil emulsions. Procedures and reagents are not yet as highly developed as in the case of oil-field emulsions, because the volumes involved are relatively small.

The recent production of butadiene from petroleum naphtha as an intermediate step in the manufacture of synthetic rubber is accompanied by the production of a water-in-oil emulsion that appears to respond in some degree to demulsifying reagents, in procedures similar to those above mentioned. A very stubborn oil-and-carbon-in-water emulsion occurs in the cooling-water system employed in such operations, which is susceptible to the application to chemical demulsifying agents.

The steam emulsion number of lubricating oils can be improved by the incorporation of small percentages of chemical demulsifying agents.

Oil wells, particularly wells drilled into calcareous formations, are frequently treated with hydrochloric acid to increase the permeability of the oil-bearing formation and improve well productivity. Emulsions of such acidic solutions and the oil being produced from the formation are extremely difficult to handle because of their stability and acidic character. By mixing with the acid a demulsifying reagent of a type which is soluble and stable in such acidic solutions, the formation of stable emulsions with the oil is prevented, so that separation of the spent acid is facilitated. Heat may be required to accelerate the resolution of the aqueous phase of the emulsion.[47]

Emulsions of water in fuel oil are sometimes encountered on ships and are troublesome, because they cannot be used as fuel, nor disposed of in harbors. Disposal at sea sometimes means hauling the emulsion a long distance from land. Chemical reagents are being used in demulsification processes like those described above, to recover the fuel oil content of these emulsions.

Another method which has been proposed for avoiding the difficulties produced by the emulsification of fuel oil with ballast water is to add a suitable demulsifying chemical reagent to the water immediately after it has been pumped into the tanks, thus avoiding emulsion formation altogether. Due to the great variability of composition of fuel oils, the reagent selected must be determined by prior tests with the particular oil involved.

National and local laws have long prohibited the pollution of navigable waters and bathing beaches by the discharge of oily waste from ships near shore. As it is often impossible for a boat to discharge all its ballast water in the open sea, especially when approaching port in stormy weather, recourse must be had to pumping ballast water from the ship's fuel tanks to shore installations equipped to make the necessary separation of oil from the water. In general, such separating plants have consisted merely of large pits where the ballast water is allowed to stand until the oil it contains has had an opportunity to rise to the surface. Since many fuel oils now have a specific gravity very nearly that of sea water, the levitation process is very slow, and large volumetric capacities are required to give the time required for separation to take place.

A process has been developed for separating ballast water, which employs an air flotation method to increase the rate of separation of oil and water.[48] The process depends upon the principle that, if a stream of fine gas bubbles is allowed to rise

through water containing finely divided oil droplets, the gas bubbles will attach themselves to the oil particles if a suitable chemical reagent is present to provide the proper surface conditions for such attachment. In commercial operation, cylindrical tanks 10 feet in diameter have been used. The ballast water is pumped into the vessel near the top, and small gas bubbles are produced at the bottom by injecting air or a gas to give the flotation action. Clear water is withdrawn from the bottom of the tank, and the separated oil from the top. High rates of flow, as great as 750 barrels of ballast water an hour, have been attained in commercial operations. The simplicity of the process and the comparatively small storage requirements make the method particularly attractive.

When wells in oil fields which are producing both oil and water are operated at high rates, additional water is usually obtained with the oil. In some such cases the tendency to form oil-in-water emulsions is greatly enhanced. For example, in one California field the production of some 8,000 barrels of oil required the concomitant lifting of only some 5,000 barrels of water; but when the field was so operated as to produce 19,000 barrels of oil daily, the production of water approached 100,000 barrels. In the latter case substantially all the water so produced contained oil in concentrations approximating 1,000 parts per million. Chemical demulsifying agents have been devised to resolve such oil-in-water emulsions which permit discharging to the streams water carrying as little oil as 5 parts per million.

In "sweetening" gasoline, by conventional doctor solution or by means of alkaline potassium isobutyrate solutions, etc., emulsions often are produced which respond readily to small amounts of demulsifying chemical reagents. Incorporation of such a reagent into the gasoline treating solution appears to prevent emulsification or to reduce the stability of any emulsions formed to the point where they are transitory in the process.[49, 50] The small volume of gasoline formerly lost in the emulsion is conserved, and the operations are improved in other respects.

Space does not permit the presentation of all demulsification problems or their solutions. The foregoing are intended to be representative instances of the application of chemical reagents, electricity, heat, and mechanical means to the problem of resolving emulsions and recovering the valuable components of such systems.

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Lubricating Greases as Colloidal Systems

C. J. BONER

Battenfeld Grease and Oil Corporation

Composition of Greases

Although lubricating greases are recognized as colloidal systems, relatively little consideration has been given to them by workers in the field of colloids. This may be because such "soap-thickened oils" are heterogeneous mixtures which are not easy to control or to understand. However, a review of information regarding such systems may be of value.

In the case of lubricating greases, some of the constituents may be colloidal in character before compounding. Thus, Morrell and Egloff [40] consider petroleum a colloidal system, especially the asphaltic type. A further complication is that soaps of petroleum acids, wool fat or rosin may be present in greases, besides those derived from animal or vegetable fats. In addition to the two main phases, any or several of the following may be present in the same grease: glycerol, other higher alcohols, uncombined fat, fatty acids, uncombined alkalies, water, unsaponifiable fractions from rosin or fat, such as sterols, etc. Some of the above may be added purposely to stabilize or modify the structure; they may be present as the result of reactions; or they may enter as impurities in some of the initial materials.

Not all soaps will produce a grease structure when dispersed in mineral oil. Lawrence [80] stated that only those soaps which, on heating, pass through intermediate plastic forms * that melt sharply at a higher temperature to isotropic liquids, gelate in oil solutions. No confirmation of this criterion for oil-bodying soaps has been published, and there may be some exceptions to it. Thus, Earle [10] prepares lubricating greases from lithium soaps of higher fatty acids and mineral oils, though according to Lawrence such soaps are non-gelating. The cation appears to be the determining factor in the type of grease structure which results when soaps are dispersed in mineral oils. The soaps commercially employed for this purpose are those of aluminum, barium, calcium, lead, lithium, magnesium, sodium and zinc. However, in agreement with the findings of Lawrence, lead and zinc soaps have little ability to thicken mineral oils. Possibly the velocity of crystallization of these soaps is too rapid for a grease structure to form. In some cases soaps of mixed bases are encountered in greases.

The fatty acids employed in soaps for production of lubricating greases seem to be limited to those above lauric, according to Lawrence.[80] This agrees with Brooks' statement [4] that the solubility of soaps in mineral oils increases rapidly with increasing molecular weight of the fatty acids employed. However, Carmichael and Bain [8] claim that a certain percentage of the calcium salt of a low molecular weight acid, such as acetic, when present together with a calcium soap of a higher fatty acid, is advantageous in that such a grease may be dehydrated without destroying the structure. Rosin acids, fatty acids from wool fat, naphthenic acids or those derived from oxidation of petroleum are also employed in soaps for grease manufacture. Licata [81]

* See paper by R. D. Vold and M. J. Vold in Vol. V of this series. J. A.

has observed that the fatty acid radical to a large extent governs the physical properties of a metallic soap and that the solubility of soaps of the same cation decreases in the following order: naphthenates, linoleates, oleates, palmitates and stearates. Lawrence [30] noted that the strength of gels in mineral oils was parallel to the hardness of the soap employed.

Preparation

Lubricating greases may be produced either by dispersing a pre-formed soap in mineral oil with the aid of heat and agitation, or by the formation of the soap *in situ* in a portion or all of the mineral oil required. Preparation of lubricating greases from dry metallic soaps and mineral oil in a colloid mill has been attempted, but the results were not promising. Some soaps, for instance aluminum soaps, will swell to some extent at low temperatures when immersed in mineral oil, but no thorough dispersion results, and the amount of swelling varies with the particular oil used.

The method of formation of a lubricating grease determines the structure to almost as great an extent as does the composition of the soap used. Thus in the case of sodium-soap greases, Fraser [14] states that factors contributing to the non-fibrous character of soda-soap greases are high cooking temperature and rapid rate of cooling, whereas low cooking temperature and slow cooling produce a fibrous structure. Farrington and Davis [11] showed microscopically that heating and agitating a soda-soap grease for four hours materially shortened the fibers. Actually, as Lawrence [30] points out, the majority of greases are manufactured at temperatures below the melting point of the soap but above the transition point from a plastic to a gel state.*

Lawrence believes that when soap is heated with mineral oil, the soap lattice opens up and oil makes its way between the hydrocarbon chains. True solution does not occur until the hydrocarbon chains and the polar $-CO_2Na$ groups are disrupted. When this occurs, the soap is in solution and the hydrocarbon chains are in potential solution. Further, Lawrence considers gelation to be a crystallization, the soap separating suddenly and in peculiar crystal habit, so that a meshwork is formed which holds the oil like a sponge. There are two reasons why the stable gel is formed only by those soaps which pass through the plastic stage. First, the fact that those soaps that do not pass through the plastic stage all have low melting points which increase with increase in chain length shows that the adhesion of the hydrocarbon chains is greater than that of the polar heads. Secondly, in the plastic state the gel structure of the soap is swollen with oil and unable to undergo particle growth according to the thermodynamic conditions which make a suspension of small crystals unstable.

Where soaps are formed *in situ* in mineral oils, the temperature may not reach the transition point, so that perhaps at no time is there true solution of the soap. As saponification proceeds, there is a growth of crystals or micelles. In extreme cases this reaches the point of coagulation, and peptizers must be added to form a stable structure.

In producing some greases provision is made for rapid chilling of the soap solution, so that crystal growth will be arrested and the soap aggregates small. This may be accomplished by running the fluid product into shallow pans or by a chiller similar to a wax chiller. In other cases the rapid addition of cold oil to the soap dispersion is effective.

Structure

Lawrence [30] considers that soap-oil systems can exist in three forms: (1) *True solution,* the viscosity of which is but slightly greater than that of the oil alone. (2) *True gel,* a stable, transparent, homogeneous elastic system. If the concentra-

* The facts mentioned here and later on, bear marked analogies to what happens in metals and alloys on thermal treatment. Diffusion, nucleation, crystal growth and shape are all important factors. J. A.

tion of the soap is too low for formation of a gel that is self-supporting under gravity a solution with anomalous viscosity is formed. The elasticity may become vanishingly small, but the viscosity is very high. (3) *Pseudo-gel* or paste of fully crystalline soap suspended in oil. The crystallites are very tiny, but grow larger on standing. With sufficient concentration of soap the system is a plastic paste. At low concentrations the soap separates. Lawrence concludes that soda- and aluminum-base greases are certainly paste types and that lime-base grease is probably a gel.

Lutz and co-workers [84] state that convential greases are presumably not homogeneous gels, because the concentration of soap in the medium is too high for this form to remain stable. They believe that crystallization occurs, leaving the limited concentration of soap in oil as a gel which supplies a framework for the now insoluble soap crystals. Further, the exact nature of this framework is uncertain, but for soda-soap greases it is likely to be a mixture of fibers, while for lime-soap mixtures it may have a cellular structure (somewhat like honeycomb) enclosing the liquid present.

Klemgard [27, p. 18] states that while greases are ordinarily classified as heat-reversible gels, a more plausible theory of grease structure is that the soap exists in the form of liquid crystals dispersed in the oil.

Farrington and Davis [11] were able microscopically to distinguish fibers in all types of greases. Aluminum- and calcium-base greases showed fibers less than one micron in length. Lime grease also showed some granular particles. Smooth soda-base greases had fibers 5 to 10 microns in length, and the fibrous type had fibers ranging up to 100 microns in length.

Whether the structure of a grease is entirely colloidal or entirely crystalline * in character should be possible to confirm by examination with polarized light. Holde [20] states that lime-soap greases appear to be colloidal amorphous solutions, and that in benzene solution such a grease exhibits a colloidal structure with a Tyndall cone. Klemgard [27, p. 27] cites examinations of both calcium- and sodium-soap greases under a microscope with crossed nicols which showed the structure to be anisotropic, indicating crystalline structure. The fact that fat and fatty acids possess the power of doubly refracting polarized light should be considered, since most greases contain one or both of these materials. The author has likewise noted that some mineral oils showed crystalline material when observed under crossed nicols.

Any crystalline material in greases may well be of colloidal dimensions. Likewise, non-crystalline colloidal micelles may be present together with the crystalline form. Perhaps soaps of any base dispersed in mineral oil assume one of several forms, similar to what has been found true of soda soap-water systems by McBain [86] and others. This may account for the variation of grease characteristics obtained with varying methods of processing.

Examination of greases of very low soap content might lead to more definite proof of the structure, but most calcium greases of low soap content are produced by diluting the greases high in soap at temperatures lower than are required for complete dispersion of the soap; therefore, such greases may not be strictly comparable with the firm products. However, Lutz and co-workers [84] state that their experience with soap-oil mixtures of low concentration indicates that at low water concentrations true solutions of soaps in oils can be made which show no detectable increase in viscosity. Such mixtures did not form gels on cooling to any temperature down to 0° F. The same soap mixtures with a water content of 0.5 per cent (based on the soap present) formed true solutions at high temperatures and assumed a gel structure on cooling, as indicated by their anomalous viscosity.

This agrees with the findings of others that lubricating greases, whether the soap is colloidal or crystalline in form, require peptizers to form a stable structure. Holmes and Maxson [21] as well as Rhodes and Wannamaker [44] found that they could

* Crystals may be of colloidal size in one, two or three dimensions. They may be elongated or plate-like, and may form aggregates of various kinds. J. A.

not stabilize neutral calcium soap dispersed in mineral oil. These workers resorted to the use of fatty acids to stabilize the grease or gel, as the former workers term it. In spite of the almost universal use of water for stabilizing such systems, Holmes and Maxson venture the opinion that the presence of free fatty acids is a more important factor for stabilization than is the presence of water. Rhodes and Allen [48] tried to form grease by dissolving dry sodium oleate in mineral oil, but reported that under heat and agitation only a small amount of soap passed into solution or permanent suspension and that the resulting product is not a true grease. These workers thus conclude that soda-base greases are not simple solutions or suspensions of dry soap in oil, but that to obtain a true grease, some substance other than mineral oil must be present. Their experiments indicated that the stabilizing material might be water or glycerol, or both.

Materials which influence the structure of soap-oil systems are classed by different workers as peptizers, fluxes, modifiers or additives. There may be sufficient distinction in the action of such materials to justify the above terms. As the patent literature lists innumerable substances which change or stabilize grease structure, only a few will be mentioned here.

In the case of aluminum-soap greases some of the claims are: Japan wax and castor bean oil; [23] resin, such as rosin or hydrogenated rosin; [7] high molecular weight alcohols, such as glycerol (5 per cent of the soap); [24] wool fat alcohols, oleic alcohol or alcohols prepared from olefins of relatively high molecular weight; [41] vegetable fat; [2] a small amount of beta-naphthol is claimed to prevent soap separation; [45] solutions of rubber, latex or polymerized isobutylene all used to give additional stringiness to the lubricant.[29, 28, 49] For calcium-base greases we find the following claims: stabilized by wool fat alcohols; [9] alcohols of relatively high molecular weight; [41] glycerol monostearate or neutral lanolin; [26] to prevent syneresis, an organic solvent boiling above 65° C and a substance miscible with mineral oil, *e.g.*, triethanolamine, diethylene glycol, mono-butyl ether of ethylene glycol, the acetates, formates or other esters of such ethers, ethylene dichloride; [10] *p*-naphthyl aminophenol or other substituted aminophenols; [18] an oil-soluble monohydric alcohol boiling below 95° C, *e.g.*, propyl, butyl, amyl or cetyl alcohol; [6] a partial ester of a polyhydroxy alcohol and a fat acid, *e.g.*, diglycol stearate; [5] addition of phenyl-α-naphthylamine.[46] Addition of vegetable oil or a polymerized ester of acrylic acid to a lithium grease is said to improve the thixotropic properties of the grease.[10] Klemgard [27, p. 859] states that the waterproof properties of soda-soap greases are said to be improved by the addition of such substances as glue, varnish, linseed oil, casein, gums, shellac, rubber, silicates or mixtures of these substances.

Lawrence [30] states that polar substances, in small quantities, aid dispersion of soap in mineral oil and alter the nature of the grease. It is suggested that the mechanism of the attachment of the added polar substance is dipole adhesion to the polar groups of the soaps, thereby reducing their mutual cohesion. This is no doubt the reason for the fluxing action of such substances. Licata [32] states that by the addition of fluxes to aluminum stearate the resulting product dispersed in mineral oil may be a thickened oil, a stringy adhesive semi-flued grease, or a high-melting point solid. Lawrence also indicates that the gel temperature of such oil systems is lowered by either glycerol or fatty acid addition. No doubt other polar substances have a similar effect.

Lawrence suggests that fatty acids form complexes of the formula: $Ca(St)_2$:HFa, where Fa may be any fatty acid. He states that such complexes are more soluble in mineral oil than neutral soap. Lutz and co-workers [34] believe that excess fatty acids present in grease mixtures probably combine with neutral soap molecules to give acid soaps. They reason that since such soaps would contain less metallic element and more hydrocarbon radical per complex than do the neutral soaps, they would be more soluble in mineral oil.

The function of water in greases is interpreted differently by various workers.

Holde [20] states that the water cannot be in molecular combination with the lime soap, since the distribution of the water not only contributes to the turbidity but can be detected under magnification. Klemgard [27, p. 26] states that on microscopic examination of calcium-soap greases, small droplets of water were visible. These were considered to be present in addition to the water bound to the soap, since examination of a transparent lime grease having a lower water content showed no free water. The fact that soap crystals are present in calcium soap greases would seem to contradict attempts to class such systems as emulsions. Lawrence [30] points out that greases have none of the characteristics of emulsions and that the function of water is that of a polar substance which aids dispersion as a peptizer. However, Höppler,[22] who has recently investigated the system calcium oleate-mineral oil, states that anhydrous calcium oleate is amorphous, but on the addition of water forms crystals in which two moles of water of crystallization are present. He claims that such crystals form elongated fibers which agglomerate to "crystal bundles." Höppler observed these "bundles" as "calcium oleate micelles" under a microscope, where they showed a fibrous and honeycomb structure if permitted to grow undisturbed. It was reasoned that in commercial manufacture of calcium-soap lubricating greases the formation of such crystals cannot be followed since, due to agitation, they are perhaps ultramicroscopic. Such crystals are presumed to felt and form a framework which enmeshes the mineral oil.

The choice of soap stocks is a determining factor in the final structure of a grease. Klemgard [27, p. 391] states that in manufacturing soda-base solidified oils (a type of soda grease which is buttery in texture and transparent or translucent) soap stocks are selected which are more soluble in the mineral oil than in the case of fibrous soda greases. Such combinations may be akin to selection of eutectic mixtures of the fats or fatty acids. Such soaps may also have a residual affinity of the soap molecules such that a coarse, fibrous texture is not produced. This is one of the reasons why acids other than those derived from animal or vegetable fats, such as naphthenic or rosin acids, may be partially employed in some products. Of course the latter acids may carry some peptizers as impurities and thus influence the structure; for example, commercial naphthenic acids frequently contain phenols.

Some of the added substances listed above may function as protective colloids. This would be especially true of such materials as glue, casein, rubber, polymerized isobutylene, etc. A similar autoprotection may explain why certain mineral oils will produce stable greases while other oils of the same viscosity fail to do so. Thus, as a whole, asphaltic or naphthenic types of mineral oils seem to form greases more readily than paraffinic types of oils. The former undoubtedly have colloidal components which contribute to this stability.

The same protective action may also be possible with two different soaps which will form micelles at different temperatures or of different size. Henry and Streeter [16] found that they could obtain desired characteristics in a lubricant by preparing aluminum mono-oleate and aluminum trioleate separately and then dispersing in mineral oil when aluminum dioleate would not serve their purpose. A number of workers have made use of the soaps of two different bases in the same grease. This is done with the idea of modifying the characteristics of the predominant soap. Thus, Maag [35] states that a small proportion of lime soap in a soda-soap grease will help to give a smooth, non-grainy structure. On the other hand, Garlick [15] feels that a little sodium soap included in a calcium-base grease will raise the melting point, and Kauffman [26] believes that such an addition stabilizes the soap dispersion and prevents separation of oil from the finished grease. Garlick [15] states that aluminum soaps are frequently added to calcium-soap greases to impart greater stringiness, adhesiveness or clarity. Klemgard [27, p 216] who added a small amount of aluminum soap to a calcium-base grease, felt that the former soap hindered the crystal formation by giving a mixed soap and by aiding in building up the proper charge on the soap particles. Lincoln

and co-workers [88] state that small amounts of aluminum soaps in soda grease serve to control the fiber character of the grease. Yagle,[48] in producing a smooth soda-base grease, employed a small proportion of aluminum soap which was said to impart additional stringiness and toughness to the finished product. Many possible combinations of soaps have been suggested for lubricants; in some cases three or four different soaps are used in the same grease. Miller and Morway [89] make claim for the addition to calcium-base greases of other metallic soaps which form "emulsoidal" colloids in mineral oil and are supposed to stabilize the compounds and prevent sweating of oil from the grease. Suitable soaps are cadmium, cobalt and manganese compounds.

The function of a small proportion of a second soap in a grease may not always be the same. If the additional soap contains some peptizer such as free fatty acids, the addition may simply be equivalent to the addition of such peptizer. This will be particularly true where aluminum soap is added to another soap system.

Properties

The colloidal structure of lubricating greases contributes certain desirable properties which make them preferable to oil in many cases. The solid or semi-solid quality of greases, together with their plasticity, permit their use where the lubricant must stay in place over long periods. The high softening point of such a system enables some greases to be used at temperatures up to 500° F without the lubricant running from the bearing.

The plasticity, together with the thixotropic nature of greases, enables them to seal bearings against the entrance of foreign material. This thixotropic quality permits the grease adjacent to the moving part to soften and if necessary flow or be drawn to the parts requiring lubrication. Any grease pushed away from such parts will return, at least partially, to its original body. Not all greases exhibit this characteristic to the same degree; and naturally the higher the percentage of soap, the less softening will occur with working.

Even with low concentrations of soap, lubricating greases show very high viscosities, relative to that of mineral oil. Since some lubricating greases are unstable, this viscosity may change greatly on "working," indicating either a coagulation of the soap or a tendency to become a sol.

If greases are gels it might be expected that the gel would re-form after heating. This is actually so in many cases, provided that any peptizing material present is not lost in heating. Thus almost all aluminum-soap greases can be melted and will return to about the original structure. The same is true with many anhydrous smooth-texture soda-base greases, as well as with greases made from lithium stearate. Calcium-soap greases have been made which were reversible, even if they contained water and this was driven off.

The fact that mineral oil in greases is often rather loosely held may indicate that any gel present is not sufficient to hold the oil. Thus, Herschel,[17] by means of a grease press, was able to remove a large proportion of the oil from calcium-base greases. In all the greases tried, increase in pressure gave proportional increase in the oil removed. Farrington and Humphreys,[12] using the same type of apparatus, found that a rise in pressure increased the ultimate oil loss, but that the nature of the soap base exerted an influence upon the amount of oil capable of being expressed. For the same grease consistency, more oil can be pressed from the fibrous sodium-soap greases than from the smoother-textured calcium- and aluminum-soap greases. This is probably caused by the finer structure and therefore greater surface area of the crystals or micelles in the latter types of grease. There probably is, as Alexander [1] has suggested, a "zone of maximum colloidality," and if this optimum condition could always be attained, little syneresis might be expected. The behavior of such

systems would indicate that there might be a "brush-heap" structure of relatively coarse crystals in cases where the oil is readily expressed.

An interesting grease structure is noted by Mead and McCoy.[38] This was aluminum oleate dispersed in hot mineral oil. On stirring the mixture cold it showed the normal elasticity of a gel; on the other hand it flowed extremely slowly, acting as a liquid of high viscosity. This was referred to as a striking example of a colloidal solution which was both fluid and elastic.

Stability

Greases are similar to other colloidal systems in that the structure can be destroyed either by coagulation or solution of the dispersed phase. Since, as Mackley [37] states, the presence of an excess of base leads to instability of a grease, Boner and co-workers [3] made use of this principle for the separation of oil from calcium grease in the course of analysis. Considerable excess of lime was added and upon heating the soap settled out, leaving the oil in a free state. Flaxman [18] made use of the same idea when he produced a fluid grease from aluminum stearate by the addition of a liquid amine. If a peptizer is present in the grease, removal of this ingredient will result in coagulation of the soap. This is the case when moisture is removed by heat from ordinary calcium-base grease.

Addition to a grease of a solvent which removes one of the phases or the peptizer will naturally destroy the structure. Lutz and co-workers [34] state that carbon tetrachloride will disintegrate a grease. Excess of a peptizer will likewise destroy the structure of a grease, since it makes the soap so soluble that a liquid rather than a gel results. Thus, a very large excess of fatty acids will break down the structure completely, especially if the grease is warmed slightly, so that in extreme cases a quite firm product will become fluid. A similar destruction of a grease structure sometimes occurs in service where, because of the use of unstable oil or catalytic action of metals, the acidity of the lubricant increases. Excess of water has a similar effect in calcium-base greases, softening the lubricant. If sufficient glycerol is added to aluminum grease under heat, the product will remain fluid, where otherwise it would have set to a firm grease. Naturally, excess water will destroy soda-base greases. Klemgard [27, p. 54] notes that same soda-base wheel-bearing greases absorb water from external sources, causing emulsification with a loss in consistency.

While some workers have found it advantageous to add a second soap to a grease to modify its structure, there are instances where this causes destruction of the grease. Licata [31] states that as little as 5 per cent of the soap as calcium or sodium in an aluminum-soap grease will liquefy the grease. Advantage is taken of this to form some lubricants. Thus Klemgard [27, p. 464] used a mixture of aluminum stearate, potassium oleate and some glycerol to form a semi-fluid air-brake lubricant. Willock and co-workers [47] thickened an oil with aluminum oleate and then added a smaller amount of calcium soap to reduce the tackiness. Such fluidification may be due to the added soap containing excess of base which might react with fatty acids and remove them as peptizers. Or, if the added soap contained moisture, this might tend to hydrolyze the aluminum soap, and the fatty acids thus set free might be responsible for a structural change.

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Colloidal Behavior in Metals and Alloys

REGINALD S. DEAN

Assistant Director, Bureau of Mines, U. S. Department of the Interior

We shall concern ourselves in this chapter only with colloidal systems which behave differently because one or more of their components is metallic in character. The hydro- and organosols and the dispersion of metals in gases are treated elsewhere in this work Although of great metallurgical importance, dispersions of metals in gases do not differ greatly in behavior from dispersions of non-metallic substances in gases. We shall deal with the colloidal behavior of metals and alloys under three general headings: Gases in Metals, Slag Metal Systems, and Metals Dispersed in Metals.

GASES IN METALS

An entirely satisfactory explanation of the behavior of gases in molten and solid metals has not been offered.

Dean and Gottschalk [1] have pointed out that the amounts of gases apparently dissolved by several metals are much greater than would be expected from a consideration of the internal pressure of liquid metals. Ample experimental evidence is also available to show that gases dissolved in liquid metals do not follow Henry's law. Direct evidence is lacking to prove that gases in molten metals are dispersed in one way or another, but the criteria of simple solution are also lacking. An explanation of the behavior of gases in both solid and liquid metals from the colloid viewpoint is best arrived at from a general consideration of metallic structure.

It has long been recognized that the properties of polycrystalline substances are not the same as those of single crystals. These differences are especially marked in metals and metallic minerals and are of the greatest practical importance in metal working and in ore treatment. The property changes in passing from a single crystal to a polycrystalline aggregate are the same as are produced by cold-working a metal or by the precipitation of a dispersed phase. Hence, we may logically assume that the property changes are due directly or indirectly to the formation of interfacial area or internal surface. Our problem then is to ascertain the physicochemical state of the metal atoms at such internal surface, and to show how this physicochemical condition accounts for the singular behavior of gases within the metallic structure. The adsorption of gas on such an internal surface in apparently single crystals of galena has been demonstrated by the writer in collaboration with Gross, Brighton and St. Clair [2] and also by Rideal.[3]

Physicochemical Nature of Metallic Interfaces

The whole subject of the physicochemical nature of metallic interfaces has been reviewed by Dean.[4] The theories that have been advanced to account for the change in properties of metals by the increase of internal surface may be conveniently divided into four groups:

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(1) Theories that postulate a new Gibbsian phase at the interface. (2) Theories that postulate nothing definite concerning the physicochemical nature of the interface and attribute all property changes to distortion of the lattice, which is incidental to the presence of increased internal surface. (3) Theories that attribute the property changes to disregistry of the lattice across the internal surface. (4) Theories that postulate a non-Gibbsian phase at the interface.

The earliest complete theory of metallic interfaces is the amorphous metal hypothesis of Sir George Beilby.[5] The amorphous theory postulates that at metal interfaces, whether at the boundaries of crystals grown from a melt or formed by cold work, a layer of amorphous metal is formed. This amorphous metal, according to Beilby, has the structure and properties of a supercooled liquid, and the properties of the resultant aggregate are those of a mixture of the supercooled liquid and solid phases of metal. He developed interesting experimental evidence of such an amorphous film on polished surfaces, and recent work with electron diffraction has confirmed his conclusions.[6]

The properties that must be assigned to a supercooled liquid do not enable its presence to account for the property changes brought about by internal surface. The writer pointed out this discrepancy many years ago.[7]

It is now generally accepted that if an amorphous layer does exist at metallic interfaces, it is not a supercooled liquid and must be assigned properties that are not consistent with the ordinary or Gibbsian definition of a phase. The theory that the hardening produced by cold work is due to elastic strain was perhaps first proposed by Heyn [8] and has been developed by Sachs.[9]

The inability of lattice distortion to account for electrical property changes resulting from cold working has been shown by Geiss and van Liempt.[10] It may be indicated that there is a discrepancy between energy storage in cold-worked metals and that possibly due to lattice distortion. Fink and Van Horn studied lattice distortion as a factor in hardening of metals [11] and concluded that lattice distortion approximating the elastic limit does not alter hardness. It may therefore be reasonably concluded that lattice distortion *per se* is not adequate to account for the effect of internal surface on property changes in metals.

These theories have been employed by Jeffries and Archer [12] and, more recently, by Taylor [13] in explaining certain mechanical properties of cold-worked metals. Their inadequacy to account for changes of electrical or magnetic properties without some additional hypothesis concerning the physicochemical nature of the metallic interface has been discussed thoroughly by the writer,[14] and more recently by Maier.[15]

The simplicity of the Beilby theory has prompted many investigators to suggest that the amorphous phase is not a supercooled liquid or a second crystalline modification but some state of aggregation not definable as a phase from a phase-rule basis. Fonda [16] and Polanyi [17] have suggested that the new phase is in reality merely an aggregate of fine crystals.

Geiss and van Liempt [10] have suggested that the atoms forming the new phase have deformed outer shells, which cause the changes in properties. The latter has followed the idea further [18] and has postulated that this atomic deformation results in higher energies for the deformed atoms, which may be calculated from the usual quantum formula,

$$E = 0.75\ Q_v = nh\nu,$$

where Q_v is the heat of vaporization. From these considerations, about 50 to 250 quanta are added to the energy of the atoms by deformation.

Maier [15] has been less definite concerning the nature of the new phase, postulating merely an accumulation of atoms having a higher heat content than the normal lattice, and stating that "convenience and expediency require a concise term for the desig-

nation of the total content of atoms not having lattice spacings either normal or distorted." He suggests that such nondescript atoms are in fact adsorbed on the lattice.

The pseudomolecule theory of hardening, first proposed by the writer [7] in 1922, had much in common with these more recent proposals. It suggested that the amorphous layer, if it existed, would not be a stable or Gibbsian phase but would resemble a monotropic form. It went further and postulated the exact structure of such a monotropic form. This postulate recognized that the metallic lattice was built of ions, not atoms, and that in addition to these ions the lattice contained electrons either in a random distribution or in a lattice of their own. It was then postulated that if the ions were displaced from their equilibrium positions they would tend to take on electrons and become atoms, and in view of the competition for electrons in such a process the ions might in some cases share electrons, thus forming dipoles, which were called pseudomolecules. They might more properly have been called merely molecules. As the ions that would form such a molecule might come from opposite sides of a glide plane, their strengthening effect was at once apparent. Their effect on electrical properties was also plain, because free electrons were bound and, hence, conductivity was reduced.

This theory was elaborated further and its advantages were discussed by the writer and Gregg in 1927.[14]

Dean [2] has given the following explicit statement of the pseudomolecule theory: *First postulate.* The ions in a metallic lattice are displaced from their equilibrium position at a surface. *Second postulate.* This displacement results in the formation of electrical dipoles, in which the ions share electrons. *Third postulate.* Energy of thermal vibration (heat content) of these dipoles is greater than that of ions in the lattice, and such energy is distributed according to a Boltzmann or probability relation.

The electrical properties of aggregates of powdered metals were shown particularly to be in accord with this theory, the resistance passing through a sharp minimum at a frequency of about 50 kilocycles, the calculated resonance frequency for the simplest form of pseudomolecules.

The gas in a solid metal may therefore be said to be adsorbed on the internal surface and held in the same way as the gas is adsorbed on an ordinary metal surface. Finch and Stimson [19] conclude that gas can be held at least five ways on a metal surface.

(i) The gas is held physically in an electrically neutral condition, in the form of a condensed layer which even at 850° is, as has been shown by Langmuir [*Trans. Faraday Soc.* 17, 607 (1922)] at least of monomolecular thickness.

(ii) The gas is held loosely in an electrically charged condition, whereby the surface itself acquires a charge, which can be removed with complete restoration of the *in vacuo* charge proper to the surface within 30 to 60 minutes by evacuation at 850°. As examples may be cited H_2, CO, CO_2, H_2O and Ar, in the case of gold; N_2 and Ar, in the case of silver; (no experiments were carried out with this metal in contact with CO, CO_2 or H_2O); and all these gases together with oxygen, but excepting carbonic oxide, in the case of nickel.

(iii) The gas is held more firmly than in (ii) in a condition approximating to unstable, loose chemical combination; for example, O_2 on gold, and O_2 or H_2 on silver. In these cases the respective gas charges can only be removed with difficulty, and the necessary time of evacuation increases with the time during which the surface was previously in contact with the gas.

(iv) The gas is held in a still firmer manner than as outlined in (iii); the surface, however, continues to exhibit the charge characteristic of the gas in question even after prolonged evacuation. The one example of this type of combination so far revealed in the course of this investigation is that of carbonic oxide on nickel.

(v) The gas is bound chemically to the surface and the resulting stable chemical compound undergoes no dissociation at temperatures up to 850°. In this case the *in vacuo* charge on the oxidized surface is the same as the *in vacuo* charge characteristic of the reduced oxygen-free surface. The one example which we have so far been able to study is

that of oxygen on nickel, where direct evidence was obtained, not only of compound formation (absorption of a large volume of oxygen by the hot surface, coupled with the change of appearance at the surface from a bright metallic lustre to a matte greenish-black), but also of the stability of the nickel oxide at 850°. Thus the oxygen, when once it is firmly chemically combined with nickel, does not give rise to the charge otherwise characteristic of that gas.

All these ways apply to an internal as well as external surface. Norton and Marshall [20] have shown that the gas held by molybdenum is present throughout the body of the metal and is removed at a rate proportional to the thickness of the metal.

The entrance of a gas into the internal surface formed either by the original crystallization of a metal or by cold-working the metal frequently stabilizes the structure, which in the first instance was an example of the condition called isocolloidal by Alexander.[21] The example given by Alexander was that of finely dispersed ice in liquid water. Obviously such isocolloidal systems, including the case of a cold-worked metal, are thermally unstable and become homogeneous when heated above a certain limiting temperature. The adsorption of gas on the internal surface of such isocolloidal systems definitely stabilizes them. In some instances such adsorbed gas may combine chemically with the material, as in the case of oxygen adsorbed on graphite, which according to Norton and Marshall [20] is desorbed as CO only on heating to 2150° C. There is no reason why a gas similarly adsorbed on a metal should not persist when the metal is melted. A liquid metal formed by melting a solid metal with gas adsorbed on its internal surface may therefore be regarded as a foam, a concept that Quincke [22] put forward for all liquids for different reasons.

The solubility of gases in metals beyond certain very small physical solubilities must, therefore, be looked upon as cases of adsorption on a sort of foam structure of essentially colloidal dimensions. The negative temperature coefficient of the solubility of gases in metals, as contrasted to other liquid-gas systems, caused Steacie and Johnson [23] to conclude that the explanation must be sought in adsorption in terms of Langmuir's formulation.*

The purer the metal the less persistent is the foam structure. Nitrogen is not adsorbed by very pure molten manganese held just above the melting point, but aluminothermic manganese held just above the melting point adsorbs nitrogen. Though chemical effects are not ruled out, it seems probable that nitrogen is here adsorbed on the foam structure which is stabilized, in all probability, by aluminum oxide. While direct evidence of the actual existence of foam structure in liquid metals is not obtainable, Dean, Barrett and Pierson [24] showed that the cell structure of directly reduced sponge iron persisted through a melting operation and was outlined by small particles of solid inclusions.

Gayler [25] observed that with even the purest commercial aluminum freed from gas and melted *in vacuo* the atmosphere to which the metal is then exposed for only a short time before casting has a marked effect on the macrostructure but a small effect on the microstructure. Hydrogen under these conditions causes a fine macrostructure to form. This holds in spite of the fact that Sieverts [26] had found under other conditions that hydrogen is insoluble in aluminum. The hydrogen in the experiments of Gayler was evidently adsorbed on a persistent foam structure. Further indirect evidence that the effective condition in the "solubility" of gases in molten metals is the existence of a foam structure rather than small changes in chemical composition is furnished by the work of Chipman and Murphy [27] on the solubility of nitrogen in liquid iron. They found that silicon and aluminum used to deoxidize molten iron increased the solubility of nitrogen and that these materials added to

* H. Moisson (*Compt. rend.*, **144**, 593 (1907) observed that when a little platinum is dissolved in mercury the latter readily emulsifies in water. J. Alexander found (*J. Soc. Chem. Ind.*, **28**, 280 (1909) that the supernatant water showed bright ultramicrons in rapid motion. J. A.

already deoxidized iron did not increase the solubility, but did increase the rate of adsorption. It is suggested that the nitrogen was actually adsorbed on a foam structure, stabilized by the deoxidation, and that aluminum and silicon in the steel merely acted as carriers to bring the nitrogen to these interfaces.

Practical Applications of the Concept of Gas-Metal Systems as Colloids

Degasification of Metals. Most technical metals and alloys evolve gases on solidification to such an extent that porous ingots are formed on casting if some form of "deoxidation" or degasification is not employed. Some of the gas evolution may be accounted for by the reactions on cooling, such as the reaction between iron carbide and iron oxide in steel melts to give CO, or the reaction between copper sulfide and oxide to give SO_2. Floe and Chipman [28] have shown that the solubility of SO_2 in molten copper can be interpreted by postulating a simple reaction between gas and metal. The killing of steel is accounted for by the reaction of a deoxidizer such as silicon or aluminum with iron oxide. Many metals and alloys, however, yield porous ingots where such gas-producing reactions are not apparently present. Studies have shown that the gases in such instances are derived from the furnace atmosphere. O. W. Ellis,[29] reviewing the work on gases in copper, finds that nitrogen is a major constituent of the gases evolved from copper ingots during solidification. He concludes, from consideration of the ratio of oxygen to nitrogen in the evolved and extracted gases, that the nitrogen evolved could not be accounted for on the basis of entrapped air and hence must have been present in the molten copper. In two examples of copper melted so as to be fairly well oxidized, nitrogen constituted 33.8-41.1 per cent and 10.2-18.1 per cent, respectively, of the total evolved gases, whereas on copper containing very little oxide only 2.8 per cent of the evolved gases was nitrogen. It would appear that stabilization of the internal surface of the molten copper by large amounts of oxide is necessary for "dissolving" nitrogen, which would be evolved on solidification. Degasification of such copper can accordingly be accomplished by removing the oxide which stabilizes the internal surface. In other words, deoxidation brings about degasification indirectly by breaking up the foam structure in the liquid and permitting chemically inert gases to escape. Leaving entirely aside the purely chemical aspects of degasification, we find that the problem of obtaining a molten metal or alloy in shape for casting into a gas-free ingot is one of eliminating its foam structure or stabilizing it so that it will not be broken down by crystallization of the metal or alloy. One way to do this is to solidify repeatedly and rapidly remelt the alloy with the idea that any gas which can be evolved during solidification will be thus evolved and removed, and that re-adsorption of the gas will not be rapid enough to bring about porosity again on solidification.

Another method applied to light metals, which has recently been receiving considerable attention, is to pass a gas through the molten metal, which will replace the adsorbed gas but will not itself be evolved during solidification, either because of the small amount adsorbed or because it will chemically combine after replacing the other adsorbed gases. The use of chlorine in treating aluminum, as advocated by Tullis [30] is an example of the latter type of degasification. The refining of aluminum and its alloys by treatment with chlorine gas and with nitrogen has been studied by W. Koch.[31] Allen [32] has found nitrogen effective in removing hydrogen from copper-nickel alloys.

Purely mechanical breaking up of the foam structure and consequent release of "dissolved" gases by subjecting the molten metal or alloy to supersonic vibrations has been proposed. British Patent 456,657, November 9, 1936, to Rudolf John and Camillo Reisinger specifies frequencies of 100-300 kilocycles.*

The most generally useful degasification method for molten metals is, however,

* See paper by Prof. K. Sollner in Vol. V of this series on "Sonic and Ultrasonic Waves in Colloid Chemistry." J. A.

the use of deoxidizers. These are the highly chemically reactive metals or metalloids, such as silicon, calcium, magnesium, aluminum, phosphorus, titanium and boron. The selection of the best deoxidizer is necessarily somewhat empirical. It must react with the oxides, nitrides or sulfides that may enter into gas-evolving reactions or that may stabilize a foam structure from which adsorbed gas may be evolved; and, at the same time, the products of its reaction must either eliminate themselves or distribute themselves in a desired manner. Any excess of the deoxidizer must either be harmless in the resulting alloy or must volatilize.

Grain Size Control in Metals

As indicated in the foregoing discussion, the problem of grain-size control in metals is closely bound up with gases in metals. The effect on grain size of nonferrous alloys of various furnace atmospheres has been studied by Gayler,[25] who concluded that with fairly high casting temperatures the atmosphere to which the molten alloy is exposed has a very marked effect on the macrostructure (*i.e.*, grain size) as compared with a small effect on microstructure.

Grain-size control in steels has become a matter of great commercial importance. Steels deoxidized with manganese and silicon are coarse-grained. Aluminum additions produce fine-grained steels. It is generally considered that aluminum additions produce inherently fine-grained steels, because they introduce numerous submicroscopic refractory particles which serve as nuclei for recrystallization. It appears, however, that the aluminum content of fine-grained steels is greater than that of coarse-grained, while the Al_2O_3 content is about the same. The fact that an actual excess of aluminum over that for ordinary deoxidation is required indicates that the presence of dispersed Al_2O_3 will not explain the result. The presence of an excess of aluminum is necessary to react with the gases (probably carbon monoxide) in the internal surface of the molten steel, and thus stabilize the foam cells. It is these stabilized foam cells that control the crystal growth of the austenite.

Hydrogen Embrittlement of Steel

Two distinct but related phenomena are referred to as hydrogen embrittlement in steel—the embrittlement caused by acid-pickling or certain boiler waters, and the defects in steel known as flakes. Both result from the fact that atomic hydrogen can diffuse through steel and under certain conditions become molecular hydrogen, no longer capable of free diffusion in the metal.

Pfeil [33] demonstrated that a loss of tensile strength is produced in iron by atomic hydrogen and that the fracture is inter-crystalline.

The tendency of the atomic hydrogen in steel to diffuse into the internal surface of the steel structure and there become adsorbed molecular hydrogen brings about flakes and similar defects in steel, according to Zapffe and Sims.[34]

Slag-Metal Systems

The dispersion of metals in solid non-metallic media is represented by several well known examples. The color of gold ruby glass has been shown to be due to ultramicroscopic particles of gold. The colorless glass formed by quick cooling has been explained as true solution, atomic dispersion, or just very fine dispersion. The theory of fine dispersion assumes spontaneous dispersion of the gold particles at high temperatures. The criteria of solution are not easily applied to mixtures of this kind.

Other well known examples of dispersion of solid metal in a non-metallic medium are the photohalides. The work of Lorenz and Eitel [35] and Lüppo-Cramer [36] has shown that the latent image is an extremely disperse sol of silver in halide. The silver particles furnish the nuclei for subsequent development.

The pyrosols, particularly those formed by the electrolysis of lead chloride, are also well known from the work of Lorenz.[37] The work of Eitel and Lange [38] indicates that these pyrosols pass into true solutions above 500° C. Again, the criteria of true solution are not easily applied.

A less familiar example of metal dispersion in slag is the mica-copper mixture described by Williams and McLennan.[39] This interesting dispersion is formed by striking an arc between a plate of copper and a rod and feeding mica into the arc. The resulting mixture is remarkable for its high positive coefficient of electrical conductivity: it is practically an insulator at room temperature, and its conductivity increases a thousand fold as the temperature is raised a few hundred degrees.

All these examples refer to the dispersion of metal in slag. The reverse condition, the dispersion of slag in metal, is of course the basis of non-metallic inclusions in metals and alloys. The retention, or lack of retention, of such inclusions in metals has been explained on the basis of melting point with the idea that liquids coalesce more readily than solids. This, of course, is fallacious reasoning, as anyone who has tried to rejoin droplets of floured mercury can testify. Boys [40] pointed out that the easiest way to collect spilled mercury was to sprinkle water about it and to sweep the wetted globules together with a card. The much more likely criterion is that of wettability. Non-wetted inclusions will certainly tend to agglomerate and be lifted out of the metal by gas bubbles.

Most cases where non-metallic surfaces are wet by metals or metal surfaces by slags are based on a chemical reaction in which a slag phase is being precipitated from a metal phase, or *vice versa*. Wrought iron is an excellent example of metal wet by slag, and in this instance, the slag is actually precipitating metallic iron by the reaction

$$3FeO \rightarrow Fe_3O_4 + Fe$$

An example of a slag-like surface being wet by a metal is the action of molten metallic manganese on silica. In this instance we have $SiO_2 + 2Mn \rightarrow 2MnO + Si$, a slag-like phase, MnO, being precipitated by the reaction of the silica and manganese. A similar reaction between Fe and SiO_2 is responsible for good adherence in enameling on iron.

Non-metallic inclusions in metals are not necessarily harmful to physical and chemical properties, as is demonstrated in the case of wrought iron. It is only necessary that these non-metallics be wet by the metal and preferably capable of spreading on metal surfaces or interfaces to form a thin layer of cement between the crystals.

Practical Applications

The Aston Wrought-Iron Process. In the Aston [41] process for wrought-iron manufacture, very low-carbon steel is dispersed in a slag high in iron oxide. The slag is maintained at a temperature below the melting point of iron. When iron strikes the slag, it is suddenly solidified and the gas evolution disperses the iron throughout the slag, forming a sponge or ball. As there is substantially no opportunity for reactions between slag and metal, the metal must be sulfur-free, contain the right amount of phosphorus, and above all be full of gas. This is accomplished by melting a suitable charge of pig iron and scrap in a cupola, desulfurizing with NaOH in a mixer, and overblowing somewhat in a Bessemer converter.

One most interesting result of this dispersion process is that solid metal is completely degasified. Evidently, the gas in the metal is not in solution or evolved by chemical reaction; otherwise, the individual metal particles would still contain gas and be themselves spongy. The gas must be distributed in a sort of foam structure, so that disintegration takes place along a continuous gas phase, leaving gas-free globules dispersed in slag.

Steel-Making Reactions. The possible importance of the dispersion of metal in slag in the ordinary steel-refining processes has not been determined. Certainly in any reaction between two immiscible liquids, the process could be greatly speeded by emulsification. The use of Twitchell reagent in the splitting of fats with aqueous acid is the best-known example of this in the non-metallurgical field. The Perrin [42] process for steel refining makes use of at least a purely mechanical emulsification by pouring a thin stream of metal into highly fluid slag.

The full implication of the possibility that substantially all steel-making reactions may be surface reactions seems to have been disregarded by students of physical chemistry of steel making. Dean and Gottschalk [1] pointed out that the gas available for reaction at the surface of even a relatively coarse suspension of gas in metal must be far greater than the number of any dissolved molecules in the same metal volume. Haglund [43] has recognized that there is very little, if any, reason to presume any considerable solubility of carbon monoxide in liquid steel.

A study of the method of occurrence of sulfur in slags shows clearly that the usual equations of desulfurization involving a homogeneous reaction with diffusion at the slag interface are based on a whole series of incorrect assumptions. These reactions usually are written:

$$\text{FeS (in metal)} \rightleftharpoons \text{FeS (in slag)}$$
$$\text{FeS (in slag)} + \text{CaO (in slag)} \rightarrow \text{CaS (in slag)} + \text{FeO (in slag)}$$

In the first place neither iron sulfide nor calcium sulfide is soluble in slag in the usual physicochemical sense. At relatively low concentrations, ultramicroscopic studies of chilled slags show them to form dispersions.[44]

Under these conditions it becomes clear that increased desulfurization obtained by increased basicity of the slag cannot be explained on the basis of a homogeneous reaction. The formation of CaS from FeS must be due to some other mechanism. The most probable is the reduction of calcium into the metal through the intermediate formation of calcium carbide. If this were the case, a dispersion of calcium carbide in the metal should prove the most effective desulfurizer. Tests by Wood, Barrett and Holbrook [45] show this to be the case.

Desulfurization with fused sodium carbonate and hydrate proceeds in a very different manner. The highly liquid slag is dispersed through the metal and reacts directly with FeS to produce Na_2S and FeO, which remain in solution in the metal. The highly alkaline slag which rises to the metal surface must, however, be skimmed immediately or resulfurization will take place by FeO diffusing into the slag and reacting to form FeS.

In the case of CaC_2 the elimination of sulfur increases sharply with reduction of carbide particle size below 48-mesh, showing that a similar dispersion is necessary. There was, however, no resulfurization from the slag formed, as was the case when desulfurization was accomplished with alkalies, probably because sulfur was removed without oxidation of iron; hence, the FeO plus carbon balance in the iron was not disturbed.

Powder Metallurgy

Compacted metal powders may be considered as a special case of metal-nonmetal dispersions. Under certain conditions of compression and sintering the elimination and aggregation of surface contamination on the particles may be sufficient to give a coherent body of metal similar in every respect to that formed by casting, forging or annealing. In general, however, powder compacts have special properties due to their extended interfacial areas. Emmett [46] has shown that iron powders form almost instantly a layer of oxide five molecules thick even at liquid-air temperatures.

The heterogeneous metallic compact is nowhere better illustrated than in cemented carbide tools. Rollfinke [47] describes their manufacture as follows: "In a ball mill the carbide mixed with nickel or cobalt is ground to a colloidal powder and then pressed at 2000 kg/cm^2 and sintered at 1000° C. Final sintering in vacuum is at 1400-1500° C." Since any true alloying of the carbide with metal probably does not take place, this is a splendid example of a dispersion of fine particles in a solid coherent metal.*

Magnetic Properties of Metal Compacts. The magnetic and electrical properties of metal compacts not only have practical importance but are of value in revealing the structure of compacts themselves.

Gottschalk [48] found that the susceptibility of magnetite compacts at low field strength dropped rapidly for fine particle sizes, that is, large interfacial areas. Observations on iron and silicon steel confirm this point qualitatively. It cannot be assumed, however, that as a general rule susceptibility decreases with grain size. Dean and Davis [49] have pointed out that the induction per unit volume of cobalt increased from 11.0 to 62.6 when the internal surface of the cobalt compact was increased by adding 0 to 97 per cent of a non-magnetic diluent, tungsten carbide. These authors also report that finely divided cobalt made through the amalgam has an abnormally high induction as well as a high coercive force. Another case of increase in magnetism of metal compacts with increased interfacial area is that of manganese. Here the investigations of Ochsenfeld [50] have established that ferromagnetism in manganese is a property of the gamma form having a tetragonal lattice, which is obtained by suitable means with high internal surface or lattice discontinuities. The decomposition of manganese nitride is a simple method of accomplishing this. Not only is such manganese magnetic, but according to Ochsenfeld it has a coercive force of 200. Kuh [51] reported that finely divided manganese obtained by distilling the mercury from a manganese amalgam was magnetic. Bates, Gibbs and Pantulu,[52] however, found that manganese by mercury became magnetic only on heating in nitrogen. Under these conditions both induction and coercive force increased, reaching a simultaneous maximum at 550° C.

We may accordingly conclude that where ferromagnetism is due to structural changes in normally paramagnetic or only slightly magnetic substances, it is accompanied by high coercive force. On the other hand, in strongly magnetic substances increase of coercive force is usually accompanied by a decrease in magnetic induction.

For magnetite Gottschalk [48] found that coercive force of compacts was a linear function of the specific surface. A similar relationship has been found for iron and silicon steel. This relationship between average particle size of magnetic powders and coercive force has been found useful for several purposes, and has been used by Dean to check the relationship between work of crushing and surface produced. The high coercive force of compacts of very fine metal powders has been utilized by Dean and Davis [49] in the production of permanent magnets.

It is interesting that, despite the tendency of metal compacts to have high coercive force due to increased surface, compacts of powdered Permalloy or especially molybdenum Permalloy are used for loading coil cores where losses must be kept to a minimum. The extent of surface increase to produce appreciable coercive force in a material of such high permeability is very large and the particles are relatively coarse—usually about 65-mesh—and are separated by a ceramic insulating material that will withstand the necessary heat treatment.[53]

Electrical Properties of Metal Compacts. Dean and Davis have discussed the electrical properties of metal compacts on the basis of the pseudomolecule theory

* In the first paper of Vol. V of this series, J. Alexander shows that carbonado ("black diamond") is an aggregate of fine or colloidal diamond crystals. J. A.

previously mentioned. Where the internal surface is grealy extended and most of the resistance of the compact is due to it, the equation for the relation between electromotive force and current becomes

$$E = IM_{\bullet} - Q/T + BT + C.$$

This equation conforms to Dean and Koster's [54] results for galena compacts. The quantity, $-Q$, in the above equation is the energy of dissociation of the pseudomolecules. To obtain this in terms of calories per gram-atom, Dean and Koster's value of Q must be multiplied by $2R$, which gives 5000 calories. This value is in excellent agreement with Maier's [55] value for the energy of transition of his omega phase in copper.

The most characteristic part of this equation of conduction is, of course, the positive temperature coefficient of electrical conduction. We have already noted that an emulsion of copper in mica, which is an extreme case of the powdered metal compact has a surprisingly high positive temperature coefficient of conduction. Metallic titanium and zirconium, as ordinarily prepared, also have a positive temperature coefficient of conduction, due entirely to the separation of their metallic grains by oxide layers. Really pure titanium and zirconium as prepared by de Boer [56] and his associates have normal metallic conduction and temperature coefficients.

In most powder metallurgy, interest in the colloidal system that initially exists centers only in the best methods of destroying it. Electrical resistance has been used by Rhines and Barrett [57] as the most effective means of following the course of diffusion in metal compacts. The transition from a dispersed system to an integral metallic one in powder metallurgy could undoubtedly be followed more effectively by temperature coefficient of electrical resistance.

Tyssowski [58] describes the preparation of copper compacts made from brittle electrolytic copper powder which has been purified by heating in hydrogen. After extrusion of the compacts at pressures as high as 76400 psi the resulting compact has become an integral piece of metallic copper with a conductivity higher than that of electrolytic copper.

Mechanical Properties of Metal Compacts. The mechanical properties of compacts, like those of cold-worked metals, depend not only on the total amount of internal surface but upon the energy distribution at this internal surface. This distribution is a function of the pressure of compacting and the subsequent sintering. In the formation of the compact, pseudomolecules are formed with a more or less random distribution of energy. According to Bal'shin,[59] the energy expended by a die in compression is divided as follows:

(a) Absorption of energy in overcoming the cohesive forces between the particles of the powder in changing their position. (b) Absorption of energy in deforming the particles and, in a number of cases, in transforming the particles into a conglomeration of fragments. (c) Absorption of energy in overcoming elastic and unbalanced strains in the pressed conglomerate. The expenditure of energy increases with increasing density because:

(1) The active cohesive force increases with two factors—increase in surface of contact of particles and decrease in the interstices between the particles. These factors, with increasing condensation, vary with the cohesion acting between the particles. (2) The consolidation of the metal with increase of density is opposed by the deformation of the particles. (3) With increase in density there is an increase in strains.

Some part of the energy of pressing remains as interfacial energy in the compact. On sintering at any given temperature only part of this is removed. There remain the lower-energy pseudomolecules formed in the pressing operation. It does not follow, therefore, that all properties of a compact are affected alike by an annealing or sintering treatment. It may be possible to soften a compact mechanically without

softening it magnetically, since coercive force is a property that appears to be affected by dipoles of an exceedingly wide energy range. On the other hand, it may be possible to bring about high conductivity in a compact without softening it mechanically.

The problem of producing a copper compact for starting-motor brushes is one of obtaining a high conductivity and at the same time a relatively high hardness. Segments must have an average hardness number of 85 Brinell after reheating for one hour at 450° F; at the same time the conductivity must be at least 9670. According to Hardy,[60] these conditions may be met by using rapid compression of the compact and hard-faced dies.

The possibility that metal compacts made from heat-treatable alloy powders may be heat-treated more effectively is suggested by an experiment of Kikuchi discussed by Jones.[61] According to this experiment, annealed compacts of duralumin had a Brinell hardness of 76.7, whereas the same compacts, when heat treated, had a Brinell hardness of 136. This is an unusual increase in hardness for duralumin.

Dispersions of Metals in Metals

Liquid-Phase Systems

A few dispersions of metals in metals are formed in systems having at least one liquid phase at the time of formation. The most important of these are the amalgams of iron, nickel, cobalt and manganese formed when these metals are electrolytically deposited from their aqueous solutions into a mercury cathode. These systems were early recognized as dispersions,[62] and the preparation of very fine iron and nickel powders for catalysts by this means has been suggested by Bennett and Frazer.[63] Nagaoka [64] in 1896 found that the magnetization of iron amalgams was proportional to the iron content and hence that the iron was not in solution. This investigator also noted that the coercive force of these amalgams was extraordinarily large. In a sample of such liquid amalgam reported by Dean, Gottschalk and Davis [65] the coercive force was 275 oersteds. We have already spoken of the magnetic properties of the powder compacts made from the finely divided metals obtained by evaporating the mercury from these amalgams.

An interesting problem has arisen in the dispersion of steel in mercury when used in boilers. According to A. R. Smith and E. S. Thompson,[66] the addition of 1 part per million metallic Ti and 100 parts per million metallic Mg completely prevents the dispersion of the steel in the mercury and, in addition, produces perfect wetting of the steel by mercury. No explanation of the phenomenon is offered.

The plastic bronzes are another example of liquid-metal dispersion or emulsion. These are usually dispersions of copper in lead and are not as a rule fine enough to be really in the realm of colloid chemistry.

Practical alloy technology contains a number of examples where a solid phase is dispersed in the liquid. The alloys of manganese with magnesium are of this type.

Dispersions of Solid Metals in Solid Metals

We now come to the most important of all colloid phases of metallurgy—the solid dispersions, which include the hardened steels and all the many alloys that modern metallurgists find to be heat-treatable. Heat-treating is essentially a colloid phenomenon.

There are many ways of bringing about a dispersion in solid alloys. They are all, however, applications of a general principle, which is to obtain an unstable atomic arrangement by a change of environment of the alloy and then to interrupt transition toward equilibrium at a point where a dispersed phase has resulted. The simplest case of such dispersion formation is the quenching of a solid solution which ages at room temperature to produce a dispersion of one of the constituents in the remaining

solid solution. An example of this is the system lead-antimony, investigated many years ago by the writer and his associates.

On first consideration the formation of a dispersion in this system seemed very simple indeed. The solid solution of antimony in lead when quenched from a temperature where it is homogeneous breaks down at room temperature to separate antimony in a finely divided form. The resulting dispersion is characteristically harder and stronger, has a lower electrical resistance, and in general behaves as would be expected for a mechanical mixture of finely divided antimony through lead. Further investigations of the kinetics of the process indicate, however, that actual separation of submicroscopic crystals of antimony may be preceded by some phenomenon which has a profound effect on the properties of the alloy as well as its further decomposition.

Ordering in Alloys. The nature of this process is indicated by certain alloys in which the separation of the constituent never takes place but which, nevertheless, are susceptible to heat treatment. A good example of such an alloy is the copper-gold alloy having the composition Cu_3—Au. This alloy, when heated to 750° C and quenched, exhibits a completely random distribution of gold atoms among the copper atoms. It is said to be completely disordered. After very long heating at 200° C the gold atoms take on ordered positions in the lattice, *i.e.*, every gold atom has three copper atoms for nearest neighbors. The most conclusive proof of this ordering is to be found in the X-ray diffraction pattern of such an annealed copper-gold alloy. As the absorption of gold is so much greater than that of copper, the gold atoms form a super-lattice readily detectable in the X-ray diffraction pattern. For a discussion of the entire subject of ordering the reader is referred to an excellent article by Nix and Shockley.[67]

Among the alloy compositions known to undergo ordering may be mentioned CuPt, CuPd, Cu_3Pd, Ni_3Mn, Ni_3Fe, FePd, and MnNi. So far as the beginning and final states of this order-disorder transformation are concerned, nothing enters the proper domain of colloidal phenomena, and if there were no intermediate stage we should have no occasion to discuss ordering phenomena in alloys here. There are, however, both theoretical and practical reasons for assuming the formation of local domains of order at temperatures much above the point where long-distance order disappears. By complete long-distance order we mean that each lattice point is occupied by the assigned atom. Obviously, in complete disorder there will be as many right as wrong atoms in a given lattice position. Where thermal forces have completely nullified the existence of long-distance order, there may remain, however, domains in which short-distance order exists, *e.g.*, each gold atom surrounded by three copper atoms. The dispersion of such domains in an otherwise ordered lattice brings about a true colloidal state, and the properties of such a state constitute the subject of our present inquiry.

As we have seen in previous sections, the coercive force of magnetic alloys is one of the most reliable measures of "internal surface." Jellinghaus [68] has reported studies on the FePd. This alloy, after rapid cooling, has a coercive force of only 2 oersteds, while on annealing at 500° C for 15 hours the H_c increased to 260 oersteds; on still further annealing, a steady value of 150 oersteds was reached. We conclude that the coercive force is due not to long-distance order but to the colloidal condition established by heating to a point where long-distance order gives way to dispersed domains of short-distance order; with sufficient time these domains themselves disappear. Burgers and Snoek [69] have shown that the coercive force is not proportional to the intensity of the superstructure lines which indicate the extent of long-distance order.

The presence of many small areas of local or short-distance order does not affect such properties as electrical resistivity provided the size of the antiphase or out-of-step domains is smaller than the mean free path of the conduction electrons.[70] This

is in line with what we have learned to expect for internal surfaces in general: namely, coercive force measures such surface very comprehensively, while electrical resistance is affected by such surface only when it has certain relationship to the electrical conduction phenomenon.

Mechanical properties like electrical resistance are affected only when the internal surface has a certain relationship to the atomic bonds with which they are concerned. Hardness and strength are in general increased by ordering processes in the same way as coercive force. Nowack [71] has shown that reheating a rapidly cooled Cu-Pt alloy brings about an increase in hardness which, like coercive force, passes through a maximum after a relatively short annealing time at 500° C. Similar behavior has been observed for CuAu, CuPd and Cu_3Au.

It is interesting to note that cold work, which brings about a decrease in long-distance order, as shown by electrical resistance, by X-ray diffraction lines and by magnetic saturation, increases hardness even in an ordered alloy. Koster [72] has concluded from a survey of published work that high hardness accompanies ordering only when there is a lattice change, but it can be developed in other cases by cold work preceding the ordering treatment. It appears, therefore, that hardness is not directly connected with ordering but with a condition of dispersion that sometimes results from the tendency of an alloy to order.

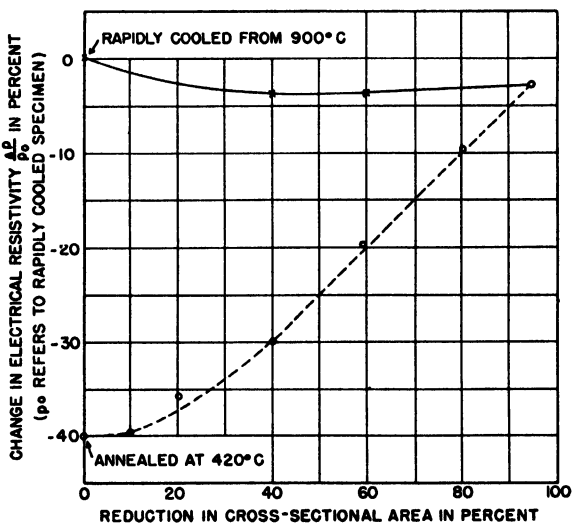

FIGURE 1. Effect of plastic deformation on the electrical resistivity of Ni_3Mn. F. C. Nix and W. Shockley, *Rev. Modern Physics*, **10**, No. 1, p. 57 (Jan. 1938).

The effect of order on modulus is even more interesting than its effect on hardening, since the elastic modulus is a much more fundamental property. Rohl [73] has reported that Young's modulus increased on ordering for Cu_3Pd and Cu_3Au, whereas it decreased on ordering for the CuAu and CuPd alloys. These results, however, do not agree with those of Guillet and Portevin,[74] who found an increase of modulus on annealing quenched alloys of the compositions Cu_3Au and CuAu. The effect of ordering on the modulus of the alloys of Mn and Ni near the ordered lattice Ni_3Mn in composition is most interesting. The relation of change in modulus on ordering to composition is shown in Fig. 3. These results are from the unpublished work of Dr. E. V. Potter in the author's laboratory. From these results, it is evident that the modulus is greatly increased by ordering only at compositions a little to

either side of the composition of the ordered lattice. Very near to this composition itself is an actual decrease in modulus due to ordering. We can conclude only that the increase in modulus is due to the formation of a fine dispersion of areas of local order when the composition is not right for a nearly complete ordering of the lattice. This conclusion agrees with the work of Siegel,[75] who found from a study of CuAu alloys that elastic constants are closely related to the degree of local order.

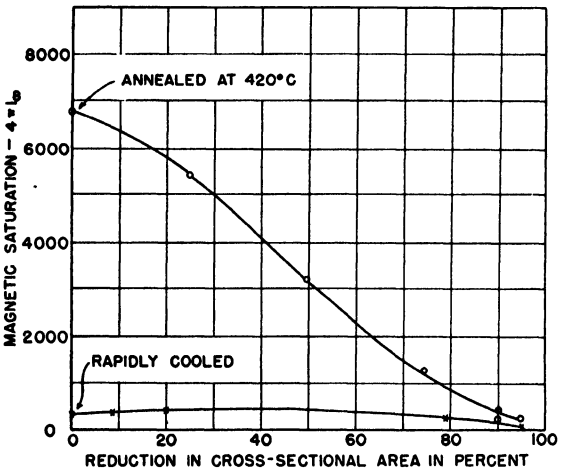

FIGURE 2. Effect of plastic deformation on magnetic saturation of Ni_3Mn. F. C. Nix and W. Shockley, *Rev. Modern Physics,* 10, No. 1, p. 58 (Jan. 1938.)

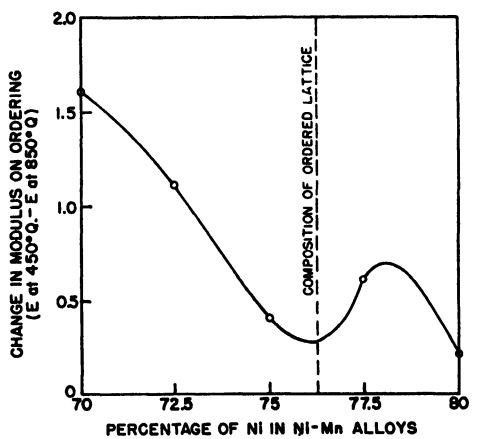

FIGURE 3. Relation of change in modulus on ordering to composition.

The author's conclusion, then, is that the mechanical and magnetic properties with which the metallurgist is essentially concerned are greatly affected by dispersions of local areas of ordering, and that the eventual separation of another phase in microscopic size is a final stage in some ordering systems which takes them out of the realm of true colloidal phenomena. It has long been recognized that dispersion-hardening was the result in the first instance of the dispersion of something other than fine particles and these had been called "knots" or "pseudo particles." The study of the ordering systems would seem to reveal their real nature. The explanation of the property changes which they bring about, however, is still most con-

veniently explained on the basis of the internal surface or pseudomolecule theory, discussed in detail in an earlier section. While ordering in ternary systems has not received much attention, it has been shown that the ordered lattice MnNi can be dispersed in solid copper to give alloys which are in every way equivalent to the usual dispersion hardening alloys, such as Cu—Ni_2Si or Cu—$CuBe_2$, except that a microscopically visible phase never separates. There is, therefore, every reason to believe that the formation of pseudomolecules by local ordering is responsible for the initial stages of the phenomenon of dispersion-hardening.

Dispersion-Hardening

The number of dispersion-hardening alloy systems is too great for anything like a comprehensive review here. Many of them were discussed in a symposium on the subject of dispersion hardening at the October 1939 meeting of the American Society for Metals in Chicago.[76] As observed many years ago by Gregg,[77] dispersion-hardening is most common in systems which consist of an intermetallic compound (or we would now add, ordered lattice) with another metal in which both components of the compound form solid solutions.

Internal Friction or Vibration-Damping Capacity of Metals

In recent years increasing interest has developed in the vibration-damping capacity of alloys as indicative of their structure. Briefly, vibration-damping is the conversion of elastic energy of vibration into heat. It will be clear that in the simplest type of lattice anything such as cold work, which affects modulus of elasticity, should affect damping capacity in the same way, since, if there is no change in the lattice, the energy lost in its dilation and contraction will be proportional to the force necessary to produce a given dilation. On the other hand, if the lattice points possess polarity, the modulus will be affected by the rotation of the unit cells by cold work and by any disordering effect of the work and may be either increased or decreased, depending on the entire average orientation with respect to the dilating force. The very great effect of orientation of crystals on Young's modulus is clearly shown in the work of Rinehart[78] on the modulus of single crystals of beta brass. He found that $1/E_{100} = 3.881 \times 10^{-12}$ and $1/E_{111} = 0.475 \times 10^{-12}$, corresponding to an elastic anisotropy of 8.2. Rinehart's work showed further that the effect of disorder on Young's modulus was great only in the (100) and (110) directions and not in the (111) direction. That is, in any polar lattice we have not only a dimensional but a rotational factor, and the damping capacity may change either directly or inversely with the modulus or first in one way and then in another, as one or the other factor dominates.

A recent study of the effect of torsional cold work on the vibration-damping capacity of several metals and alloys has been made by Dean and Potter. The results of these investigations may be summarized as follows:

In simple cubic metals and alloys, such as copper, brass, aluminum, electrolytic iron and nickel, the change of modulus and damping with cold work are quite closely parallel; with Permalloy, zinc, manganese-copper alloys and non-aging Armco iron, however, the modulus is affected in one direction and the damping capacity generally in the opposite. Permalloy is the most definite example of this. Here we see that very small amounts of cold work profoundly affect both modulus and damping of the fully annealed alloy. The modulus increases from 14.5 to 17 and the damping drops from 3.0 to less than 0.2 per cent. As Permalloy is known to be an exceedingly sensitive ordered lattice, we may assume that the predominant effect here is a destruction of long-distance order, resulting in increased modulus and decreased damping. In other words, by cold work Permalloy becomes very much less like a simple metal. The manganese-copper alloys with their extremely high damping capacities are much less affected by cold work; but here again, the modulus

appears to increase as the damping decreases after an initial increase in damping at very small amounts of cold work. Zinc is an example of a hexagonal lattice rotated by cold work. We know very little about non-aging Armco iron, but it behaves as if it were an ordered lattice somewhat like Permalloy. These results shed some light on the nature of damping itself. Apparently, high damping is characteristic of certain lattices in a high state of perfection, such as nickel and Permalloy. It is even possible that all very pure metals and ordered alloys, that is, undistorted and uninterrupted isotropic lattices, have high damping capacity.

The very great rate of drop of damping capacity of copper and electrolytic iron with a little cold work indicates that with sufficient purity and careful enough annealing these might have damping capacities as high as nickel or Permalloy. There is nothing to indicate that brass or aluminum would ever join this group; but brass is not an ordered lattice, and aluminum has a very low modulus and its purity is not comparable to copper, electrolytic iron, nickel or Permalloy. It is also true that such chemically and structurally pure metals have virtually zero elastic limit, so that high damping in the unstressed metals may be nothing more than plastic deformation by even the small stresses used in measuring. If, then, we assume that damping in very pure metals and ordered lattices is not an elastic phenomenon and confine our attention to metals and alloys that have been given a finite elastic limit by moderate cold work or by alloying, we find first a group of metals and alloys for which damping decreases with cold work (copper, electrolytic iron, Permalloy); a second group for which damping increases with cold work (brass, zinc, Armco iron and aluminum); and finally a third group for which damping first increases and then decreases rapidly (nickel and Mn—Cu alloys).

The first group may be considered normal: high-purity, continuous, isotropic lattices in which cold work has only one effect—to decrease vibration-damping capacity. The alloys of the second group are anisotropic or discontinuous lattices in which cold work increases damping capacity. The third group represents systems with areas of local order where cold work tends to bring about lattice continuity an effect that overcomes the normal tendency of cold work on such lattices to lower vibration-damping capacity.

We thus see high damping capacity as a characteristic of continuous lattices which, in most metals and fully ordered alloys, is readily destroyed by cold work or by introduction of even small discontinuities. However, certain metals and alloys form dispersions of local-order areas which are not obliterated by cold work and which bring about retention of damping capacity approaching that of pure metals in alloys which have been cold-worked or heat-treated to give them finite elastic limits. The best example of this is found in the manganese-copper system, in which atom mobility is so low that, over a wide range of compositions and heat treatments, dispersions of local-order areas are formed which are only moderately affected by cold work. For example, in the alloy of 80 Mn—20 Cu, more than 100 pounds per inch torsional cold work can be done on a rod without decreasing the damping capacity of a quenched alloy below its initial damping capacity of 2 per cent. With the same amount of cold work, Permalloy is decreased from 3 to 0.15 per cent and nickel from 1.85 to less than 0.5 per cent. With the cold work applied as tensile stress, more than 60,000 pounds per square inch can be applied without decrease of vibration-damping capacity below the initial unstressed value. The maximum damping capacity in the Cu—Mn alloys is obtained by slow cooling, which gives maximum opportunity for the formation of areas of local order. Next highest damping capacity in this system is obtained by reheating after quenching. In this case the ordering process is accompanied by considerable increase in hardness and electrical conductivity, indicating that the areas of local order are large enough to have an effect of electrical resistance.

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Colloidal Factors in the Electrodeposition of Metals

LOUIS WEISBERG

Consulting Chemist and Chemical Engineer, New York

Electrodeposited metals show enormous variations in structure. Some consist of coarse crystals which may be observed at fairly low magnification or sometimes even with the unaided eye. In others, the structure is too fine to be resolved by the microscope and can be detected only by means of x-rays or electron diffraction. It is believed that the particle size in some instances extends down to about 50 Angstrom units.

Interference with Crystal Growth

If an electrodeposit could be formed under ideal conditions, one would expect it to have a perfectly regular crystal structure, free from discontinuities or imperfections of any kind. In fact, according to modern ideas of the metallic state, the deposit would constitute a single large crystal. In practice, ideal conditions are never realized. Interference with crystal growth occurs in so many ways that discontinuities and imperfections in electrodeposits are the rule, rather than the exception.

Deposits are seldom free from inclusions. If dirt or suspended matter of any kind is present in the electrolyte, some of it always gets carried into the deposit. It has been shown that inclusions of this nature account for the porosity often found in nickel deposits.[1] In certain applications where thick nickel deposits of exceptional smoothness are required, the Tyndall beam has been used to test the clarity of the electrolyte and insure proper removal of suspended matter.

Many electrodeposits show cracks or fissures. Sometimes these are large enough to be seen with the naked eye, although more often they can be seen only under a microscope. Nearly all electrodeposits are porous when thin, which may be due to dirt inclusions, as already mentioned, or to microscopic cracks.

Cracks and fissures may originate from several causes. Some are due to hydrogen adsorption and embrittlement.[2] Metal deposition is usually accompanied by some discharge of hydrogen ions. Part of the hydrogen thus neutralized may be adsorbed by the metal, where it is present as hydrogen atoms which occupy interstices in the metal lattice. To make their escape from the metal, these atoms must first combine to form molecular hydrogen. This hydrogen gas collects in intergranular cavities and there builds up pressures which may be high enough to tear the metal apart and cause cracks or blisters.

Cracks and fissures may also result from the fact that the metal is deposited in a highly stressed condition. The stresses are then relieved by cracking. The magnitude of the forces involved may be appreciated from the fact that if nickel is deposited to a thickness of several thousandths of a centimeter on one side of a flat sheet of steel, the steel sheet acquires a perceptible curvature as a result of the pull exerted by the nickel. The origin of the stress in electrodeposits is not fully understood. It has been suggested that it may be associated with hydrogen adsorption by the metal. It is noteworthy that deposits formed from electrolytes containing col-

loids are more likely to be highly stressed than deposits formed under other conditions.

In thin deposits, it is often possible to see a continuation of the crystal structure of the underlying metal.[3] This structure may persist for a certain thickness, but as the deposit grows, the structure gradually changes to one more characteristic of the metal being deposited.

Deposition of crystals with preferred orientation occurs frequently. The degree of orientation is influenced by the presence of colloids and by their concentration in the electrolyte.[4]

Variations of current density have been observed to produce discontinuities in the structure of an electrodeposit. Interruption of the current or even a marked change in current density may frequently be detected on microscopic examination of a section perpendicular to the lines of current flow.

In the case of an irregularly shaped cathode, crystal growth takes place in different directions at different points on the cathode. It presumably occurs in the direction of current flow. Crystal growth in different directions obviously may result in interference with the development of normal crystal structure.[5]

Alloy deposits present additional interesting features. Some show a superlattice structure. In such cases, the deposits are usually brittle and often cracked. Some alloy deposits have a different color from cast alloys of the same percentage composition. This is the case with brass electrodeposits. Adding ammonia to a brass plating solution may change the color considerably without producing a significant change in the proportions of copper and zinc in the deposit. On annealing, the brass deposit approaches the color of the cast alloy. This behavior might be related to grain size, since alloy electrodeposits are usually finer-grained than cast alloys. Or, it might be related to a change in the ratio of the number of free electrons to atoms, since there is a pronounced correlation between this ratio and the structure of alloys.[6]

Pits form on the surface of electrodeposits when a hydrogen bubble adheres at one spot and prevents the electrolyte from making contact with the cathode at that point. The hydrogen bubble may be formed in the first place either by discharge of hydrogen ions or by escape of adsorbed hydrogen from the metal. Adherence of the bubble may be assisted by some irregularity in the surface of the metal or by dirt lodged on the surface.

Colloid Formation at the Cathode

Mention has already been made of the fact that metal deposition is usually accompanied by some discharge of hydrogen ions. The extent to which hydrogen-ion discharge takes place depends on a number of factors, such as the relative energy requirements for the two processes, the relative supply of metal and hydrogen ions, the current density and the temperature. Hydrogen-ion discharge at the cathode reduces the hydrogen-ion concentration in the layer of solution nearest the cathode. This is equivalent to a rise in pH value. In time, the rise in pH may spread through the entire body of electrolyte, but in any case a considerable differential in pH between the cathode interface and the main body of solution is eventually established. Diffusion, convection currents, and agitation all tend to reduce the differential; but even with the most vigorous agitation, the pH value in the cathode film may be several units higher than in the rest of the solution.

A number of investigators have attempted to measure this rise in pH at the cathode. None of the methods used is entirely free from objection, and it is unlikely that any investigator so far has succeeded in getting a correct sample of the solution at the cathode interface. Most of the reported values are probably lower than the maximum value actually attained in the cathode film. In the case of a nickel-plating solution with a pH of 3.5, Henricks has reported that the pH approached 7.0 at the cathode interface.[7]

Although this value may be somewhat on the high side, there is little doubt that the pH near the cathode becomes high enough to cause precipitation of basic nickel compounds. With such a precipitate being formed near the cathode, some of it is sure to be occluded in the metal deposit. The precipitate is likely to be colloidal and may carry a positive charge. In that case, it would be swept up to the cathode and carried into the deposit under the influence of a sharp potential gradient.

Nickel deposition affords a particularly good illustration of these phenomena. Nickel deposition is influenced more by the pH value of the electrolyte than by any other factor. Accordingly, it is general practice to buffer nickel-plating solutions. The substance almost universally employed for this purpose is boric acid, which was introduced by Weston in 1878. With no buffer in the electrolyte, nickel deposits are excessively hard, and the maximum current density that can be used without producing "burned" or rough deposits is low. On addition of boric acid, the deposits become softer and the maximum current density can be substantially increased. Although the buffer action of boric acid is most effective at a fairly high pH—say above 6—and so is exerted mostly at the cathode interface, its beneficial effects may be seen even in nickel solutions operating at a pH below 2.0.

The hardness and structure of nickel electrodeposits have been investigated by Macnaughtan and Hothersall and their associates.[8] They have shown that the hardness is not related to hydrogen discharge, as was long supposed, but that it is greatly influenced by the pH value of the solution. In general, there is a sharp increase in hardness at a critical pH, which varies somewhat with the composition of the electrolyte. In solutions buffered with boric acid, the presence of ammonia or alkali metals tends to harden the deposit, *i.e.*, to lower the critical pH value, whereas chloride ion has the opposite effect. The grain size, on the other hand, decreases with increasing pH. The hardest deposits show the smallest grain size and tend to be lustrous. Buffering with boric acid tends to make the deposits matte and crystalline and at the same time softer.

These results suggest that the relationship between hardness and pH may be explained by interference with crystal growth as a result of the precipitation of colloidal basic nickel compounds at the cathode interface. The respective effects of alkali-metal ions and chloride ions could then be explained reasonably by their influence in stabilizing or flocculating the colloid.

The presence of basic nickel salts, nickel hydroxide or nickel oxide in nickel deposits is not readily established by chemical analysis, but Macnaughtan and Hothersall were able to establish the presence of non-metallic matter in nickel deposits by annealing them under conditions favorable to grain growth. On heat treatment, soft deposits recrystallize to give large equiaxial grains with clean boundaries; with harder deposits grain growth takes place with segregation of non-metallic material at the grain boundaries.

It has not been established whether the hardness depends only on the grain size of the nickel, or whether, as has been suggested by Desch, it may also be affected by the presence of non-metallic particles in a critical state of dispersion. It is possible, of course, that both factors may be involved.

Viers and Case[9] claim to have established a connection between the grain size of nickel deposits and the tendency toward pitting. Since grain size appears to be controlled by inclusions of colloidal basic matter in the deposit, the same factor would appear to influence the tendency of certain nickel-plating solution to produce pitted deposits.

Other metal electrodeposits have not been studied as thoroughly as nickel. Soft copper deposits produced from acid copper sulfate solutions show very large grains on annealing and little evidence of non-metallic inclusions. Copper deposits from cyanide solutions are usually hard and fine-grained; on annealing they show con-

siderable non-metallic matter at the grain boundaries. It has been shown that hard chromium deposits contain some oxide.

Colloidal Addition Agents

We have seen that colloids can be formed at the cathode through the action of an electric current. Colloids are sometimes purposely added to the electrolyte. For example, glue is used in copper and lead refining to produce smooth deposits. Tragacanth, goulac and condensed milk may be mentioned as examples of other colloidal materials that have found application on a considerable scale.

Finding suitable colloidal addition agents has been done heretofore on a purely empirical basis. It is not difficult to find colloids that produce marked effects on an electrodeposit. Almost any substance introduced into the electrolyte produces some effect. Many colloidal materials are so variable, however, that their action cannot be controlled satisfactorily. Besides, the desired effect is frequently accompanied by others that are extremely undesirable. Certain zinc solutions give deposits that tend to become very rough as the thickness increases. Adding a small quantity of glue makes these deposits smooth. Glue, however, is useless in this case because it makes the deposits extremely brittle, and for most purposes zinc coatings are required to be ductile.

The effect of pH on colloids like glue is known to be important. In an electrolytic cell, the pH at each electrode interface as well as the pH of the main body of solution must be taken into account. In addition, electrokinetic effects may also come into play.

The idea that smooth deposits can be obtained by the use of mucilagenous materials such as glue and various gums has undoubtedly achieved some success. Nevertheless, the trend in selecting addition agents nowadays is to avoid materials of this class and to favor substances whose composition is more sharply defined and which moreover are available in a high degree of purity.

Surface-Active Addition Agents

Quite a few of the newer addition agents are surface-active materials. A great many synthetic products of this type have been investigated and some very useful ones have emerged. For example, pitting caused by the sticking of hydrogen bubbles is prevented by the use of addition agents which are able to lower the interfacial tension enough to bring about quick release of the bubbles. Some of the most effective materials for this purpose comprise normal straight-chain or slightly branched chain alcohol sulfates of 8 to 14 carbon atoms [10] and alkyl-substituted benzene or naphthalene sulfonates.[11] Many wetting agents are able to produce the necessary lowering of interfacial tension, but caution is necessary to avoid those which produce adverse effects or decompose on electrolysis to give products which produce such effects. Since the interfacial tension is not easy to measure, these agents are generally controlled by surface tension measurements, usually with a stalagmometer. A surface-tension lowering to 35 dynes per centimeter is sufficient to prevent pitting in most cases.

Brighteners

Perhaps the most important of all addition agents are the so-called "brighteners." A bright deposit, in platers' language, is one that shows specular reflection and hence requires no buffing, or at most little buffing, to bring up a luster. Savings in buffing costs and general improvement in the quality of deposits produced from bright plating solutions have caused these to become very popular within the few years that have elapsed since they were introduced. How little various brighteners apparently have in common becomes evident on enumerating some of the most important ones. One of the earliest nickel brighteners to be used was gum tragacanth.[12]

This is no longer important, having been replaced by improved types. Brighteners for nickel plating include certain alkyl aromatic sulfonates,[13] aryl sulfonates, preferably napthalene polysulfonates,[14] sulfonated rosin oil,[15] various sulfonamides,[16] triarylmethane dyes,[17] formaldehyde,[18] crotonaldehyde, and other aldehydes. Two or more brighteners are frequently used together. Small quantities of other metals such as zinc, cadmium, selenium, and cobalt enhance the brightening action of the foregoing materials.

For cadmium, important brighteners are wool and other proteins,[19] sulfite cellulose waste,[20] Postum,[21] better known as a coffee substitute, naphthylamine sulfonates,[22] furfural resins,[23] and aldehyde-ammo reaction products.[24, 25] For zinc commercial use has been made of thiourea,[26] ammonium thiocyanate-formaldehyde resin,[27] polymerized methyl ethyl ketone,[28] sodium sulfide,[29] sodium sulfide with polyvinyl alcohol,[30] gelatin with oxyheterocyclic compounds,[31] and piperonal.[32] The principal brightener used for silver is carbon disulfide, which is used in minute quantities; other brighteners characterized by a C-N-S linkage have been described.[33] Bright copper deposits are obtained from complex salts of copper sulfate with polyalkyl amines,[34] such as diethylenetriamine, or with pyrophosphates.[35]

What can so diverse substances have in common that would account for their ability to act as brighteners? Quite a number of them are surface-active, but all surface-active materials are not brighteners. It has been suggested that most brighteners are capable of being adsorbed by the deposited metal. Henricks [36] has pointed out that many brighteners inhibit the action of acid on metals or can be readily reduced at the cathode to give compounds which have this property. The formation of complex ions through coordination with the depositing metal has been suggested as an essential requirement.[37] But not all complex compounds result in bright deposits. Schloetter [38] claims that bright deposits may be produced solely through control of grain size. Thus, according to Schloetter, any nickel deposit having a grain size under one ten-thousandth of a millimeter is necessarily bright. Henricks [39] postulates the formation of colloids at the cathode which are adsorbed and which produce brightness by controlling the size and orientation of the deposited metal crystals.

The idea that a colloid is formed and carried into the deposit resembles the theory advanced by Macnaughtan and Hothersall to explain the hardness and grain size of nickel deposits. As to the nature of the colloid and how it is formed, Henricks suggests that it may be produced by electrolytic reduction of the brightener itself or of a compound formed by the brightener with the metal being deposited. The high pH value at the cathode interface may also be a factor. Most nickel brighteners are effective within a limited pH range, and the brightening action may be enhanced by the presence of a suitable buffer, for example, formic acid.[40]

There is considerable evidence that some of the brightener is carried into the deposit. Thus, up to several tenths of a per cent of carbon as well as some sulfur have been found in bright nickel deposits produced by organic addition agents.[41] In the case of silver deposits made in solutions containing carbon disulfide, sulfur has been found in the deposit.*

The surface-active characteristics of some brighteners or of the products formed from them by electrolysis are indicated by the fact that they can be removed from the solution on treatment with activated carbon. The use of carbon to remove undesirable decomposition products formed from certain brighteners is usually essential to successful operation. Treatment with activated clay is sometimes used to supplement carbon treatment.

Nearly all brighteners cause more or less reduction in grain size and tend to increase the hardness of the deposit. This is analogous to the effects produced by

* As S. E. Sheppard has shown, traces of silver sulfide formed by "impurities" in photographic gelatin, act as nuclei in development. See his paper in Vol. V of this series. J. A.

colloidal basic nickel compounds precipitated as a result of the pH increase in the cathode film.

Support for the view that colloids are involved in the mechanism of brightening comes from the fact that many bright deposits have been found to show a banded structure.[42] Some investigators go so far as to say that this structure is characteristic of all bright deposits and may be made to appear in every case, providing suitable means of etching are employed. In all cases, the banded layers are parallel to the surface of the deposit—that is to say, perpendicular to the direction in which the deposit has grown. This type of structure suggests a periodic process similar to the well known Liesegang-ring phenomenon. If Liesegang-ring formation is always associated with the presence of a colloid, it seems reasonable to infer that the banded structure associated with bright deposits can be produced only in the presence of a colloid.

A noteworthy observation in connection with banded structure has been reported by Meyer.[43] By connecting a recording microvoltmeter in the circuit, he was able to detect periodic fluctuations in voltage. On calculating the thickness of deposit which should be produced during these periods, the length of the periods was found to correspond fairly well to the measured thickness of the bands.

Insofar as the banded structure indicates an orderly arrangement of the metal crystals in planes parallel to the surface of the underlying metal, it is easy to understand the high reflecting power of the deposit thus formed. Mention should be made of the fact that a number of investigators have attempted to determine the orienation of the crystals in bright deposits.[44] Orientation has been found in some cases, not in others. The results reported by different investigators have not always been concordant.

To summarize our present knowledge in regard to brighteners, the presence of colloids or the formation of colloids at the cathode seems to be an essential requirement. It also appears that this colloid must be carried into the deposit, either by entrapment, by the action of a potential gradient, or by adsorption. In regard to adsorption, it is to be noted that many brighteners are surface-active or are reducible at the cathode to surface-active materials. Inclusion of the colloid in the deposit produces interference with normal crystal growth, which results in most cases, at least, in the characteristic banded structure. The part played by reduction in grain size and by orientation of the crystal faces is not yet entirely clear. Some of the measurements that have been made of grain size are certainly open to question,[45] and as has already been mentioned, observations on orientation are not concordant.

Stress and Embrittlement

It might be expected that bright deposits showing a banded structure would have poor physical properties, as laminated deposits generally do. This is not infrequently the case, but surprisingly enough, many bright deposits have high tensile strength and excellent elongation. An excellent illustration of this is afforded by comparing two substances, namely, hexamethylenetetramine and formaldehyde, both of which give deposits with a high degree of specular reflection.[46] The former gives extremely brittle deposits, while the latter gives deposits which can be bent, twisted or deformed to a remarkable degree without causing the deposit to fail. Triphenylmethane dyes alone generally give brittle deposits, but it is claimed that when these brighteners are used in conjunction with certain naphthalene disulfonates, embrittlement is avoided and good, ductile deposits are obtained.[47]

It has already been mentioned that many electrodeposits as formed are highly stressed. Thus if a thin cathode is plated with nickel on one side only, the pull exerted by the nickel causes the cathode to become curved. The addition of certain naphthalene sulfonates or sulfonamides is reported to relieve the stress sufficiently to eliminate the tendency toward curvature, and may even cause the curvature to

reverse. There is undoubtedly a connection between stress and embrittlement in electrodeposits and the action of colloids, but our understanding of this connection is very limited.

Anodic Effects

A high authority on electrochemistry once made the remark that the cathode knows nothing of what goes on at the anode. The remark has since been widely quoted and much too widely accepted, for as we shall see, the cathode is inevitably influenced by what happens at the anode.

The anode seldom dissolves with 100 per cent current efficiency. Some oxygen is usually evolved and a corresponding quantity of acid is formed. Thus, there is a pH drop at the anode interface just as there is a pH rise at the cathode interface. The acid formed at the anode diffuses into the main body of electrolyte and eventually makes itself felt at the cathode interface by reducing the pH rise there. This reduction in pH may be enough to influence, or even prevent altogether, the precipitation of basic colloidal compounds at the cathode interface.

The anode does not always dissolve uniformly. Attack often follows the grain boundaries. Accordingly, crystal aggregates of varying size may get loose. Inclusions in the anode also get loose. Some of the loose particles may reach the cathode, where they cause the deposit to become rough. Accordingly, it has become a common practice to enclose the anodes in bags.

Sometimes the anodes contain impurities which form insoluble compounds with a component of the solution. These compounds sometimes adhere to the anode surface and sometimes drop off as colloidal slimes. The slimes formed in copper refining contain enough precious metals to be important in the economics of the process.

Insoluble films sometimes form on the anode, because the conditions are not favorable for the metal to dissolve. For example, a copper anode in a cyanide electrolyte may become coated with insoluble cuprous cyanide, if the solutiion does not contain a sufficient excess of "free" sodium or potassium cyanide. A more interesting example of this kind is the behavior of tin anodes in stannate solutions. At low current densities, tin dissolves in such solutions as stannous tin. Accumulation of even a very small quantity of stannous tin in the solution causes the tin deposited at the cathode to become spongy. However, if the anode current density is increased beyond a certain critical point, which depends on the composition of the solution, and especially on the alkalinity, a greenish-yellow coating is formed on the anode and the tin goes in solution as tetravalent tin. Under these conditions, excellent deposits of tin are obtained. If the anode current density is increased still further, the coating turns black, the current falls off, and no more tin goes into solution—the production of good tin deposits is no longer possible. This black coating is hard, impervious, and difficult to remove by brushing. The greenish-yellow coating, on the contrary, is soft and slimy and can be readily wiped off. It is almost certainly colloidal in nature.

Conclusion

We have seen that the structure and many of the physical properties of electrodeposited metals are influenced by the presence of colloids. When colloids are not initially present, they may be formed at the cathode by reduction or as a result of the pH rise, which usually takes place in the cathode interface on electrolysis. Colloids may be formed at the anode by oxidation or as a result of the pH drop at the anode interface. Evidence of colloidal inclusions in the deposit is presented and their effects on such properties as hardness, grain size, brightness, stress, and embrittlement are considered.

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See also papers by Wm. Blum in Vol. III, and by W. G. France in Vol. V of this series. J. A.

Surface Treatment in Fusion Welding, Pressure Welding, Brazing, and Soldering

JOHN J. CROWE AND FREDERICK C. SAACKE

Air Reduction Sales Co.

Introduction

Types of Welds. The American Welding Society has defined a weld as "a localized consolidation of metals by a welding process." Welding processes are then divided into three groups; fusion welding, pressure welding, and brazing, in which the fusion weld requires melting of the base metal; brazing requires melting of the filler metal but not the base metal, and pressure welding requires the use of pressure to consummate the weld. Soldering may be considered a process akin to brazing but operating at temperatures below 1000° F.

The strength of fusion welds is not unexpected, since the development of a homogeneous metallic seam (or localized consolidation of metals) is visible to the observer watching the mechanical intermixing of the molten filler metal and molten base metal. In brazing, soldering, or pressure-welding operations, the lack of a mechanical bond is patent, and yet high strengths are readily developed under the proper conditions. It is the effect of surface conditions on the quality of joints made by these processes with which this paper will deal.

Requirements of a Welded or Soldered Joint. For "a localized consolidation of metals" to exist, there must be *uniform, intermolecular contact.* These terms are significant in that no reference is made to heat or fusion. It would seem quite reasonable to obtain this condition by mechanical means alone.

The adhesion between mechanical gage blocks illustrates this principle. With gage blocks finished plane to a millionth of an inch, it is possible to wring them together (squeezing out most of the air film) and have them adhere with sufficient force to hold a direct load tending to separate them, well in excess of anything that can be attributed to the atmospheric forces on the gage blocks. It is obvious that there is no mechanical keying, heating, or glueing but only the attraction of one piece of metal to another when the intervening surface film of air is made sufficiently thin and discontinuous.

More recently,* unprepared brass surfaces have been welded by the pressures developed under the impulse of detonating charges in routine tests of explosives. It was evident that the pressures developed were sufficiently high to plastically deform the contact surfaces and bring together clean metal surfaces in intermolecular contact wherever oxides and inclusions could be pushed aside without developing sufficient heat to change the structure or soften the cold-worked metal at this point.

These joints cannot be considered "welds," chiefly because of the discontinuity of the adhesion and the resulting instability or weakness of the joint. The problem in welding is to join parts with the contacting surfaces in *uniform,* intermolecular contact, and the problem of securing *uniformity* of jointure is the practical question involved.

* Leroy R. Carl, *Metal Progress,* 102, July, 1944.

Effect of Interface Discontinuities. As might be expected, the intermolecular forces existing between metals cannot extend across slag or flux inclusions, air or gas films, and gas pockets, and the strength of a joint depends upon the cleanliness of the joint or freedom from these non-metallics. A non-metallic film one molecule in thickness is probably sufficient to reduce materially adhesion between adjacent metal surfaces, and the presence of such films would not be apparent to the untrained observer.

A piece of aluminum can be cleaned by any known mechanical or chemical means; but after exposure to the air, it will not be tinned or wetted by the application of molten solders (without a flux). On the other hand, if the surface of the aluminum is scratched, wire-brushed, or abraded under a cover of molten solder, the exposed aluminum will alloy with almost any solder of tin, cadmium, zinc, or aluminum. The oxide film on clean aluminum forms with such rapidity on exposure to air that only by removing the film under molten metal can alloying or wetting of the metal interface occur.

In a similar manner, mercury * will not wet the edges of a piece of iron that has been broken in the air, but will wet the surfaces when the piece is broken under mercury. Under these circumstances, the mercury will alloy with the iron quite readily.

Problems of Surface Treatment

Surface Cleanliness. The average surfaces to be welded or joined are either dirty repair jobs or, if in production, are usually covered with films of oil, grease, rust, oxides, protective paint, or atmospheric grime. Mechanical methods of cleansing such as machining, chipping, grinding, filing, wire-brushing, or wiping will serve to clean many of the surfaces sufficiently for subsequent fusion-welding operations in which dirt, dross, or metallic oxides formed on heating are floated on top of the molten puddles and mechanically separated from the weld metal pool to avoid contaminating the subsequent joint. They will also suffice for those pressure-welding operations in which the closely fitted surfaces are kept fairly clean by exclusion of air and deformed sufficiently to break up the continuity of whatever slight oxide film is present, or in which surface fusion is followed by forceful contact and the resulting expulsion of the fused metal and metal oxides.

Mechanical methods of cleaning will not suffice for brazing operations or for many of the fusion welding or pressure welding operations. With many of the metals being joined, oxide films are present that must be removed and kept from reforming if any suitable type of weld is to be made.

To maintain cleanliness during the pre-welding heating cycle, as well as to remove oxides from the surfaces being welded, chemical cleaners or fluxes are usually used. Quite often the fluxing element is an alloying element of the filler metal, but usually the fluxes are introduced as separate chemical compounds.

Surface Contour (Fit-Up). In securing uniformity of metallic contact, one must meet and overcome numerous practical considerations. The parts to be joined must be properly fitted to make a suitable weld joint. Fusion welds or brazed joints usually require a groove or fillet at the contact edges of suitable proportions to receive the molten weld metal. Where sections are of irregular shape or of different sizes, special care is necessary to insure a groove of uniform depth and cross-section. In many pressure welding processes, the edges or contact faces must fit closely to minimize oxidation on heating, or be so shaped that contact starts at the center and progresses toward the outside surfaces to maintain cleanliness by squeezing out the oxides that form on heating. In others, the type of surface preparation depends upon the amount of pressure available for welding.

Means for Contacting Surfaces. In fusion welding or brazing, the forces re-

* P. W. Bridgman, *Proc. Nat. Acad. Sci.*, **46**, 325 (1911); also Vol. V, this series, p. 334.

quired to bring the weld materials into intimate contact are very slight. In most cases, the force of gravity is sufficient to cause agglomeration of the molten drops of filler metal. In pressure-welding operations, much stronger forces are necessary. Aside from flash-welding operations, the metal parts must first be brought into close contact; and since the greater part of the base metals being joined is cold and stiff, considerable pressure is required to maintain proper contact. The degree of pressure exerted controls the extent of contact, its effect on current density and rate of heating, amount of plastic deformation, control of molten metal in the spot weld, etc. Further pressure increases are necessary to bring about distortion of the grain structure and the boundary films of gases and oxides by upsetting of the heated base metal. The extent and care with which the base-metal surfaces are prepared, cleaned, and pressed or fused together thus very often determine the quality of the subsequent weld.

Methods of Surface Treatment

Surface cleaning. *Mechanical Cleaning.* The surfaces of base metal parts being joined must not only be cleaned prior to welding, but must be kept clean during the preheating and welding operations. Mechanical removal of the surface film, although a necessary precaution in preparing joints for welding, is usually insufficient by itself to maintain the cleanliness that intermolecular metallic contact requires. In several welding processes, the effect of the oxidation during heating is minimized without using chemical cleansers by careful thermal and pressure control.

In flash-welding operations, oxidation at the contact faces is allowed to occur; but since the surfaces are eventually liquefied, the subsequent application of pressure squeezes the molten metal and entrapped oxides out of the joint, leaving the relatively clean base metal surfaces in intimate contact.

In spot-welding operations, the heating time takes only a few hundredths of a second; and with close contact and fast heating, oxidation is reduced to a minimum. In spite of this, many materials, such as aluminum and its alloys, require chemical cleaning to insure a minimum of oxidation from the heating cycle.

In fusion-welding operations, particularly on iron or steel where the metallic oxides liquefy at temperatures below the melting point of the base metal, the elimination of non-metallics or metallic oxides is aided by the lower densities of these impurities, which permit them to float on the surface of the liquid puddle and if molten, to blow out of the way under the force of the gas welding flame or the metal arc.

In brazing and pressure-welding operations where the base metal is either solid or, if molten during the welding operation, is so protected that mechanical separation of surface oxides or slag cannot be obtained, methods other than mechanical cleaning prior to welding must be used.

Chemical Cleaning. In general, the chemical cleansers or "fluxes" as they are usually called, are salts which in the fluid condition at elevated temperatures are capable of combining with and thereby liquefying and removing relatively large proportions of solid metal oxides. Such fluxes may be either liquid or gaseous at operating temperatures. Their purpose is two-fold. First, they should dissolve metal oxides readily, not only in the welding temperature range but also at the lower temperatures during preheating when oxidation begins to occur rapidly. Second, the fluxes should be fluid during the preheating period as well as the welding period, since they maintain chemical cleanliness fully as much by mechanically separating the oxidizing atmosphere from the metal surfaces of the joint as by dissolving oxides that have formed. Even fluxes in the solid state may accomplish this protection. When covered electrodes are used, the metal core wire often burns faster than the flux covering and throws molten metal across the arc gap, part of which is completely enclosed and protected by the extending edge of the electrode covering.

The salts for operations at welding temperatures over 1100° F form mixtures of oxides of metals, such as boron, silicon, manganese, titanium, calcium, sodium, potas-

sium, etc. Borax, which breaks down into sodium and boron oxides when heated, has been a major component of brazing or bronze welding fluxes for years.

For the brazing or welding of materials below 1500° F, the sulfates and halides of the alkali metals are particularly useful in providing the proper fluidity and oxide solvent action required. The chlorides and fluorides of sodium, potassium, lithium, and strontium are responsible for the oxyacetylene brazing and welding of aluminum, magnesium, and their alloys.

At still lower operating temperatures in the soft-soldering of metals, the fluxes generally used are powdered rosin or a solution of zinc chloride, alone or combined with sal ammoniac.

Surface Contouring. The joint edges may be prepared by any of the mechanical methods available for forming the metals being joined. Where forge-welding uses a hammer or press to develop a weld, a suitable edge contour can be obtained by using the same hammer or press for forming and shaping. In making flash butt welds of solid sections, the edges may be sheared, rough-turned, sawed, or oxygen cut without too much attention to accuracy. Upset butt welds, on the other hand, whether heated by electricity, thermit, or combustible gases, usually require parallel faces mechanically machined to rather close limits.

Fusion weld joints may be prepared by forming, machining, or oxygen-cutting methods. To avoid adding filler metals, the abutting plate edges are often flanged so that when fused together, sufficient weld metal is available to leave a reinforcing bead and insure complete fusion without undercut. The choice between mechanical machining or oxygen machining usually rests with the equipment and personnel available, besides the contours desired and speed of preparation necessary. In this respect, the use of oxygen cutting is considered a big factor in speeding up welded construction.

Methods of Contacting Surfaces. *Forge and Pressure Welding.* Welding, as we know it today, probably did not begin until forges became available for the development of high temperatures. The earliest welding was probably a forge-welding operation using a hammer to combine manually iron parts at a white heat in the plastic state. This type of welding was responsible for the term "forge" welding, although today an electric furnace may replace the blacksmith's forge and a steam hammer, power press, or rolls may replace the hammer-wielding smith. It is only a few steps to the substitution of other sources of heat in the development of pressure-welding with the use of thermit in pressure thermit welding, oxygen and acetylene in oxyacetylene pressure welding, and electric power in resistance welding.

Fusion Welding and Brazing. When more powerful heat sources become available through the discovery of the oxyacetylene flame or the development of the electric arc, it was recognized that pressure was no longer necessary to consummate a weld, since with suitable high temperatures the metals could be melted and the gap between adjoining plate edges bridged by the addition of molten filler metal to mix with and bond the plates together. Where the adjacent faces of the base metal are melted in forming a weld by the addition of filler metal, a fusion weld is obtained. From this point, it is only a step to the development of brazing materials which melt at temperatures below the melting point of the base metal, but which bind the two base metal parts together in a weld if the base metals have been properly cleaned before the addition of clean filler metal. Brazing has since been distinguished from soldering by artificially defining 1000° F as the operating temperature above which the process is called "brazing" and below which it is called "soldering."

Cold Welding. A consideration of the role that heat and pressure play in creating intimate contact between metal parts suggests that heat may not always be necessary —in other words, that metals can be welded cold. Some materials, like gold and platinum, are highly resistant to oxidation and at the same time are quite malleable—so much so, in fact, that it would seem possible to combine metals of this type and

secure uniform, intermolecular contact by cold-forming operations. Actually, this has been done and the compacting of gold leaf into small dental cavities is one example of a "cold weld" that depends for its "welding" properties upon the ability of clean (oxide-free), uncontaminated gold surfaces to be brought into close contact by hammering or pressing without the application of heat. Aluminum has also been welded cold in this manner, although the tendency of aluminum to oxidize prevents the fabrication of a joint free from oxides.

Progress Due to Proper Surface Treatment

Plate Edge Preparation; Economies of Oxygen Machining. The welding industry in World War II owes a great deal to the oxyacetylene cutting torch, without which the speed, efficiency, and economy of the welded design would be greatly handicapped. The facility with which steel plates and shapes can be cut and beveled to finished size without further machining has made the oxyacetylene cutting torch a component part of the equipment for welded construction.

Recent improvements in tip design have increased cutting speeds 25 per cent with excellent control of cut contour, so that plate edge preparation for welding can be speeded up and simplified accordingly. The further development of oxygen grooving tips combined with cutting tips has facilitated weld repair and has permitted the oxygen-machining of plate edges with curved contours with resultant economies in labor and capital expense.

The metallurgical effects of the oxyacetylene cutting process on the cut edges of steel plate are well recognized; they require subsequent heat treatments only with medium carbon and alloy steels when mechanical bending or forming operations are to follow the cutting operation.

Improvements in Welding. The history of welding may well be traced in the developments of fluxes for protecting the molten weld metal and maintaining surface cleanliness.

The first major improvement in arc welding was due to the development of coatings that effectively blanketed the molten weld metal puddle from the oxygen and nitrogen of the atmosphere. This, together with subsequent coating modifications, improved the weldability of steel and lead to the present acceptance of arc welding as a manufacturing process of merit.

Commercial fluxes have been applied not only as permanent rod coatings but as tapers burning near the arc, as gas atmospheres, or as granulated particles covering the weld puddle.

Tables 1 and 2 illustrate the effects of different types of melt protection in controlling oxygen and nitrogen content together with the physical characteristics of steel weld metal with various nitrogen contents.

Table 1. Chemical Analyses of Metal Arc-weld Metals and Change in Composition from Original Electrodes

	Weld Type	Degree of Protection	Carbon (%)	Loss of C (%)	N_2 (%)	Increase in N_2 (%)
1.	Core Wire		0.13-0.18		0.005	
2.	Boiler Plate		.15- .30		.008	
3.	Bare Electrode	None	.021	88	.125	2,400
4.	Covered Electrode, slag producing, long arc	Minimum	.06	63	.07	1,300
5.	Ditto, but medium arc	Medium	.10	37	.05	900
6.	Ditto, but short arc	Good	.11	31	.027	440
7.	Ditto, but short arc plus gas flame	Maximum	.11	31	.015	200
8.	Bare electrode, gas protection	Good	.08	50	.031	520
9.	Covered Electrode, gas producing	Maximum	.075	55	.019	280
10.	Bare Electrode, Arc buried in powdered flux in groove	Maximum	.07	52	.011	120

Table 2. Influence of Nitrogen on Physical Characteristics of Steel Welds

Nitrogen (% by wt)	Yield Point (psi)	Ultimate Strength (psi)	Elongation (% in 2")	Red. of Area (%)	Charpy Impact (Ft Lb)
0.019	46,000	61,000	36.5	65	31.5
.032	46,000	63,000	29.0	51	30
.058	51,000	66,000	26.5	36.5	20.5

* J. C. Hodge.

The flux coatings are responsible for AC welding, for AC and DC reverse polarity all position electrodes, for DC straight polarity horizontal or flat fillet electrodes, and for AC and DC high-speed electrodes ("hot rods"). The coatings are used to control weld metal analysis, physical characteristics of weld metal, arc stability, deposition rate, spatter, penetration, operating polarity and numerous other characteristics to simplify the operators' problems of control.

Typical of such compounds are the following:

Gas forming: cellulose, wood or wheat flour
Slag forming: silica, clay, manganese dioxide, iron oxide, feldspar, rutile, amphibole
Binders: water glass
Arc stabilizers: calcium carbonate
Inert fillers: asbestos
Deoxidizers, degasifiers: ferro-manganese, ferro-silicon, silico-manganese

Recently, the use of granulated, gas-free, conductive flux compounds has made submerged melt welding an effective combination of high welding speeds and quality. Single vee-butt joints in 1½" steel plate are welded in a single pass at speeds of 8 inches per minute, while ½" plate is welded at speeds of 23 inches per minute.* Minimum tensile strengths of 60,000 and 70,000 psi are maintained in the as-welded condition, with ductilities in excess of 20 per cent.

Still more recently, the introduction of helium and argon as the protective atmospheres in tungsten arc welding have created unusually effective methods for welding aluminum and magnesium.

In the latter case, although the arc welding of magnesium in helium atmospheres is no faster or better than gas welding, lap and edge joints may be welded with relative impunity, since there is no longer the possibility of entrapping corrosive flux inclusions at the unwelded contact surfaces.

In the early days of gas welding, the first really satisfactory work in the field of cast iron, brass, bronze, and aluminum welding started with the development of suitable fluxes. Ten years ago when the solvent action of molten alkali bifluorides or fluoborates for chromium oxide was first recognized, fluxes permitting the silver alloy brazing of stainless steel were introduced. More recently, liquid fluxes based upon the protective and cleansing properties of molten boron oxide films have improved the quality of brass and bronze welding and brazing by fully 20 per cent, so that brazed joints in steel can be made that are stronger than the steel itself. (See Fig. 1.) The completely new field of aluminum brazing started with the modification of the alkali halide type of aluminum welding flux by the use of strontium halides to allow cleaning aluminum surfaces at temperatures not much more than 50° F below their melting point. Gaseous fluxes (ethyl borates) have been developed for introduction into the gas ducts of the torches that permit adequate fluxing on clean metal parts with the deposition of a minimum of flux residue.

In resistance welding, many problems in surface cleanliness have been overcome by precleaning operations to insure reproducibility of results, particularly on aluminum.

* AWS 1942 Welding Handbook.

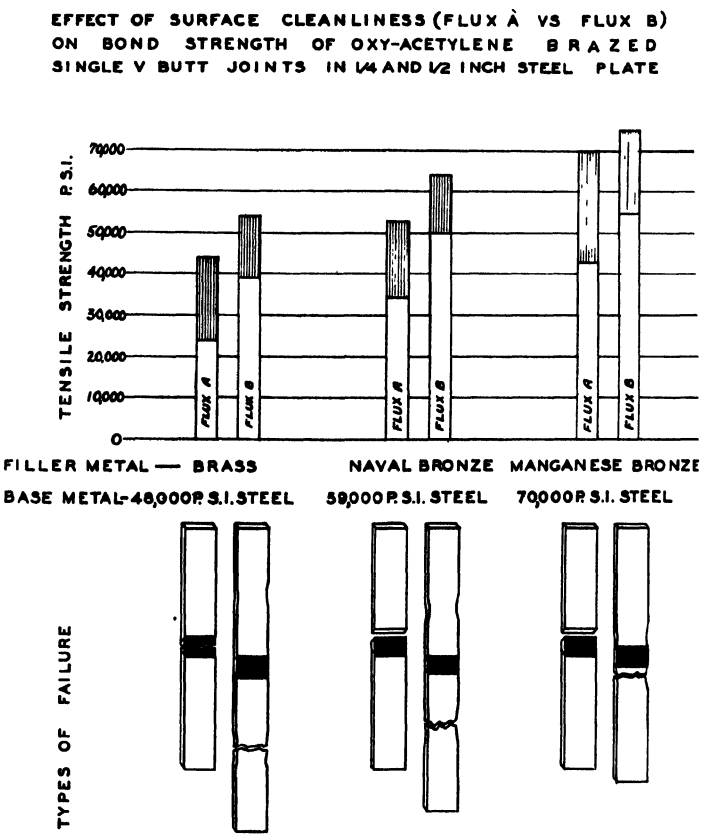


FIGURE 1.

Personnel Safety Problems

The introduction of chemicals into the welding operation has created a safety hazard that must be recognized and anticipated. Welding operators everywhere are familiar with the hazards of working on galvanized or zinc-coated steel, and are readily aware of the need for ventilation to prevent excessive inhaling of the zinc oxide fumes that form from the oxidation of the volatile zinc vapors. They are not ordinarily apprehensive, however, of dangers that might lie in handling liquid fluxes and breathing the fumes from flux coatings or volatile fluxes.

Because of the almost universal use of such materials as the alkali halides in the welding and brazing of certain types of materials, the precautions to be observed in using these materials should be pointed out to the welding operators. Unless effective measures can be taken to avoid health hazards, materials of a toxic nature should be avoided.

Summary

As a result of the proper choice of chemical cleansers that are not only efficient but comparatively simple to handle safely, the welding industry has reached a point where the general attitude toward welding is often encountered in such remarks as, "It becomes habitual, whenever a new problem arises, to think immediately in terms of the welding processes, which are so handy in mill work that other methods are seldom even considered."

Physical Chemistry of Dyeing

E. I. VALKO

Onyx Oil & Chemical Company, Jersey City, New Jersey

The theory of the dyeing process is based on knowledge of the properties and the behavior of both fibers and dyes. The last two decades have witnessed a significant progress in both fields. This fact, as well as the application of modern physicochemical methods to the study of the dyeing process itself, have resulted in the development of a new theory of dyeing. This represents an advance over older theory, not only because of incorporation of recently gained knowledge, but also more precise formulation of the problems and recognition of the limitations resulting from the present incompleteness of knowledge of intermolecular forces.

In the older theories much emphasis was placed upon the fact that some of the phenomena involved in the dyeing process were of a colloidal character. The newer theory stresses the intimate relationship between the phenomena of dyeing and those associated with molecular solutions. This change of attitude parallels the general tendency of demonstrating the identity of the fundamental laws governing both true and colloidal solutions, and is in contrast to the practice prevalent in the early days of colloid science, of overemphasizing the peculiarities of colloidal systems. As colloidal chemistry merges into physical chemistry, from which it took its origin, so the colloidal chemistry of dyeing becomes the physical chemistry of dyeing.

Physical Chemistry of Fibers

Organic fibers (animal, vegetable and synthetic) have a common characteristic in that the ultimate molecular building units of their principal constituent are macromolecules.[10, 40, 44, 53, 85, 89] These belong to the group of linear polymers or polycondensates, *i.e.*, chemical compounds in which a large number of identical or similar atoms or groups of atoms are linked together by covalent bonds. The main constituent of the vegetable fibers is cellulose, a polycondensate of glucose; those of the two animal fibers wool and silk are keratin and fibroin respectively, polycondensates of amino acids. The synthetic fibers nylon and Vinyon are copolycondensates of diamines and dicarboxylic acids; and of vinyl chloride and vinyl acetate respectively. The molecular weight of such substances is only an average value, but even so, it is likely to differ from sample to sample. On the basis of numerous investigations, it is generally estimated that the cellulose in native fibers has a molecular weight of more, possibly much more, than 100,000 (according to Gralén and Svedberg from 1 to 2,000,000 [28]); in rayon it is more than 20,000. Similar orders of magnitude have been found for the molecular weight of the other synthetic fibers.

Most fibers are composed partly of crystalline and partly of amorphous material. It has been found that the macromolecules of the crystalline part are straight and lie parallel to each other. The results of optical investigations indicate a similar, although not so rigid, organization for the amorphous part. However, even the crystalline part of the fibers is not formed of large single crystals, but of aggregations of submicroscopically small crystals which are called crystallites. X-ray analysis allows some estimate of the size of the crystallites. The crystallites of ramie were found to

have a length of certainly not less than 600 Å, although the results are consistent with any length greater than this limit.[81] The diameter of the crystallites is about 55 Å. The length of cellulose crystallites in viscose rayon was found to be 300 Å; their width 40 Å. The width of crystallites of cellulose in sulfite pulp was found to be about 13 to 17 Å; their length was too great to be determined by this method.

The x-ray method applied does not distinguish whether the perturbation of the x-ray interferences is due to foreign material or vacuoles, or simply to irregularities in the lattice structure. Indeed, the term crystalline, in the case of fibers, does not have exactly the usual meaning. The crystalline regions do not represent discrete particles with sharp boundaries. Crystallinity in this case, describes merely the fact that neighboring linear macromolecules are arranged in a spatial regularity relative to one another, in the form of bundles. This regularity is interrupted by disturbances. The lower the crystallinity of the fibers, the more frequent are these disorganized regions. The regular spatial arrangement is determined by the repeating units of the macromolecules. A single macromolecule can, however, traverse disorganized regions, so that it belongs to different crystalline regions. As a consequence, the size of the organized regions, *i.e.*, the "crystallites," is not determined by the length of the macromolecule.

Dry fibers absorb moisture from a humid atmosphere or from water, and give it up upon subsequent exposure to a dry atmosphere.[85, 89] The absorption equilibrium has been determined for different fibers at varying temperature and vapor pressure. Generally, the moisture content at constant humidity decreases with increasing temperature, thus indicating a negative heat of absorption (evolution of heat). This has been confirmed by direct calorimetric measurements. However, at high temperatures and humidities, the moisture content increases with increasing temperature. This always seems to be the case at 100° when the relative humidity is near 100 per cent.

Water being the vehicle through which the dye penetrates the fibers in most dyeing processes, knowledge of the distribution of water in the fibers is one of the most important requisites for a full understanding of the phenomena of dyeing. Unfortunately, there are still some gaps in our present knowledge of the distribution of water of swelling.

The distribution of the water appears perfectly homogeneous under the microscope, the system thus resembling a solid solution or hydrate. There remains, however, the possibility that the water is distributed in channels of submicroscopic size, and there is much evidence to favor this view. X-ray investigations have shown that the take-up of water does not alter the structure of the crystalline part of cotton, ramie, viscose and cuprammonium rayon, wool, silk, etc. This holds, even when the fiber is immersed in water and takes up 20 to 30 per cent or more water, based on its own weight. This led to the conclusion that water enters only the regions between the crystals which may be the amorphous part of the fiber (intercrystalline or intermicellar swelling). It is to be expected that the water of swelling will prefer the intercrystalline, amorphous regions to the crystalline regions, providing the chemical composition of both is the same. The entering water must overcome the cohesive forces of the material. Substances in the amorphous state possess weaker cohesion than the same substances regularly arranged in a space lattice.

Regenerated cellulose in the form of sheets, manufactured by the viscose or cuprammonium process, is an eminently suitable material for the study of the distribution of the water. By measuring the rate of flow and the minimum pressure required to allow the passage of gas through the sheet, the average cross section of the pores traversing the sheet can be calculated. On the basis of these calculations the value for the pore diameter appears to be approximately 40 to 60 Å.[42, 85, 89] The permeability of the membrane, as manifested by dialysis, is in agreement with this value.[89] It must be noted that the permeability of the cellulose film is closely related to its swelling. Under a given pressure, water is forced through the film more

quickly than is a non-aqueous solvent, such as alcohol or xylene, which produce only slight swelling. If the foil is first swollen in water, ethanol will flow through it even faster than water, because it has a lower viscosity. The pores which allow permeation of the membrane do not exist as such in the dry fiber, but are created or opened up by the swelling process. Dry cellulose film is practically impermeable, even to gaseous nitrogen.[80] Although fibers cannot be tested for their permeability to gases, there are no reasons to doubt that their system of submicroscopic channels is similar. For instance, viscose fibers swell in water until they contain 0.85 grams of water per gram dry weight, whereas in ethanol, the take-up is only 11 per cent. However, as the water-swollen fiber is soaked in alcohol, the take-up is then 45 per cent alcohol.[46] The average pore width of water-swollen wool has been estimated to be 35 to 41 Å,[76] which is of the same order as the estimated pore size of cellulose fibers.

The differences between the amount of the moisture taken up by different fibers under identical conditions may be due either to differences in the length or in the width of the pores traversing the fibers, or to both. Because the pores are opened up only by moisture, this means that the higher moisture content is due either to a larger number of regions of amorphous structure, *i.e.*, to a smaller size of the "crystallites," or to a weaker cohesion of the whole material, allowing the crystallites to be pushed farther apart by the entering water. The indications are that the differences are due mainly to the first factor and only to a lesser extent to the second. By mercerizing, or by dissolving and precipitating cellulose, its water absorption can be increased considerably. The higher water absorption of mercerized cotton and cuprammonium rayon is mainly due to the smaller size of the crystallites which can also be expressed as larger internal, submicroscopic surface or as a larger proportion of amorphous material.

Repeated attempts have been made to determine the internal surface of cellulose by measuring the amount of gases, liquids, or dissolved substances absorbed. The required calculations generally involve the assumption of a complete monomolecular coating, for which there is seldom evidence. As a matter of fact, the results so obtained differ widely. The increased reactivity of mercerized cotton and of regenerated cellulose, when compared with native cotton, *e.g.*, toward hydrolyzing agents (Nickerson [52]) or, in non-aqueous solutions, toward thallous sulfate (Assaf, Haas, and Purves [2]) may under certain assumptions be correlated with the relative amount of amorphous material in these fibers.

Physical Chemistry of Dyes

All the water-soluble dyes used in the textile industry are electrolytes. In aqueous solution they dissociate into positively and negatively charged ions, namely into the colored dye ion, the charge of which is due to the presence of ionogenic groups such as sulfonic acid, carboxylic acid, phenolic, amino groups, etc.; and the counter-ion, which is an ordinary colorless cation such as sodium ion, or an anion such as chloride ion. Therefore, when considering aqueous solutions, it is more correct to speak of dye anions (in the case of acid and direct dyes), and of dye cations (in the case of basic dyes), rather than of dye molecules.

The shape of molecules can be determined by x-ray analysis of crystals, by measurement of the interference of cathode rays on gases, and by measurement of the dipole moments of liquids and solutes. Although these methods are more or less restricted to rather simple molecules, by using the rule of constant interatomic distances and of constant bond angles, it is possible to deduce the shape of more complex molecules, if their chemical formula is known. This has been done for dye ions,[85, 89] and a few of the results are illustrated in Figs. 1 to 5.

Early observations of the behavior of aqueous solutions of dyes led to the conclusion that the dyes were not present as single molecules or ions, but rather as larger particles, each containing a great number of dye ions. Physicochemical meth-

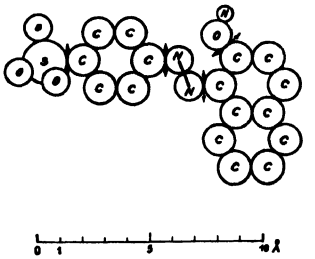


FIGURE 1. Model of the Orange II molecule, drawn to scale in planar projection. Hydrogen atoms mostly omitted.

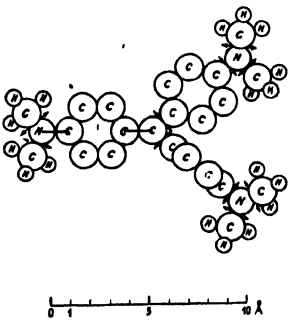


FIGURE 2. Model of the Crystal Violet molecule, drawn to scale in planar projection. Hydrogen atoms mostly omitted.

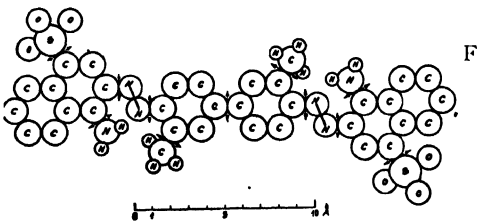


FIGURE 3. Model of the Benzopurpurine 4B molecule, drawn to scale in planar projection. Hydrogen atoms mostly omitted.

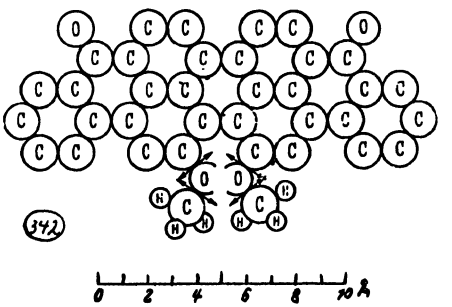


FIGURE 4. Model of the 12,12′ Dimethoxydibenzanthrone (Caledon Jade Green) molecule, drawn to scale in planar projection. Hydrogen atoms mostly omitted.

ods were applied in order to obtain quantitative data on the size of the dye particles in solution. However, the calculations required were frequently based on incorrect assumptions. Seemingly unimportant factors were overlooked in the experiments, and this led to erroneous results. The whole field was in a rather confused state until recently, when a critical sifting of the old results together with new exact measurements and calculations completely changed the situation. Today, although only a comparatively small number of the great multitude of dyes has been investigated with requisite thoroughness, the results are reliable and representative for large

classes of dyes. A comparison between the results obtained through completely independent methods reveals a gratifying agreement. While previously very little if any work was done to determine the particle size of dyes under the very conditions of the dyeing operation, *i.e.*, at the required temperature and salt concentration, a significant advance has been made in this direction during the last decade (Rose,[62, 63] Morton,[46] Lenher and Smith,[37] Valko [83, 89]).

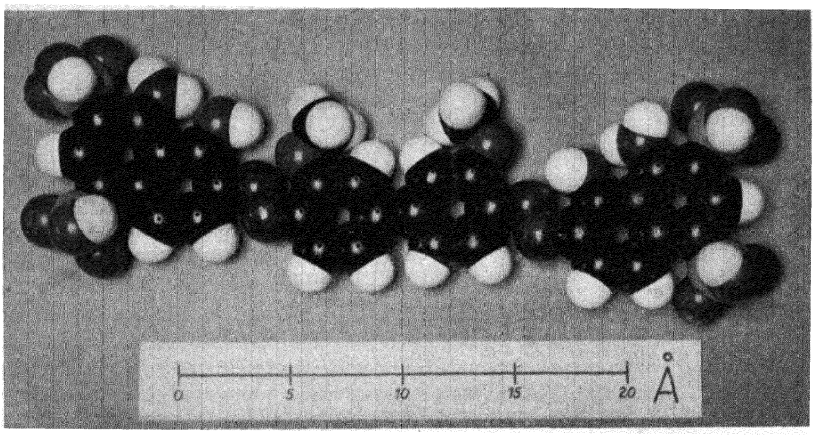


FIGURE 5a. Molecular model of Sky Blue FF built with the atomic models of H. A. Stuart to scale. Viewed perpendicular to the plane of the molecule.

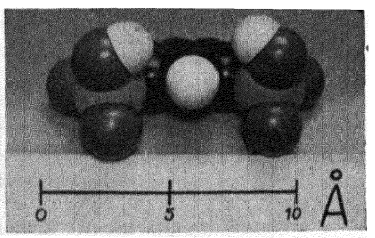


FIGURE 5b. Viewed in the plane of the molecule in the direction of its longer axis.

The methods which are suitable for determining the number of dye ions aggregated into particles in aqueous solutions are: osmotic pressure (freezing-point depression, rise in the boiling point, vapor pressure); conductivity, transfer number; diffusion; light absorption.

For details of the experimental methods and calculations, the original papers as well as comprehensive reviews [85, 89] should be consulted. However, brief mention must be made of some of the necessary criteria, which have frequently been neglected in earlier work.

The osmotic pressure, measured with a membrane permeable to water and ordinary ions, and impermeable to large ions and molecules, such as the dyes, is subject to the Donnan equilibrium.[11] Hence, data on the concentration of all the ions present are required for the proper evaluation of the results.[58]

The vapor pressure is equally influenced by all the particles, molecules and ions present. Soluble impurities must be excluded and the share of the counter-ions must be taken into consideration. Each ion present contributes to the conductivity. Therefore, electrolytes beside the dye salt must to be excluded or their concentration known. The coefficient of diffusion of an ion, such as the dye ion, in a solution can

not be correlated with its size, unless the concentrations and concentration gradients of all the ions present are known.[29, 30, 48]

The possible types of association of the dye ion in aqueous solutions can be schematically represented by the following three formulas. For a dye cation:

D^+	$(nD)^{n+}$	$(mDA.nD)^{n+}$
I	II	III

for a dye anion:

D^-	$(nD)^{n-}$	$(mCD.nD)^{n-}$
I	II	III

D denoting the dye ion, A and C the anionic and cationic counter-ion, respectively. The first form represents complete dissociation into single ions; the second, association of the dye ions while still retaining their state of ionization; the third, the formation of larger aggregation products with the inclusion of counter-ions when a comparatively small fraction of dye ions is attached to the surface of the particle, leaving in the solution the compensating counter-ions. The first form is that of the typical electrolyte; the third, that of the typical colloidal particle. The intermediate form, called ionic micelle, is characteristic of colloidal electrolytes, a group which besides the dyes or at least a part of the dyes, includes the soaps and other highly surface-active ions.*

The expected effects of these various forms of association on the results obtained, using the physicochemical methods listed above, will now be considered. Measurements of the osmotic pressure carried out in the presence of excess of electrolytes, in order to eliminate the Donnan effect, and using a semi-permeable membrane, would lead to a normal molecular weight, in the case of the first form; to a considerable increase of the molecular weight, expressed by a decrease of the osmotic pressure, in the second form; and to an extremely high molecular weight, expressed by immeasurably low osmotic pressure, with the third form. For the vapor pressure lowering, the first form would give a value twice as high as a non-ionizing molecular solution of the same molar concentration; the second, a value equal to a molecular solution of the same molar concentration; and the third an infinitely low value. The conductivity of the first form would appear normal; that of the third, very low. The second form may possess a normal conductivity, but it may have also a conductivity somewhat higher than normal, due to the high mobility of ionic micelles.[56, 60, 61] The situation is still more complicated by the fact that most dye ions are polyvalent, bearing two, three or four electric charges, and that if the solutions are not very dilute, the interionic forces cause a further deviation in the thermodynamic and conductivity properties. For instance, as a consequence of the interionic attractive forces the high mobility of the ionic micelles may be reduced below the value of the mobility of the single dye ion.

Under these circumstances, the results of osmotic pressure and conductivity measurements can not be expected to give very exact data on the degree of association of dye ions. Nevertheless, the numerous measurements which have been carried out, definitely eliminate the possibility that a significant fraction of any of the dyes is present in the form of truly colloidal particles (III), at least in salt-free solutions which alone permit the evaluation of conductivity measurements for this purpose. Basic and acid dyes show conductivities approximately like ordinary electrolytes, while direct dyes, in some cases show an abnormally low conductivity in concentrated solutions. Even these low values correspond to a fairly strong ionization (at least 50 per cent). The results of osmotic measurements likewise exclude the possibility of formation of truly colloidal particles.

Among the methods used for determining the degree of association (DA) of dyes,

* See papers by J. W. McBain in Vols. I and V of this series. J. A.

measurement of diffusion occupies a unique place. In the presence of an excess of an electrolyte, the rate of diffusion is a measure of the particle size, regardless of whether the dye is present as a single ion, as ionic micelle or as colloidal particle. The radius of the particle can be calculated, assuming a spherical form, from the Stokes-Sutherland-Einstein equation:

$$D = \frac{RT}{6\pi\eta r N}$$

where D is the coefficient of diffusion, R the gas constant, T the absolute temperature, η the viscosity, r the radius, and N Avogadro's number. A probable value must be assumed for the density of the particles on the basis of the macroscopic specific weight, in order to obtain the weight of the particles. The error involved in assuming a spherical form for comparatively small particles, such as are dealt with here, has been shown to be relatively small, except in the case of extremely anisodiametric particles, such as elongated chains, etc. Thus, using the macroscopic density and neglecting the hydration, we are in a position to calculate the DA. However, the usefulness of numerous determinations was seriously impaired by the failure of earlier investigators to take into account or to eliminate the influence of electrolytic dissociation and rate of diffusion. Fortunately, this failure has been avoided in the course of the investigations carried out recently. The following discussion is based on these recent results.[87, 56, 88-89]

The particle size generally depends on the temperature and the concentration of both the dye and the electrolytes present. Thus, the degree of association of dye ions represents the result of a reversible equilibrium.

Contrary to previous statements, which were based on incomplete evidence, it has been found that with increasing salt concentration the particle size invariably increases, with the exception of those dyes which do not show any tendency to asso-

Table 1. The Degree of Association of Acid Dyes (Valko)

Dye	Color Index No.	Temperature (° C)	% Concentration of Dye	*M* Concentration of Electrolytes	Degree of Association
Orange GG	27	25°	0.005-0.5	0.01-1.00	0.98
"	27	60°	0.02	0.02	0.70
"	27	90°	0.02	0.02	0.95
Methyl Orange	142	25°	0.0009	0.01-0.06	1.05
Orange II	151	25°	0.005-0.01	0.02	1.2
		25°	0.002-0.1	0.05-0.2	1.7
		25°	0.05	0.2	2.6
		60°	0.02	0.05	0.82
		90°	0.02	0.05	0.87
Azo Crimson S	54	25°	0.005-0.05	0.02-0.05	1.1
		25°	0.01	0.1	1.4
		25°	0.1	0.1	2.0
Ponceau 4 GBL		25°	0.01	0.05	1 4
Brilliant Ponceau G		25°	0.01	0.05	1.1
Naphthol Yellow S		25°	0.02	0.02	0.74
Amido Black 10B	246	25°	0.02	0.05	2.00
Tartrazine	640	25°	0.02	0.05-0.5	1.54
Milling Yellow O		25°, 60°, 90°	0.02	0.02	1.94
Metanil Yellow		25°	0.01	0.05	1.14
		90°	0.01	0.05	0.78
Fast Red AV	176	25°	0.005-0.01	0.005-0.02	3.0
		25°	0.02	0.05	9.15
		60°	0.02	0.05	1.1
		90°	0.02	0.05	3.4
Polar Yellow R		25°, 60°	0.01	0.05	350
		90°	0.01	0.05	1.8
Palatin Fast Blue GGN		25°	0.01-0.05	0.01-0.075	1.3
		60°	0.01	0.075	1.1
		90°	0.01	0.05	2.6

ciate and remain dispersed in the form of single ions under all experimental conditions. The law of mass action requires that the DA increase with increasing dye concentration, and this is confirmed by the experimental data. Generally, the association diminishes with increasing temperature which means that it is an exothermic reaction. However, in a few cases, the DA was larger at 90° than at 60°.

The results summarized in Table 1 show that the acid wool dyes are partly dispersed into single ions and partly form aggregates, the size of which, however, does not exceed that of three dye ions at 90°. Even Polar Yellow R Conc., which displayed a particle size corresponding to a molecular weight of about 250,000 or a DA of 350 at room temperature, possessed a DA of only 1.8 at 90°, *i.e.*, it was present mainly as a dimer. Orange GG proved to be present as single ion, even at room temperature and in the presence of 1*M* sulfuric acid. Milling Yellow D dimerizes in the presence of a moderate concentration of salt at room temperature as well as at 90°. Fast Red AV has a DA of about 3 at 90°. In all these cases (except when the DA is 1) the particle size is likely to be regarded as an average value of the various associated forms present. With a DA of 2, for example, a large part of the dye may be present as the monomer and another large part as a trimer, unless experiments show that the DA is constant in a broad range of temperature and salt concentration, in which case it is likely that the dimeric form has exceptional stability.

DA values between 1 and 2.6 have been obtained for the soluble chromium complexes of dyes of which Table 1 presents only one example.

Even a greater variation of the DA was observed with direct dyes, as demonstrated on Sky Blue FF by Fig. 6. At room temperature this dye showed any DA

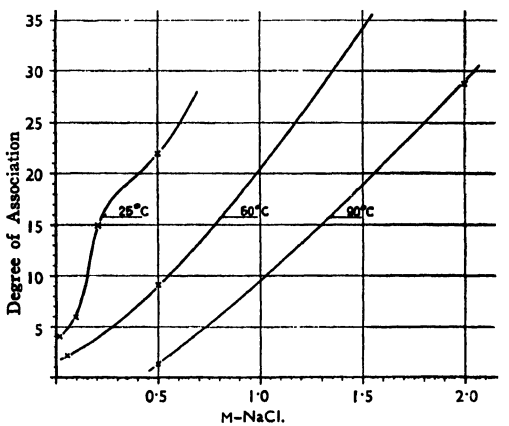


FIGURE 6. Degree of association of direct dyes at 25° C as a function of the concentration of NaCl. From diffusion measurements. (Valko)

value between 3 and 1,000, depending on the salt concentration. At 90° with 0.05*M* NaCl, which approximately corresponds to the concentrations used in the dye bath, a DA of only 1.4 was measured, indicating that a large part of the dye was present as single ion. However, in 2*M* NaCl, the DA at 90° reached a value of 29.

Fig. 7 shows that Benzopurpurine 4B has a DA of about 6 at room temperature, in 0.01*M* NaCl, while in 0.05*M* NaCl the DA is well above 800. A similar but slightly lower sensitivity of the DA toward the salt concentration was displayed by Congo Red. Evaluation of the conductivity measurements showed that in pure water the DA of Benzopurpurine 4B is only 2-3, that of Congo Red only 2-4 at 90°. Even in moderate salt concentration such as occur in the practical dye bath, the DA of Benzopurpurine 4B is likewise only 2-3, according to the results listed in Table 2. Another direct, dye, Benzo Light Red 8 BL, has a DA of 6 at 90° C in the presence of 0.05 per cent NaCl.

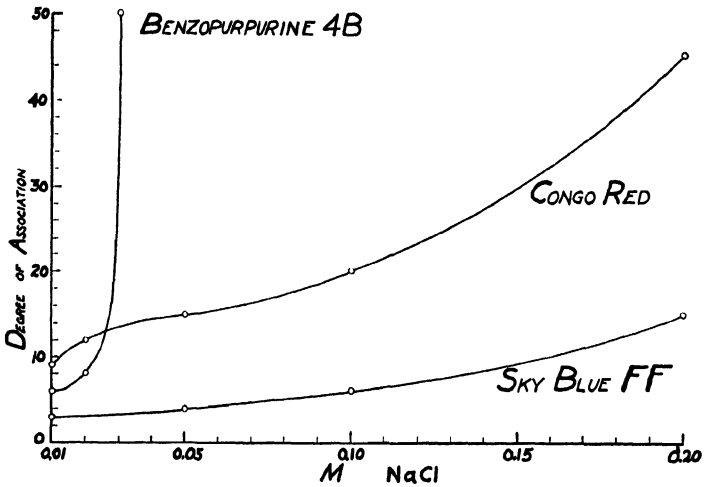


FIGURE 7. Degree of association of Sky Blue FF at various temperatures as a function of the concentration of NaCl. From diffusion measurements.

Table 2. Radius of Particles of Benzopurpurine 4B (Lenher and Smith)

NaCl Conc. *M*	Radius in 10^{-8} cm			
NaCl	At 25°	50.5°	65.2°	94.2°
0.01	9.0	8.2	—	—
0.025	26.4	10.0	—	—
0.05	62.2	12.9	10.6	—
0.075	—	36.3	—	—
0.1	Precipitated	—	16.2	8.1

Vat dyes, such as dimethoxydibenzanthrone (Caledon Jade Green), dibenzpyrene quinone, etc., showed in a reduced soluble state at room temperature, in solutions approximating the composition of the ordinary dye bath, DA values between 2 and 4 and similar values were obtained for the salts of the sulfuric acid esters of the reduced vat dyes known as Indigosols.[88]

Table 3. Particle Size of Cationic Dyes at 25° (Valko)

Dye	g. Dye per 100 ml Solution	Conc. *M* of Electrolyte	Degree of Association
Methylene Blue	0.005	0.01-0.02	1.8
	0.02	0.05	2.2
Crystal Violet	0.005	0.01	2.1
	0.01	0.05	2.6

As shown in Table 3, among the basic dyes, Methylene Blue at 20° in the presence of moderate salt concentration displayed a rate of diffusion corresponding to the molecular weight of a dimer. The DA of another dye cation, Crystal Violet, was found to be only slightly higher. Methylene Blue and its non-methylated parent substance Thionine belong to the few dyes the DA of which has been determined by the measurement of the light absorption.[54] The absorption was measured in a broad range of concentrations, and the spectrum obtained was assumed to be the superposition of the spectra of the monomeric and dimeric dye cations. The equilibrium between the two forms is ruled by the law of mass action of binary dissociation, and on this basis the dissociation constant of the dimer could be successfully calculated (compare however Sheppard and Geddes[78]). Its value for Thionine, at 26-7° was found

to be 1×10^{-3}, for Methylene Blue, 2.8×10^{-4}. The latter dye accordingly showed a somewhat stronger tendency to dimerize. For two concentrations of Methylene Blue for which the earlier diffusion measurement lead to DA values of 1.8 and 2.2, the optical method permitted to calculate DA values of 1.4 and 1.7, respectively. However, the diffusion measurements were carried out in the presence of salts, which certainly increases the association.

With Thionine, the dependency of the dimerization equilibrium on the temperature was determined, and this allowed the heat of dimerization to be calculated. Its value, at room temperature, is 6,820 cal/mole. The free energy of the dimerization, calculated on the basis of the dissociation constant, is 4,096 cal/mole, and the entropy 9.1 cal/mole/degree.

All these results indicate that the importance of the size of the dye particles in the dyeing process has frequently been overestimated. It is now known with certainty that *under the conditions of the dyeing process* (that is, salt concentration and temperature) *not only numerous acid wool dyes, but also some direct cotton dyes, are dispersed either completely or very nearly into single ions.*

Kinetics of the Dyeing Process

Dyeing is generally a slow process. Commercially, it is not infrequent to allow one hour or more for the textile to pick up the dye in the dyebath, and even then equilibrium is sometimes not approached. Careful investigations of the kinetics of the process of absorption of direct dyes by cellulose sheets, have proved extremely valuable in the theory of the dyeing process, since they avoid complications brought about by the irregularities of the natural fibers, as well as by variations of the physical properties along the cross-section. The results of these studies definitely show that the rate-determining step is the diffusion of the dye from the surface of the cellulose into the interior.[7, 49] The establishment of the absorption equilibrium on the surface is practically instantaneous if the dye bath is agitated. The terminating step, *i.e.,* the linking of the dye molecule to the cellulose molecule, can likewise be regarded as an instantaneous process. The slowness of the dyeing process is caused by the slowness of the diffusion of the dye through the fiber.

In practical dyeing, the bath is gradually exhausted during the process. While the adsorption equilibrium almost immediately establishes itself between the surface of the fibers and the original concentration of the dye bath, the diffusion of these adsorbed dye ions into the interior of the fibers necessitates their replacement from the bath. This disturbs the original equilibrium, and the density of the dye on the surface of the fiber diminishes as the concentration of the dye in the bath decreases. For theoretical studies of the kinetics of the dyeing process, it is convenient to apply very large bath ratios so that the dye concentration in the bath remains practically unchanged during the dyeing process.[17, 24, 27, 28, 48, 49]

The diffusion of the dye in the fiber obeys Fick's law, but the rate of diffusion in the cellulosic material is much slower than in free water. There does not seem to be any direct relationship between the rate of free diffusion of the dye and its rate of diffusion in the cellulose. The rate of diffusion in cellulose, and therefore the rate of the dyeing process, depends on the salt concentration and the temperature. With increasing salt concentration, the rate increases until it reaches a maximum value, and thereafter decreases with further increase in salt concentration. The rate of diffusion invariably increases with increasing temperature. The dependence temperature is extremely pronounced. For Sky Blue FF, the time necessary to reach an absorption corresponding to half the maximum absorption increases in the ratio 1:700, when the temperature is raised from 25° to 100°. However, the ratio varies with the dye, being *e.g.,* only 77 for Fast Red K.[17]

The diffusion of the dye in the cellulosic material is obviously a very complicated process. First of all, it is certain that only a small fraction, if any, of the dye present

can move freely in the submicroscopic water-filled channels, the greater fraction being adsorbed in the wall of the channels. Depending upon the adsorption equilibrium, the free fraction may be only one-tenth of a per cent, or even much less, of the dye present. Furthermore, the dimension of the dye molecule, or at least its longest axis, is, as it was shown in the early part of this article, of about the same order of magnitude as the diameter of the channels.[46] In the case of dimerization, and of course even more so in the case of poly-association, the narrowness of the pores will certainly diminish the rate of diffusion. It does not seem unlikely that the diffusion of the dye in the fiber proceeds essentially in the adsorbed state, *i.e.*, the dye ions creep along the surface of the submicroscopic channels.[83] There also seems to be a third factor which contributes to the complications, namely, the electric potential of the dye ion and of the fiber.[46] A satisfactory mathematical treatment of the effect of the adsorption on the diffusion is lacking, and consequently a complete theory of the process is remote.[8] Nevertheless, the empirical description of the penetration of the dye into the fiber and its characterization by a diffusion coefficient, the value of which depends on the nature of the dye, the salt present, and the temperature, represents a certain clarification of the problem.

The diffusion of the dye in the fiber proved to be likewise the rate-determining process in the take-up of acid dyes by animal fibers.[78] Consequently, the finer the fiber the greater is the speed of dye sorption. With increasing temperature the rate of sorption increases. At rooom temperature, weeks and months are required until wool is completely saturated with a dye acid. Some dyes penetrate slowly in wool even at 50° and there are also some dyes which even at 90° do not reach sorption equilibrium in three hours.[16]

The rate of dyeing of natural fibers, with their microscopically inhomogeneous structure, presents an even more complicated situation than is found with regenerated cellulose. It has been shown that the scale cells of wool form an outer hull which represents a considerable hindrance to the passage of dyes. If the scales are removed by rubbing the hairs with sandpaper, the dye penetrates much quicker.[78] Fibers cut to short length adsorb dye more rapidly than longer fibers because penetration through the cut ends is easier than through the scales. This was proved by determining the influence of hair length on the speed of dye absorption [78] as well as by direct microscopic observations.[66] Similar phenomena may occur with cotton. Certain observations with rayon indicate that as a consequence of the mechanics of the spinning process, even in man-made fibers there are differences between the properties of the periphery and those of the interior.

Many questions remain to be answered regarding the kinetics of dyeing. However, out of these studies arose a further advance, namely, the clear distinction between the characteristics of the dyeing process related to equilibrium and those related to kinetics. Before, it was not infrequent to attribute a low affinity to a dye, simply because a comparatively low amount was absorbed during a given period of time, for instance, one hour. In many of these cases, a comparatively high absorption is observed if the dyeing period is sufficiently long to allow a state of equilibrium to be fully established.

Equilibrium of the Dyeing Process

The dependence of the amount of dye adsorbed at equilibrium on prevailing dyeing conditions is the most valuable experimental information which we have as a basis for the theory of dyeing. The nature of the dye and of the fiber, the temperature, the concentration of the dye, and of the electrolytes present, including the hydrogen ion, have been long since recognized as the determining parameters of the sorption of the dyes. Recent measurements have brought forth much new data; these are more reliable, because the dyes were carefully purified and the existence of a state of equilibrium was ascertained. However, only a few sections, although

important, of the whole extensive field are covered by this data. Such a section is represented, for example, by a number of direct azo dyes investigated regarding their behavior towards regenerated cellulose film and cotton.[17, 24, 27, 28, 48, 49, 50] It was found that:

(1) At equilibrium the amount of sorbed dye invariably increases with increasing concentration of sodium chloride. Other salts have a similar effect, although there are significant differences in their efficiency. As early as 1909, Knecht and Batey [34] stated: "It is well known that many direct dyes, such as Benzopurpurine will only dye a cotton fiber in the presence of an inorganic salt, such as Glauber's salt, sodium chloride, potassium chloride, etc."

(2) The amount of sorbed dye invariably decreases with increasing temperature. This fact was frequently overlooked because of the relatively slow establishment of the sorption equilibrium at lower temperatures. From a dye bath containing 0.005 per cent Fast Red K and 0.5 per cent NaCl cellophane takes up 1.84 grams per 100 grams of cellulose at 25°, and only 0.268 grams at 100°. With Heliotrope 2B, the corresponding values are 0.96 and 0.066 grams of dye adsorbed. In the first case, the sorption dropped with increasing temperature to about 14 per cent of its original value; in the latter case, it dropped to about 7 per cent. The drop depends also on the nature of the fiber, (cellophane or cotton).

(3) With increasing concentration of the dye, the sorption value appears to tend toward a saturation value, the sorption isotherm nearly following Langmuir's equation. However, the saturation value depends on the salt concentrations and on the temperature and varies with them over a range of several orders of magnitude.

(4) Generally, cellophane (and other types of regenerated cellulose such as cuprammonium and viscose rayon) takes up more dye than cotton under identical conditions. The only exception is in the presence of a low concentration of salt, when the take-up is lower with the regenerated cellulose. With increasing salt concentration, the ratio of the amount of dye taken up by cellophane to that taken up by cotton approaches the limiting value, which is considerably greater than 1. The ratio depends on the temperature, with Heliotrope 2B, decreasing from 2.4 at 20° to 1.3 at 90° (dye concentration 0.005 per cent, NaCl concentration 0.5 per cent). Furthermore, the ratio depends on the nature of the dye, varying for example between 3.2 and 1.7 under identical conditions.

Another class of dyes is represented by the few experiments carried out with "naphthols." Here the influence of salt and of temperature were found to be identical with that of direct dyes. Likewise, an increasing sorption was observed with increasing salt concentration of the vat dyes in the form of their leuco compounds. It is reasonable to assume that the first step of the dyeing process with alkaline solutions of naphthols and of reduced vat dyes is essentially of the same mechanism as the dyeing with direct dyes. The steps following thereafter (coupling, oxidation), are of course entirely different from the phenomena of direct dyeing (see below).

Certain aspects of the equilibrium of wool with acid dyes have been likewise studied in detail. Most of these investigations were directed toward the determination of the dependency of the sorption on the hydrogen ion concentration of the solution, as well as toward the determination of the maximum amount of dye taken up. Some of the older observations were verified, other, however, were considerably modified. The following are fairly well established facts: [45, 16, 79]

(1) The amount of dye anion taken up increases with increasing hydrogen ion concentration between pH 5 and pH 2.5. However, there is a definite sorption of the dye even at pH values above 5, *i.e.*, on the alkaline side of the isoelectric point.

(2) The maximum amount of dye taken up corresponds to 0.7-1.0 milliequivalent per 1 gram of wool. This is the same quantity as, or slightly higher than the maximum amount of common acid, *e.g.*, hydrochloric, taken up by wool. The maximum is reached with dyes at a lower hydrogen ion concentration than with common acids.

(3) From a mixture of common anions and dye anions, the latter are preferentially sorbed.

(4) In the region between pH 1.5 and 5, much more acid is sorbed at a given pH from a solution of a dye acid than from a solution of a common acid.

(5) The amount of dye acids sorbed at a constant pH decreases with increasing temperature.

Theory of Dyeing

Certain rules which were found to govern the dyeing process were presented in the foregoing sections. This section deals with the cause and the molecular mechanism of the process, *i.e.*, the theoretical explanation of the observed facts.

Generally speaking, the dyeing process leading to a reversible equilibrium represents a partition of the dye between two phases: the solution and the fiber. The dye accumulates in the fiber, as indicated by the more or less complete exhaustion of the dye bath. The question is as to the cause of the preference of the dye for the fiber.[8, 64, 85, 89]

A distinction can be made between processes which are caused by the kinetic movement of molecules and those caused by intermolecular attraction. In the first case, the change of heat content is either vanishingly small, as in the case of the expansion of an ideal gas and the dilution of an ideal solution, or there is an increase of the heat content, as in the case of the melting of crystals and the evaporation of liquids. In the second case, there is a decrease of the heat content, as in the case of the crystallization of a liquid, the condensation of a vapor, the formation of water from oxygen and hydrogen, etc. Because the kinetic movement of the dye molecules is certainly more impeded in the fiber than in the solution, and because their crowding into the smaller space of the fiber occurs against their tendency to reach a more probable state of distribution, it is to be expected that the take-up of dye by the fiber is not a consequence of the thermal movement of the molecules. That the sorption of the dye is caused by molecular forces is evidenced by the shifting of the sorption equilibrium with increasing temperature in the direction of diminished take-up, which proves that the dyeing process is exothermic. The problem is to specify these forces as quantitatively as the present knowledge of molecular interaction permits.

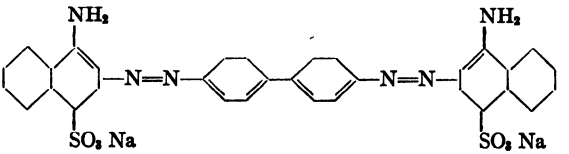
It is convenient to give separate consideration to the two kinds of molecular forces: the specific non-ionic attraction on the one hand, and the coulombic attraction or repulsion between the free electric charges of the ions, on the other.

There cannot be much doubt that the ultimate cause of the exhaustion of the dye from the bath onto the fiber is the action of specific, non-coulombic attractive forces between the molecules of the dye and the fiber. These forces are obviously of the same general type as those which cause other phenomena of molecular association, *e.g.*, the condensation of vapors, the solvation of a solid, etc., *i.e.*, they are van der Waals forces. The nature of these is understood to some extent. They are due to the orientation of permanent dipoles, to the induction of polarizable molecules, and to a wave-mechanical interaction of internal electronic motions, called dispersion or London forces. A specific kind of interaction which is usually stronger than any of the previously mentioned kinds, and which is called hydrogen bond or hydrogen bridge, occurs between molecules containing hydrogen atoms which are connected with electronegative atoms, as in the amino and hydroxyl group.

At present it is not possible to decide which one of these forces is mainly responsible for the interaction between the dye ion and the fiber. Both the fiber molecule and the dye ion possess strongly dipolar groups, such as hydroxyl, amino, carbonamide, etc. The dye ion is highly polarizable and capable of strong wave-mechanical interaction. Moreover, the fiber and the dye contain groups of pronounced hydrogen bonding tendency. It is safe to assume that all these forces contribute their share to the attraction of the dye ion for the fiber. However, consideration must be given

to the fact that through the adsorption of the dye by the fiber, both dye and fiber molecules suffer to some extent a loss of their hydration. It is obvious that this loss must be compensated by the energy gained by the interaction between the fiber and the dye. This requirement complicates the explanation of the dyeing process.

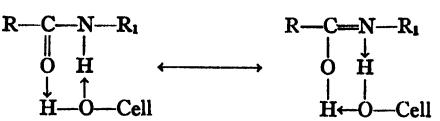
The best approach to this problem is obtained by considering the common characteristics of that class of dyes which shows highest affinity for cellulosic fibers, *i.e.*, the direct or substantive dyes. Their most important characteristic is the presence of a long chain of conjugated double bonds in the dye ion.[69, 36, 33] This can be demonstrated by the structure of Congo Red.



Frequently the enolized carbonamide group appears to be a member of the conjugated system. A powerful argument in favor of the importance of the presence of the conjugated chain has been found in the fact that substitution by an alkyl group of the hydrogen atom attached to the nitrogen of the amide group destroys the affinity of the dye for the fiber.[86] The substitution prevents enolization and consequently interrupts the conjugated chain.

Because of their importance for the color of the molecule, conjugated double bonds are present in all organic dyes. However, other conditions remaining unchanged, the affinity appears to increase with increased length of the chain of conjugation.

It cannot yet be said how the conjugated double bonds affect the linking of the dye to the fiber. Conjugated double bonds can be significant for practically every type of intermolecular forces. Wave mechanics teaches that a chain of conjugated double bonds has a common electron cloud. This electron cloud is polarizable, for example, through the interaction with permanent dipoles, such as the hydroxyl group of cellulose. Furthermore, it can be demonstrated that a single long-wave electronic absorption bond in the molecule, such as exhibited by a system of conjugated double bonds, increases the dispersion forces. Finally, there is a possibility, although without direct experimental evidence, that the hydrogen bonding capacity of electronegative atoms is increased when they are directly attached to a chain of conjugated double bonds. The fact that the conjugated system in dye molecules is always between two polar groups which contain either hydrogen (NH_2) or oxygen (SO_3) or both (OH) may have some significance in this connection. The role of the carbonamide group built as a link in a chain of conjugated bonds was explained by the assumption that it gives rise to cyclic hydrogen bridges by interaction with the hydroxyl groups of the cellulose.[13, 85]



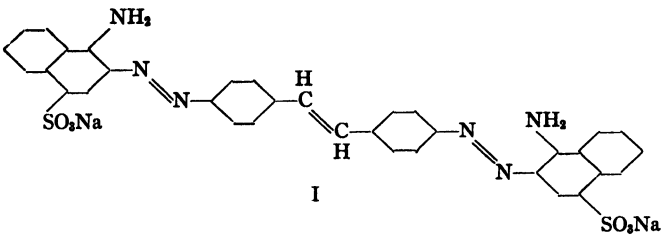
In A the carbonamide group is in the keto-form, while in B it is enolized. The stability of the hydrogen-bridges depends on the tendency of the carbonamide group to enolize and this tendency increases under the influence of conjugation.

It seems, therefore, that all kinds of van der Waals forces are active in the adsorption of dyes by cellulose fibers. Further investigation is required to estimate the contribution of the different types of forces.

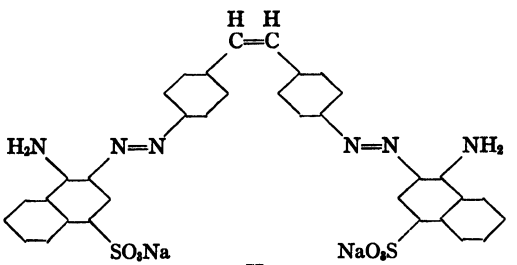
The influence of the shape of the dye ion and of the distribution of the polar and

ionogenic groups in it, can be understood, at least in principle, if the adsorption of the dye ion is regarded as a manifestation of molecular interaction.

The assumption that a dye of elongated shape (I) is more substantive than a similar type of folded shape (II) could not be confirmed:[67]

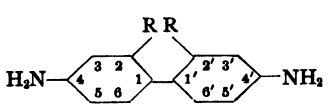


I



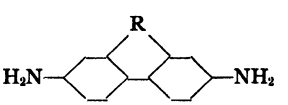
II

However, flat or planar shape seems to be a requisite for substantivity.[32, 38] Thus, the 2,2′ derivatives of Benzidine (III) are not substantive unless cyclization occurs in these 2,2′ positions, *e.g.*, through amino or methylene group (IV).



R = Cl, SO_3H, CH_3.

III



R = NH, SO_2, CH_2.

IV

On the other hand, the leuco compound of 9,9-dimethoxy dibenzanthrene is substantive, although it cannot be strictly planar (Fig. 4) unless the ring system is distorted.[85] In view of the tendency of condensed ring systems to attain planar configuration, this possibility cannot be neglected. The same holds for the recently synthesized substantive derivatives of *o*-terphenyl.[1] It remains an open question whether the non-planar configuration is detrimental to substantivity because it impedes the formation of an adequate resonance system, or because it hinders the necessary apposition of the dye to the cellulose molecule.

Essentially, the same considerations hold for the molecular forces acting between dyes and the protein fibers, wool and silk, as for those between dyes and cellulose. Besides free amino and carboxyl groups, wool and silk contain carbonamide as well as hydroxyl groups. All these are capable of forming hydrogen bonds. However, it appears that the presence of a relatively short chain of conjugated double bonds is sufficient to lend the dye enough affinity for protein fibers. The probable reason for this behavior, as distinguished from that of cellulose, will become evident by considering the influence of Coulomb forces in the take-up of dye-ions by the fiber.

The sorption equilibrium of the dyes with the fibers is complicated by the existence of the electrical forces acting between fibers and dyes. Whether these Coulomb

forces exert repulsive or attractive action depends only upon whether the sign of the charge of the dye ion is the same as or opposite to that of the fiber. However, the initial electrical charge of the fiber is a decisive factor only as long as the amount of dye ions taken up is smaller than the original amount of the electrical charges of the fiber. In most cases, the dye ions, when sorbed by the fibers, influence their electrical potential to such a great extent that the original charge of the fibers become a matter of no importance.

While the sorption of the dye ions affects the electrical potential of the fibers, the electrical potential is one of the factors determining the sorption of the dye ions. No complete understanding of dyeing phenomena can be expected before the nature of this electrostatic interaction is thoroughly known.

The dye ions do not accumulate on the microscopic surface of the fibers, but permeate them and, microscopically, are homogeneously distributed throughout the fibers. This cannot occur in such a way that the corresponding counter-ions remain outside the fibers. According to the law of electroneutrality, cations are to be accompanied by an equivalent amount of anions, and *vice versa*. The accumulation of dye ions in the fiber can be accomplished only when an equivalent amount of counter-ions accumulates in the fiber. Analytical determination confirmed that with every equivalent of dye, an equivalent of counter-ions is sorbed. The sorption of counter-ions is opposed by their kinetic energy which tends to distribute them uniformly in the space available. Expressed in terms of statistical mechanics, the sorption of the counter-ions is opposed by the law of probability. The final sorption equilibrium is reached when the attraction between the fiber and the dye is balanced by the kinetic energy exerted not alone by the dye ions, but also by the corresponding counter-ions. The higher the concentration of the counter-ion in the solution, the smaller is the required relative increase of their concentration in the fiber. Since the concentration of the counter-ions can be increased by adding salt to the solution, the sorption of the dye is facilitated by increase of the salt concentration. Higher valency of the counter-ions promotes sorption of the dye ions, since less osmotic work is required for the accumulation of an electrically equivalent amount of counter-ions bearing more than one charge. Any non-Coulombic attraction between dye and counter-ion or between fiber and counter-ion promotes the sorption of the dye; and any loss of energy of hydration of the counter-ions suffered in entering the fiber, counteracts it. In other words, consideration needs to be given to the change of heat content of the counter-ions caused by their transfer from the solution into the fiber.

A quantitative expression can be formulated for the dependence of sorption of the dye ions on the concentrations of ions in a simplified case.[18, 19] The consideration of this formula helps us understand the more complicated cases. Let us assume first that the amount of dye sorbed is relatively small, so that the number of available sites in the fiber is not considered variable, but constant. This is justified even for the conditions of the practical dyeing process. The capacity of the fibers for dye amounts to several per cent on the weight of the fibers. It was found by independent investigations [86, 88, 50] that cotton, for instance, can sorb a direct dye in an amount of 9 per cent of its own weight. Corresponding values for viscose rayon were 22 per cent, viscose staple fiber 36 per cent, cuprammonium rayon 37 per cent, cellophane 44 and 24 per cent. On the other hand, in commercial dyeing the amount of sorbed dye (calculated as pure compound) very seldom reaches 1 per cent by weight.

The Boltzmann Law for the distribution of a compound between two kinds of sites can be applied

$$C_{D,\,\text{FIBER}} = C_{D,\,\text{SOL.}}\, e^{\frac{-W_D}{RT}}$$

$C_{D,\,\text{fiber}}$ is the molar concentration of the dye ion in the fiber, $C_{D,\,\text{sol.}}$ the concentration of the dye ion in the dye bath, W_D is the work which is gained by transferring

one mole of the dye from the solution into the dye bath. This work can be separated in the non-Coulombic energy which represents the intrinsic affinity of the dye ion to the fiber molecule and into the electric energy which is equal to the product of charge and electric potential difference [4] between fiber and solution. Denoting the non-Coulombic energy with $W_{D,A}$ for a univalent dye, we can write

$$C_{D,\text{ FIBER}} = C_{D,\text{ SOL.}}\, e^{\frac{-W_{D,A} + F\Psi}{RT}}$$

(F is the Faraday). For a monovalent counter-ion, for instance, Na^+, the analogous equation is valid:

$$C_{Na,\text{ FIBER}} = C_{Na,\text{ SOL.}}\, e^{\frac{-W_{Na,A} - F\Psi}{RT}}$$

If we assume that in the fiber no other ions are present than the dye ion and the sodium ion, the concentration of these in the fiber must be equal, and if the intrinsic affinity of the sodium ions to the fibers can be neglected, it follows that [19]

$$C_{D,\text{ FIBER}} = \sqrt{C_{Na,\text{ SOL.}} \times C_{D,\text{ SOL.}}}\; e^{\frac{-W_{D,A}}{2RT}}$$

It is remarkable that the electric energy does not appear in the expression, in spite of the fact that it is the only reason for the sorption of the cations and for the dependence of the amount of sorbed dye ions on the amount of the cations.[19] Although the cations have no specific attraction to the fibers, their concentration has the same effect on the sorption of the anions as the concentration of the latter. With higher concentration of salts, ions of the same sign of charge as the dye ions will enter the fiber in an amount which can no longer be neglected and the above equation will not be valid. The concentration of salt usually present in practical dyeing operations is not high enough to cause a serious error by neglecting this effect. The validity of the above equation is more seriously impaired by the fact that the dye ions are generally multivalent, that several kinds of counter-ions are present and that the specific attraction of the counter-ions to the fiber molecules or to the adsorbed dye ions cannot be neglected.

Several other conceptions have been suggested to describe quantitatively the role of electric forces in the dyeing process. Some of these makes convenient use of previously known principles, for instance, of those of the Donnan equilibrium.[75, 15, 28] The fiber and the solution are considered as two phases in equilibrium with each other, all ions being freely diffusible, with the exception of the sorbed dye ions. In agreement with the law of electroneutrality, an equivalent amount of counter-ions must be present in the fibers in excess of any salt which may be there, and the product of the concentration of any pair of monovalent cations and anions inside and outside of the fibers must be equal. Consequently, the concentration of free, unadsorbed dye ions in the fiber is only a fraction of the concentration of free dye ions in the solution. With increasing salt concentration the distribution of ions inside and outside the fibers becomes more uniform, and the concentration of free dye ions in the fiber increases. Since an adsorption equilibrium is established between the free and adsorbed dye ions in the fiber, the amount of dye adsorbed increases with increasing concentration of the free dye ions in the fiber, that is, with increasing salt concentration. In applying the theory to the experimental conditions, assumptions must be made on a more or less arbitrary basis, particularly as to volume of the fiber phase and as to activity coefficient of the ions in the fiber phase, by which a fair agreement can be reached.

The relation of this treatment to the simple electric theory can be demonstrated if the membrane potential is considered as the quantity on which the distribution of the

ions depends. This membrane potential has obviously the same function as the electrical potential in the theory above outlined.

It has been repeatedly suggested that the salting out effect may be of significance in the role of the electrolytes added to the dye bath;[85, 81, 47, 82] and it has been pointed out in that connection that the solubility of direct dyes is greatly reduced by the presence of electrolytes. However, the fact should not be overlooked that the apparent reduction of solubility is mainly due to increase in concentration of counter-ions, this concentration being one factor in the solubility product; that the affect of the concentration of counter-ions is duly taken into account in the electrical theory outlined above, as well as in the Donnan theory; and that the genuine salting out effect is likely to be negligible at the salt concentrations of the commercial dyeing operations.

The adsorption of dye ions in the direct dyeing of cellulose fibers occurs always against the opposition of electrical forces. The situation is different in the acid-dyeing of wool. The protein molecule in the absence of electrolytes contains ionized ammonium and carboxyl groups in approximately equal numbers. These groups balance each other electrically by internal salt formation. Generally, in wool dyeing, the dye salt is added to the bath together with an acid such as acetic or sulfuric. It may be assumed that the following ions are present: sodium, hydrogen, anions of the acid, and dye ions. At first hydrogen ions are taken up by the protein molecule, mostly by the ionized carboxylic groups. As a consequence, an equivalent number of ionized ammonium groups of the protein molecule lose their counter-ions, and according to the law of neutrality they must take up an equivalent number of anions. It has definitely been demonstrated that, because of their high rate of diffusion, the small anions are taken up first.[14, 16] At equilibrium, however, these anions are replaced almost completely by dye ions, provided the latter are present in sufficient number. The distribution of the common anions and of dye anions between fiber and solution does not involve any electrical forces. This replacement occurs only because of the higher non-Coulombic specific attraction of the dye anions for the fiber. Thus, the acid-dyeing process can be described in terms of ionic exchange.

The higher specific attraction of the dye anions to the ammonium groups of the protein can be expressed in terms of a lower dissociation of the salt formed by the protein cation and dye anion. The mass action law of electrolytic dissociation has been used to formulate a quantitative treatment on this basis.[79] However, the assumptions and simplifications which have been required to bring this theory into agreement with the experimental data involved the neglect of the electrostatic compulsion of the counter-ions to enter the fibers. Instead, the implicit assumption has been made that undissociated dye acids are adsorbed by the fibers.[19] Thus, the physical picture on which the theory was based deviated considerably from the actual molecular process.

Because in the acid-dyeing of protein fibers electrical forces favor the adsorption of the dye ions (the fibers are as a consequence of the adsorption of hydrogen ions positively charged) these need not possess as high an affinity for the fibers as in the direct dyeing of cellulose, where the electrical forces oppose the adsorption of dye ions. Large anions, even if they do not contain long chains of conjugated double bonds, are sorbed by protein fibers in acid solutions.[79] However, the adhesion of these ions is not high enough to withstand the laundering process when this is carried out, as usual, at high pH values. Acid dyes which are fast to washing contain a chain of conjugated double bonds, as do neutral dyeing wool and silk dyes.

The specific affinity of the anions of acid dyes for protein fibers is demonstrated by the observation registered in the previous section, that from a mixture of common anions and dye anions the latter are adsorbed preferentially, and that there is a definite sorption of the dyes even at pH values above 5, *i.e.*, on the alkaline side of the isoelectric point. The specific affinity of the dye ions accounts also for the ob-

servation that much more acid is sorbed at a given pH from the solution of a dye acid than from the solution of a common acid.

The adsorption of leuco salts, and of the salts of acid sulfate esters of the leuco compounds of the vat dyes, is governed by the same factors of specific affinity and electrical forces than the adsorption of direct dyes. A long chain of conjugated double bonds links the pair of ionic groups in both kinds of dye molecules.[69] The substantive naphthols likewise contain the long conjugated system.[69, 86] Salt concentration influences the adsorption of all these dyes in the same way as that of the direct dyes.

Cellulose and protein fibers exhibiting crystalline x-ray patterns retain them unchanged when dyed with direct and acid dyes, respectively.[44, 45, 8, 88] This proves that the dyes do not enter the crystallized regions. A further proof for this is the fact that the amount of dye taken up by cellulose fibers from the same dye bath is higher, the greater the capacity of the fibers for moisture adsorption. Therefore, mercerized cotton takes up more dye than native cotton, and regenerated cellulose take up more dye than mercerized cotton. To explain this, it is not necessary to assume any other difference between these fibers than that in the number of available sites for the dye ions. The only notable exception to this relationship is the take-up of direct dyes by cellulose at low salt concentrations. Here, the presence of carboxylic groups in bleached cellulose material may, through electric repulsion, decrease the amount of dye anions taken up by regenerated cellulose, such as cuprammonium or viscose rayon, below the amount taken up by native cotton.[28] Presence of sufficient concentration of salt suppresses the effect of the carboxylic groups in the cellulose and allows the adsorption of the dye to parallel the moisture regain of the fiber.

Different conditions prevail in the case of dyeing of cellulose acetate. The sorption of the dye does not occur on the walls of the water-filled submicroscopic channels, but homogeneously through the whole mass of the fiber. Therefore, solubility of the dye in the cellulose acetate (and in organic solvents generally) seems to be one of the characteristics of the dyes used for cellulose acetate.[90]

Particle Size of Dyes on the Fiber

After the dye molecule is adsorbed by the fiber it may undergo further changes during the subsequent treatment. In the simplest case, that of direct dyeing, this consists in drying alone; with other groups of direct dyes in after-treatment with heavy metallic salts such as chromium or copper compounds; with naphthols in coupling with diazo compounds; with vat dyes, in oxidation by air or by peroxides; with the acid sulfates of the leuco compounds in oxidative hydrolysis. With the three last groups a treatment with hot or even boiling soap or detergent solution precedes the final drying operation.

The reaction with chromium or copper salts, the coupling and oxidation, causes a chemical change in the dye molecule. Simultaneously with this chemical change and particularly in the course of the after-treatment, the dye undergoes certain physico-chemical changes which are the subject of this section.

Fibers which have adsorbed acid, direct and vat dyes or naphthols from the dye bath and have been dried but otherwise not after-treated, do not reveal the presence of dye particles under the microscope. Even after the oxidation of the vat dyes and the coupling of the naphthols, the dyes do not condense to microscopically visible particles in the fibers. However, when the fibers with the developed azo dye undergo the after-treatment with boiling water, in most cases the dye particles become microscopically visible.[25, 65, 4] Indigo readily forms aggregates in the fibers when after-treated with boiling water. With Indanthrene dyes, however, only protracted steaming under pressure yields microscopically visible particles.[4] Some azo dyes

which do not form microscopically visible aggregates after the usual after-treatment, do this likewise when steamed under pressure.[25]

Somewhat more information on the changes occurring during after-treatment was obtained by x-ray studies of heavily dyed cellulosic material.[88] It was found that the vat dyes could be classified into three groups according to whether they remained amorphous in the fibers, or formed crystallites only upon after-treatment with steam or water, or crystallized upon oxidation without being subjected to any after-treatment. Indanthrene Blue RS belongs in the first group. On the diagram of a cellulose film (cellophane) containing as much as 30 per cent of the dye, the only visible pattern is that of the undyed material, namely, that of mercerized cellulose. The diagram does not change when the material is subjected to after-treatment with boiling water or soap solution. The behavior of only one direct dye, Sky Blue FF, was investigated and yielded the same result. The cellulose film contained 20 per cent dye and the after-treatment was carried out with a concentrated solution with sodium chloride in order to prevent the removal of the dye. It is not unlikely that all direct dyes exhibit the same behavior.

The second group consists of dyes which are amorphous on the fiber after adsorption and oxidation, but form crystallites upon after-treatment. This type of behavior seems to be the most frequent with the vat dyes. A typical representative of this group is Caledon Jade Green. Only the lines due to the pattern of mercerized cellulose can be recognized after the oxidation of the dye. Following the customary after-treatment with boiling soap solutions, the diagram is a superposition of the pattern of the cellulose and of that of the dyestuff. Under the microscope, the dyed material remains completely homogeneous even upon after-treatment. The size of the crystallites does not exceed the limit of visibility. Estimated on the basis of the width of the diffraction rings, the radius of the crystallites is in the range of $5\text{–}10 \times 10^{-6}$ cm. While earlier microscopic studies showed that aggregation to very minute particles occurred only upon steaming for three hours upon 50 lbs pressure per sq in,[4] the x-rays showed that even mild after-treatment produced an aggregation to crystalline particles, which were microscopically invisible.[88] Another member of the group is Indanthrene Brilliant Scarlet RK. The shade of cellulose dyed with this dye is strongly shifted from yellow to red by after-treatment. The x-ray diagram reveals that the color change is due to the crystallization of the dye.[88, 85] Even soaking in cold water for several hours is sufficient to affect the crystallization, which with this dye yields microscopically visible particles.

Finally, the third group consists of dyes which crystallize in the cellulose fiber upon oxidation, even before they are subjected to any after-treatment. Only indigo could be identified by x-ray as a member of the group. Here treatment with boiling soap solution brings no change of the diagram. The presence of indigo crystallites has also been microscopically observed on the cellulose fiber, though only after treatment with boiling water. On wool, the appearance of indigo crystallites on after-treatment was recorded by x-ray.[8]

In order to understand the phenomena of aggregation of vat and naphthol dyes on the fiber, one should bear in mind that the sorption of naphthols and vat dyes, including the leuco ester salts, is due to molecular attraction between cellulose molecules and dye molecules. Crystallization of the dye prior to drying or oxidation and coupling respectively, is unlikely, because the dye bath is not supersaturated with dye. Through oxidation or coupling, however, the dye becomes insoluble and its attraction to the molecules of the fiber may change. Therefore, the presumably monomolecular layer of the dye on the wall of the submicroscopic pores of the fiber becomes unstable or metastable. Depending upon the strength of adhesion of the dye and its tendency to crystallize, the monomolecular film will be more or less easily disrupted and form aggregates of submicroscopic or even microscopically visible par-

ticles. Because the dye molecules cannot attain enough mobility for condensation unless the submicroscopic channels of the fiber are sufficiently open, swelling of the fiber must precede crystallization. High temperature promotes the crystallization probably by decreasing the adhesion of the dye to the molecules of the fiber, and this may also be the function of soap and other dispersing agents usually applied in the after-treatment.

The formation of crystalline particles in the fiber can proceed only after an enormous widening of the pores, even if the particles remain microscopically invisible. Consequently, the migration of the dye to the surface or, in the case of cotton, into the lumen, frequently accompanies the crystallization.

A few technically important aspects of the phenomena of the crystallization of the dyes on the fiber may be mentioned here.

(1) Alteration of the shade. There is generally an increase of the particle size connected with the crystallization of the dye in the fiber. With comparatively opaque dyes the original transparent color partially passes over into the reflection color due to the increased diffraction. Simultaneously, the absorption spectrum of the transmitted light changes,[85] since the environment of the dye molecule in the monomolecular absorbed state is different from that in the crystalline state. The effect of the environment in displacing the absorbed band of the dye may be attributed to van der Waals forces.[72]

(2) Dulling of rayon. This occurs only when the size of the dye particles exceeds a certain limit.[85]

(3) Fastness to light. In general, this increases upon crystallization, probably as a consequence of the diminished total surface of dye particles.

(4) Fastness to rubbing. The greater the tendency of the dye to crystallize, the lower is its fastness to rubbing. The fastness to rubbing can be diminished by excessive soaping.[4, 85]

(5) Tendering of cellulose fibers. The presence of some of the vat dyes causes an increase of the rate of degradation of cellulose under the influence of atmospheric conditions (light and oxygen). This catalytic effect of the dyes is generally reduced by crystallization. The effect probably depends on the contact of the dye molecule with the cellulose molecule and, consequently, with diminished total surface of the dye, is bound to decrease.[26]

Fig. 8 illustrates schematically the possible changes in the size of particles during the entire vat-dyeing process. On the top (A) is shown the particle of the insoluble dye in commercial paste or powder form. (At the magnification shown, only a segment of the assumedly spherical particle is sketched). Below this is shown (B) the dye as a leuco salt in solution. In this soluble form the dye is able to penetrate the submicroscopic channels of the swollen cellulose fiber, the average pore diameter of which is $4\text{-}6 \times 10^{-7}$ cm. Adsorption of the leuco compound gives rise to formation of a probably monomolecular layer on the wall of the pores. The thickness of the dye layer amounts to about 5×10^{-8} cm, corresponding to the thickness of the dye molecule. Except for extremely heavy shades, the monomolecular film is far from being a continuous one. This state is indicated by line (C) of the figure. The next line (D) illustrates the monomolecular film after oxidation, but before further after-treatment. The change concerns only the chemical structure of the dye ion, *i.e.*, the loss of electrons. On the collapse of this film during the after-treatment, dye particles are formed, the size of which in most cases remains below the limit of microscopic visibility, not exceeding 2×10^{-5} cm. Nevertheless, in most cases the size of these particles considerably exceeds the original diameter of the fiber pores. The bottom (E) shows the microscopically visible dye particles formed, *e.g.*, by after-treatment of Indanthrene Brilliant Scarlet RK.

The formation of crystallites recognizable by x-rays requires the agglomeration of at least about 1,000 dye molecules, while the particles of commercial paste and

powders contain dye molecules in the order of ten million. A still higher number of dye molecules are present in each microscopically visible particle.

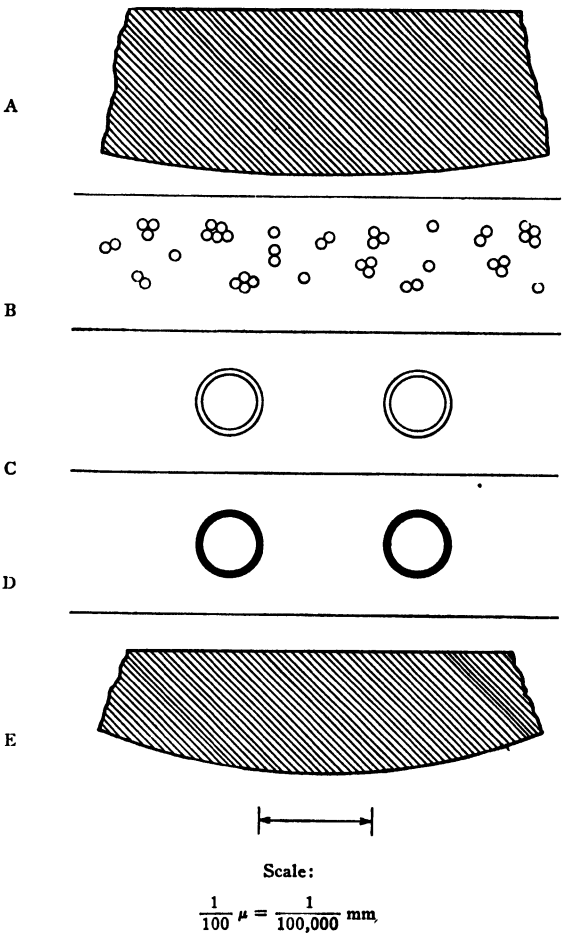


FIGURE 8. Schematic representation of the changes of the particle size of vat dyes during the subsequent dyeing operations. Explanation in text.

Level Dyeing

The problem of level dyeing of textiles was attacked from different angles, and some of the aspects have been satisfactorily elucidated. Two possible causes of the unevenness of dyeing must be distinguished, namely, the lack of uniformity of the fiber, made manifest by lack of uniformity either in the amount taken up at equilibrium or in the rate of diffusion of certain dyes in the fiber; and differences in the accessibility of the fibrous material, such as between the open and closely woven part of the fabric between the surface and interior of a thread, etc. It is evident that if the lack of uniformity consists only of a difference in speed of diffusion or in accessibility, prolonged exposure to the dye bath would lead finally to complete levelness of the dyeing. If, however, the lack of uniformity is due to a difference in the magnitude of the sorption at equilibrium, *i.e.*, due to a difference in the extent of available in-

ternal surface or difference of the attractive forces, even after an infinitely long dyeing period, levelness will not be obtained.

An example of the lack of uniformity of the textile causing unlevel dyeing, is that of wool partly exposed to the action of light and air. It has been shown that wool staple from the back and shoulder of the sheep dye unlevel, staple from the belly dye uniformly.[5] A correlation with the chemical constitution of the fiber was established by the finding that the sulfur content of the hairs which were exposed to light is reduced on the tip section and to a somewhat lesser extent in the middle section; however, it is unchanged in the root section.[41] The effect of this damage is different against different dyes, some giving darker, and some lighter dyeings on the exposed parts; this is probably because the exposure increases the speed of diffusion of the dye by allowing a greater swelling of the fiber, but, at the same time, it reduces the affinity of the dyes for the fiber.[55] The development of different hues on exposed and unexposed parts of wool, when level acid dyeings are after-treated with chromium in an acetic acid dyebath, is due to the presence of excess sulfhydryl and aldehyde groups in the exposed wool, which cause more complete reduction of the chromium compounds than is the case with unexposed wool.[55]

Where the tendency to unlevel dyeing is due to differences in the accessibility of the fibrous material, those dyes give the most uniform dyeing which have the highest rate of diffusion in the fiber, relative to their rate of exhaustion from the bath. The rate of exhaustion is again the result of two factors: the rate of diffusion in the fiber and the affinity of the dye to the fiber. Accordingly, those dyes give unlevel dyeing which combine high affinity with low rate of diffusion in the fiber. Such dyes tend to dye the cross-section of the fibers non-uniformly, but give a heavily dyed surface layer and an undyed core. The rate of the desorption of such dyes from the place of higher take-up is relatively low; consequently they require too long a time for the redistribution necessary for initial differences of the shade be leveled out. It seems that the magnitude of the activation energy of the diffusion of the dye in the fiber is the physical quantity which is mostly intimately related to the phenomenon of leveling. Since a high affinity of the dye is related to its better fastness against wet processing, a reasonable balance must be found between the properties of the dye in respect to its fastness and leveling. The selection of dyes in commercially branded series is the result of such a compromise between the two properties.

According to their ability to give even dyeings on viscose rayon, the direct dyes have been grouped into three classes.[6, 9, 91] In the first class are dyes with low substantivity and high diffusion speed in the fiber. These give level dyeing. In the second class are dyes with low substantivity and low diffusion speed. These level well in low salt concentration, but may cause lack of levelness at high concentration of salt necessary to obtain exhaustion of the bath. In the third class are dyes of high substantivity and low rate of diffusion. Only by carefully avoiding high salt concentration is level dyeing obtainable with these. At a constant temperature and salt concentration, different direct dyes show considerable variation in speed of diffusion, the range varying in a ratio of more than 2500:1 on viscose rayon yarn.

Similar conditions are met in acid wool dyeing.[77] High temperature promotes uniform distribution of the dye by reducing the affinity of the dyes and simultaneously increasing the speed of diffusion.[21] A further method of controlling the affinity of the dyes to the fiber, which is available here, is the adjustment of the pH. Addition of sodium sulfate is likewise often used to increase the levelness of the acid dyeing. The adsorption of the sulfate ions reduces the positive electric potential of the fibers and thus diminishes the Coulombic attraction of the dye anions.

As a result of the complex nature of the level dyeing process, the use of so called leveling agents is manifold and cannot be explained by a single mechanism. First of all, surface-active agents, as a consequence of their wetting action, promote a more uniform contact between fibers and dye bath by eliminating the air trapped between

the fibers. Goods which are completely free from fatty impurities do not require such a dyeing assistant, since they wet instantaneously with water. It is to be noted that, by the mechanism just mentioned, only the penetration of the dye solution between yarn and fibers can be promoted. As far as is known, the penetration into the single fibers is not influenced by reducing the surface tension of the dye bath. It is, therefore, preferable to exclude the wetting process from any consideration of the leveling action. If this is done, it can safely be said that the efficiency of the leveling agents is based on a reduction of the tendency of the dye molecules to deposit on the fiber. A distinction can be made between leveling agents possessing affinity for the fiber and those with affinity for the dye.[84] The leveling agents with affinity for the fiber achieve their effect by occupying the sites on the fiber which otherwise would be open to the dye molecules, while the leveling agents with affinity for the dye act by combining with the dye molecules in the solution. The first case is a matter of competition between dye and leveling agent for a place on the fiber, while in the second case fiber and leveling agent compete for the dye. From this point of view it is obvious that the leveling agent with affinity for the fibers does not need to affect the size of the dye particles in order to gain full efficiency, while those with affinity for the dye will generally affect the size of the dye particles by combination with the dye ions, and that in most cases results in an increase in particle size. In the special case of the ionically dispersed dye, leveling agents can only cause an enlargement of the particles. This opinion originated from the results obtained by studying the influence of the leveling agents on the size of the dye particles through diffusion experiments,[84, 74] and it is opposed to the idea frequently met, that leveling agents act by reducing the size of the particles in the dye.

Examples of leveling agents with affinity for the fiber are the higher molecular colorless anions applied in the acid dyeing of wool. These high molecular colorless anions, especially of sulfonic acids and acid sulfuric acid esters, compete with the dye anions for the available surfaces on the fiber, particularly also for the surfaces which due to their easy accessibility otherwise would adsorb too many of the dye anions.[51, 70, 71, 79] The colorless anions promote redistribution of the dye anions by replacing them temporarily on the fiber. This type of leveling agent functions in cellulose dyeing merely as wetting agent.[74] Examples of leveling agents with affinity for the dye are ligninsulfonic acid, dextrin, gelatin, polyglycol ethers of fatty alcohols, and high molecular cations, applied in the dyeing of cellulose fibers with direct and vat dyes.

Conclusions

In the foregoing a brief outline has been given of the results achieved by application of modern theories and methods to some aspects of the dyeing process. It is obvious that the complete field has not been covered. Among others, the field of mordant dyes [20] was omitted, partly because the present state of knowledge is still far from satisfactory, partly because the practical significance of this dyeing method has been extremely reduced in recent years. However, reference should be made to the advance made in recognizing the significance of co-ordinative valency forces acting between the chromium atom of the chromium complexes of dyes and the fiber molecules.[84, 16, 20] Omitted also is the field of textile printing, which in economic importance approximates or even surpasses that of dyeing. Practically no systematic investigation has been carried out as yet on the kinetics and the equilibrium of the printing process with soluble or solubilized dyes which, from the physico-chemical point of view, presents itself as a special case of dyeing characterized by a relatively high concentration of dye and electrolyte in the dye solution (printing paste), and a relatively short period of dyeing at high temperature (ageing).

The correlation between the size of dye particles and their behavior in dyeing played so dominant part in the earlier treatments of colloidal chemistry of dyeing

that it could not be ignored here. On the basis of experimental evidence and theoretical considerations, it is unlikely that the association of dye ions into larger aggregates can cause or even facilitate their sorption by the fiber, since aggregates of dye ions can hardly penetrate the submicroscopic pores of the fibers. It is more likely that these aggregates, when present in the dye bath, merely serve as a reservoir for the monomeric and possibly dimeric dye ions which alone can enter the fibers. It has been shown that under the conditions under which dyes form definitely colloidal particles, so that single or dimeric dye ions are not available in sufficient number, no commercially satisfactory dyeings can be obtained.[22] However, as a rule, dyes which exhibit a higher tendency for association (revealed by their particle size at low temperature and in the presence of high salt concentration) possess a higher affinity to cellulose fibers than those which exhibit lower tendency for association.[62, 63, 64] This can easily be explained by taking into account the fact that the tendency toward association is the indication for the ability of the dye for intermolecular attraction which is also the basis for the affinity of the dye for the fiber.[87] Likewise, the fact that increased concentration of salt increases the take-up of the dye and similarly increases the degree of association, can be explained by the assumption that the reduction of electrical repulsion between dye ions on the one hand, and between dye ions and fiber on the other, promotes both these types of molecular association.

The pigment printing processes have not been made yet the subject of fundamental investigations. It is probable that typically colloidal phenomena will be more significant for them than for the other textile dyeing and printing processes.

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Colloidal Factors in Laundering

ROBERT A. PHAIR

H. Kohnstamm and Co., Inc.

COLLOIDS IN LAUNDERING

Even a superficial study of the chemistry of laundering shows that much of it lies in the realm of colloids. The fibers themselves are colloidal; the attraction between the fabrics and the staining or soiling material in the range of colloidal phenomena. Sizing materials are largely colloidal in nature. Water carries in suspension or in sol form, iron, manganese, clay and organic matter. The calcium and magnesium present form colloidal precipitates with most of the water softening compounds and with many of the detergents used. Even the forces which hold many of the dyes on the fabrics are in the colloidal range. There remains much to be done before the complete picture of the chemistry of laundering is clear. We will make no special attempt here to study washing methods, but will show some of the interesting effects on the fabric of certain compounds in the washing or as brought out by the washing. Since cotton constitutes more than 90 per cent of the goods washed, most of our attention will be directed to the washing of goods made of this fiber.

DESTRUCTIVE ACTION OF ACIDS ON COTTON

Mineral Acid Sour and Formation of Circular Destruction

In the processing of cotton in bleacheries, mineral acids are used as "sours" to decompose traces of hypochlorite and to remove metallic contact stains. Non-destructive acids are used as "sours" in steam laundry practice for neutralizing alkali and for removal of stains. The effect of acids on cotton is an important phase of laundering.

The destructive effect of strong or moderately strong acid solutions on cotton is well known. It has not been so well recognized that under certain circumstances, concentrations as low as $1/200N$ can cause considerable damage to cotton. Clayton [1] in his study of laundry sours has found that low concentrations of strong acid can cause tendering when the cotton containing it has been ironed at 205° C.

A study of the causes of certain damages to cotton fabrics reported by Phair and Lukash [2] showed further cases where very small concentration of strong acids caused great damage. Many of these damaged pieces were destroyed around the outside rim of a circle; the inside was intact and almost unaffected. This damage was duplicated by soaking cotton muslin in a $1/200N$ sulfuric acid solution, wringing out and drying uniformly. If the fabric is ironed at this stage, the damage will be relatively slight and uniform over the whole piece. However, if a few drops of water are dropped on the fabric and allowed to spread until it will spread no more, ironing at 200° will cause the fabric to be carbonized and destroyed around the edge of the wet area, leaving the center practically unaffected. If the cotton is dried after the drops of water have been allowed to spread and then ironed, the same result will be obtained. Where much weaker solutions of acid are used, the damage is less,

but it can be detected around the outside of the wet area by the Fehling's solution test. On laundering such pieces the weakened cotton eventually gives way entirely, leaving a more or less circular hole with sharply cut edges.

It would appear that the acid in the fabric is dissolved by the water and carried to the periphery of the water "spot" by the peripherally rushing capillary streams. Furthermore, since the water is preferentially absorbed by the cotton, the acid should become more concentrated as it spreads. The water "spot" generally dries before there is any marked backward diffusion from the periphery toward the center. If insufficient time is allowed for the drops of water to spread to their maximum, the damage is confined to a band around the inside of the wet area instead of a sharp line.

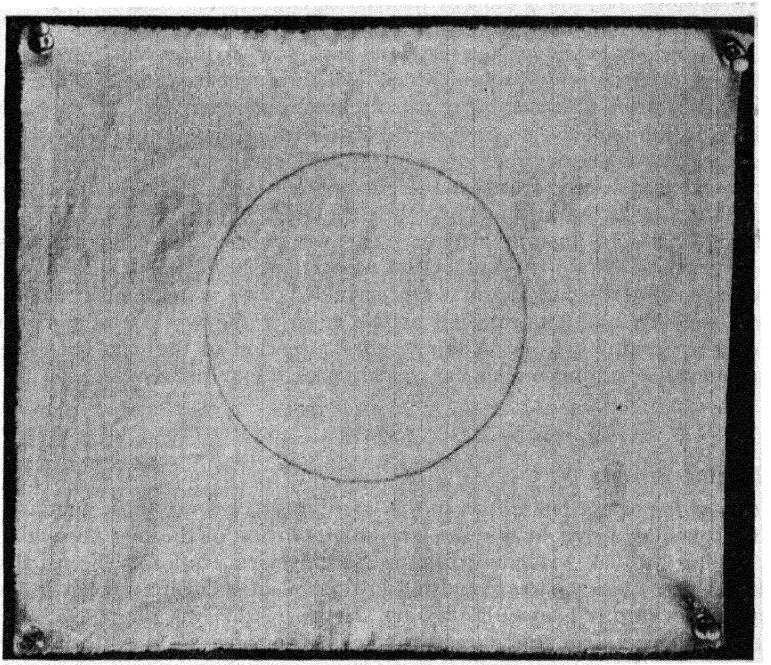

FIGURE 1. The effect of spreading water on dry fabric containing a small amount of sulfuric acid. Concentration of the acid at the rim of the drop is shown by carbonization under the heat of the ironing.

A review by M. Samec [2a] of the literature on the adsorption of acids by cotton shows no uniformity of results. The effect of concentration seems to be very great. Our work was done with much more dilute acid than that used by other investigators. S. Lepatov [3] has shown that cotton has little or no adsorption for dilute acids; in fact, for some acids, including sulfuric acid, cotton has a negative adsorptive coefficient. In other words, the cotton actually swells, absorbing water from the dilute acids, thus concentrating the acid as its solution spreads.

Since bleacheries use sulfuric acid or sometimes hydrochloric acid as a "sour," it is very important that the acid be thoroughly rinsed out. Even if the amount of acid present in the fabric be very small, any contact with water might cause a concentration of acid at the periphery of the wet area, and cause damage on long standing.

Solutes tend to follow moving water streams and to become concentrated at surfaces where the water evaporates.[3a] A familiar example of this is the white in-

crustation found on the surface of ordinary red bricks. The rain dissolves calcium sulfate in the brick, and as the brick dries, capillarity causes the calcium sulfate to come to the surface and crystallize there.

Another example of this transport to the surface of loosely held soluble material is found in some laundry blues when used under conditions unsuited to them. For instance, if a so-called sour blue, fixed on the fabric at a pH 6, is used at pH 8, blue trouble is apt to develop. When wet garments so blued are placed on the heated press, the unfixed blue migrates to the heated surface where evaporation is taking place. This is apparent particularly in the seams or neckbands and pockets and gives very unsatisfactory results.

"Winter Damage"

Similarly, we find another example in the so-called "winter damage," which caused such serious losses in New England and New York in the winter of 1924-25. This damage occurred only to "wet wash," which is sent from the laundry in a damp condition to be dried at home, being usually hung outside to dry. Where the fabrics were dried in the laundry, no such damage resulted. Some of the affected garments showed the characteristic lines of sulfuric acid similar to those described above. It was found that winter frosts and slight precipitations scrubbed from the air the sulfurous acid from the burning of sulfur-containing fuels, and this sulfurous acid became sulfuric acid upon oxidation. The wet fabric also could be expected to absorb directly a certain amount of the acid atmospheric impurities. When these fabrics were allowed to dry and were sprinkled with water before ironing, as is usually done, the acid concentrated at the edge of the wet areas and caused the damage upon ironing. J. B. Wilkie [4] called attention to the catalytic acceleration of iron and other substances on the oxidation of the sulfur dioxide.

Soaps

The Washing Process

The most important operations in the washing process are those containing soap. Lennox [5] has shown that by far the largest proportion of the dirt present in a load of work being washed is removed in the first sudsing operation. The usual washing formula calls for a succession of sudsing operations of sufficient number to insure the elimination of the dirt before the rinsing starts.

The function of soap seems to be a combination of wetting, with deflocculation, or lubrication and suspension effects. Soaps possess these powers to an extraordinary degree. The alkali salts of the phosphoric acids and silicic acid possess suspension effects without having wetting or deflocculating powers comparable with soaps. The addition of these products to soaps in proper amounts improves the cleansing effect, probably by a combination of at least two factors. The alkali undoubtedly restrains the soap from hydrolyzing and forming less active hydrolysis products. Furthermore, the anionic portion of the builder may have specific properties which may aid in the overall effect. We know that the silicic acid in sodium silicate is usually present in colloidal form and aids in the suspending action of the soap. As will be mentioned later on, the salts of polyphosphates can sequester calcium and magnesium in the water so that they will no longer precipitate out the soap. The orthophosphates have an appreciable water-softening power as well as a certain amount of ability to suspend dirt and emulsify oils.

Alexander [6] has shown that there is a zone of maximum colloidality for colloidal dispersions. Soaps seem to function best within their zone of maximum colloidality. These zones vary depending on the fatty acids in the soap, concentration, salting out effects, temperature and other factors. If we take a 10 per cent solution of a soap made from a solid fat, such as tallow, and vary the temperature from 20 to 100°, the

solution will be a gel at the lower temperatures. At the higher temperatures the sol will be extremely thin. At neither of these two temperatures does the soap function best. The temperature at which tallow soap functions best is approximately 70°. Coconut oil belongs to the class of low-titered oils; that is, the solidifying point of its melted fatty acids is below 30°. Such low-titered soaps have their best effect lower in the temperature scale and can be used in cold or lukewarm water.

"Soap Specks"

As can be expected from the fact that soaps are compounds of long chain aliphatic acids and bases, they possess important colloidal properties. Since the long chain or non-polar portion of the molecule is in the anionic part, soaps are anionic detergents. As much of the dirt to be removed carries a positive charge, if an insufficient amount of soap is used, the suds "break down" and "soap specks" are caused. In the worst cases, the amount of suds in the wash-wheel may have seemed ample in the beginning. Later on, however, the amount of suds will be greatly reduced and may disappear entirely. This may be caused by the neutralization of the charge on the soap particles by the opposite charge on the dirt. Such "soap specks" can be avoided by making certain that there is always a sufficient excess of anionic detergent.

Insoluble flecks of soap and dirt are important sources of trouble, and may be caused in several other ways. Thus, if the water contains sufficient calcium or magnesium which has not been precipitated or sequestered, the dirty soap will be rendered insoluble and form dirt-soap specks. As there is usually enough soap present in the sudsing operations to keep the insoluble soaps deflocculated, the "soap specks" do not show themselves in those operations but do show in the rinses.

If the temperature of a soap bath is allowed to rise much above the optimum point, "thinning out" occurs. "Soap specks" can be caused by this reduction of suspending power resulting from too high a temperature. When the dirty soap solution is heated above the thinning out temperature, soap and dirt are precipitated as "speck." Here again the trouble is more apt to occur in the rinses, where only a small amount of soap is present. This particular type of "soap speck" can be avoided by using soap at its proper temperature and and using enough soap operations to ensure removal of all the dirt before rinsing.

Similarly, under certain conditions, the gray soap-dirt compound is precipitated in a fine dispersion instead of forming specks. This causes graying of the work. To maintain the proper whiteness, sufficient hypochlorite is usually used to bleach out whatever gray soap-dirt deposit has been formed.

Generally speaking, the lower-titered soaps are more soluble, rinse out better, and are less affected by salt or hardness. The higher-titered soaps give a larger volume of suds and have better suspending power. There is a place for each type in the laundry.

Action of Hypochlorites on Cotton

Effect of Amount of Hypochlorite on Fabric

Sodium hypochlorite is used in the washing of white cotton and linen fabrics to remove resistant stains and to whiten the fabric. It is often used, as well, for removing stains in laundry work that is classified as being "fast color." Small amounts of hypochlorite with temperatures under 65° do not cause any undue amount of cellulose degradation. However, where larger amounts of "bleach" are used, especially at higher temperatures, considerable modification of the cellulose occurs. This oxycellulose has much less resistance to further oxidizing action of the hypochlorite than the original fabric. Much of the bleaching power is then used up on the fabric, leaving less for stain removal. This makes it very difficult to cut down

the quantity of hypochlorite used when large quantities have previously been used, since such a reduction is usually apparent at once in reduced stain removal and whiteness of the fabric. Such a reduction of bleach to save tensile strength losses must be accomplished gradually if the quality of the laundry work is not to be sacrificed.

Action of Alkali on Oxycellulose

The modified cellulose formed by action of hypochlorite adsorbs considerable alkalinity, which is not readily removed by rinsing. If this alkalinity is not neutralized, there will be formed on ironing a yellow or brown compound that will destroy the whiteness of the work. This is one of the reasons for the use of a sour after the washing and rinsing operations. The neutralized oxycellulose, in the next wash, takes up alkali from the soap and alkalies present in the first operation, making it necessary to compensate for such loss in alkalinity of the bath by adding more alkali.

This modification of cellulose causes it to take on changed characteristics. Since practically all white laundry work contains more or less oxycellulose, it is not safe to assume that experiments done in the laboratory with pure cellulose will be duplicated in the field. For instance, basic colors such as methylene blue are taken up and hold to a much greater degree than in the case of cellulose itself.

Effect of pH of Bleaching Bath on Tensile Strength and Stain Removal

Sodium hypochlorite has a considerably higher oxidation potential at higher temperatures and at lower pH, than at lower temperatures and higher pH. The hypochlorite can be expected to act more vigorously at pH 10 than at pH 11. However, in this laboratory it was found that at pH 11 and higher, the bleaching effect, although slower, acts more selectively; that is, the less resistant stains were attacked to a greater degree because the bleach was not consumed by the fabric. There is also less tensile strength loss if the bleaching is carried out at pH 11 than if carried out at pH 10.

Action of Hypochlorite on Chlorine Absorbing Resins and Finishes

Many years ago, Cross and Bevan [7] published an experience covering the destruction of partially bleached linen fabrics due to the formation of insoluble slowly decomposable chlorine compounds from nitrogenous matter present. Recently, a number of new products have been introduced into the textile industry. Some of the most popular of these materials are finishing, stabilizing and crease-proofing resins of the urea-formaldehyde type. Similar resins had also been recommended at that time for binding the pigments to the fabric in textile printing. A considerable amount of this finishing agent was used in shirtings prior to 1940. The writer found that these resins combined with chlorine from hypochlorite solutions to form chloramine compounds which did not rinse from the fabric, and were similar in many respects to those reported by Cross and Bevan. In this case, hydrochloric acid was formed by the decomposition of the chloramine compound by the subsequent ironing. The fabric was severely hydrolyzed and its value destroyed. It was found that such trouble occurred only where bleaching and subsequent operations were carried out at low temperatures. Higher temperatures in these operations decomposed the chloramine compounds and no hydrochloric acid was produced on ironing. This damage also occurs where chlorine-absorbing resins are used in the vehicle for textile printing.

Action of Metal Catalysts on Fabrics in Bleaching Bath

Very small quantities of copper and larger amounts of iron can act as catalytic agents and cause a great acceleration of the bleaching effect of hypochlorites.[8] For

this reason it is quite essential to remove copper or iron stains from fabrics which are to be subjected to washing operations which include treatment with hypochlorite. Otherwise, the life of the fabric may be shortened or holes caused. This catalyst removal is one of the functions of the laundry sour.

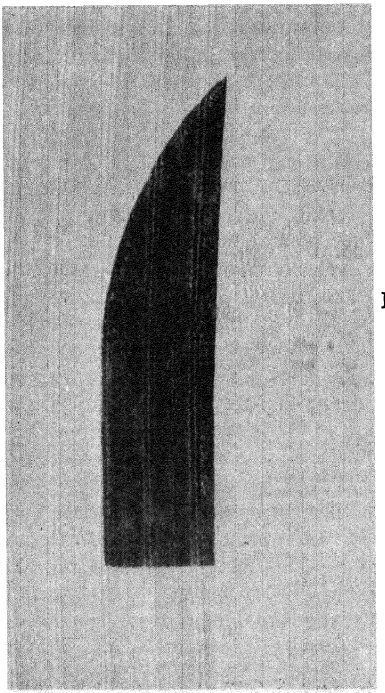

FIGURE 2. The effect of a hot iron on shirting finished with a urea-formaldehyde finish, which had been washed with a laundry formula containing hypochlorite. A piece of unsized muslin similarly washed and ironed was not affected.

ACTION OF SILICATES IN KEEPING COLLOIDAL IRON COMPOUNDS FROM THE FABRIC

In 1935, Kind reported that the presence of silicate of soda in the washing operation gave the clothes a whiter appearance. Some have even held that this was due to the adsorption of silicon dioxide on the fabric. The silicate of soda has a large effect in keeping ferric hydroxide and other positively charged colloids in suspension, whereas in its absence these positively charged compounds would be adsorbed by the negatively charged fabric, causing discoloration. This suspending action is stronger at pH 10 than at pH 12, probably because the silicate at the lower pH is much more colloidal and hence more effective. Within recent years, the silicates have taken an increasingly important place among soap builders in the laundry. Iron is almost always present in laundry water and small amounts can have a large part in causing loss in whiteness.

OILY STAINS, THEIR EFFECT ON COTTON AND THEIR REMOVAL

Oxidation of Fabric Caused by Oils

The author has reported that certain oils such as cotton or corn oils do cause an oxidation of the cotton fabric, if these oils are allowed to remain on the fabric for some time before washing. The damaged cotton reacts to the Fehling's solution and methylene blue tests in the same way as the oxycellulose resulting from the overbleaching of cotton. Work done in this laboratory demonstrates that the oil

on the fabric first increases its peroxide content without affecting the fabric to a great extent. However, after the peroxide content has reached its peak, the loss in tensile strength of the fabric proceeds with a simultaneous reduction of the peroxide content. It would seem that the spontaneous combustion which sometimes takes place in oily rags may be due more to the actual oxidation of the rags themselves by the peroxides of the oil than to the heat of oxidation of the oils themselves. Salad dressings, salad oils, and other products containing saponifiable oils often cause holes or tendering on tablecloths when allowed to remain on them for some time without washing.

Refined Corn Oil

	Peroxide Value (Wheeler Method) in Millimoles	Tensile Strength (after removal of oil by washing) in lbs/in
Original Oil	3.00	—
Original Fabric	—	70.2
After 3 days exposure to light indoors	26.1	68.2
7 days	57.6	67.7
11 days	306.	61.8
14 days	773.	59.5
18 days	693.	48.2
21 days	553.	48.0
25 days	405.	46.2
28 days	355.	43.5

Coconut Oil

	Peroxide Value (Wheeler Method) in Millimoles	Tensile Strength (after removal of oil by washing) in lbs/in
Original Oil	3.4	—
Original Fabric	—	69.3
After 2 days exposure to light indoors	4.3	67.5
4	6.9	67.3
11	19.2	67.2
18	29.6	63.3
25	24.2	60.0
32	23.4	54.0
39	18.8	50.2
46	18.2	47.2

Colloidal Clay and Its Use in Oil Removal

The ancient fullers of wool found that fuller's earth could be used for the removal of grease from raw wool. Colloidal clays such as bentonite are now used for cleansing very oily or greasy materials such as wiping rags and mechanics' overalls. Apparently, the clays have a superior adsorptive power for the oil, in comparison with the fabric. It is interesting to note that a good cleansing operation will remove the oil from the fabric and not allow it to redeposit on the buttons of the overalls or on the metal of the wheel. The bentonite colloid has such a strong affinity for the oil that the oil will not redeposit.

Solvent Soaps

Pickering[9] has found that soap solutions themselves have some solvent action on oils. This solvent action is sometimes increased by admixture of some solvent such as pine oil, carbon tetrachloride, or petroleum solvents. In certain cases where oil stains resist the action of the washing formula, solvent soaps may be used with good results. When these solvent soaps contain sufficient soap to emulsify thoroughly the solvent that they contain, additional soap to that which would have been required without the use of the solvent soap is not necessary. However, if there is an insufficient amount of emulsifier present in the solvent soap, it will consume soap, and then more soap will have to be added.

Newer Detergents

It has been recognized for many years that soap has many serious disadvantages in addition to its many excellent characteristics. The fact that soap is precipitated by hard water and is decomposed by acids limits the conditions under which it may be used. The first development along the line of improving these unfavorable characteristics was Turkey red oil. This was made by the action of sulfuric acid on castor oil. The improvement was only partial and it was accompanied by a loss in cleansing power per unit of fatty acid present.

Turkey red oils were followed, after a considerable period, by the alkyl-naphthalene sulfonates which included the Nekals and similar products. These products had good wetting power but little detergent action. In recent years, the progress has been increasingly rapid. Today, the number of these products is legion. They have been synthesized by balancing the various hydrophilic groups with lyophilic groups to produce compounds having the desired properties as nearly as possible.

These detergents may be divided into three general classes: (1) anionic; (2) non-ionic; and (3) cationic.

In the first class, the long chain aliphatic group, primarily responsible for the detergent properties, may be found in the anionic part of the molecule. Similarly, the cationic class has the long chain in the cation portion. Those detergents which do not ionize belong, of course, to the non-ionic group.

Cleansing compounds of the anionic class are the most common and are compatible with soap since soap also is anionic. The non-ionic compounds are compatible with both anionic and cationic compounds.

The cationic compounds reduce the sudsing and cleansing power of the anionic compounds. Since cotton carries a negative charge in the washing operation, cationic detergents tend to be substantive because of the mutual neutralization of charges. This may be an advantage where a small amount of cationic finishing compound is almost completely adsorbed by the cotton and thus produces a finishing result. But if we want rather to cleanse the fabric, this substantivity is a decided disadvantage, not only because of the constant weakening of the cleansing bath caused by the adsorption of the cationic compound but also because the adsorption may fix the dirty detergent to the fabric and cause greying.

Many cationic products are substituted ammonium salts which combine with hypochlorites to form insoluble chloramine compounds. Since cationic products are also used in finishing, care should be taken that no destructive chloramines are formed, where the finished goods are subjected to bleaching in the household or laundry.

In general, it can be said that for the usual cleansing job, soap is most economical and has the advantage over the newer detergents. Soap functions in a number of different ways, among which are penetration, deflocculation or lubrication, suspension, and, according to Pickering, by solvent power. The newer detergents possess these properties in various degrees. Some are good wetting-out agents having good penetrant power, but do not possess much deflocculating power. Others have sufficient suspending power to carry off the dirt, but do not have great penetrant power. Many possess great lime and acid resistance whereas others do not. It is essential to pick the right product for the job. Since these products are more expensive than soap, they find increasing use in those fields where their special advantages warrant the extra cost.

Sequestering Polyphosphates

Usually when hard water must be used in the washing bath, some water-softening agent is added to prevent or reduce the precipitation of insoluble calcium or magnesium soap. These water-softeners usually throw down the hardness in the form

of more or less insoluble precipitates, which tend to react with the soap to form insoluble soaps, especially with the higher titered soaps which form the most insoluble lime and magnesium soaps.

This problem was approached from another angle. If the hardness producing elements could be sequestered in the form of complex ions so that they would not precipitate soap, the problem would be largely solved. Sodium hexametaphosphate was found by Hall [10] to have this sequestering effect. In fact, the hexametaphosphate actually dissolves precipitated insoluble soaps from the fabric, regenerating the active sodium soap.

Sodium tetraphosphate was also found by Bryan and Fiske [11] to possess very strong sequestering power on both calcium and magnesium. It has a higher pH than hexametaphosphate, which is an advantage for laundry purposes.

Tetrasodium pyrophosphate acts similarly, although it is principally effective on the magnesium and less so on the calcium. Since calcium is usually present in much greater amount than magnesium, the total effect of the pyrophosphate is considerably lower than that of the hexametaphosphate and tetraphosphate.

In the competition between soap and the newer detergents, it will be of interest to note the extent to which these sequestering phosphates will maintain the present position of soap.

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Phycocolloids: Useful Seaweed Polysaccharides

C. K. TSENG

Scripps Institution of Oceanography of the
University of California, La Jolla, California

Phycocolloids [2] are algal polysaccharides derived from brown and red seaweeds, able to form colloidal systems when dispersed in water. Earlier, they were variously called "vegetable isinglass," "vegetable gelatin" or "seaweed glue." In recent years these terms have not been in general use, since we now know that they are not nitrogenous compounds as was first thought. They have come to be more popularly known as "seaweed gums" and "seaweed mucilages" instead, as the gums and mucilages are derived from plant sources and are also polysaccharides.

There are, however, certain important differences between gums and mucilages from land sources and the seaweed polysaccharides, although they do resemble each other superficially (cf. Norman, 1937). Generally speaking, the gums and mucilages are polyuronides, containing more than one type of monosaccharide unit, whereas the seaweed colloids contain a single type of monosaccharide unit, and, with the exception of alginic acid, are not polyuronides. Although alginic acid resembles the gums in being a polyuronide, it is unique in being exclusively composed of mannuronic units.

Phylogenetically, the primitive marine plants known as brown and red algae, from which we obtain our commercial seaweed colloids, are not directly related to the modern land plants from which the gums and mucilages are derived. There are therefore numerous differences between the seaweeds and the land plants in their chemical constitution and their assimilation products. For instance, it has been well established in recent years, that chlorophyll *b* is not present in the brown and red algae, which have, instead, chlorophyll *c* and *d*, respectively.[3] The kinds of reserve food of these seaweeds are also different from those of the land plants. Similarly, the seaweed colloids, which are mostly cell-wall constituents, are, as might be expected, different from their counterparts in the land plants. Thus it is not inappropriate to treat them separately and to divorce them from gums and mucilages: hence the new term *phycocolloid*.

In fact, several decades ago, Marchand (1879) proposed a similar term "phycocolle" for the so-called "Japanese isinglass," now known as agar. Marchand's term means "seaweed glue" and carries a somewhat different meaning from "phycocolloid." Another term, "gelose," was proposed by Payen (1859) to designate the refined extract from "mousse de Chine" under which name agar was known when first introduced into France from China. Payen's "gelose" and Marchand's "phycocolle" are therefore synonymous. Later authors use the term gelose to designate all

[1] Contributions of the Scripps Institution of Oceanography, New Series No. 252.

[2] From Greek φῦκος (seaweed) and κόλλα (glue) + -oid.

[3] Strain, H. H., and Manning, W. M., "Chlorofucine (Chlorophyll γ), a green pigment of diatoms and brown algae," *J. Biol. Chem.*, **144**(3) 625-636 (1942). Manning, W. M., and Strain, H. H., "Chlorophyll d, a green pigment of red algae," *J. Biol. Chem.*, **151**(1), 1-19 (1943).

the gel-forming substances derived from the red algae, including carrageenin. The term, however, should be restricted to these jellifying substances and should not be applied to all of the seaweed colloids, since some of them, the alginates for instance, are not strictly gel-forming substances.

While seaweeds have long been utilized for various purposes (Tressler, 1923; Chase, 1942; Dillon, 1943; Tseng, 1944b), their organic extracts, the seaweed colloids, have been more recently introduced as commercial articles. The economic importance of these substances has been constantly rising in recent years, and there are indications that they will soon occupy an even more prominent place among the industries. Thanks to the efforts of scientists, we have now some idea as to the chemical nature and physical properties of these unique substances. Nevertheless our present knowledge of the phycocolloids is still far from complete. Any attempt at a classification of these substances is therefore premature. It is quite certain, however, that there are at least two general groups: the alkali-soluble polyuronides of the algin type, and the water-soluble substances as represented by agar and carrageenin, which are ethereal sulfates of varying degrees of complexity (Norman, 1937). The sources, preparation and uses of the seaweed colloids have been briefly reviewed by various authors (Field, 1920; Tressler, 1923; Chase, 1942; Dillon, 1943; Scheffer, 1943; and Tseng, 1944a, b, and c, 1945). Their properties and chemical nature have also been reviewed by Clayton (1932), Norman (1937), Gortner (1937), and Hassid (1944).

Historical and Terminological

Agar

The first phycocolloid discovered and prepared as a purified extract was undoubtedly agar. In the form of a sweetened and sometimes flavored gel, agar has been known in the Oriental countries for ages. It was, however, not until the middle part of the seventeenth century, presumably in 1658, when the process of purifying and dehydrating agar in its present form was accidentally discovered by an inquisitive and ingenious Japanese innkeeper, Tarozaemon Minoya, according to a story quite commonly accepted by the Japanese agar manufacturers. Minoya happened to note one morning that some of the agar jellies which he had thrown outdoors and which had evidently frozen the night before, had thawed and dried in the sun to become translucent, membranous, porous flakes. Thus, the method of making agar utilizing natural freezing, thawing, and drying was evolved, which to date is still being used by the majority of the Japanese agar manufacturers. Even in the so-called modern process, while some mechanization has been introduced, the fundamental principles of extraction and purification are still the same.

This gelatin-like substance is extracted principally from the red seaweed *Gelidium Amansii*. It is known in Japan as "kanten," meaning "cold weather," an allusion to its being made only in winter, and in China as "tungfen," meaning "frozen powder." The word "agar," which we now use to designate this product from Japan and China, is neither Japanese nor Chinese. It is Malayan, and is used in the double form agar-agar, as names in that language are usually repeated. It originally referred to certain seaweeds, especially *Euchcuma muricatum* of the East Indies, and to a less extent, also to the jelly made from this seaweed (Tseng, 1944a). The story of how the Malayan term came to be applied to the Japanese product has, to the writer's knowledge, never been told. The writer has reason to believe that it probably came about in this way: The Chinese immigrants to the East Indies imported the Japanese kanten to the East Indies for their own use—as they usually do with other food articles when they settle in other countries. Later, they also sold some of this product to the natives. To avoid introducing a Japanese or Chinese name, they merely called it agar-agar, which term was also used by the Malayans to apply to seaweed jellies in general. The Dutch and other Europeans in the East Indies eventually learned to use this Japanese product for making fruit and vegetable jellies, and finally when

they went home, they introduced the art of making agar jellies to their friends and relatives in Europe. Thus a Malayan term became permanently attached to a Japanese product.

It may be of some interest to note that agar was first introduced into France by M. de Montravel in 1856 (Payen, 1859). It was then called "mousse de Chine" (Chinese moss) and later "Japanese isinglass." Payen initiated the term "gelose" to apply to the jellifying principle, as noted above, and until the early 1920's agar was called by various names. In Germany, however, Reichardt (1876), Bauer (1884) and others had already consistently used the term agar as we are using it now.

Agar was still very little known when Koch first used it as a culture medium for his famous experiments on tuberculosis bacteria. Undoubtedly Koch himself did not realize the significance of the discovery of this new medium as an epoch-making technical improvement. He disposed of the introduction of this new material to the bacteriological laboratories by a single, insignificant sentence, in his now classical preliminary note on the tubercle bacillus (1882): "So wachsen sie beispielsweise auf einer mit Agar-agar bereiteten, bei Blutwären hart bleibenden Gallerte, welche einen Zusatz von Fleischinfus und Pepton erhalten hat." The idea of using agar as a medium for bacteriological culture was actually first conceived by a housewife, Frau Fanny Eilshemius Hesse (Hitchens and Leikind, 1938, 1939). Frau Hesse had been using agar in her kitchen for years in the preparation of jellies, and was fully aware of its value as a gelatin-substitute. It was said that she received the recipe from her mother, who in turn had obtained the formula from some Dutch friends formerly living in Java. Evidently when her husband, Dr. Walther Hesse, complained about the difficulty of using gelatin in cultivating pathogenic microbes, she suggested that he try agar instead. The success in such a trial was communicated to the great Robert Koch by letter probably late in 1881. A few years after Koch formally announced the use of agar as a new culture medium, this curious seaweed product penetrated the bacteriological culture rooms throughout the world. From kitchen on one hand, and the bacteriological laboratory on the other, agar worked its way into science and industry until it reached its present stage of prominence among the colloids.

Carrageenin

From another red alga, *Chondrus crispus,* more popularly known as carrageen [4] or Irish moss, another gelatin-like substance is extracted. Among the several names applied to this gelose,[4] carrageenin seems to be the most appropriate from the point of view of both simplicity and explicitness. So far as the writer's information goes the term was first used by Stanford (1862).

In many ways the carrageenin of the Occidentals corresponds to the agar of the Orientals, both serving similar purposes in their respective dietary. Agar, however, has been made as a purified extract for almost three hundred years, whereas it is only in recent years that carrageenin has been extracted on a large commercial scale. Undoubtedly because of its high percentage of the colloid, as much as 79 per cent on a dry weight basis according to some investigators, the ground and powdered carrageen will serve most purposes, and there was no necessity to go to the trouble of preparing the extract. In fact, even now, the large proportion of the carrageen product on the market is still in the form of bleached entire plants or powder.

This gelatin-like substance was first extracted from *Chondrus crispus* by C. Schmidt (1844). There is no definite information concerning the time when carrageenin was actually commercially extracted from the plant. In 1871, a United States

[4] Carrageen is sometimes spelled "carragheen," and "carrigeen." It is preferred to the more popularly used name "Irish moss" for simplicity and to avoid using the word "moss" which refers to a group of small land plants. Carrageenin, the extract, is also known as "Irish moss extract," "*Chondrus* polysaccharide," "carrageen extract," and "*Chondrus* extractive."

patent was granted to Gustave Bourgade for extracting this colloid by the alcohol-precipitation method. This appears to be the first described method for extracting carrageenin on a large commercial scale. Previously, a few patents had been granted for preparing carrageen for the market (Weild, 1866; Rand, 1869a and 1869b), but they all dealt with methods of packing and powdering the seaweed.

Whether Bourgade actually started commercial production of the carrageen extract by his patented method is not known. In the early days there was not much demand for a really pure product, and commercial extraction of the colloidal substance would probably be unsuccessful financially. It is only in recent years, when certain industries require a highly purified carrageenin without the accompanying undesirable odor and taste of the powdered seaweed, that there has been a market for such a purified product. In the last few years, several U. S. patents have been granted for processing it.

Funorin

In the Orient, plants belonging to the red algal genus *Gloiopeltis,* especially *G. tenax* and *G. furcata,* have long been utilized as a sizing material for textiles and paper (Turner, 1809; Suringar, 1872; Tseng, 1933, 1935, 1944b). The thalli contain a very high percentage of a gluey principle, which is very soluble in water. When the plants are left in lukewarm water they soon disintegrate and go into solution almost completely, without leaving any significant amount of residue behind. There is, therefore, no necessity of isolating this colloidal substance for general commercial uses, at least for the time being. In recent years some research has been conducted on the chemical nature and physical properties of this mucous substance (Aoki, 1935-38 and Yanagawa, 1937). While there is still no definite knowledge about its chemical constitution, there is little doubt of its being a polysaccharide. It is probably more closely related to carrageenin than to agar. To this gluey substance present in *Gloiopeltis,* or funori in Japanese, the term "funorin" has recently been applied in order to keep the nomenclature of the seaweed colloids uniform (Tseng, 1944b).

Algin

Undoubtedly many beach-lovers have noticed, from time to time, huge piles of kelp washed up on the beach. Many have also noticed that, after a rainy day, "blisters" are formed on the kelp frond, which contain viscous fluid. Some have further noticed that after being left in the sun for some time, the viscous fluid becomes jelly-like and scatters over the surface of the frond. But, up to 1883, no one ever thought of this as being of any commercial significance. In 1883, however, the ingenious English chemist and seaweed industry promoter, Edward C. C. Stanford, recognized the possible value of such a substance. He undertook a series of experiments and found that this kelp exudate,[5] when moist, was miscible with water but coagulated by alcohol and by mineral acids. When evaporated to dryness it became insoluble in water, but was very soluble in alkalies. Hence he arrived at an alkali-extraction method in which the kelp was macerated for 24 hours in sodium carbonate in the cold. The resulting glutinous mass was very viscous and was filtered through a coarse linen sack. The solution when evaporated to dryness presented "an appearance which is not unlike gum tragacanth," and was called "algin," derived from the word "alga."

[5] In view of the fact that algin probably occurs *in situ* (cf. *infra*) as the insoluble calcium alginate, it is not improbable that the substance contained in the viscous fluid is not algin, but rather the water-soluble laminarin. In the extraction of algin, Stanford subjected the entire kelp to soda digestion, and evidently took it for granted that the algin thus extracted was the same substance as that present in the viscous fluid of the "blister." The writer is not aware of any critical investigation on the chemical nature of this particular substance. It is quite definite, however, that the "blisters" on the fronds of *Laminaria* were responsible for attracting Stanford's attention, and eventually led to the discovery of algin.

Stanford further discovered that, if a mineral acid was added, a gelatinous precipitate was obtained, which dried to a hard, horny substance. This was first thought to be "algin" in its pure insoluble form, but later (1884) it was correctly identified as a new acid, to which Stanford gave the name alginic acid. Stanford had confidence in the great commercial possibilities of algin and its derivatives and carried out extensive investigations to determine the properties and possible uses of his products. Later, he started manufacturing algin on a commercial scale in Scotland. Unfortunately for Stanford the time for extensive applications of alginic products was not yet ripe. There was evidently not enough market for his products. Moreover, these were crudely prepared, as shown by their nitrogen contents, and the cost of production was high. Consequently his enterprise was not financially successful. Stanford, however, had sown the seed of a new industry. In the few decades that followed, more and more was learned about the manufacture and uses of algin and its derivatives. It was not until the last decade or so, however, that the algin industry became a reality and achieved commercial success.

When the term "algin" was first introduced, Stanford (1883) used it to designate the "unique substance of remarkable properties" present in the viscous fluid found in the blisters or sacks formed on the surface of kelp plants when they were soaked in fresh water. Strictly speaking, therefore, algin refers to the natural state of this substance as it occurs in the kelps. While little is definitely known yet about the condition of the algin *in situ,* it has been assumed by some to exist naturally as the calcium salt of alginic acid (Kylin, 1915; cf. Norman, 1937). On other occasions Stanford also referred to algin as being "insoluble in water" and "very like horn," which implied that he had the acid, instead of its salts, in mind. In discussing its applications, however, he used the term to refer expressly to the soluble sodium alginate. It is in the latter sense that the term "algin" is used in commerce today, although it is self-evident that sodium alginate does not occur in the plant *in situ.* In a broader sense, algin refers to all alginic compounds, the acid and its salts all included.

Laminarin

Of the other polysaccharides now known to occur in seaweeds, laminarin has considerable possibilites in industrial applications and has received much attention in recent years. Laminarin was discovered by Schmiedeberg in 1885. It is now known to be the reserve carbohydrate of the brown algae, although it differs considerably in properties from the starches of the land plants. A United States patent was recently granted to LeGloahec and Herter (1940) on a commercial process for extracting laminarin by treating the seaweed with an alkaline-earth metal salt such as calcium or barium chloride.

Chemical Analysis of Phycocolloid Seaweeds

The useful seaweeds utilized in the commercial production of phycocolloids, their habitats, and the methods of harvesting and drying some of them are illustrated in Figures 1-16.

Agarophytes

The gelose content of agarophytes or agar-bearing seaweeds has long attracted the attention of chemists. Simmonds (1857) reported an analysis of *Gracilaria lichenoides* (*Fucus amylaceus*) by Professor O'Shaughnessy as follows: 54.50 per cent vegetable jelly, 15.00 per cent true starch, 18.00 per cent ligneous fiber, 6.50 per cent sulfate and chloride of soda, 4.00 per cent gum, and 1 per cent sulfate and phosphate of lime. Another analysis of the same plant was reported by Greenish (1882). The important constituents are: 15.07 per cent moisture, 7.48 per cent albuminoids,

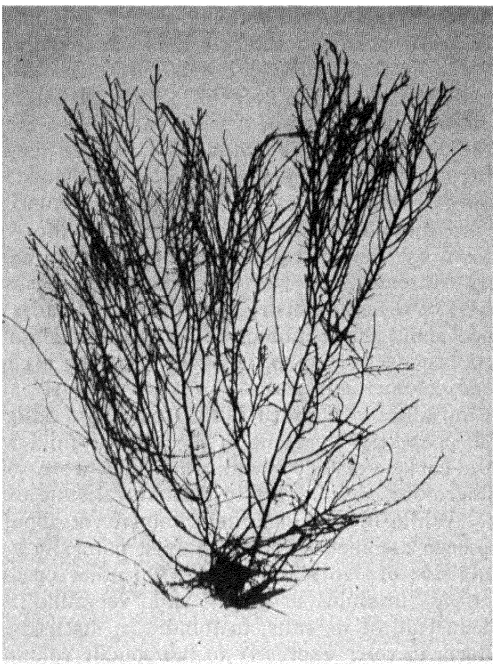


FIGURE 1. *Gelidium Amansii.* A young female plant of the principal oriental agarophyte from Tsingtao, China. About half natural size. (*Courtesy of "The Scientific Monthly."*)

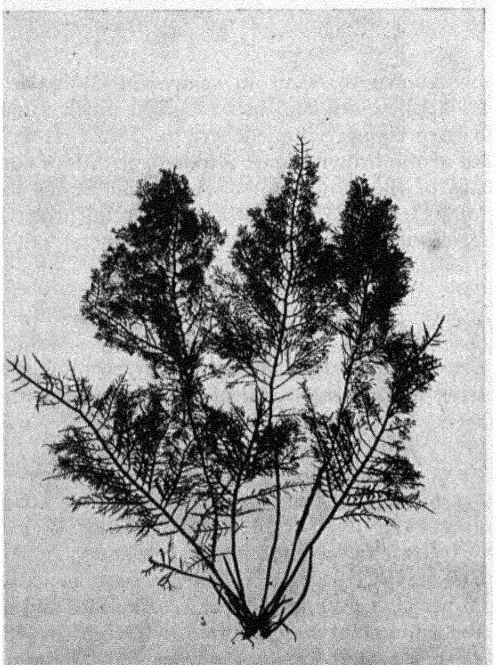


FIGURE 2. *Gelidium cartilagineum.* A young female plant of the principal American agarophyte from La Jolla, California. About one-fourth natural size. (*Courtesy of "The Scientific Monthly."*)

Figures 2, 3, 4, 5, 6, and 7 were published previously in *The Scientific Monthly* with the courtesy of The U. S. Fish & Wildlife Service. The author wishes to thank the Service for the privilege of re-using them in the present article.

FIGURE 3. Habitat of *Gelidium cartilagineum*. (*Courtesy of "The Scientific Monthly."*)

FIGURE 4. *Gelidium* diving boat. (*Courtesy of "The Scientific Monthly."*)

FIGURE 5. Life-line tender hauling in a basketful of *Gelidium* harvested by the diver. (*Courtesy of "The Scientific Monthly."*)

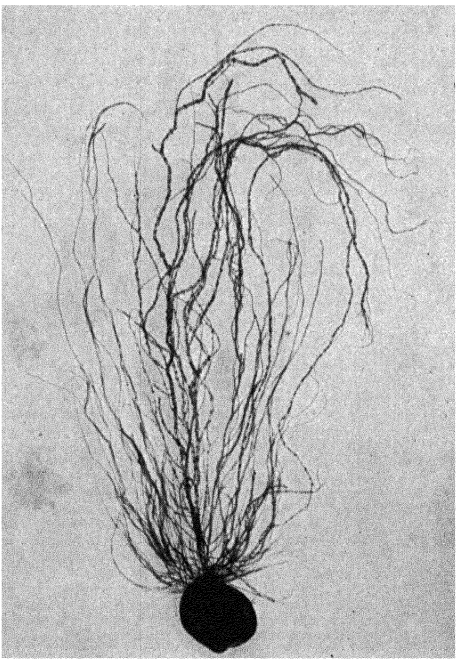


FIGURE 6. *Gracilaria confervoides.* A female plant of another important American agarophyte from San Diego, California. About one-fourth natural size. (*Courtesy of "The Scientific Monthly."*)

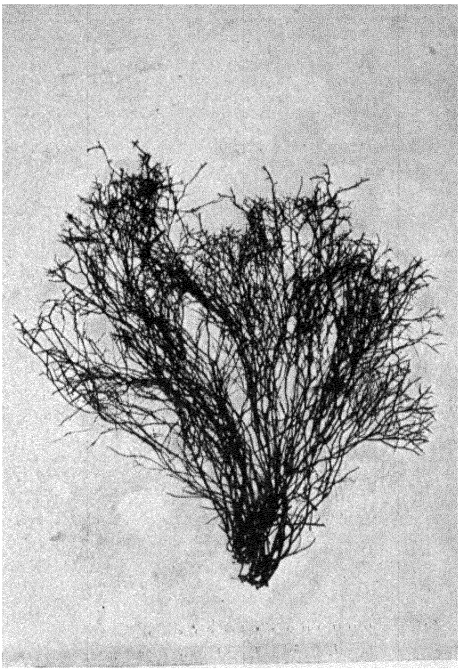


FIGURE 7. *Gelidium nudifrons.* An asexual plant of the "hair agar," from Laguna Beach, California. About one-fourth natural size. (*Courtesy of "The Scientific Monthly."*)

10.24 per cent ash, 36.71 per cent gelose which he called metarabin, 4.17 per cent wood gum, and 10.17 per cent cellulose. *Gracilaria lichenoides,* commonly known as Ceylon moss, and botanically known under several synonyms, such as *Fucus amylaceus,* is one of the classifical agar-bearing seaweeds, and has been used for ages by the Asiatics in jelly making. König (1884) reported analyses of a few Oriental agarophytes by himself, Kellner, and Nagai and Murai. A later report by Matsui (1916) on the analysis of three Japanese agarophytes is summarized in Table 1. Miyake and Hayashi (1939) reported a recent analysis of air-dried *Gelidium Amansii* as follows: 11.83 per cent moisture, 4.24 per cent ash, 0.69 per cent ether extract, 8.67 per cent acid or alkali-soluble substances, 15.03 per cent total N, and 54.54 per cent soluble, non-nitrogenous compounds.

Table 1. Analysis of Three Japanese Agarophytes, Based on Dried Materials (Matsui)

	Tengusa (*Gelidium Amansii*) (%)	Yegonori (*Ceramium hypnaeoides*) (%)	Ogonori (*Gracilaria confervoides*) (%)
Ash	4.23	3.04	3.54
Lime	0.28	0.48	0.39
Magnesia	0.52	0.94	0.84
Alumina	....	0.45	0.55
Nitrogen	2.01	2.19	0.69
Crude protein (N × 6.25)	12.56	13.67	4.29
Fiber	17.89	12.25	4.32
Galactan	23.70	24.88	22.14
Pentosan	2.30	5.19	1.21
Methyl pentosan	0.93	2.13	0.97
Reducing sugars after hydrolysis with dil. acid	23.20	48.38	45.20

So far as American agarophytes are concerned, the only published records are those of Field (1921), who reported the gelose content of the following species of

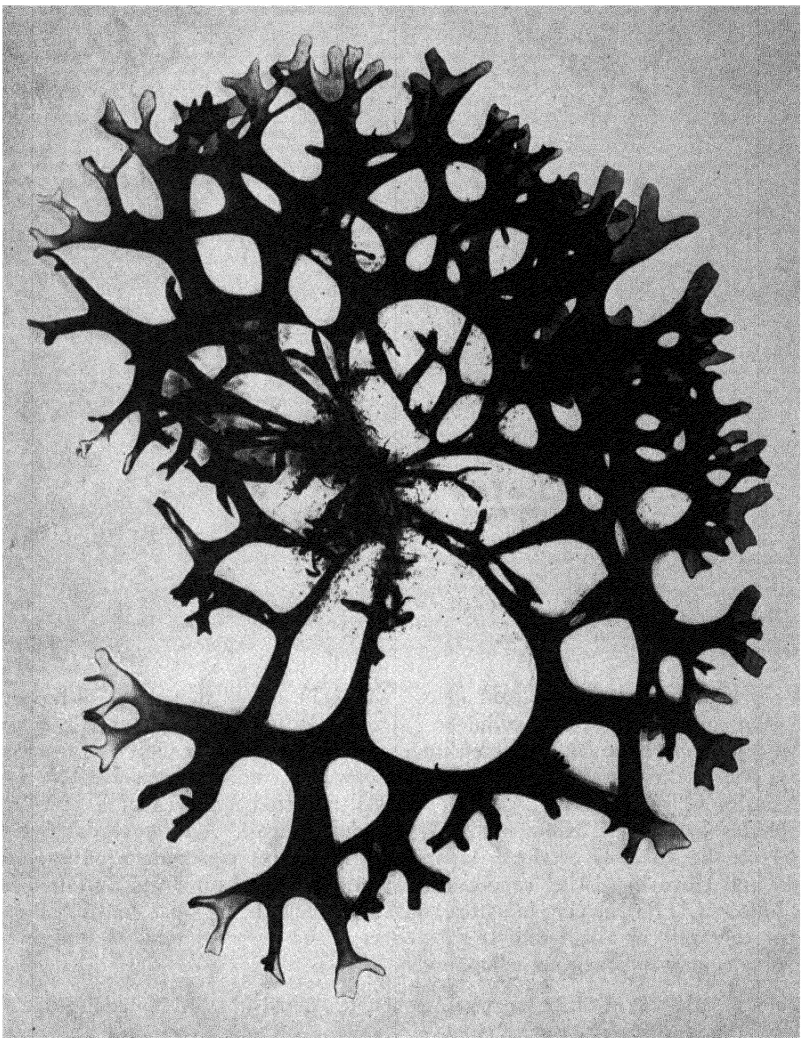


FIGURE 8. *Chondrus crispus.* An asexual plant of carrageen, or "Irish moss," from Hingham, Massachusetts. About natural size. (*Courtesy of "The Scientific Monthly."*)

Gelidium from California, based on sun-dried weight as follows: *G. cartilagineum* 40 to 45 per cent, *G. Amansii*[6] 28.9 per cent, and *G. australe*[6] 32 to 37 per cent. Recently three samples of California agarophytes were analyzed by C. F. Lee of the U. S. Fish and Wildlife Service. The results of the analysis are presented in Table 2. The reducing sugars are dextrose equivalents of Cu_2O precipitate. In (a), direct hydrolysis was made of dry plant with dilute HCl; and in (b), the plant was washed

[6] According to Gardner (1927) the Pacific American *"Gelidium Amansii"* is not that species, but rather *Gelidium pyramidale*. This species, however, more correctly belongs to the genus *Pterocladia,* hence it should be *Pterocladia pyramidalis*. The California *"Gelidium australe"* of the early American authors is also found to be different from the Australian species and is renamed by Gardner (1927) *Gelidium pulchrum.*

in cold HCl first to remove calcium, soaked in water, and then hydrolyzed with dilute acid. In the direct determination of the phycocolloids, the samples were extracted three times with distilled water under reflux, boiling at least two hours for each extraction.

Table 2. Analysis of Three California Agarophytes, Based on Sun-dried Materials (C. F. Lee)

	Gelidium cartilagineum (%)	*Gelidium nudifrons* (%)	*Gracilaria confervoides* (%)
Moisture content	9.31	10.07	8.07
Ether extract	1.04	0.85	1.04
Protein (N × 6.25)	25.5	15.4	14.3
Crude fiber	11.1	10.2	5.8
Reducing sugars (a)	25.0	26.4	37.7
Reducing sugars (b)	21.5	27.7	19.6
Total ash	7.39	5.59	10.78
HCl insoluble ash	0.21	0.25	2.98
Calcium	0.944	0.280	0.302
Magnesium	0.428	0.635	0.504
R_2O_3 (NH_4OH ppt.)	0.11	0.22	2.35
Phycocolloid, Direct	33.9	50.0	37.7

FIGURE 9. Carrageen harvesting boat, showing a harvester at work. (*Courtesy of The United States Fish and Wildlife Service.*)

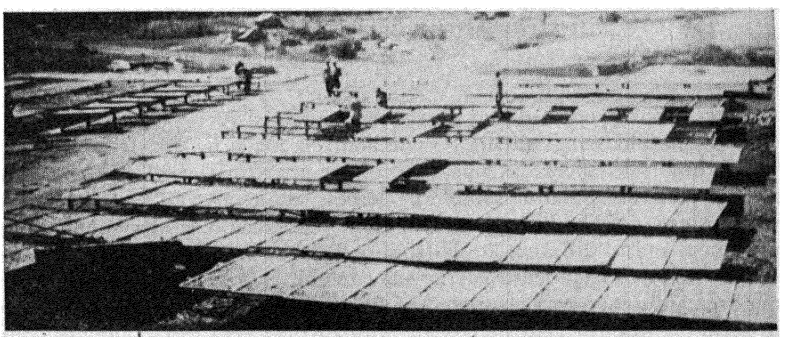


FIGURE 10. Carrageen drying ground, Scituate, Massachusetts. (*Courtesy of The United States Fish and Wildlife Service.*)

Very little is known concerning seasonal fluctuations of agar content of agarophytes. According to Aoki (1940), agar content of *Gelidium Amansii* is highest in spring and lowest in summer.

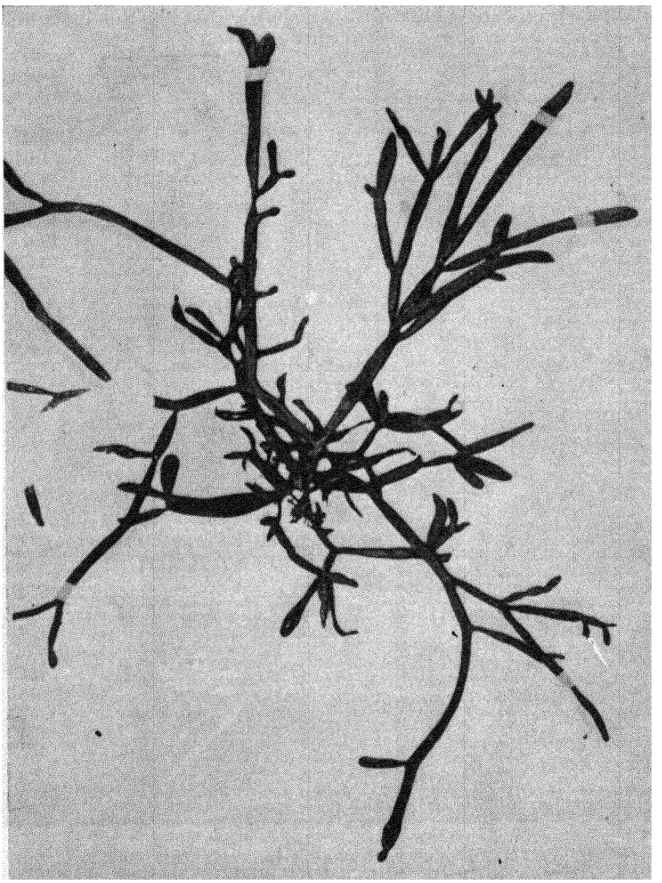


FIGURE 11. *Gloiopeltis furcata.* An asexual plant of funori from Chekiang, China. About natural size.

Carrageen

Simmonds (1857) reported that carrageen contained 77 or 78 per cent of "mucilaginous and gelatinous ingredients." The analysis made by Dr. Davy showed that it contained three substances: 28.5 per cent of a gummy matter soluble in cold water, 49.0 per cent gelatinous matter soluble in boiling water, and 22.5 per cent insoluble matter. Stanford (1862) introduced the term carrageenin to designate the gelatinous substance, and to differentiate it from ordinary gum and gelatin. Analysis by Field (1921) showed that fresh carrageen contained 79 to 80 per cent water, and the water-free substance was composed of 65 per cent gelatinous matter, 2 to 3 per cent nitrogen, 0.7 to 1 per cent lipoids and 10 to 15 per cent ash. The ash contained calcium oxalate, sodium, potassium, and magnesium with chlorine, bromine, iodine, and sulfur. Haas and Hill (1921) reported that air-dried carrageen contains 2.54

to 18.20 per cent moisture, 70 to 75 per cent carrageenin, and on the average, 14.6 per cent ash and 1.93 per cent nitrogenous matter.

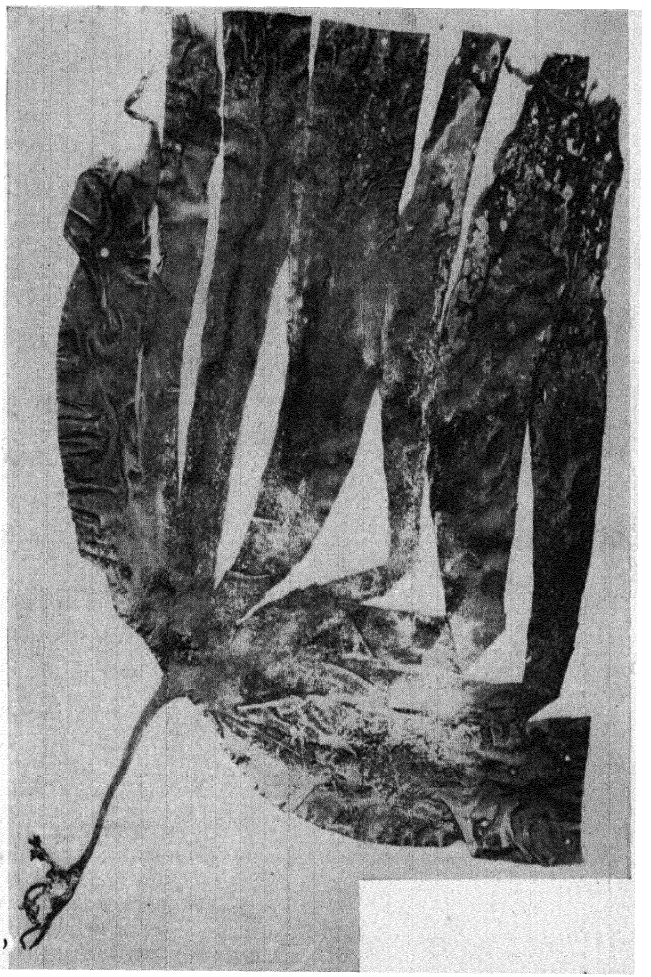


FIGURE 12. *Laminaria digitata.* An important American alginous seaweed. Horse tail kelp from Penikese Island, Massachusetts. About one-fifth natural size. (*Courtesy of Professor Wm. Randolph Taylor.*)

Butler (1936) found definite seasonal variations in the protein, ash and carbohydrate content of *Chondrus crispus.* While carrageenin contains calcium and sulfate radical besides the carbohydrate, the last mentioned is present in such a predominant percentage as to make it safe to assume that the seasonal variations of the carbohydrate also indicate similar variations in the carrageenin content. The carbohydrate content reaches its maximum in July, being about 82 per cent of the whole plant. Then it gradually drops until it is lowest in the period from January to April, falling to almost 61 per cent. After April, the trend reverses, and the carbohydrate content rises steadily until July.

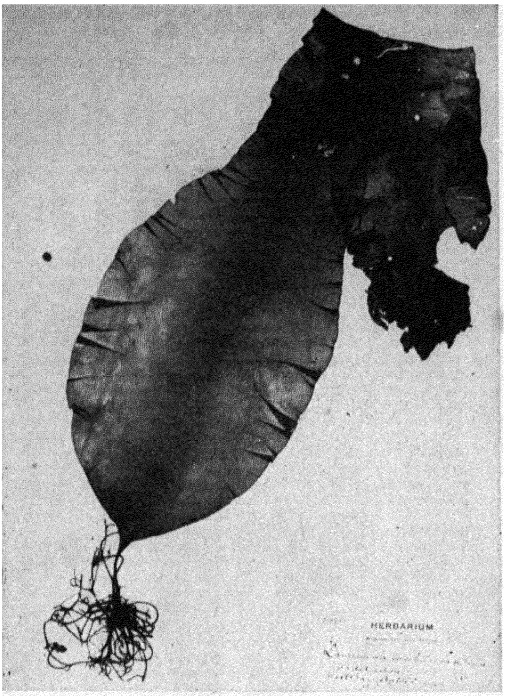


FIGURE 13. *Laminaria saccharina.* An important American alginous seaweed. Broad leaf kelp from West Barnstable Dunes, Massachusetts. About one-fifth natural size. (*Courtesy of "The Scientific Monthly."*)

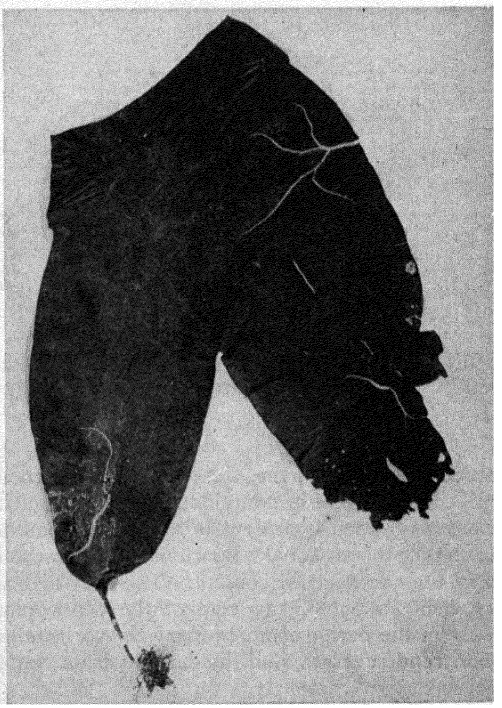


FIGURE 14. *Laminaria japonica.* An important oriental alginous seaweed. Young Japanese kelp plant from Chefoo, China. About one-fifth natural size. (*Courtesy of "The Scientific Monthly."*)

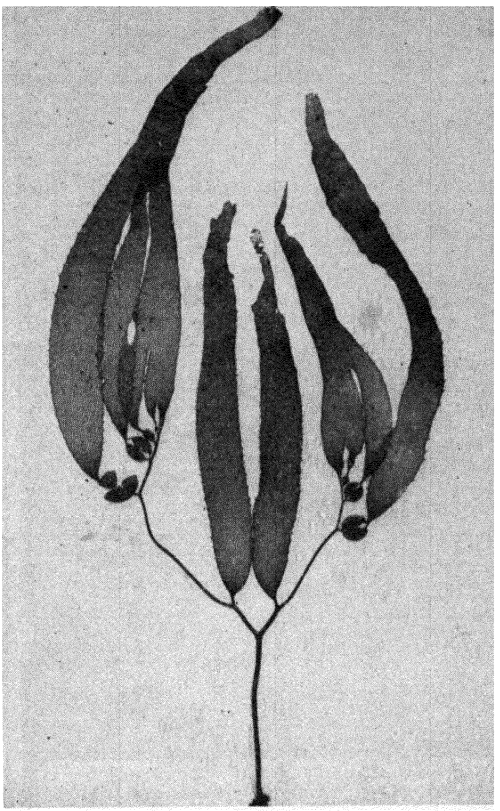


FIGURE 15. *Macrocystis pyrifera.* The principal American alginous seaweed. Young giant kelp plant, about four months old, from La Jolla, California. About one-fifth natural size. (*Courtesy of "The Scientific Monthly."*)

Funori

While funori or *Gloiopeltis* has been used extensively as a sizing material in the Orient for ages, it is only in recent years that it has been studied chemically. The two principal species and their manufactured products have been analyzed by Yanagawa (1937), the results being summarized in Table 3.

Table 3. Analysis of Gloiopeltis, Based on Air-dried Material[7] (Yanagawa)

	G. tenax I		*G. furcata* II		III		IV		Average II-IV	
	Plant	Product	Plant	Product	Plant	Product	Plant	Product	Plant	Product
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Fat	0.04	0.01	0.02	0.02	0.07	0.02	0.04	0.04	0.04	0.03
Protein	11.00	8.25	14.69	14.25	17.69	13.75	16.69	14.19	16.36	14.06
Fiber	0.78	1.25	1.36	1.69	1.56	2.31	1.22	1.76	1.38	1.92
Ash	14.32	16.21	13.48	16.11	13.27	19.09	12.21	18.99	12.99	18.06
Carbohydrate	60.93	62.83	61.21	56.53	61.77	58.43	57.81	57.83	60.26	57.60
Total sulfate	18.55	18.22	14.91	17.30	10.52	13.80	15.79	15.01	13.74	15.37
Sulfate in ash	5.62	6.77	5.69	5.90	4.88	7.40	3.76	7.82	4.78	7.04

[7] "Plant" refers to the sun-dried *Gloiopeltis* while the "product" is bleached and partially fermented.

Table 4. Analysis of California Coast Kelps (Hoagland)

Alginous Seaweed Used	Number of samples analyzed	Percentage composition calculated to fresh material									Percentage composition calculated to a water-free basis							
		Moisture	Total salts	Total organic matter	Nitrogen X 6.25	Ether extract	Crude fiber	Pentosans	Water sol. alcohol precipitate	Sodium carbonate sol. acid ppt. (Algin)	Total salts	Total organic matter	Nitrogen X 6.25	Ether extract	Crude fiber	Pentosans	Water sol. alcohol precipitate	Sodium carbonate sol. acid ppt. (Algin)
Macrocystis pyrifera Harvestable portion San Diego	8	86.3	5.24	8.45	1.02	0.046	0.98	1.06	0.91	2.56	38.2	61.7	7.4	0.34	7.2	7.7	6.6	18.7
Macrocystis pyrifera Harvestable portion Pacific Grove	4	87.7	5.28	7.00	1.65	0.049	0.93	0.77	1.07	1.77	42.9	56.9	13.4	0.40	7.6	6.3	8.7	14.4
Macrocystis pyrifera Non harvestable portion San Diego	8	87.7	5.16	7.11	1.33	0.054	0.89	0.98	1.08	2.15	42.0	57.8	10.8	0.44	7.2	8.0	8.8	17.5
Nereocystis Luetkeana Entire plant Pacific Grove	4	91.7	4.52	3.74	0.90	0.088	0.42	0.53	0.71	1.17	54.5	45.1	10.8	1.06	5.1	6.4	8.6	14.1
Pelagophycus porra Entire plant San Diego	2	89.7	5.43	4.91	0.77	0.028	0.64	0.87	0.60	1.66	52.7	47.7	7.5	0.27	6.2	8.4	5.8	16.1
Egregia laevigata Entire plant San Diego	2	83.7	5.78	10.52	1.89	0.144	1.47	1.60	1.48	3.04	35.5	64.5	11.6	0.88	9.0	9.8	9.1	18.7
Egregia Mensiesii Entire plant Pacific Grove	3	83.6	5.48	10.88	2.82	0.110	1.43	1.48	0.90	3.14	33.4	66.3	17.2	0.67	8.7	9.0	5.5	19.1
Laminaria Andersonii Entire plant	1	78.5	5.70	15.80	3.22	0.40	2.24	2.15	0.37	4.90	26.5	73.5	15.0	0.65	10.4	10.0	1.7	22.8

FIGURE 16. *Macrocystis pyrifera.* Leafy parts of fronds floating on water. (*Courtesy of the United States Fish and Wildlife Service.*)

Kelps

Reports on the chemical analysis of kelps are mostly concerned with the potash and iodine contents. Stanford (1883) reported that air-dried *Laminaria stenophylla* contained 30 per cent water-soluble substances, 5 per cent acid-soluble matter, 35 per cent algin, 10 per cent cellulose and 20 per cent moisture. Hoagland (1915) conducted an important investigation of the organic constituents of kelps from American Pacific coast. The results of his analysis are summarized in Table 4.

Rigg (1916) calculated the amounts of potassium chloride, iodine, algin, etc., in a ton of the fresh giant kelps from the data given by Cameron (1915), Frye (1915), Rigg (1915), Hoagland (1915), and Turrentine (1912). His figures for the two alginous kelps are given in Table 5.

Table 5. Content in Pounds of a Ton of the Fresh Fronds of Two Giant Kelps (Rigg)

	Water	KCl	Iodine	Other salts	Algin	Crude Fiber	Nitrogen
Nereocystis Luekeana	1834	53.7	0.22	25.1-37.7	23.4	8.4	2.9
Macrocystis pyrifera	1736	52.5	0.61	26.7-55.7	44.4	19.3	4.3

As shown in Tables 4 and 5, algin content of kelps varies from plant to plant, and from one plant part to another. Table 6 summarizes the varying algin content of various algae from various sources (Tressler, 1923).

Hoffmann (1939) summarized the algin content of several European alginous seaweeds, based on the work of Lunde and his associates. The percentage of algin

Table 6. Algin Content of Various Algae, on Water-Free Basis

Name of Alga	Plant Part	Algin (%)
Macrocystis pyrifera	leaves	16.2
Macrocystis pyrifera	stems	18.2
Nereocystis Leutkeana	leaves	14.4
Nereocystis Luetkeana	stems	13.6
Pelagophycus porra	leaves	16.1
Pelagophycus porra	stems	15.9
Egregia laevigata	entire plant	18.7
Egregia Menziezii	entire plant	19.1
Laminaria Andersonii	entire plant	22.8
Laminaria digitata	stem	33.3
Laminaria digitata	leaves	31.9
Laminaria stenophylla	stem	39.2
Laminaria stenophylla	leaves	40.1

on the basis of sun-dried material is as follows: *Laminaria digitata* 15 to 40 per cent, *L. saccharina* 15 to 35 per cent, *Alaria esculenta* 30 to 35 per cent, *Fucus serratus* 18 to 28 per cent, *F. vesiculosus* 18 to 28 per cent, *Himanthalia lorea,* in the winter, 38 per cent.

Kelp also contains, besides algin, large amounts of laminarin. The occurrence of these polysaccharides is, however, not limited to kelp. Some non-kelp brown seaweeds are found to be good sources for these substances. Colin and Ricard (1930) analyzed fifteen species of brown algae and found that, while algin occurs in all except three, laminarin is present in only five of them (Table 7).

Table 7. Algin and Laminarin Contents of Brown Seaweeds (Colin & Ricard)

Name of plant	Date of Collection	Laminarin		Algin	
		% fresh weight	% dry weight	% fresh weight	% dry weight
Laminaria flexicaulis	4-8-28	10.9	42.3	3.8	14.7
L. saccharina	5-10-29	19.4	49.0	4.8	12.1
Chorda filum	3-9-28	0	0	1.5	14.3
Fucus serratus	21-9-29	3.7	17.1	3.5	16.2
Ascophyllum nodosum	28-9-29	1.2	4.3	5.2	18.6
Himanthalia lorea	7-8-29	0	0	0	0
Bifurcaria tuberculata	7-8-29	0	0	0	0
Halidrys siliquosa	22-8-29	0	0	3.0	10.6
Pelvetia canaliculata	27-8-29	0	0	5.2	11.4
Cystoseira ericoides	7-8-29	0	0	1.3	7.8
Dictyota dichotoma	7-8-29	0	0	0	0
Padina pavonia	20-9-29	0	0	0.9	5.0
Dictyopteris polypodioides	20-9-29	0	0	1.8	11.0
Taonia atomaria	8-8-29	0	0	1.0	—
Asperococcus bullosus	9-8-29	0	0	0.9	6.7

Both algin and laminarin show definite seasonal variations. Dillon (1943) reported that algin content of *Laminaria digitata* gathered on the Irish coast is highest in March, being about 31 per cent of the plant, and lowest in September, being only about 16 per cent. Laminarin, on the other hand, reaches its maximum (about 24 per cent) in September and its minimum (less than 1 per cent) in March and April (Fig. 17). These observations are in general agreement with the results obtained by Lunde (1937) for plants of the same species gathered off the Norwegian coast.

Dillon (1943) also reported that species, closely related they may be, differ in the nature of the seasonal variation of their polysaccharide content. In another species, *Laminaria Cloustonii,* the maxima for both constituents are reached somewhat later. This kelp has its highest algin content (about 23 per cent) in May and its lowest (about 13 per cent) in September; its laminarin content is highest (about 18 per cent) in October, and lowest (about 2 per cent) in June (Fig. 18).

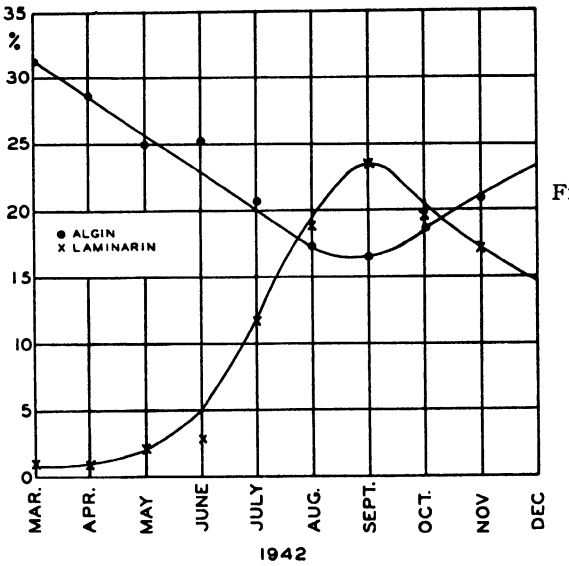


FIGURE 17. Seasonal variations of algin and laminarin in *Laminaria digitata*. (After Dillon, 1943).

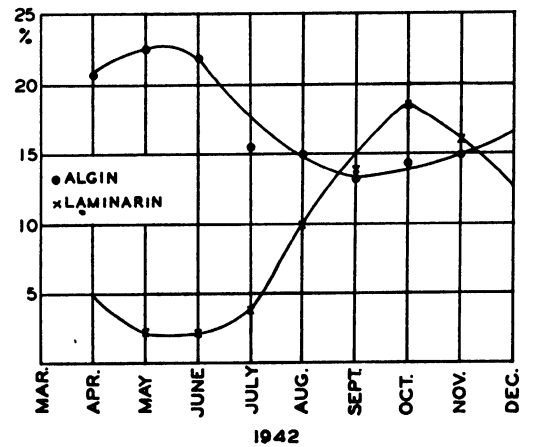


FIGURE 18. Seasonal variations of algin and laminarin in *Laminaria Cloustonii* (after Dillon, 1943).

CHEMICAL NATURE OF PHYCOCOLLOIDS

Agar

Proximate Analysis of Commercial Agar. The utilization of agar in medicinals and in making bacteriological culture media requires that it be as free from proteinaceous materials and as low in ash as possible. Hence the U. S. Pharmacopoeia in its recent editions defines agar not only on the basis of its source and nature, but also as to its contents of foreign organic matter, acid-insoluble ash, and moisture. According to the U.S.P. requirements, therefore, proximate chemical analysis must be made. In recent years with the formation of the Association of Agar Manufacturers in Japan, all the agar produced in that country is inspected and classified into different grades, and one of the important criteria is its proximate chemical composition, especially its acid-insoluble ash.

In the early days, however, Japanese agar was so inconsistent in its quality that research workers found it very difficult to standardize the preparation of culture media. Hence in many laboratories the agar had to be purified before use. With a view to checking the fluctuation of the quality of commercial agar, Whittaker (1911) analyzed 17 samples and found a great deal of variation: moisture 11.39 to 16.50 per cent, crude fiber 0.16 to 4.27 per cent, crude protein 1.16 to 3.58 per cent, carbohydrate 74.91 to 80.53 per cent, and ash 3.23 to 7.50 per cent. He therefore suggested that the quality of agar for bacteriological purposes be standardized and that such an agar be specified to contain not more than 15 per cent moisture, 0.5 per cent crude fiber and 2.5 per cent ash.

There are several other reports besides Whittaker's on proximate analyses of commercial agar. Two earlier ones are by Smith (1905) and Davidson (1906). Smith reported two analyses, one by Kellner and the other by the Japanese Imperial Fisheries Bureau. Davidson obtained the data of analysis from a report on the second Japanese Exhibition of Marine Products. Another analysis was later reported by Forbes, Beagle and Mensching (1913). Feller (1916) made an intensive study on the analysis, purification and chemical properties of agar, and analyzed 16 samples. Only one analysis of American agar has been published so far. It was based on samples prepared by the American Agar Company at San Diego, California, and was published first anonymously (1927), then by MacKinnon (1930). Table 8 summarizes the results of analysis as reported by the above mentioned authors.

Table 8. Proximate Analysis of Air-dried Commercial Agar

	Japanese Agar						American Agar
	Japanese Imperial Fisheries Bureau (Smith, 1905)	Kellner (Smith, 1905)	Davidson (1906)	Whittaker (Average of 4 samples) (1911)	Forbes, Beagle and Mensching (1913)	Feller (Average of 15 samples) (1916)	Anonymous (1927) MacKinnon (1930)
Moisture	22.29%	22.80%	21.79%	14.52%	15.29%	16.57%	18.41%
Crude fiber	6.73	——	3.54	0.80	0.89	0.80	0.14
Crude protein (N × 6.25)	6.85	11.71	5.95	2.20	1.88	2.34	1.12
Carbohydrate (N-free extract)	60.32	62.05	64.59	68.57	77.34	76.15	76.94
Ether extract	3.81	3.44	4.13	——	0.37	0.30	0.19
Silica				0.40	——	0.68	——
Ash				3.89	4.23	3.85	3.20
Ca				0.62	0.60	0.92	
Mg				0.33	0.48	0.57	
Na				0.17	0.11	0.25	
K					0.11	0.07	
Cl				0.13	0.03	0.22	
S				1.69	1.77	2.65	
P				0	0.02	0.05	
Fe & Al				0.16	——	——	

The crude fiber, crude protein, ether extract and silica are now known definitely to be impurities, which can be greatly reduced by repeated purification. The ash can also be materially reduced. Some of the ash components, however, are found to be constituents of the agar molecule itself, and therefore cannot be reduced without affecting its chemical structure. Recent investigations have shown that natural agar is a calcium or magnesium salt of a sulfuric acid ester of a galactan, or a mixture of both such salts. Hence sulfur, calcium and magnesium are always present in agar in much larger amounts than the other ash constituents, which are impurities.

There are other foreign matters found in the proximate analysis of commercial agar. Arsenic was reported to be present by Tassilly and Leroide (1911). They found 0.025 and 0.02 mg arsenic per kilo, respectively, in two samples examined. The origin of this arsenic was obscure. It might have been introduced with the sulfur dioxide sometimes employed in the bleaching process in Japan. Czapek (1922) records the presence of pentosans to the extent of 1.66 per cent, and also of enough iodine to impart to CS_2 a red-violet color (cf. also Itano, 1933). A few years ago the Japanese agar imported by England was reported to contain boric acid. Kimura (1939) was requested by the Agar Manufacturers' Association of Osaka to investigate the matter. He found that *Gelidium Amansii* itself contained on the average 0.0296 per cent of boric acid, and agar about 0.0334 per cent. The borax content can be attributed to that in the epiphytic organisms, probably some of the bryozoans, on the plant itself. The use of boric acid in the manufacture of agar in Japan is strictly prohibited by law.

Growth Substances in Commercial Agar. Besides various inorganic impurities, commercial agar also contains certain amounts of growth substances, as conclusively shown by various experiments in recent years. Probably the first to show the presence of such substances were Allison and Hoover (1934). They used *Bacillus radicicola* as the test organism, and detected the presence in commercial agar of Coenzyme R, which is now considered to be identical with biotin or vitamin H. Hawker (1936) working on *Melanospora destruens* found that a scanty growth developed on a mineral-glucose medium containing 1.5 per cent agar, and that no growth occurred in the medium without the agar. These observations were interpreted as showing the presence of traces of the second of two growth factors which must be present for the development of this organism. This second factor was later demonstrated also to be biotin.

Fries (1938) reported that *Polyporus abietinus* and *Polyporus adustus* grew and formed aerial mycelium on a mineral-sugar medium containing ammonium nitrate and 1.5 per cent agar, and that the growth on a medium containing washed agar was much less than that on unwashed agar. Since both of these organisms are thiamine-deficient and do not grow in a liquid medium lacking thiamine, or its pyrimidine intermediate, growth on the agar medium can only be interpreted as due to the presence of thiamin. Robbins (1939) presented evidence that agar exerted a favorable effect upon *Phycomyces Blakesleeanus* and that this effect was probably due to the presence in commercial agar of appreciable quantities of biotin and traces of thiamine or its intermediates.

The presence of thiamine in agar was first determined quantitatively by Day (1942). From the relation between the amount of thiamine and the dry weight of *Phycomyces* grown in liquid culture, it was calculated that one lot of Difco agar contained about 0.1 mμ mole thiamine per gram, Eimer and Amend flake agar about 0.01 mμ mole, and crude, shredded agar about 0.09 mμ mole. It was also found that on leaching the agar with five per cent aqueous pyridine, the thiamine was largely or completely removed.

Chemical Constitution of Agar. There were two stages in the development of studying the constitution of agar. At first chemists desired to know what actually was the carbohydrate which had such an outstanding ability to form a jelly in small concentrations. Later when chemists realized that the carbohydrate exists in a very complex form they began to investigate its constitution.

Payen (1859) was undoubtedly the first to extract the gelatinizing carbohydrate (which he called "gelose") from *Gelidium Amansii* brought by Montravel from China, then called "Chinese moss." His gelose, as mentioned above, is what we call agar today. Payen characterized this substance by its ternary composition, absence of nitrogen, complete solubility in boiling water and its remarkable power of forming, on cooling, a colorless transparent jelly, and incorporating in this form 500

times its weight of water. He assigned to it the formula $C_6H_{10}O_5$. Reichardt (1875) identified the carbohydrate as pararabin ($C_{12}H_{22}O_{11}$), a substance he had previously prepared from carrots and beet roots. Morin (1880) found that the gelose of Payen gave mucic and oxalic acids on oxidation with dilute HNO_3. He determined the rotatory powers of solutions of gelose and concluded that its properties were very similar to those of the gums. Porumbaru (1880) assigned to it the formula $C_6H_{12}O_6 \cdot H_2O$ and stressed its analogy with glucose. Greenish (1882) gave it the formula $4C_6H_{10}O_5 \cdot H_2O$. He reported that it did not reduce Fehling's solution and was not fermentable by yeasts even after hydrolysis with dilute sulfuric acid. He obtained seven carbohydrate-like compounds by various treatments of this gelose, and among them were arabinose and glucose. Since Greenish used the whole plant of *Gracilaria lichenoides* in his investigation, it is reasonable to presume that these sugars might be impurities and did not necessarily originate from agar. Bauer (1884) was the first to identify agar with galactan, a product obtained by Muntz from lucerne seeds and various non-starchy plants with the formula $C_6H_{10}O_5$. The early authors were all interested in the form of carbohydrate to which agar belongs. They did not suspect that sulfur and calcium played an important role, and that the structure of the molecule was so complicated.

Modern investigation of the constitution of agar probably started with the research of Neuberg and Ohle (1921). They showed the presence of combined S in agar by the fact that when the substance was dissolved with HCl to which a few drops of HNO_3 and $BaCl_2$ had been added, a precipitate of $BaSO_4$ resulted. They also showed that, although the ash of agar contained from 0.8 to 0.9 per cent of calcium, Ca ions could not be detected by oxalate precipitation in agar solution. Similarly, sulfate ions could not be demonstrated, although the ash contained 0.62 to 0.65 per cent S. That it was not due to protective colloid action was shown by the addition of small amounts of Na_2SO_4 which were precipitated by $BaCl_2$. They concluded therefore that the sulfur occurred as ethereal sulfate intimately related to calcium ion.

Samec and Isajevič (1921) found that prolonged dialysis of commercial agar in distilled water failed to reduce the percentage of ash below 1.31, or that of the sulfate below 1.03. They showed that heating dialyzed agar to 120° rendered part of the sulfate dialyzable. They believed agar to be chemically analogous to amylopectin, and to be a gelose sulfate, with the possible inclusion of silicate. It was suggested that a gram atom of S corresponded to 9320 grams of a compound having the formula $(C_6H_{10}O_5)_{57}SO_4H_2$. These investigators (1922) later suggested the formula $(C_6H_{10}O_5)_{54}SO_4H$ with a molecular weight of 8900.

Fairbrother and Mastin (1923) also presented evidence that agar consisted principally of the calcium salt of an acid sulfuric ester. They found that on hydrolysis with dilute HCl, almost all the sulfur content of agar appeared as sulfuric acid. That heating an agar sol also yielded SO_4 ions was believed to be a matter of hydrolysis as follows:

$$2H_2O + (R{\cdot}O{\cdot}SO_2{\cdot}O)_2\,Ca \rightleftharpoons 2ROH + CaSO_4 + H_2SO_4$$

Attempts were made by these authors to prepare the free agar acid $R{\cdot}O{\cdot}SO_2{\cdot}OH$ by soaking agar in 0.01*N* HCl and water alternately. By this procedure a product containing no ash except some silica was obtained. When this was dissolved in water by heating, it failed to gel again even after long standing. The same authors showed that other metals could replace the calcium of agar without impairing the setting to gels. They were able to prepare a potassium agar by heating agar with a slight excess of potassium oxalate. The quantity of potassium in the resulting agar was approximately equivalent to the calcium which was originally present. The potassium agar sol filtered readily and set to a very firm gel. Discussing the constitution of the agar gel, these authors suggested that "in the neutral state, the mi-

cellae consist of undissociated salt and sulfuric ester ion, both possibly polymerized,

$$[H_3O]_x\,[(R{\cdot}O{\cdot}SO_3)_2\,Ca]_y\,[R{\cdot}O{\cdot}SO_2{\cdot}O']_z$$

The Ca ions exist in the intermicellar spaces."

The formation of a free agar acid by replacing the Ca ion with H ion was later confirmed by Hoffman and Gortner (1925). These authors were able, by electrodialysis of agar, to remove the calcium almost quantitatively, resulting in the formation of the free acid. This was found to be more highly dissociated than most organic acids; a 1 per cent solution of it had a pH value of 2.475, and was apparently ionized to the extent of about 56 per cent. It was neutralized by NaOH below a pH of 4.0. No sulfur was removed by electrodialysis. All the sulfur was apparently present as acidic sulfuric ester. It was further found that the solutions of as much as 5 per cent of the free acid would not gelatinize upon cooling, but that upon neutralization by the addition of a base, firm gels were obtained. Organic bases such as aniline and the alkaloids reacted with the acid similarly. The gelation of agar was therefore held to be the gelation of a salt and not that of a complex polysaccharide. These authors calculated that the minimum molecular weight of the free agar acid was about 3000, probably corresponding to the formula R-O-SO_3-OH, where R was a large polysaccharide residue.

That other metallic ions may replace calcium without impairing the setting of the gel was also confirmed by de Waele (1929), who further found that the sulfate ion can also be replaced by a cation such as Cl or NO_3 without impairment of the gel setting. At a pH less than 2.0 the Ca was replaced by hydrogen ion and the resulting compound would not gel. Neutralization with any base, such as calcium, sodium or potassium hydroxide, alkaloid or aniline, however, replaced the hydrogen ion with an anion, and restored the gelling ability of the substance. Heating an agar solution of a pH 2.0 caused hydrolysis, and resulted in the formation of simple sugars reducing Fehling's solution.

Lüdtke (1929) found that the sulfuric acid hydrolyzate of agar contained levulinic acid, the amount increasing with the time of hydrolysis, and that agar was only 35 to 40 per cent *d*-galactose. He therefore seriously doubted if agar was essentially a *d*-galactan as generally believed.

Takahashi and Shirahama (1931, 1932a) reported the isolation of hydrato-kanten δ and λ. After autoclaving agar solution at 130° for 2 hours, a white jelly was obtained upon cooling, which was separated by centrifuging. These authors called this hydrato-kanten δ. It was a white amorphous powder, soluble in hot water and precipitated on cooling. From the filtrate a precipitate was obtained by the addition of 95 per cent alcohol, and was called hydrato-kanten λ. It was a yellowish brown powder, soluble in water and in dilute alcohol. It had high ash content, consisting of Ca and SO_4 and small amounts of Mg, Na, and K. Later (1932b, 1934), these authors freed the hydrato-kanten λ of the mineral components by electrodialysis, thereby obtaining the free λ acid, which was named by the authors kanten-acid. When a solution of the acid was treated with a mixture of alcohol, ether, and benzene, it was precipitated as a white powder. The formula $RR'(SO_4)_nM$ was suggested for this substance, where M is principally Ca. They suggested that the loss of gelatinizing power of this substance after hydrolysis resulted from the separation of the two carbohydrate residues, R and R', a view contrary to that of Samec and Isajevič that the gelatinizing power of the gel was dependent upon the ethereal sulfate group.

The existence of *l*-galactose in agar was first demonstrated by Pirie (1936), who isolated hepta-acetyl *dl*-galactose by the acetolysis of agar. That *l*-galactose is an integral part of the agar molecule was later definitely established from the fact that a derivative of *l*-galactose was found among the hydrolysis products of methylated

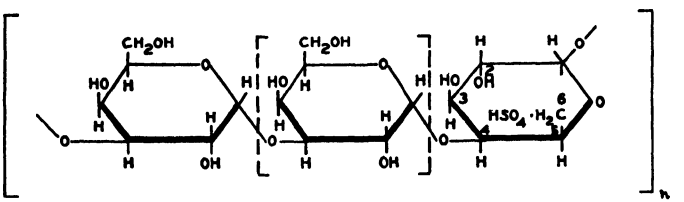
agar (Hands and Peat, 1938a, 1938b; Percival, Somerville and Forbes, 1938; Forbes and Percival, 1939; Cottrell and Percival, 1942).

Neuberg and Schwietzer (1937) by shaking crude agar with water for 20 hours obtained from the filtrate a yield of about 90 per cent of a substance almost free from sulfur, which formed a gel like ordinary agar, whereas the remainder containing a relatively high proportion of sulfur (5 per cent) would not gelatinize.

Percival and Somerville (1937), using the acetylation and methylation procedures, were first to establish the fundamental features of the structure of agar. By acetylation they obtained an agar acetate, which yielded, on removal of the acetyl groups with alkali, a substance indistinguishable from agar in its gel-forming properties, showing that no degradation had taken place on acetylation. The acetyl residues were then replaced by the more stable methyl residue and the methylated product turned out to be a new crystalline trimethylgalactose, shown to be 2,4,6-trimethylgalactose. They concluded that the major part of the agar molecule consists of *d*-galactose residues united by 1,3-glycosidic linkages, chiefly of the β-type. The sulfuric acid group esterified with galactose was split off during acetylation or methylation, since no sulfur could be detected in agar acetate or methylated agar.

Araki (1941) isolated from the hydrolytic products of methylated agar a disaccharide which was apparently penta-methyl-*d*-galactoside-3,6-anhydro-methyl-*l*-galactoside, the *d*- and *l*-galactose derivatives probably united through the first and fourth carbon atoms. It was further shown that the methylated *l*-galactose derivative contained a 3,6-anhydro or hydrofuranol ring. The 3,6-anhydro form of *l*-galactose thus obtained was assumed to be a residue formed in the course of hydrolysis of *l*-galactose-6-sulfuric acid ester, rather than an original constituent in agar.

Jones and Peat (1942) presented evidence that agar is the sulfuric ester of a linear polygalactose. According to these authors, agar consisted of a chain of 9 *d*-galactopyranose residues attached by 1,3-linkages, and terminated at the reducing end by one residue of *l*-galactose, which was esterified at carbon atom 6 with sulfuric acid and attached to the chain through position 4. The constitution of agar is best represented by the following formula:



Agar (After Jones and Peat, 1942).

By such a structural formula it is possible to explain the isolation of *l*-galactose from agar, as well as the separation of 2,4-dimethyl-3,6-anhydro-*l*-galactose and 2,5-dimethyl-3,6-anhydro-*l*-galactonic acid from methylated agar. The absence of sulfuric acid residues from acetylated and methylated agar is also satisfactorily accounted for. Jones and Peat believed that "a sulfate fulfills a similar function in the biological synthesis of agar to that of a phosphate in the enzymatic synthesis of starch from glucose 1-phosphate." They suggested further that, "On this supposition, the initial material in the biological synthesis of agar is *d*-galactose 1-sulfate, from which is formed a chain of *d*-galactose residues combined by 1,3-glycosidic linkages. When ten such *d*-galactose members have been united, a change in the synthetic procedure becomes operative, and the tenth member, bearing its sulfuric acid group, undergoes the intramolecular transformation just described, whereby it is converted into the *l*-galactose residue . . . with agar the sulfuric acid remains, with its orientation readjusted, as an integral part of the molecule."

Percival and Thomson (1942) obtained somewhat different relative proportions of the hydrolysis products of the methylated agar derivatives. They pointed out that the methoxyl content for a model of methylated agar as suggested by Jones and Peat should be 42 per cent, whereas the highest recorded value is not greater than 35 per cent for a representative sample. According to these authors, therefore, the structure of agar as presented by Jones and Peat is oversimplified.

Barry and Dillon (1944) in a recent publication disagreed with Jones and Peat in the number of galactose units in the latter's formula. They worked on agar made from *Gelidium latifolium*, and after repeatedly purifying it, found an ash content of 2.59 per cent and a sulfur content of 0.364 per cent. The latter figure corresponds to one SO_4 group to every 53 galactose units. These authors also presented evidence that the 3,6-anhydro-*l*-galactose isolated from agar in the form of its 2,4-dimethyl derivatives is not an artifact of the methylation process, but rather a constituent of the agar molecule. They contended that agar cannot contain as much as one non-reducing end group for every 140 galactose units, which is in agreement with the lack of detectable amounts of tetramethylgalactose in the hydrolysis products of methylated agar, as Percival and Thomson (1942) had previously found.

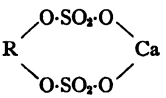
An excellent review of the recent important advances on the chemical constitution of agar and other seaweed polysaccharides has recently been presented by Hassid (1944).

Carrageenin

Chemical Composition and Constitution. Stanford (1862) was probably the first to call attention to the "peculiar gelatinous principle" of *Chondrus crispus*, which he called "carrageenin." He made the following remark: "It contains $C_{12}H_{10}O_{10}$ according to Schmidt, and $C_{24}H_{19}O_{19}$ according to Mulder." The presence of galactose was reported by Flückiger and Obermayer (1868). Among the products of the action of acid upon this extract, Bente (1875, 1876) found levulinic acid and a sugar which showed little or no optical activity. Haedicke, Bauer and Tollens (1887) found that the aqueous extract of *Chondrus* yielded mucic acid corresponding to 28 per cent of galactose. Sebor (1900) confirmed the presence of galactose and fructose, found small quantities of pentosan and proved the absence of raffinose. He stated that he had found evidence for the presence of glucose. Müther and Tollens (1904) also mentioned the presence of glucose. Abderhalden (1911) assigned the formula $C_6H_{10}O_5$ to this substance, without giving the necessary evidence. On the basis of an earlier analysis by Stocks and White (1903), however, it appears that carrageenin does not possess that formula. These authors found in the ash-free substance 37.94 per cent C, 5.92 per cent H, 54.95 per cent O, and 1.19 per cent N. Tollens (1914) found that carrageenin contained galactose and fructose residues, the latter in such quantity as to induce him to place this substance among the fructosans. He did not, however, assign to it any definite formula.

These investigators have contented themselves with establishing the presence of certain carbohydrate residues by hydrolysis of the *Chondrus* extract, or by distillation with mineral acids or oxidation with nitric acid. Sebor, however, did go a little further in expressing the opinion that carrageenin is a complex carbohydrate produced by the union of galactose, dextrose, and levulose residues, together with a small quantity of contaminating pentosan or methylpentosan. The first attempt at the chemical constitution of carrageenin was made by Haas (1921). While the attention of earlier authors has been attracted by the high ash content of this substance (Flückiger and Obermayer, 1868; Czapek, 1925) it was Haas who first realized its significance. He showed that the aqueous extract of carrageen gave the reactions of calcium ion but not of sulfate ion; and that after hydrolysis, the addition of barium chloride produced a plentiful precipitate of barium sulfate. He therefore concluded that the calcium sulfate obtained by various investigators by incineration

was not present as such in the plant, but rather produced by the decomposition of an ethereal sulfate pre-existing in the undecomposed material. This also explains the observation made by earlier workers that the high ash content of this substance could not be reduced by dialysis. On the assumption that such a compound must contain two sulfuric acid residues for each atom of the bivalent calcium, Haas suggested the following formula:



where R represents the polysaccharide complex. This assumption that carrageenin is a colloidal electrolyte, an ethereal sulfate of calcium, has been experimentally proved by the fact that the ratio between the sulfate by hydrolysis and that by incineration is about 2:1. Upon incineration, this substance loses half its sulfur, given off in the form of sulfuric acid, while the remaining half is converted into calcium sulfate.

Harwood (1923), making use of physico-chemical methods, found the evidence contradictory and offered an alternate formula $Ca(O{\cdot}SO_2{\cdot}O{\cdot}R)_2$. He pointed out that without further experimental work it is impossible to choose between the alternative formulas. He seems, however, to be inclined to agree with Haas that the first formula is more acceptable. Nelson and Cretcher (1931), on the other hand, criticized Haas' assumption of this disulfate ester on the grounds that the analytical data are insufficient to indicate this composition of the esters and to preclude the presence of polymerides of monosulfate esters.

Haas and Russell-Wells (1929) noted that the loss of gelatinizing power of carrageenin resulting from mild hydrolysis is not accompanied by production of free sugars, although reducing properties are developed. They found that the resulting solution contained two ethereal sulfates separable by dialysis; the one retained by the dialyzer had reducing properties, and the one passing through had not. They also established the presence of glucose.

Butler (1934) improved the method of isolating the carrageenin by first extracting it from the thoroughly washed plants with water for 5 to 6 hours on a boiling water-bath; then centrifuging and filtering the extract while hot; and finally concentrating the filtrate and precipitating the carrageenin by adding alcohol. The extract was purified and dehydrated by repeated washing with alcohol. The ash content of the resulting product was fairly uniform, about 19 per cent, and included appreciable quantities of potassium. Sulfate accounted for an average of only 58 per cent of the ash. The ratio of sulfate in the ash to sulfate in the acid hydrolyzate was found to be more nearly 1:3 than the 1:2 called for by Haas' formula. By dialysis against potassium chloride, the potassium salt of the carrageenin was obtained, which was free of calcium and the ash of which gave almost quantitative figures for K and SO_4. Ammonium salts were similarly prepared, and also pure calcium salts from the potassium salt. By this means Butler was able to show that the assumption that the original carrageenin is a calcium salt is erroneous, since the pure regenerated salt differed greatly in analysis. In the case of the pure potassium and regenerated calcium salts, an almost precise ratio of 1:2 ash-sulfate to hydrolyzed sulfate was obtained. According to Butler, the constitution of the pure potassium salts is more correctly represented by one of the two formulas:

$$[R(O{\cdot}SO_2{\cdot}O{\cdot}K)_2]_n \quad \text{or} \quad [R(O{\cdot}SO_2{\cdot}O{\cdot}K)_3]_n$$

The carrageenin is presumed to occur *in situ* as a mixture of acid, potassium, and calcium salts. Since the sulfate has been found to form 28 per cent of the potassium

salt, the molecular weight of potassium carrageenin would be $n \times 685$ on the basis of the first formula, or $n \times 1030$ on the basis of the second one.

It has been shown by various authors that the aqueous extracts of carrageen are not quite nitrogen-free. Butler (1935) showed further that the nitrogen could not be removed or appreciably reduced by repeated precipitation. The nature and form of association of this nitrogenous material is not yet known. Protein is probably absent, since the biuret test is usually negative. That the nitrogen is not chemically combined is proved by the fluctuating percentages of nitrogen in all preparations. Furthermore, its quantity in the polysaccharide complex was found to depend on the amount of nitrogen originally present in the plants, averaging about 13 per cent of the latter.

The fundamental features of the structure of carrageenin molecule were recently established by Buchanan, Percival and Percival (1943), who showed that this polysaccharide, similar to agar, contains galactose residues joined by 1,3-linkages. The sulfuric ester group, however, is attached to carbon atom 4 in galactose and not to position 6 as in agar. The galactosidal linkages combining the residues appear to be of the α-type. This does not take into account the mode of union of the unidentified portion of the molecule. These authors have confirmed the presence of small quantities of glucose by the isolation of crystalline tetra-acetyl-β-methylglucoside and tetramethylglucopyranose, as well as by the isolation of glucosazone.

Hot and Cold Extracts of Carrageen. Haas and Hill (1921) were the first to notice that a hot-water extract of carrageen is not a single substance but is composed of at least two constituents, which can be separated by their different solubilities in cold water. The one extractable by merely immersing the plant in cold water is called cold extract (C.E.), and the other extractable only in hot water is called hot extract (H.E.). While the cold extract gives only viscous solutions with water, aqueous solutions of the hot extract readily gel upon cooling. The C.E. and H.E. also differ in their hygroscopic properties, and in their ash and nitrogen content (Table 9).

Table 9. Comparison of Cold and Hot Extracts of Carrageen (Haas and Hill)

	Moisture (%)	Ash Content (%)	Nitrogen Content (%)
Cold Extract	23	21.50-27.07	0.99
Hot Extract after removing C.E.	19	16.30	1.09
Hot Extract without first removing C.E.	21	22.70	0.82

Haas (1921) made a more detailed study of the cold and hot extracts. He found that the behavior of these two substances is different toward salt solutions. While both the H.E. and the C.E. are precipitated from their solutions by half saturation with ammonium sulfate, the H.E. only is precipitated by half saturation with sodium chloride or magnesium sulfate, the C.E. remaining unaffected. Rochelle salt is found to increase considerably the gelling power of the H.E., while it does not so affect the C.E. The H.E. also differs from the C.E. in giving a deep violet color when warmed over a water-bath with alcoholic solutions of α-naphthol and sulfuric acid, indicating the presence of a ketonic sugar.

Russell-Wells (1922) found evidences showing that the C.E. consists of calcium and ammonium ethereal sulfates, its ash containing magnesium, sodium, potassium and traces of iron, besides sulfate and calcium; and that while these ions are all found in the ash of the H.E., the latter contains very small amounts of the alkali metals and relatively more calcium. This investigator also succeeded in preparing the ammonium salts of both extracts by replacing the calcium ion with ammonium. This is effected by the addition of ammonium phosphate or oxalate which combines with the calcium ion to form respectively the insoluble phosphate or oxa-

late. The ash content of the resulting ammonium salt of the C.E. is only 5.87 per cent compared with 21.26 per cent of the original extract; and that of the H.E. only 4.38 per cent compared with the original 17.6 per cent. The ash in both cases consists very largely of magnesium, which must therefore be present in an un-ionized condition in the original extracts. In addition to magnesium the ash of the ammonium salt of the C.E. contains potassium and sodium but no calcium. It was also found that the main oxidation products of both extracts consist of mucic, oxalic and tartaric acids, and that more mucic acid, but less oxalic acid, is obtained from C.E. than from H.E. Pentose radicals are present in both, but more in the cold than in the hot extract.

Butler (1934) studied the cold and hot extracts made by the Haas method, and compared them with her standard which was extracted by hot water and purified and dehydrated by precipitation in alcohol. She further dialyzed the cold and hot extracts to rid them of the adherent salts, which she contended were responsible for the marked difference in ash contents of both extracts. Table 10 summarizes the results of the various tests and analyses of these extracts. There still remains a difference of 4 per cent between the ash contents of the dialyzed fractions of both extracts. The ash content of the standard extract, as expected, is intermediate between the two fractions. That the ash of the dialyzed C.E. contains more phosphorus than that of the dialyzed H.E. probably helps to explain the higher percentage of ash in the former.

Table 10. Comparison of Various Carrageen Extracts (Butler)

Tests	C.E.	C.E. (dialyzed)	H.E.	H.E. (dialyzed)	Standard
50% alcohol	No. ppt.		Good ppt.		Good ppt.
Molisch	+		+		+
Biuret	−		−		−
Reduction	−		−		−
Reduction after hydrolysis	+		+		+
Potassium	+		−?		+
Phosphate	+		−		+
Chloride	None visible		−?		−?
Calcium	?		+++		++
Sulfate	−?		−		−
Sulfate after hydrolysis	+		+		+
Ash	27.43%	21.47%	17.24%	17.63%	19.47%
	26.43		17.35		19.42
	27.49		16.80		−
Nitrogen	0.32		0.16		0.24
	0.30		0.15		0.24
% SO_4 in ash		59.36	63.34	60.90	58.74
% SO_4 in original salt calculated from ash		12.75	10.85	10.74	11.74
% SO_4 in original salt by hydrolysis		28.79	27.03	27.83	27.51

Buchanan, Percival and Percival (1943) reported that galactose is the main component of both extracts, and that the galactose residues constitute at least 31 per cent of the C.E., and 33 per cent of the H.E. They also detected small quantities of glucose in H.E., but none in C.E. They emphasized that the main differences between the two extracts, however, appears to be that H.E. is chiefly a calcium salt, whereas C.E. is a mixture of sodium and potassium salts. Table 11 summarizes their analysis of ash of the two extracts. Each extract contained about 1 per cent pentose. The C.E. was also found to yield a trace of ammonia on boiling with 8 per cent sodium hydroxide solution.

Seasonal Variations of Chemical Composition of Carrageenin. Butler (1936) studied the seasonal variations of carbohydrate, ash, and nitrogen content of both carrageen and carrageenin. In general, the plant and extracts show the same series

Table 11. Analysis of Ash of Carrageen Extracts (Buchanan, Percival and Percival)

	Ash in Extracts (%)	Ash Constituents			
		SO_4	Ca	K	Na
C.E.	22.4	63.8	5.5	24.5	13.7
H.E.	18.7	66.6	29.9	2.5	1.0

of fluctuations, the changes in the extracts occurring somewhat later. During the early part of the year the percentage of ash is fairly high and that of carbohydrate low. Conversely, from May to July the ash content is low and the carbohydrate high. From about October, however, the percentage of both fall off together. The nitrogenous content is highest in the spring months and lowest in summer (Fig. 19).

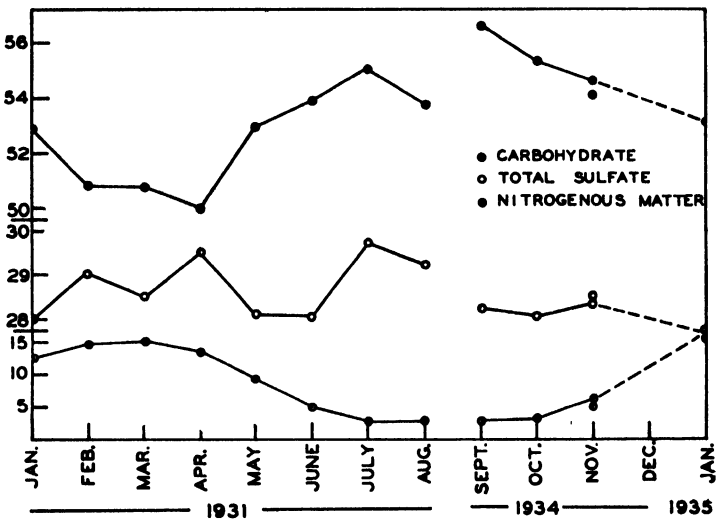


FIGURE 19. Seasonal variations of carbohydrate, total sulfate and nitrogenous matter in carrageenin (After Butler, 1936).

The ratio of sulfate in ash to total sulfate is determined in order to interpret the types of ester predominating in the different seasons. It was found that from the beginning of the year until May, this ratio is about 0.333, indicating a predominance of the acid salt. It rises to a value of about 0.500 in about August when the ash content rises, indicating the predominance of esters of the normal type from May until October. After October, until January there appears to be a gradual return to the acid type of salt. Similarly, the relation of the carbohydrate to total sulfate also indicates that the acid salt may predominate from January to about May. Butler therefore suggested the hypothesis that "the supply of the carbohydrate complex synthesized during the summer months is largely of the normal ester type, and that after the supply of these has been used up, the acid type of ester alone remains to be metabolized."

Algin

When Stanford (1883) discovered algin in *Laminaria stenophylla* he reported it to contain as much as 3.77 per cent of nitrogen. Later Stanford (1886) gave the composition of alginic acid as being carbon 64.985 per cent, hydrogen 5.700 per cent, oxygen 25.020 per cent, nitrogen 1.995 per cent, and ash 2.30 per cent. He assumed that nitrogen was an essential constituent and even advanced a definite formula: $C_{76}H_{76}O_{22}(NH_2)_2$. As pointed out by Hoagland (1915), such a formula is without

justification, since the elementary analysis was made on a highly contaminated sample. Later investigations by Krefting and others have demonstrated that pure alginic acid is nitrogen-free.

Krefting (1896, 1898) produced a "tang acid" from Norwegian laminarias, which he claimed to be similar to Stanford's alginic acid, but nitrogen-free. Earlier, Villon (1893) and later Kylin (1913, 1915) described similar preparations from other seaweeds, thus indicating its wide distribution in brown seaweeds from different localities. Investigating the organic constituents of kelps on the American Pacific coast, Hoagland (1915) found algin in all the five species under investigation, their algin content ranging from 14.1 to 22.8 per cent on a water-free basis (cf. Table 4).

Hoagland and Lieb (1915) made a detailed study of algin prepared by them from *Macrocystis pyrifera* and purified until practically ash- and nitrogen-free. The neutralization equivalent was found to be 325. They proposed an empirical formula, $C_{21}H_{27}O_{20}$, with a molecular weight of 599, and containing two replaceable hydrogen atoms. The product was subjected to acid hydrolysis, the water-insoluble fraction removed by filtration, and the filtrate treated with phenylhydrazine. A pentosazone was isolated having melting point, optical rotation and solubilities resembling closely those of *l*-xylosazone. On the basis of these observations alginic acid might be considered a compound composed of an unknown acidic nucleus in combination with pentose sugars.

Atsuki and Tomoda (1926) suggested that the acidic nucleus in algin from *Laminaria* is glucuronic acid. This was probably because their preparation lost 20 per cent of its weight as carbon dioxide when boiled with hydrochloric acid. These authors, however, did not present evidence in proof of the configuration of the acid.

Schmidt and Vocke (1926) prepared alginic acid from *Fucus serratus* and claimed to have isolated from the hydrolyzate *d*-glucuronic acid in the form of its cinchonine salt. Proof of the identity of this salt, however, is limited to the determination of its melting point and is therefore inconclusive.

Cretcher and Nelson (1928), and later Nelson and Cretcher (1929) isolated alginic acid from *Fucus serratus, Laminaria agardhii* and *Macrocystis pyrifera,* and critical studies were made on the algin from the latter two sources. Pure alginic acid has been shown to be a polymer of the anhydride of an aldehyde sugar acid in which all aldehyde groups are conjugated and all carboxyl groups free. These authors were doubtful of the presence of xylose, and believed that any pentose found in the hydrolysis liquor might have arisen from the decarboxylation of a uronic acid unit. The acid has a neutralization equivalent varying from 176 to 184 with different samples. It does not reduce Fehling's solution. On hydrolysis a uronic acid was obtained with a cinchonine salt melting at 152°, different from that of either glucuronic or galacturonic acid. It may be oxidized to a dibasic six-carbon sugar acid. The diamide and diphenylhydrazide of this acid had constants agreeing closely with analogous compounds prepared from pure *d*-mannosaccharic dilactone. These authors therefore assumed that the alginic acid contained *d*-mannuronic acid. The observation that alginic acid is a pure polyuronide of *d*-mannuronic acid was very interesting, inasmuch as this uronic acid had not been known previously to exist. Later, *d*-mannuronic acid lactone and the corresponding mannosaccharic lactone from *Macrocystis pyrifera* were isolated in a crystalline condition (Nelson and Cretcher, 1930). The lactone has also been obtained by hydrolysis of alginic acid from *Fucus serratus* and *Laminaria saccharina* (Nelson and Cretcher, 1932). The melting point and optical rotation of the cinchonine salt from these two seaweeds agreed with the value reported for that from *Macrocystis.*

At about the same time, Bird and Haas (1931) independently identified mannuronic acid as the main constituent unit in the alginic acid from a species of *Laminaria.* Miwa (1930) also arrived at similar conclusions on the alginic acid from *Undaria pinnatifida.* These investigators, however, did not all agree as to the prop-

erties of the cinchonine salts obtained from the hydrolysis liquor. Table 12 summarizes the properties of these salts prepared by different investigators. Nelson and Cretcher (1932) believed the discrepancies to be due to differences in the degree of hydrolysis. While the presence of glucuronic acid has been suggested by Schmidt and Vocke (1926) and Miwa (1926), it has never been established. Nelson and Cretcher prepared cinchonine mannuronate from crystalline mannuronic lactone and found its constants to agree very well with those of the cinchonine salt they obtained by hydrolyzing the alginic acid.

Table 12. Cinchonine Salts of Uronic Acids from Algin

Investigators	Plants Investigated	M.P. (° C)	$[\alpha]_D$
Nelson and Cretcher (1928, 1929, 1932)	*Macrocystis pyrifera*	152	+113.6°
	Fucus serratus	153	+114.3°
	Laminaria saccharina	152	+111.2°
	From crystalline mannuronic lactone	154	+113.3°
Schmidt and Vocke (1926)	*Fucus serratus*	204	——
Miwa (1930)	*Undaria pinnatifida* and other algae	174	+140.3°
Bird and Haas (1931)	*Laminaria sp.*	195-197	+112.8°
		161	+154°

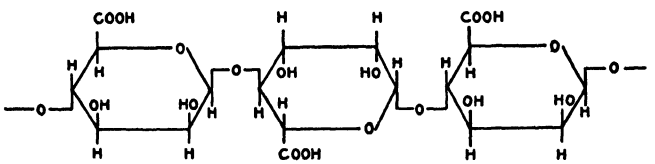
Dillon and McGuinness (1931), by titrating the wet alginic acid preparation and subsequently determining the weight of the salt, obtained an equivalent weight of 198. The barium content of a salt, prepared by addition of the calculated quantity of barium chloride to the neutralized preparation, gave an equivalent of 195. According to these authors, the results indicate that dry alginic acid is a latone; if this is so, the polymerizing unit is not the uronic anhydride but the complete mannuronic acid group itself. This view is supported by later analyses of acetylated alginic acid by Barry, Dillon and O'Muineachain (1936).

By improved methods of preparation, Schoeffel and Link (1933) have isolated the free α- and β-*d*-mannuronic acids in a crystalline condition. The identification has been established beyond doubt by comparison with synthetic *d*-mannuronic acid lactone obtained by reduction of *d*-mannosaccharic acid dilactone (Niemann and Link, 1933). In all cases the physical constants of the lactone of the naturally occurring alginic acid, and of the brucine and cinchonine salts prepared from it, were in close agreement with those of the synthetic acid lactone and its alkaloidal derivatives.

The above-mentioned investigators were chiefly concerned with the nature of the constituent units of alginic acid, the empirical formula of which has been generally agreed to be $(C_6H_8O_6 \cdot H_2O)_n$. The advancement of our knowledge regarding the form of the aggregation or polymerization of the constituent units has been greatly hindered because of the extreme difficulty involved in obtaining derivatives of alginic acid of the ether or of the ester type. While Gomez (1933) did report that he acetylated algin with acetic anhydride and sodium acetate, his products do not correspond in acid or in acetyl number to any definite acetyl derivative, and he isolated no products soluble in organic solvents. Barry, Dillon and O'Muineachain (1936) were the first to achieve success in the acetylation of alginic acid. They expressed their belief that Gomez did obtain a small amount of acetylated product, but that his compound was mixed with a large quantity of unchanged alginic acid. After several failures in attempts with the conventional reagents, they were forced to try less common or entirely new catalysts with acetic anhydride. Finally they met with success by using hydriodic acid. They found that pretreatment of alginic acid with glacial acetic acid containing a little hydriodic acid caused acetylation with acetic anhydride to take place rapidly. This resulted in a 60 per cent yield of three compounds, all having the formula $(C_6H_9O_7)(COCH_3)_3$ and appearing to be acetates

of alginic acid in varying degrees of polymerization. These authors believed alginic acid to be a polymer, not of a uronic acid anhydride, but of the complete uronic acid.

It remained, however, for Hirst, Jones and Jones (1939a, 1939b) to determine the structure and mode of linkage of the mannuronic acid units. By subjecting alginic acid to partial degradative methanolysis by means of methanolic hydrogen chloride, these investigators completely methylated the partially degraded alginic acid. When treated with methanolic hydrogen chloride under pressure, this yielded the methyl ester of 2,3-dimethyl-*d*-mannuronide which was then hydrolyzed to 2,3-dimethyl-*d*-mannuronic acid. The last was oxidized to 2,3-dimethyl-*d*-mannosaccharic acid by bromine water treatment. Further oxidation with HIO_4 gave glyoxylic acid and the half-aldehyde of *meso*-dimethoxysuccinic acid, from which the crystalline methyl *meso*-dimethoxysuccinate was obtained quantitatively. From this and other evidence these authors concluded that, in the mannuronic units of alginic acid, hydroxyl groups are attached to carbon atoms 2 and 3, while bridge and ring linkages are attached to carbon atoms 4 and 5, respectively. Although the evidence was not sufficient to decide between pyranose and furanose structures, the former was favored in view of the resistance of alginic acid toward hydrolysis, and its large negative rotation. Thus, the mannuronic acid units are linked in such a way that the carboxyl group on each unit is free to react while the aldehyde group is shielded by linkage. The following formula represents the arrangement of the mannuronic residues in alginic acid according to Hirst, Jones and Jones.



Alginic Acid (After Hirst, Jones and Jones, 1939).

Similar conclusions as to the structure and mode of linkage of the mannuronic acid units have been reached by Lucas and Steward (1940), who oxidized the alginic acid by means of periodic acid. A substance, presumably the corresponding polymeric dialdehyde acid, was obtained, which undergoes hydrolysis in dilute acid; a 42 per cent yield of glycoxal was obtained from the hydrolyzate. Oxidizing the polymeric dialdehyde acid by means of bromine water resulted in a 25 per cent yield of *meso*-tartaric acid. These results show that the scission of the mannuronic acid units of alginic acid takes place between the second and third carbon atoms. These authors therefore concluded that the hydroxyl groups are attached to the second and third carbons, while bridge and ring linkages are attached to the fourth and fifth carbons, as claimed by Hirst, Jones and Jones. Unfortunately, no conclusion was reached with regard to furanoside or pyranoside structure, or to α or β configuration at the first carbon atom.

By viscometric measurements Heen (1937, 1938) calculated the molecular weight for alginic acid to be 14,100 and for sodium alginate 15,400.

Other Phycocolloids

Funorin. The most imperfectly known among the seaweed colloids is undoubtedly funorin, the gluey substance from *Gloiopeltis*. Although Japanese scientists in recent years have studied the chemical and physical properties of this substance, nothing is known yet regarding its chemical constitution. The limited information available points to its being a galactan.

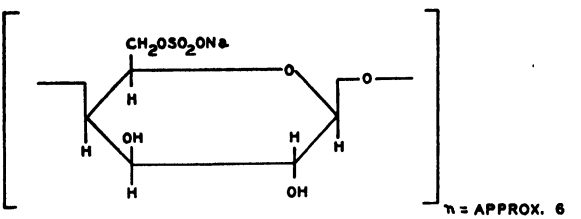
Iridophycin. From a California red seaweed, *Iridophycus flaccidum*,[8] Hassid

[8] Erroneously called *Iridaea* (*Iridea*) *laminarioides* by various authors, cf. G. M. Smith, 1944, "Marine Algae of the Monterey Peninsula," p. 288.

(1933, 1935, 1936) has isolated a galactan ethereal sulfate, which upon hydrolysis gives only galactose. For the sake of convenience and uniformity, the name iridophycin is tentatively given to this polysaccharide. The ash content of the preparations exceeds 25 per cent, and consists chiefly of sodium sulfate. The ratio of sulfate in the polysaccharide to sulfate in the ash is approximately 2:1, indicating the presence of a simple ethereal sulfate with the following empirical formula for its sodium salt:

$$[(C_6H_9O_4)\cdot O\cdot SO_2\cdot O\cdot Na]_n$$

The free acid prepared by electrodialysis has a pH of 3.6 in a 1 per cent solution. By means of acetylation and methylation this investigator has obtained evidence that it belongs to the 1:4 normal pyranose type, and that the sixth carbon atom bears the ethereal sulfate group. According to Hassid, the formula of the sodium salt may be represented as follows:



Iridophycin (After Hassid, 1935).

While iridophycin has as yet no commercial applications, it is a potentially useful product able to serve purposes similar to those of carrageenin. Information reaching the writer indicates that a commercial firm is seriously contemplating the manufacture of this extract after the war.

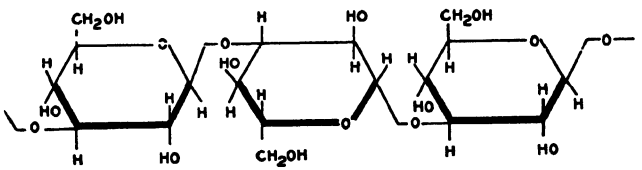
Laminarin. Since its discovery by Schmiedeberg (1885) laminarin has been studied by Krefting (1909), Torup (1909), Kylin (1913, 1915, 1918), Gruzewska (1921, 1923), Colin and Ricard (1929, 1930) and recently extensively by Barry (1938, 1939, 1941, 1942) and Barry, Dillon and McGettrick (1942). The recent investigations of its chemical constitution have been reviewed by Hassid (1944).

Laminarin has the empirical formula $(C_6H_{10}O_5)_n$ and yields only glucose on hydrolysis. Unlike algin, the other major constituent of *Laminaria,* laminarin is water-soluble, and is the reserve carbohydrate of kelp, analogous to, but considerably different from, the starch of land plants. Krefting (1909) and Torup (1909) obtained laminarin by extracting dry *Laminaria digitata* with baryta water and subsequently acidulating the extract with acetic acid. The resulting material differed from Schmiedeberg's extract in being insoluble in cold water. Kylin (1913, 1915, 1916) obtained laminarin from several species, and believed it to consist of a mixture of closely related polysaccharides which can be separated in aqueous solution by differential precipitation with varying concentrations of alcohol. Gruzewska (1921, 1923) studied laminarin from the physico-chemical point of view. She states that its aqueous solutions have a granular appearance under the ultramicroscope, and that the grains are of different sizes, only the small ones showing Brownian movement. On standing the particles form clusters, leading eventually to spontaneous deposition. The precipitation is accelerated by the presence of acids and oxygen, and is retarded by alkali. This behavior is believed to be due to polymerization. Gruzewska suggests that the different modifications of Kylin's preparations could be explained with reference to the extent to which spontaneous aggregation might take place when the aqueous solutions were subjected to alcohol treatment. Colin and Ricard (1929,

1930a) isolated laminarin by extraction with baryta water and purification with 85 per cent alcohol. They also obtained two fractions different in solubility in alcohol, but believed it unjustified to conclude that laminarin is a mixture of different polysaccharides, as Kylin claimed.

Barry (1938) discovered a very easy method for isolating laminarin with one particular species, *Laminaria Cloustonii*. He found that if fronds of this kelp are covered with 5 per cent HCl, laminarin separates out from the plant in a solid state in about 24 hours. It may then be shaken into suspension, filtered or centrifuged, and purified by dissolving in warm water and allowing it to deposit slowly from the filtered solution. Barry shows that laminarin consists exclusively of glucose, when hydrolyzed by dilute HCl, and that it is an unstable colloid whose rotatory power increases uniformly with dilution.

Working on the constitution of laminarin, Barry (1939) found that on methylation followed by hydrolysis it yielded 2,4,6-trimethylglucopyranose; hence it differs fundamentally from starch and cellulose in that the glucose residues are combined by 1,3-glycosidic linkages, and not through carbon atoms 1 and 4. The negative rotation of laminarin suggests that the linkages are of the β-type. Its probable structure is glucose-3-β-glucoside. The following formula represents the arrangement of the glucose residues in the laminarin:



Arrangement of Glucose Units in Laminarin, Showing the 1,3-β-glucosidic Linkages (after Barry, 1939).

Hydrolysis of laminarin with oxalic acid or with an enzyme from snail digestive juice produced a new disaccharide, for which the name "laminaribiose" was suggested (Barry, 1941). The extent of oxidation of laminarin with periodic acid was used by Barry (1942) and Barry, Dillon and McGettrick (1942) as an "end-group assay" for this polysaccharide. Estimation of the dicarboxylated end group indicated that laminarin contains a chain of 16 glucose units. This chain length was not in agreement with that obtained by the Haworth-Hirst method of end-group assay, which indicated a chain length of about 74 glucose units.

Mode of Occurrence of Phycocolloids in Nature

With the exception of laminarin, the other phycocolloids are cell-wall constituents. The facts that cellulose is absent or present only in small amounts, and that other polysaccharides occur in very large amounts in the plants, clearly indicate that these substances replace cellulose partly or entirely in building up the seaweed cell walls. Russell-Wells (1922) examined sections of the thallus of *Chondrus* microscopically, and noted that the cell walls become very thick and swollen in distilled water. She therefore remarked: "This is what one would expect if they [cell walls] were largely composed of H.E. and C.E., since, on being placed in water, dried scales of these materials absorb much moisture and swell up enormously." The dry weight of carrageen consists of only 1.3 per cent cellulose, whereas the cell walls appear under the microscope to constitute the greater part of the section, and about 80 per cent of the dry weight of the plant consists of the hot and cold water-extractable substances. Therefore the only explanation possible is that this polysaccharide carrageenin is the principal cell-wall constituent.

Hassid (1936), speaking of the *Iridophycus* polysaccharide, made a similar remark: "The plant does not contain any cellulose, and since the content of galactan is about 40 per cent of its dry weight and constitutes the main bulk of the plant, it appears that this substance plays the same part in building up its cell wall as does that of cellulose in the higher plants." For the same reason, agar and algin are considered the cell wall constituents of the respective seaweeds.

The condition of phycocolloids in seaweeds is, however, more difficult to determine. In most cases, analyses of the ash helps to visualize the form of the metallic salts of these polysaccharides as occurring in the plants. Kylin (1913) suggested that algin occurs in nature in the form of the calcium salt of alginic acid. Bird and Haas (1931) believe, however, that it occurs in two forms: one a soluble calcium, magnesium, alkali-metal salt, present to the extent of about one-sixtieth of the total algin, and the other in the free state which appears to be the material extracted by cold dilute sodium carbonate. They base their argument on the premise that, since *Laminaria* contains about 60 per cent of its total dry weight as algin, it would require the calcium content of the kelp to be 5.11 per cent, if algin were present as the calcium salt. But the calcium content actually amounts to only 1.99 per cent. Bird and Haas' assumption, however, has been challenged on the ground that although alginic acid is a relatively strong acid, *Laminaria* and *Macrocystis* tissues are not acid either to taste or to indicators, and they fail to liberate carbon dioxide from a carbonate as alginic acid does.

On prolonged dialyses of alginic acid preparations from fresh and air-dried *Laminaria,* Dillon and McGuiness (1931) found significant differences in ash content. From air-dried material the preparation was rapidly reduced to an ash content of 0.6 to 0.7 per cent, but that of the preparation from fresh material fell to a minimum of about 3 per cent and then slowly rose again to about 10 per cent. This led these authors to believe that the alginic acid is combined with colloidal compounds of calcium and iron, and that desiccation either destroys the colloidal character of these compounds or renders them insoluble, so that they are removed by filtration of the algin prepared from the dried frond.

When Haas (1921) found carrageenin to be an ethereal sulfate of a polysaccharide he suggested that it was a calcium salt. Butler (1934), however, presented evidence that the aqueous extract of *Chondrus* is not a single substance, but a mixture of several—a mixture of "the same or very closely allied substances." Studying the seasonal variations of the chemical composition in carrageen, Butler (1935) found evidence of the occurrence of the two different types of esters. The acid type predominates from January to May, the normal type from May till October, and after October, there is a gradual return to the acid type of salt. On the basis of the ash analysis Buchanan, Percival and Percival (1943) express their beliefs that the calcium, sodium and potassium salts of carrageenin are all found in the plant, and that "the main reason for the difference in physical properties between the two extracts appears to be that H.E. is chiefly a calcium salt, whereas C.E. is a mixture of sodium and potassium salts."

According to most investigators, agar occurs in nature in the form of a calcium salt. This explains the high calcium content in its ash. The rather high magnesium content which, like calcium, cannot be easily freed from the agar by simple purification seems also to indicate that a portion of natural agar exists as a magnesium salt. Iridophycin occurs as its sodium salt (Hassid, 1933, 1935, 1936).

Results of recent investigations of phycocolloids seem to favor the assumption that these polysaccharides occur in nature in mixtures of two or more kinds of salts, and that the relative proportions of these salts in the plant vary with seasons, places, and species. The sole exception is laminarin which is a reserve carbohydrate of the brown algae, analogous to starch of the land plants, and which does not contain metallic elements in its molecules.

Properties of Phycocolloids

Agar

As a hydrophilic colloid agar has many outstanding properties, such as its ability to absorb large amounts of water, its enormous gelling power, and its striking hysteresis.

Swelling of Agar. While agar is not soluble in cold water, it absorbs large amounts of water and swells considerably, with evolution of heat. One gram of dry agar swelling in water may evolve as much as 35.5 calories (Rosenbohn, 1914) [9]

The amount of water absorbed depends on several factors. When dry agar is placed in water, it is natural to suppose that the drier the agar the more water it will absorb. This is not the case, however, as shown by the investigation of Clarke (1925) on the swelling of agar as a function of its initial water content (see Fig. 20). Clarke found that, while the water absorbing ability of agar gradually increases

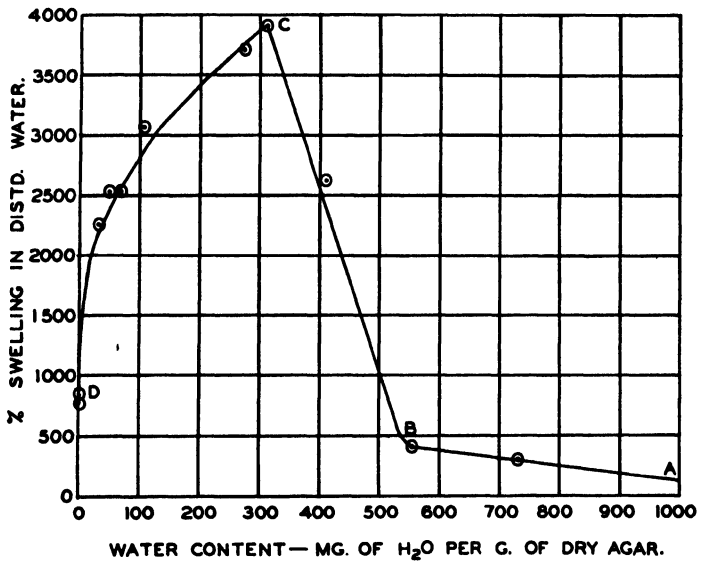


FIGURE 20. Swelling of agar gels in relation to original water content (After Clarke, 1925).

as the water content decreases, a sudden inflexion takes place at the point B (554 mg water per gm agar), and the amount of water absorbed increases rapidly until a maximum is reached at the point C (313 mg water per gm agar); and that having reached this maximum, water absorption drops until a low point (D) is reached with totally dry agar. The point B is of further significance, because not only does a sharp change of water absorption occur there, but also a change in optical properties. Fresh agar gels are opaque, but on drying, become abruptly transparent at this particular point. Perhaps this indicates a change in gel structure.

The swelling of agar depends also on the kinds and concentrations of the hydrating solutions. In dilute solutions of neutral chlorides, for instance, the swelling is greater than in water. Such increases begin in KCl and NaCl at concentrations between $0.001M$ and $0.01M$. Increases are not observed with the bivalent cations Mg^{++} and Ca^{++} until dilutions of $0.0001M$ are reached. The increases of water ab-

[9] Harvey (1925b) reported that the heat of water imbibition evolved by a gram of dry agar amounted to only 2.7 calories on the basis of the average of five determinations.

sorption in acids and in bases show maxima on both sides of neutrality. On the acid side, the maximum occurs in about 0.0001*N*, with a pH of 3.01; with univalent bases, the maximum occurs at 0.001*N*, with a pH of 11, and with bivalent bases, at 0.0001*N* (MacDougal and Clarke, 1925; MacDougal, 1928). Fairbrother and Mastin (1923), on the other hand, reported that acids decrease the swelling of agar to a degree practically in linear relation to the pH value of the solution, irrespective of the kinds of acid. In very dilute NaOH, however, agar swells more than it does in water alone, but in more concentrated solutions the swelling is less than that in water. Amino acids such as glycocoll, alanine, and phenylalanine increase the hydration to the extent of 165, 151 and 161 per cent, respectively, above that attained in pure water, when they are used in 0.01*N* concentration (MacDougal and Spoehr, 1920).

At higher concentrations, electrolytes reduce the swelling of agar in two ways (Dokan, 1924; Michaelis, 1925). First, there is a reduction in the electric charge of the colloid due to the valence of the ion bearing the opposite charge. This effect is noticeable as low as 0.001*N*. Up to 0.1*N* the anion, irrespective of valence, is of no importance, while the cation exhibits a valence effect. Secondly, there is a dehydration effect following the lyotropic or Hofmeister series, due to competition between the electrolyte and the colloid for the water present. This effect becomes increasingly important at about 0.1*N* concentrations, but is negligible below this. Anion and cation are equally effective, and valence is not a factor. Thus, for chlorides, the cationic series is Li<Na<K, and for potassium salts the anionic series is CNS<I<NO_3<Br<Cl<acetate<SO_4<citrate. Table 13 illustrates this lyotropic effect (Dokan, 1924).

Table 13. Swelling of Agar in 0.002 Equivalent Normal Solutions of Various Chlorides after 24 Hours (Dokan)

Chlorides	Swelling (%)
Water	100.00
KCl	82.22
NaCl	74.84
LiCl	73.40
$MgCl_2$	50.63
$CaCl_2$	49.18
$BaCl_2$	45.85
$AlCl_3$	35.42

Dokan also showed that the hydroxyl ion behaves toward the negatively charged agar just like any other monovalent anion, and when its concentration is high enough to exert lyotropic effect, it falls between Br and CNS in the series. The hydrogen ion, on the other hand, is highly effective in very low concentration, and is even stronger than trivalent cations. Similar results were obtained by Iwase (1927).

Working with a 2.2 per cent gel, de Jong (1929) found that all neutral electrolytes in concentrations up to 1 per cent cause a linear contraction. The cation is the only active agent; non-electrolytes such as sucrose and amyl alcohol in similar concentrations have no effect. The contraction is believed to be a capillary-electric phenomenon influenced solely by the valence of the cation and independent of the nature of the cation or the valence and nature of the anion. This electric discharge type of contraction is reversible, the original volume of the gel returning when the electrolyte is leached out. Alcohol in high concentrations also produces a linear contraction of the gel to the extent of 7 per cent, which is also reversible. Its action is believed to be due to the dehydration of the agar. Hydration and electrokinetic potential are therefore the important factors determining the volume of agar gels at the swelling equilibrium.

The swelling of agar also depends upon the time factor. Harvey (1925b) found that the absorption is more rapid at first, as Table 14 shows:

Table 14. Increase in Weight of Soaked Agar in Five Minute Intervals

Time of Soaking (Minutes)	Weight of Soaked Agar (Gms)	Increase in Weight (Gms)
0	1.00	
5	8.46	7.46
10	13.00	4.54
15	14.75	1.75
20	15.80	1.05
25	16.95	1.15
30	17.25	0.35
35	17.81	0.56
40	18.36	0.55
45	18.41	0.05
50	18.65	0.24
55	18.70	0.05
60	18.74	0.04

Fairbrother and Mastin (1923) have obtained similar results with agar in water, acid and base (Table 15).

Table 15. Velocity of Swelling of Agar (Fairbrother & Mastin)

	Water Absorbed as per cent of dry agar							
Days Elapsed →	0.25	1	2	3	4	7	14	29
Water	760	1,034	1,179	1,304	1,362	1,530	1,690	1,778
0.01*N* HCl	467	523	525	545	544	553	558	565
0.01*N* NaOH	661	760	808	855	887	940	1,009	1,085
0.002% Acetic acid	490	607	671	706	723	744	789	812

Viscosity of Agar Sol. Heat, pH, and the presence of electrolytes affect the viscosity of agar sol. At neutrality agar sols reach maximum viscosity (Harvey, 1925a). Viscosity decreases with the increase of salt concentration (Harvey, 1925a), and is reduced by heating (Harvey, 1925b). Table 16 summarizes the findings of Harvey.

Table 16. Influence of Heat, pH and Salts on Viscosity of 1 per cent Agar Sol, Measured by Ostwald Viscometer at 45° C, Relative to Water

Influence of Heat		Influence of pH		Influence of salts			
Duration of Boiling (Minutes)	Relative Viscosity	pH	Relative Viscosity	Salts Conc. (%)	Relative Viscosity		
					K_2SO_4	$MgSO_4$	$Al_2(SO_4)_3$
0	1.16	2.3	1.16	0.05	1.19	1.17	1.15
5	1.09	4.9	1.23	0.10	1.184	1.166	1.144
10	1.06	7.1	1.26	0.20	1.182	1.162	1.142
15	1.05	8.6	1.25	0.30	1.180	1.160	1.140
20	1.044	9.5	1.22				
25	1.04	10.7	1.16				
30	1.035						

Kruyt and de Jong (1922), investigating the influence of electrolytes on the viscosity of agar sols, attribute the action to a discharge based on an electro-viscous effect. The agar micelles, carrying a weak negative charge, undergo a reduction of charge due to the adsorption of the cationic electrolyte. The valence of the anion exercises no influence, while that of cation is the deciding factor. According to a later detailed report by Kruyt and de Jong (1928), the viscosity is strongly reduced

by all electrolytes in dilute concentration, and salts of univalent cations, such as KCl, NaCl, LiCl, NH_4Cl, KCNS, K_2SO_4 and $K_4Fe(CN)_6$ in equivalent concentrations produce practically the same reduction in viscosity. Salts of bivalent cations, such as $BaCl_2$, $SrCl_2$, $MgSO_4$ and $CdSO_4$, produce a greater decrease. Trivalent and quadrivalent ions exert a still greater influence. In all cases, however, decreases in sol-viscosity soon subsides to nearly constant values. Organic ions, such as fuchsin, produce a greater rate of decrease in viscosity than does KCl. With greater concentration of electrolytes, where the electro-viscous effect is absent, the relative decrease in viscosity is a function of the hydration of the ions. The influence increases over the lyotropic series: $K_2SO_4 < KCl < KNO_3 < KCNS$.

Shul'man and Karel'shtadt (1939) found that the viscosity of 0.5 per cent solution of agar is lowered by $BaCl_2$ more than by KCl, and that the effect is stronger in osmotically dialyzed than in electrodialyzed solutions. It is therefore concluded that electro-viscous effects take place, and that the ions of the double layer are removed by electrodialysis, leading to the weaker effect in such systems.

The temperature coefficient of viscosity of an agar sol is very high for concentrated solutions, and viscosity increases rapidly with lowering of the temperature. Banerji and Ghosh (1939) concluded from these high-temperature coefficients that the high viscosities of agar sols are due mainly to a certain orientation of the colloidal micelles, which gives them a structural rigidity. This view was confirmed by the effect of sowing a sol of agar with an already formed gel. The observed viscosity values were in excellent agreement with the theoretical values.

By its dehydrating effect upon the micelles, ethyl alcohol decreases the viscosity of agar sol (Cluzet and Ponthus, 1938). Fernau (1920) found that under the action of radium rays for four days, 4 cc of 0.1 per cent agar solution lost its viscosity entirely. That this was due to hydrolytic decomposition of the agar polysaccharide by the rays was shown by reduction of Fehling's solution after radiation.

Flocculation of Agar Sol. Agar sols which are diluted with alcohol or acetone at 50° and then cooled show numerous bright particles in vigorous Brownian motion which may be observed under the ultramicroscope. Similar dilution with water, however, shows only a Tyndall cone. The dehydration effect of alcohol upon agar sols causes a transformation from the original emulsoid system into a suspensoid system, which is now sensitive to the influence of electrolytes. The same effect is obtained by removing the electric charge from an agar sol by addition of minute amounts of electrolytes; further addition of alcohol will bring about immediate flocculation. Thus, there are two stability factors involved in an agar sol, namely hydration and electric charge, the removal of both being necessary to produce flocculation (Kruyt and de Jong, 1928). There is a difference between these two factors, however. While the dehydration of the particle is reversible, the removal of the electric charge is not. The dehydration of the uncharged agar is also irreversible. This is shown diagrammatically in Fig. 21.

Agar sols can also be precipitated by tannin (de Jong, 1923, 1927b). Tannin does not produce flocculation if the sols are free from electrolytes. It transforms the sols from the emulsoid to the suspensoid state, with great reduction in viscosity, and increase in sensitivity to electrolytes having ions of opposite charge. Thus tannin has dehydrating properties and acts somewhat like alcohol. The disappearance of emulsoid properties from a tannin-treated agar sol is also indicated by loss of gelatinizing power.

There is one striking difference between the dehydrating action of alcohol and of tannin. While amounts of alcohol in excess of 50 per cent by weight are required to produce the dehydrating effect, only 1 per cent tannin will suffice. The mechanism of dehydration in the two cases must necessarily be different. It is believed that tannin is a substance which lowers the surface tension considerably, and that the large effect in small concentration is therefore due to the adsorption of tannin by

the colloidal particles. Alcohol, on the other hand, effects the dehydration purely on the mass-law equilibrium between water and itself (Kruyt, 1930).

Emulsoids in general can be precipitated by large quantities of such electrolytes as $MgSO_4$ and Na_2SO_4, a phenomenon generally known as "salting out." Both the cation and the anion play a role in this phenomenon. The cation causes electric discharge of the agar particles and the anion acts as a dehydrating agent, following the effect of the lyotropic series: $SO_4 < Cl < Br < NO_3 < I < CNS$ (Kruyt and de Jong, 1928).

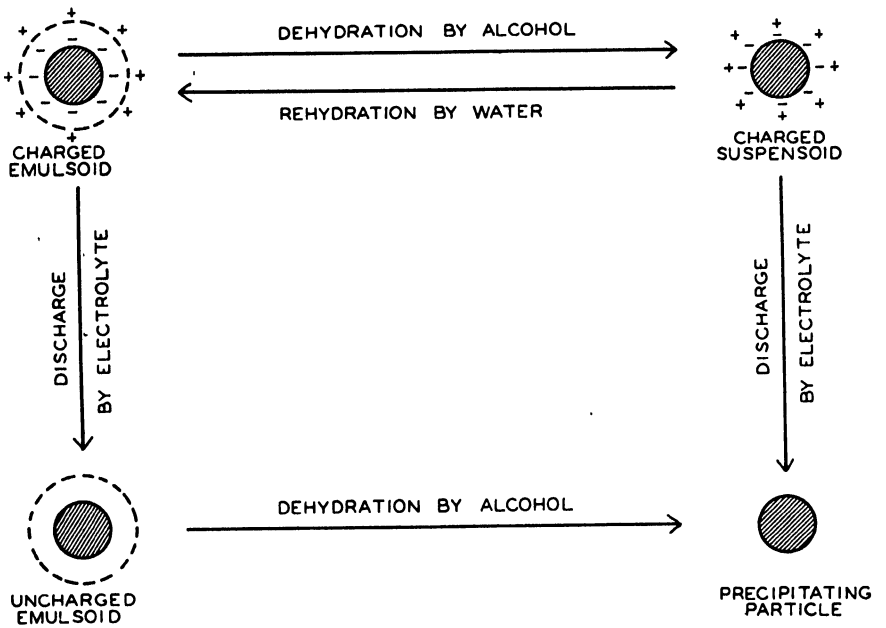


FIGURE 21. Diagram illustrating the stability of agar sols. (After Kruyt, "Colloids," John Wiley & Sons, 1930.)

Sol-Gel Transformation. It is a well known fact among those who have used agar in the laboratory that an agar sol, when cooled to about 40°, may form a firm gel, if the concentration is not less than 1 per cent. The actual setting temperature depends on the concentration and other factors. The gelation of agar is a classical example of hysteresis, because of which it is possible to examine the physical properties of both agar sols and gels over a considerable temperature range.

Hatschek and Humphry (1924) prepared clear 7 per cent agar sols by holding the solutions at 80° for 2 to 4 hours. By this treatment, the insoluble constituents gradually unite to a dirty gray coagulum, readily filtered out by glass wool. Such sols differ in optical properties from the corresponding gels, the sols being clear in transmitted and reflected light, whereas the gels are clear only in transmitted light and distinctly opalescent in reflected light. Aging the gels for several days at 62° does not decrease the opalescence of the gels. These authors further observed that the electrolytic conductivity of a sol containing an electrolyte, for instance, 12.5*M* $CuSO_4$ solution determined at 50°, was less than that of the corresponding gel system at the same temperature. They also noted that increasing the agar concentration increased the difference in conductivity. The results have been confirmed and extended by Iwase (1927), but no explanation has yet been offered.

Donnan and Krishnamurti (1930) made an extensive investigation on the scattering of light by agar sols and gels. They used 1 per cent agar sol at temperatures ranging from 80° to 25°. They observed a change in the light scattering at about 35°; below this temperature, however, the light scattering increased rapidly, signifying an increase in number and/or size of the colloid micelles. This effect precedes the sol-gel transformation and continues even when the agar sol sets to a firm gel. Heating the gel does not cause any appreciable change in light scattering until about 40°. From that temperature on there is a gradual decrease of light scattering, and a progressive diminution in bulk of the colloidal micelles constituting the gel. At about 90° the gel reverts to a sol which possesses the same light-scattering capacity as the original sol. Donnan and Krishnamurti believe that as the temperature is elevated "more and more of the material constituting the gel micelles passes into the intermicellar liquid, until finally the structure or framework constituting the gel disappears and we obtain a sol which may be polydisperse, and may contain a large proportion of the agar in a molecularly or nearly molecularly disperse form." In gels the agar is probably present as relatively large aggregates or micelles. These authors also found experimental evidence that the gel scatters more light than the sol, the difference becoming less as the temperature increases (Table 17).

Table 17. Intensity of Scattered Light (*I*) in 1 per cent Agar Sol and Gel at Various Temperatures (Donnan & Krishnamurti)

Temperature (° C)	*I* (Sol)	*I* (Gel)	$\frac{I\text{ (Gel)}}{I\text{ (Sol)}}$
40	10.9	107.4	9.9
50	10.6	97.7	9.2
60	10.6	88.0	8.3
70	10.5	73.5	7.0

Investigating the same problem, Hatschek (1929) observed that the graph obtained by plotting *I* (gel) against concentration of gel gave a maximum at about 13 per cent agar. He believed that hydration was not the only factor involved in the increase of Tyndall effect when an agar sol sets to a gel, but that pronounced hydration of the particles leads to an increase in their size. Due to the hydration of the agar, the total volume of the system agar plus water is reduced, resulting in an increased refractive index. While increasing the concentration of agar increases the value *I* (sol), the value in 2 per cent sols is only 19.0 at 35°. The concentration effect is very marked, however, in the case of *I* (gel); and a value of 220 is reached for a 2 per cent agar over the temperature range from 20° to 50°. Obviously the concentrated gels contain numerous large colloidal particles.

It is therefore recognized that cooling an agar sol causes a great increase in the number of micelles before gelation sets in, and that similarly, reducing the temperature results in a marked increase in the total volume of these micelles long after the firm elastic gel has been obtained. On the other hand, raising the gel temperature causes a progressive diminution of the total volume of the micelles before the gel-to-sol temperature is attained (Hatschek, 1929).

Stoloff (1943) made a comparative study of the gelling temperature and gel strength of various concentrations of agar and agar-like substances extracted from various seaweeds, including that of carrageen (Table 18). An interesting observation is that agar extracted from *Gracilaria confervoides* of North Carolina has two gelling temperatures, 43° and 59°. This corresponds to observations on the viscosity of this colloid at lower concentrations, followed as the sols cool. Two sudden rises in viscosity were noted, indicating two transitional temperatures and probably the presence of two components in this particular *Gracilaria* agar. Attempts to effect their separation were, however, unsuccessful.

Table 18. Physical Properties of Seaweed Extracts (Stoloff)

Seaweed Extract	Conc. (%)	Gelling Temp. (°C)	Gel Strength (Gms gel-breaking load)	Remarks
Carrageen Ext.	1	31	15	Solutions viscous
(commercial, improved)	3		90	
	5		300	
Gracilaria cornea	1	46	0	Solutions viscous
Ext. (Florida)	2		10	
	3		15	
Gracilaria floridana	1	48	20	Solutions viscous
Ext. (Florida)	2		110	
	3		210	
Gracilaria confervoides	1	46	95	
Ext. (Australia)	1½		167	
Gracilaria confervoides	1	47	120	
Ext. (California)	1½		190	
Gracilaria confervoides	½	43	113	
Ext. (North Carolina)	1	and	407	
	1½	59	650	
Gracilaria confervoides	1	37	187	
Ext. (South Africa)	1½		337	
Strip agar (commercial)	1	37	80	
	1½		270	
Japanese agar	1	38	70	
	1½		80	
Reclaimed agar	1	39	113	
	1½		287	
Bacto-agar (new sample)	1	39	215	
	1½		350	
Gelidium agar (Lab. extract)	1	39	360	
	1½		450	

Syneresis of Agar Gels. Gels shrink and exude some liquid from their surfaces upon standing. This phenomenon was first observed by Graham, who gave it the name *syncresis*, which is, as W. Ostwald stated, one of the most characteristic properties of a gel. The "bleeding" of an agar slant, or the so-called "water of condensation" found at the bottom of agar slants and on their surface is a familiar example. The liquid which exudes from the agar gel is not pure water but rather a dilute solution, the composition of which is determined by that of the original gel (Healy, 1926). Pijper (1919) suggested calling it "agar serum." The value of an agar medium for bacteriological culture depends, to some extent, upon the degree of syneresis. In recent years because of an agar shortage, jellifying substances such as carrageenin have been suggested as agar substitutes. In certain gels, however, there is enough syneresis to interfere with counting colonies found on plates and with the isolation of pure cultures; such gels are thus made useless for routine bacteriological work. Stoloff (1943), for instance, found that *Gracilaria* agar in 24 hours exudes ten to twenty times as much liquid as similar concentrations of *Gelidium* agar. This large amount of exudate causes the gel to slip in its container and induces spreading of colonies.

Rossi and Marescotti (1933) studied the syneresis of agar gels containing different concentrations of NaCl, NaBr, NaI, KCl, KBr and KI. They found that, with the exception of KI, the syneresis liquid was neutral to litmus, and that its salt content not only differed from, but was also higher than, that in the original gel. The rapidity with which syneresis took place varied in the presence of different salts. Later, these authors (1936) found that if two salts, such as NaCl and NaI, are added instead of a single one, the resulting liquid from the syneresis contained lower concentrations of these salts than did the original gel. Thus it appears that the addition of a salt to agar already containing another salt can greatly modify the behavior of the colloid.

Rossi and Scandellari (1936) made a similar study, but used organic substances, such as urea, hexamethylenetetramine and sucrose instead of the salts. They found that these substances behaved like the salts. On the assumption that gelatinization is a result of separation of agar in spongy form and in such a way as to occlude the dispersing liquid within vacuoles, they concluded that the separated agar tends to absorb water and solute; that an equilibrium is established between the solution of salts, water and adsorbed solute; and that this equilibrium varies with the nature of the solute and with its concentration in the agar, thus resulting in different concentrations of salts in the syneresis liquid and in the agar gel itself.

Generally speaking, some gels show increased syneresis with rising concentration, while others behave in the reverse way. Agar belongs to the second type (Kuhn, 1928).

Gross Structure and Pore Size of Agar Gels. Ambronn (1891) found that thin layers of agar, when frozen and dried on glass plates, appeared microscopically as a fine network, resembling parenchymatous cells of plants. The walls of the meshes were also like those of normal cells, having a decided double refraction. The minor axes of the particles lay perpendicular to the surface of the partition caused by freezing. Carey (1920) found that agar gels have a decidedly lamellated microscopic structure, with numerous biconvex lentiform cavities. Such cavities were finer in stronger gels and larger in weaker ones; there appeared to be a gradual change from the coarser to the finer structure as the concentration of the agar increased. Since all the gels except those dried at room temperature showed such lamellated structures, it was suggested that the specific gel structure was due to the rapidity of the drying.

To show the effect of concentration of agar upon the structure of the gels, Friedman (1930) made several determinations of the rates of diffusion of urea and glycerin in various concentrations of purified gels. As the gel concentration increased from 0.8 to 5.15 per cent, the diffusion of urea slowed down 36 per cent. Glycerin behaved similarly. Since the diffusion of a non-electrolyte was determined to a large extent by the molecular weight or size of the diffusing molecule on the one hand, and the size of the openings in the solid framework of agar gels on the other, the latter can be calculated if the former is known, together with the radius of its molecule and certain other correction factors. Friedman determined the values for the radii of the "pores" in agar gels, based on two different diffusates (Table 19).

Table 19. Size of Pores in Agar Gels (Friedman)

Agar Gels (%)	Radii of pores in millimicrons (mμ)	
	Determinations based on urea as diffusate	Determinations based on glycerin as diffusate
2	2.90	5.65
5	0.74	1.43

The large values for the radii from the glycerin determinations would be expected from the tremendous effect which glycerin has on the agar. It was shown that glycerin increased the rate of diffusion of urea in agar gel by 50 per cent, indicating that the former had modified the gel structure to allow this faster diffusion. Dextrose and trimethylene glycol have similar effects, but ethyl alcohol retarded the rate of diffusion.

Influence of Chemicals on Rigidity of Agar Gels. Feller (1916) found that addition of 5 per cent HCl to agar sols resulted in rather soft and crumbly gels. Addition of peptone, on the other hand, made a firmer gel. KCl seemed to decrease slightly the gel strength of agar. Michaud (1922) found that both acid and base greatly decrease the modulus of rigidity of agar gels. The effect of concentrated acids is greater than that of concentrated bases. In dilute gels, the reverse is true.

The action of the base is linear, whereas that of the acid is parabolic. Hydrolyzable salts behave like acids or bases; non-hydrolyzable salts decrease the gel rigidity to an extent of about one-tenth of the effect of the hydrolyzable salts. Organic substances behave variably.

Carrageenin

Carrageenin absorbs water rapidly and the absorption is accompanied by considerable swelling. It dissolves readily in warm water and will set to a firm gel upon cooling if present in sufficiently high concentrations. In its gelatinizing power, carrageenin is intermediate between agar and gelatin resembling rather the latter. While agar dissolves only if the water is heated for some time to 90° or higher, carrageenin, like gelatin, dissolves easily in warm water (about 60°). Agar readily forms a firm gel in concentrations as low as 1 per cent; carrageenin is able to form a rather soft gel at 3 per cent, and a firm one at 5 per cent. The melting temperature of carrageenin gel is much lower than that of agar. Haas and Hill (1921) found that a 3 per cent carrageenin gel melts at 27° to 30° and a 5 per cent gel at 40° to 41°, whereas a 1 per cent agar gel melts at 90° or higher. The melting point of carrageenin gel is very similar to that of gelatin. There is, however, one important difference. The melting points of a 3 per cent gel and that of a 5 per cent gel of gelatin do not differ much, being 27.7° and 29.5°, respectively. There is a difference of more than 10° between the melting point of 3 and 5 per cent carrageenin gels. The latter can therefore be used for bacteriological cultures, without liquefaction when incubated at or slightly above blood temperature. The gelatinizing power of carrageenin gel is not destroyed by boiling. Haas and Hill reported that a 3 per cent solution after 3½ hours' reflux boiling sets on cooling. The gelatinizing power is increased greatly by the addition of Rochelle salt. Heating carrageenin solutions with acids rapidly destroys their gelatinizing power (Haas and Russell-Wells, 1929).

In their study on the colloidal properties of carrageenin, Gutbier and Huber (1922) noted that the viscosity of a dialyzed low-ash carrageenin solution decreased upon aging and after heating. There is a marked increase in viscosity as the concentration of the carrageenin solution is increased (Table 20).

Table 20. Viscosity of Carrageenin Solution in Relation to Age, Heat and Concentration, Determined at 25°, Relative to Water as Unity (Gutbier & Huber)

Age (days)	0	1	2	5	15	33		
Viscosity	15.29	14.87	14.11	10.52	7.74	7.19		
Mins. boiled	5	15	25	45	75	135	165	
Viscosity	6.89	6.43	6.19	5.80	5.47	5.01	5.01	
Conc. (%)	1.07	0.89	0.76	0.67	0.59	0.45	0.35	0.18
Viscosity	36.96	31.17	18.18	14.15	11.71	9.02	7.39	4.45

Gutbier and Huber also found that the addition of electrolytes reduced the viscosity of the solution until a constant value was reached, at about 0.12*N* for HCl, NaOH and NaCl. A more extensive investigation of the action of electrolytes on viscosity of carrageenin solution was made by de Jong and Gwan (1929). These authors found the viscosity to be extremely sensitive to electrolytes even in traces. Thus, as little as 1 milliequivalent of an electrolyte causes pronounced decrease in viscosity. The valence of the cation is the important factor (cf. Kruyt, 1930).

Pfister (1941) and Blihovde (1941) reported that the viscosity of carrageenin solution depends to a large extent on the manufacturing method. One per cent solutions may vary in viscosity from a few centipoises, following ordinary methods of preparation, to several hundred or even a thousand centipoises under improved methods of manufacture.

The merit of carrageenin as a protective colloid has been investigated by Gutbier, Wolf and Kiess (1922). These authors found that when 5 parts of carrageenin

solution and 2.5 parts of 0.1*N* $AgNO_3$ solution were treated with 0.1 per cent hydrazine hydrate solution, a very stable sol of colloidal Ag was obtained which could then be purified by dialysis.

Funorin

Investigations by Aoki (1935) showed decreases in the viscosity of funorin solutions in the presence of dissolved substances such as NaOH, H_2SO_4, $MgCl_2$, $MgSO_4$, $CaSO_4$, or NaCl (Table 21). It was also found that heating the sol decreased its viscosity. The two species commonly used yielded funori products differing in viscosity (Table 22). While it was alleged by Aoki that the viscosity was also influenced by the solution used in bleaching the product, the differences do not seem significant enough to warrant such a conclusion.

Table 21. Influence of Chemicals on Viscosity of 0.5 per cent Solution of Dry Powder of *Gloiopeltis furcata*, Determined by Redwood's Viscometer, Measured in Seconds (Aoki)

Chemical	Temp. (° C)	Concentrations of Chemicals Used				
		0%	0.001%	0.01%	0.1%	1.0%
NaOH	21.0	46.0	45.2	44.4	41.2	37.0
H_2SO_4	21.0	45.6	44.4	41.6	36.8	34.0
$MgCl_2$	17.5	45.8	45.0	43.0	38.0	31.4
$MgSO_4$	19.0	44.6	45.0	44.0	37.0	34.8
Na_2SO_4	18.0	45.6	45.4	44.0	41.8	37.0
$CaSO_4$	18.5	45.3	45.0	43.0	39.4	—
NaCl	17.7	46.0	45.0	44.0	40.0	31.4

Table 22. Viscosity of 0.5 per cent Solution of Dried Powder of *Gloiopeltis furcata* (Fukuro-funori) and *G. tenax* (Hon-funori) in Different Concentrations, Determined by Redwood's Viscometer at 24° C, Measured in Seconds (Aoki)

Species of *Gloiopeltis*	Time of boiling (minutes)				
	0	5	15	30	60
G. furcata	42.6	41.2	38.6	37.4	36.0
G. tenax	70.6	63.4	60.0	55.6	53.0

Aoki (1937a) found a correlation between the habit of the plant and the viscosity of its sol. The viscosity increases with the size of the plant, but decreases with the number of branches (Table 23). He divided his specimens into three size-groups, the large ones averaging 5.4 cm high and 0.30 cm in diameter, the medium ones 3.6 cm high and 0.19 in diameter, and the small ones 2.0 cm high and 0.16 cm in diameter. A seasonal variation of the viscosity of the material was also found, the summer product being the most viscous.

Table 23. Habit of *Gloiopeltis furcata* and Viscosity of 0.5 per cent Sol Prepared from Its Dried Powder, Determined with Redwood's Viscometer at 15° C, Measured in Seconds (Aoki)

Size-group	Number of Branching				
	0	1	2	3	4
Large	134	130	119	118	112
Medium	125	119	116	116	111
Small	118	115	116	112	111

The temperature at which a 0.5 per cent solution of the dry powder of *Gloiopeltis* was heated influences the viscosity of the treated sol (Aoki, 1937b). There appears to be an optimum temperature for the preparation of each species of *Gloiopeltis* under investigation (Table 24).

The influence of various chemicals on the viscosity of funorin from *Gloiopeltis furcata*, and *G. tenax* was investigated by Aoki (1937c). The viscosity reached a maximum when placed in 30 per cent of the monohydric alcohols methanol, ethanol and isoprophyl alcohol, 100 per cent ethylene glycol, 30 per cent acetone, and 40 per

Table 24. Influence of Temperature History on Viscosity of 0.5 per cent of Dry Powder of Two Species of *Gloiopeltis* and That of the Prepared Bleached Product Funori, Determined by Redwood's Viscometer at 15°, Measured in Seconds (Aoki)

Temp. (° C)	Fukuro-funori (*G furcata*)	Hon-funori (*G. tenax*)	Funori (Product)
15	76.2	122.2	98.4
20	83.4	——	112.6
30	——	——	132.6
38	102.8	150.2	158.4
40	99.8	——	——
50	99.0	150.0	176.4
60	92.0	148.0	199.8
70	99.0	140.6	203.2
80	88.6	133.8	215.0
90	86.8	126.8	206.8
100	75.4	112.8	203.6

cent formalin. Carbolic acid up to 5 per cent was found to exert no influence. The same author (Aoki, 1938a) found that the viscosity of the products from plants growing at different tide levels also differed; generally those of the deeper waters gave less viscous sols than those of the shallower waters. Commercial preparations, however, do not necessarily vary in their viscosity directly in accordance with their assigned grades.

The viscosity of the funori was found to increase during storage. For some reason aging favors viscosity of the product (Aoki, 1938b). While maximum viscosity of the extract is reached by heating at a certain temperature for a definite time, the viscosity decreases with the duration of heating. Sodium peroxide, generally employed as bleaching agent, does not influence the viscosity of the resulting product if employed at concentrations lower than 0.1 per cent; when the chemical is used in excess of this strength, however, the viscosity decreases with the concentration used.

Yanagigawa (1937) found that if fermentation occurred during the process of manufacture of funori, the resulting product was less viscous than otherwise. Pretreatment of the product with sodium bicarbonate decreased the viscosity and adhesive power, but not its luster.

Algin

The term "algin" is used in two senses. In the broader sense it refers to alginous compounds in general, including alginic acid, sodium and other metallic alginates. Commercially it is used in a narrower sense, referring to sodium and other soluble alginates.

Alginic acid is insoluble in cold, and only slightly soluble in boiling water. When moist, it is capable of absorbing several times its weight of water; reports that it may absorb 200-300 times are very doubtful and lack confirmation. When dried, it becomes very hard and horny and resistant to solvents. In fact, dried alginic acid is so hard that it can be turned on a lathe. It is insoluble in alcohol, ether, and glycerol. As a colloid, alginic acid may be considered as an irreversible gel. It is capable of absorbing salts to the extent of 60 per cent of its own weight, but has no selective action for potassium (Hoagland and Lieb, 1915).

Alginic acid does not reduce Fehling's solution, but rapidly forms reducing substances if dried at 100° or if boiled with dilute acid. Its optical activity is high, and the rotation values obtained by different workers from various sources are in fair agreement, varying from −132.6° to −169.2°. The published data on neutralization equivalents, determined by titration, vary greatly (Table 25).

The theoretical equivalent weight for a true polyuronide with all carboxyl groups free is 176. Nelson and Cretcher's and Miwa's values were the only ones approach-

Table 25. Optical Rotation and Neutralization Equivalents of Various Alginic Acid Preparations

	$[\alpha]_D$	Neutralization Equivalents
Hoagland and Lieb (1915)	−169.2°	325
Atsuki and Tomoda (1926)	−130°	221
Schmidt and Vocke (1926)	−140°	185
Nelson and Cretcher (1929)	−133°	179
Colin and Ricard (1930)	−134°	202
Miwa (1930)	−133°	177-9
Dillon and McGuinness (1931)	—	195-8
Schoeffel and Link (1933)	−136°	195
Barry and Dillon (1936)	−132.6°	190.5-194.2

ing this theoretical figure. The deviations among the various preparations are probably due to the varying time and temperature of drying to which the extremely sensitive alginic acid was subjected by the various investigators.

As previously mentioned, alginic acid is a colloidal polyuronic acid with weak acid properties, but is sufficiently acidic to liberate carbon dioxide from carbonate. When the carboxyl groups of alginic acid react with compounds containing ions of the alkali metals, or of ammonium or magnesium, the corresponding alginates are formed. These are all water-soluble and possess marked hydrophilic colloidal properties. A small percentage of these alginates yield highly viscous solutions. Alginates of the lower amines, such as triethanolamine and the various alkaloids, are also water-soluble. Alginates other than those mentioned above are insoluble in water. Therefore, upon addition of solutions containing metallic ions such as calcium, the insoluble alginates are precipitated. Stanford (1866) prepared several alginates. A series of five soluble and twenty-two insoluble alginates was prepared by Lieb by the addition of metallic salts to solutions of sodium alginate. The soluble alginates were precipitated by alcohol and the insoluble ones from alginate solutions slightly acidified with acetic acid (Table 26, after Hoagland, 1915).

On drying or warming alginic acid, depolymerization occurs. Therefore instead of preparing the unstable acid, its salts, especially the soluble ones, are the standard products. Commercially, sodium alginate, and to a lesser extent the ammonium salt, are the important ones. Sodium alginate readily dissolves in either hot or cold water upon stirring, yielding a viscous solution. The solution is not coagulated by heat nor gelled by cooling. Its viscosity depends on the percentage of the algin used, the degree of polymerization of the algin molecule, which is largely governed by methods of manufacture, and the presence of traces of ions such as those of the alkaline-earth metals. Commercial algin therefore varies greatly in its viscosity. A 1 per cent solution may have a viscosity of 0.1 to 150 poises (Steiner, 1941). Osborn and DeKay (1941) found that a 1 per cent sodium alginate solution has a viscosity of about 1000 centipoises at 17°; at a concentration of 5 per cent, an immobile gel is formed.

Algin solutions are not coagulated or precipitated by alkalies and their salts, magnesium and ammonium salts, some acids such as boric, carbolic, gallic, pyrogallic, and arsenious, mercurous iodide and chloride, or the halogens. They behave similarly toward starches, glycerol, sucrose, dextrose and other sugars, casein, proteins, soluble oils, gums, soaps, ethylene glycol, and wetting agents (Stanford, 1884; Steiner, 1941; Osborn and DeKay, 1941). Mineral and organic acids other than these will precipitate insoluble alginic acid from an algin solution. Similarly, organic solvents such as methanol, ethanol, and acetone will coagulate algin from the aqueous solution when added in sufficient quantity.

Since alginates other than those of the alkali metals, ammonium, and magnesium are insoluble in water, addition of solutions containing metallic ions such as calcium, barium, iron, bismuth, nickel, copper, lead, mercury, arsenic, etc., to algin solutions

Table 26. Metallic Alginates and Their Properties (Hoagland)

Soluble Alginates

Metal	Metallic salt used	Color of fresh precipitate	General properties of precipitate
Li	Li-acetate	Silver white	Gelatinous, transparent
Na	NaOH	White	"Stringy," brittle when dry
Mg	Mg-acetate	do	Transparent, gelatinous
NH_4	NH_4OH	Light yellow	Light, gelatinous
K	KOH	Transparent	Light, fluffy

Insoluble Alginates

Al	$AlCl_3$	White	Gelatinous, brittle when dry, brown color
Ca	$CaCl_2$	do	Gelatinous, glossy when dry
Cr	$Cr(NO_3)_3$	Light blue	Heavy, nongelatinous
Mn	$Mn(C_2H_3O_2)_2$	Light red	Gelatinous, good gloss to paper when dry
Fe^{++}	$FeSO_4 \cdot 7H_2O$	Light brown	Gelatinous, brittle when dry
Fe^{+++}	$FeCl_3$	Brown	Gelatinous
Co	$Co(NO_3)_2$	Reddish	Gelatinous, good gloss to paper when dry
Ni	$NiCl_2$	Light green	Gelatinous
Cu	$CuSO_4$	do	do
Zn	$ZnSO_4$	Colorless	Gelatinous, silvery gloss to paper when dry
Sr	$Sr(NO_3)_2$	Light brown	Heavy gelatinous, transparent when dry
Ag	$AgNO_3$	White	Gelatinous, becoming dark red when dry
Cd	$Cd(NO_3)_2$	Colorless	Gelatinous, becoming horny
Sn^{++}	$SnCl_2 \cdot H_2O$	White	Thick, gelatinous
Sn^{++++}	$SnCl_4$	do	do
Ba	$BaCl_2$	do	Gelatinous, good gloss to paper when dry
Pt^{10}	$PtCl_4$	Light brown	Gelatinous
Au^{10}	$AuCl_3$	Red	do
Hg	$Hg_2(NO_3)_2$	White	Dense, white, gelatinous
Pb	$Pb(C_2H_3O_2)_2$	Colorless	Gelatinous, like isinglass when dry
Bi	$Bi(NO_3)_3$	White	Gelatinous
U	$U(SO_4)_2 \cdot 4H_2O$	Yellow	Thick, gelatinous

[10] Precipitated from alcohol solution.

will result in the precipitation of the corresponding insoluble alginates. By adding a small quantity of such an ion to an algin solution, therefore, it is possible to obtain a mixed salt which exists as a semigel and is almost completely soluble. This chemical gelation has found extensive uses in industry. Commercially, calcium salts, especially the relatively insoluble ones such as calcium citrate, have proved very satisfactory for this purpose. By using such salts the release of calcium ions can be controlled, and the resulting solutions may either be thickened or converted into rigid gels in accordance with the amount of calcium present. Other calcium salts, such as the acid pyrophosphate and the tartrate, have also their special fields of use. Acids such as citric acid are found to increase greatly the rate of setting of the gel and its ultimate firmness. Hard water contains sufficient calcium salts to give algin sols a higher viscosity than sols made in distilled water.

Insoluble alginates of the metallic ions which form complex ions upon the addition of ammonia, *i.e.*, silver, copper, cadmium, ferric iron, cobalt, nickel, chromium, manganese, zinc, etc., and those of the amphoteric metals, such as aluminum, dissolve upon the addition of concentrated ammonia. When these solutions are dried, the original insoluble alginates are formed again.

The dispersion of soluble alginates in small amounts of water generally requires warming the mixtures to about 160° F, which procedure is sometimes a distinct disadvantage in commercial applications of these products. Certain chemicals, such as borax, when added in very small concentrations, are able to reduce the solubility of the alginates and consequently to facilitate complete wetting and dispersing of the borated algin particles (Mertel and Schaller, 1941).

The pH of sodium alginate resulting from the stoichiometric combination of alginic acid and sodium hydroxide is approximately 7.7. It is practical, however,

to employ this algin within a pH range of about 4.0 to 10.0. If the pH goes much below 4.0, the alginic acid tends to precipitate, while above 10.0 the algin loses viscosity rapidly and tends to be unstable (Steiner, 1941). Increases in temperature reduce the viscosity of algin solution but do not cause any notable depolymerization below 50°. Unlike agar, and in common with gelatin, algin solutions are readily decomposed by bacterial action if allowed to stand for prolonged periods. Hence preservatives are often needed for algin compositions.

Preparation of Phycocolloids

Agar

As mentioned previously, agar is insoluble in cold but soluble in hot water at 90° to 100°. Therefore it can be easily extracted by boiling the agarophytes in water, congealing the solution by cooling, cutting the gel in whatever form wanted, freezing it by natural or artificial means, and finally thawing and drying it in the sun or by artificial heat. This same basic principle of making agar is used by the old-fashioned home industry in Japan and by modern industry in America as well. While agar can be precipitated by the addition of alcohol, tannin or salts, such methods have not yet been reported to be actually employed in the industry. Evidently the freezing-thawing method of purification is still more economical.

Japanese method of manufacture. While there are some modern agar factories in Japan, the majority of the Japanese establishments are still making agar by the traditional method, utilizing natural freezing, thawing, and drying. The process has been described by Smith (1905a), Davidson (1906), Tressler (1923) and Dickover (1927).

Preliminary treatment

If the agarophytes coming to the manufacturers are not cleansed and bleached, they have to be subjected to the following treatments:

Cleansing. The agarophyte is placed in a kind of stone mortar in which it is beaten and pounded until most of the shells, sand, and other impurities adhering to the seaweed are removed. It is then placed in a basket made of bamboo and immersed in fresh water to remove the remaining foreign matter.

Bleaching. In the Japanese process the agarophyte is generally bleached before it is subjected to the extraction process. The manufacturers are very particular about the choice of season and weather for the bleaching of their raw material. Usually this procedure is carried out at the end of August or the beginning of September, when the summer heat has abated slightly. Rainy weather is to be avoided; otherwise rotting may take place, thus decreasing greatly the production of the bleached product. The seaweed is thinly spread on bamboo or rush mats, through which the water drains away, or it may be spread directly on the ground. It is left in this condition for several days and nights, and is sprinkled with water frequently. Dew greatly facilitates the bleaching. When partially dry, the agarophyte is turned over. The time required to complete the bleaching varies with weather conditions, but usually takes several days. With exceptionally favorable weather twenty-four hours may be sufficient. When the plants are bleached almost colorless, they become matted together and form loose-meshed sheets. They are then rolled up in bundles of fixed weight and stored away until the time for extraction.

Extraction

While *tengusa* (*Gelidium Amansii*) is the principal agarophyte used in the manufacture, several other species are employed chiefly as cheap substitutes in varying portions, and some for special purposes. For instance, *egonori* (*Ceramium hypnoides*) is used in the manufacture of bar or square agar to impart a finer looking appearance to the product. The amount of the supplementary agarophyte added to

the *tengusa* in the cooker varies from place to place and from one manufacturer to another. Usually, it is added to 20 to 40 per cent of the total quantity of agarophyte used. For square agar, the *egonori* is added in the proportion of 10 to 20 per cent, and for shredded agar, 30 to 40 per cent.

The *tengusa* and the supplementary agarophyte are boiled with about fifty times their weight of water in an iron kettle, which is placed over a specially constructed furnace. In some establishments direct steam is used in place of fire heat, and wooden vats are employed, the steam being admitted from below. If the supplementary agarophyte used requires longer time for the extraction, as for instance, *toriashi* (*Acanthopeltis japonica*), it is subjected to the extraction process about one hour before the addition of the *tengusa*. After about five to six hours' boiling with frequent stirring, one part of sulfuric acid or ten parts of vinegar per 1000 parts of the agarophytes are introduced to hasten their digestion. Some water is added, and the boiling continues for another half hour. The extraction is then completed, and a thick gelatinous liquor is obtained. It is said that boiling the seaweed gently over a slow fire for a longer period produces better results than if a very hot fire is used to boil the agarophyte vigorously.

Gelation

The hot liquor is separated from the residue by straining through coarse hemp or cotton cloths stretched tightly over a frame. The filtered liquor is collected in a large vat or tank beneath. This is followed by a more complete separation of the dregs by squeezing the solution through a linen cloth of finer meshes in a press. The dregs are collected and boiled again for about four hours and strained similarly. The filtered liquor in the vat is then ladled out and poured into wooden trays about 2 feet long, 1 foot wide, and 3 inches deep. The liquor will solidify in about eighteen hours. The resulting gel is called "tokoro-ten." The jelly is then cut into the desired shape. If shredded agar is desired, the jelly is cut by knives into blocks 1 foot long and 2 inches square. These blocks are then forced through a coarse wire grating which cuts the jelly into slender sticks 10 to 14 inches long and about one-eighth of an inch thick.

Freezing

The jelly blocks or sticks are spread out on bamboo mats or on boards placed on elevated trestles outdoors. Complete freezing generally requires from two to three cold nights. Water crystallizes out during the freezing, and when the frozen gel thaws, the water runs out, carrying with it the salts and other impurities which are soluble in cold water. This leaves the agar in relatively pure condition. After thawing, the wet agar is left to dry in the sun. Threaded agar is tied in small bundles weighing about 8 ounces each. The block agar or square kanten is marketed as such.

Since the traditional Japanese method of agar manufacture depends almost entirely on atmospheric conditions, the time and the place for making agar are vitally important. The suitable season is generally from the latter part of November to February or March of the following year, when the temperature is cold enough for the freezing process. The selection of place depends on its winter temperature, the quality of its water, and the topography of its ground. The most suitable temperature is between 25° and 35° F. An ideal locality is bounded on the northwest by mountains or hills, with a stretch of meadow or plain to the southeast. The mountains or hills serve to intercept the moist north wind in the winter months, and the meadow or plain serves for spreading the agar gels to be frozen in the cold nights, and to be thawed and dried in the sun. A clear sky, favorable to frost, is desirable, so that the time required for the congealing can be minimized. A dry atmosphere is advantageous to the processes of gel hardening and drying.

American Process of Manufacture. The present process of manufacture of *Gelidium*-agar in America is principally the same as that devised by John Becker (1929d). The process has been described by various authors (Anonymous, 1927; Becker, 1929d; MacKinnon, 1930; Robertson, 1930; Tseng, 1944c, 1945). Fig 22 is a plant flow sheet of the present process, and the following is a description of it.

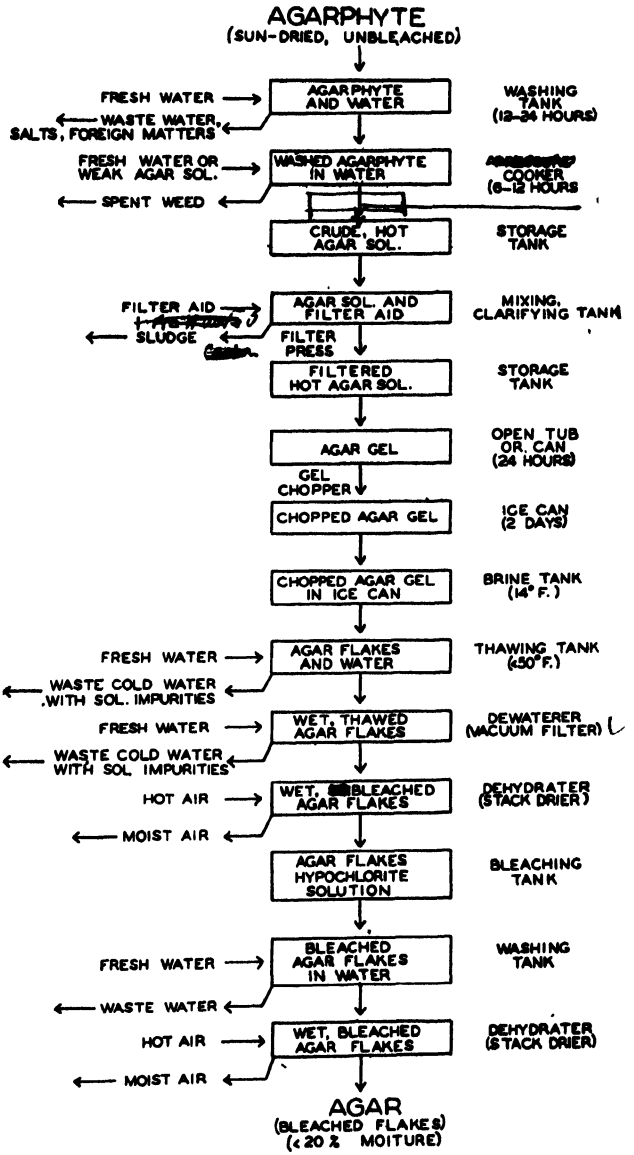


FIGURE 22. American process of agar manufacture. Plant flow sheet diagram.

Washing

The *Gelidium* coming to the factory is sun-dried and unbleached, unlike the Japanese agarophytes which are generally first bleached in the field. It is thoroughly

washed with fresh water in large open tanks for 12 to 24 hours (Fig. 23). This helps to remove the foreign matter, and to eliminate most of the soluble salts leaching out of the plants. The water used for this purpose is generally the waste water coming out of the refrigeration system.

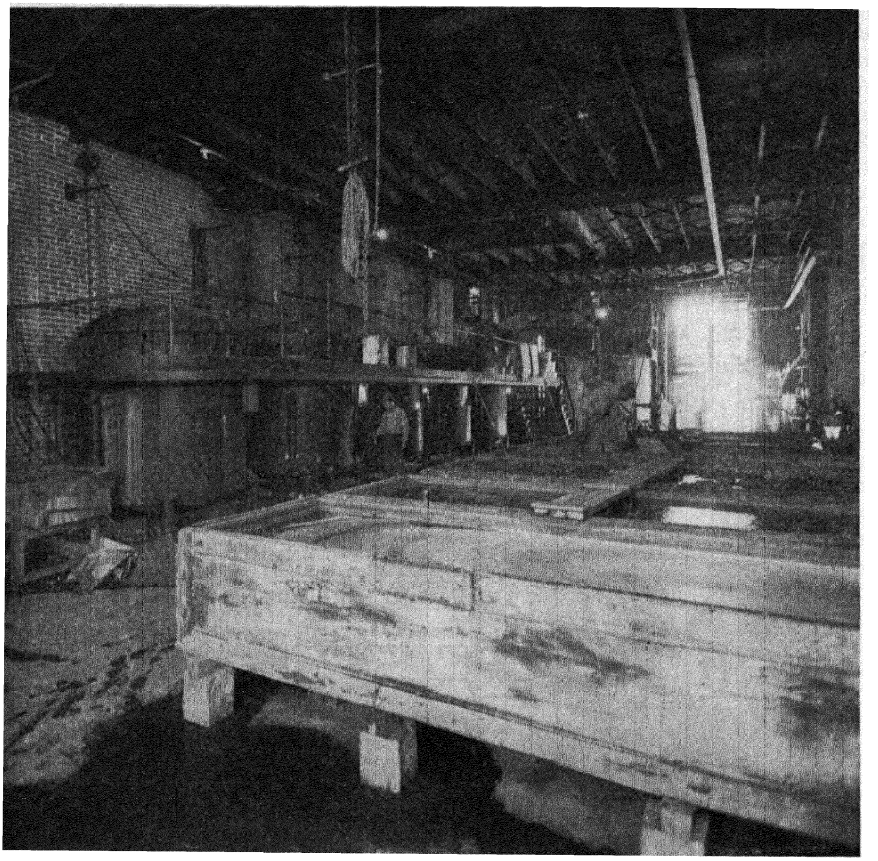


FIGURE 23. Manufacture of agar. Soaking vats on the right, pressure cookers on the left, and filter press in the rear. (*Courtesy of "The Scientific Monthly."*)

Extraction

The thoroughly washed agarophyte is then transferred in iron dump baskets by crane to a digester. This is generally a pressure cooker, holding about 1,200 gallons and heated by steam coils (Fig. 23). Alternately, it may be an open air cooker. About one pound of the agarophyte is added to each gallon of water, or of dilute agar solution from previous digestion of partly spent weed. The ratio between the water and the agarophyte used is variable, depending principally upon the quality of the raw material, especially the amount of epiphytic plants and animals on the *Gelidium*. It is digested under steam heat at a pressure of 15 lbs per sq in for six hours. Following a modified countercurrent method of extraction, the partly spent agarophyte receives two more extractions for 8 and 12 hours respectively, first with dilute agar solution and finally with water.

Purification

The resulting crude hot agar solution is then drawn off to a storage tank. At this stage, it contains, besides agar, various soluble salts, pigments and other impurities, from which it has to be freed. The principle of the purification used in the American process is the same as that in Japan. By a freezing-thawing process the cold water will carry away most of the soluble impurities, thus purifying the agar. The purification process consists of the following steps:

Filtration. The hot liquor is treated with filter-aid in a mixing, clarifying tank, and filtered at about 30 pounds' pressure in a filter press with cloths previously impregnated with the same filter-aid. Previously, activated carbon was added to the hot liquor at this stage to decolorize the solution. In the present process, however, this is omitted and hypochlorite bleaching is substituted at a later stage.

Gelation. The clarified hot agar solution then fills a series of open tubs, trays, or cans, and is left to gel at ordinary room temperature for a day. Formerly a special combination of congealer and sizer was used, but is not employed now because of certain defects.

Freezing. The solidified agar gel is next passed through a gel chopper. The chopped gel is dropped into ice cans of 100-pound capacity. The cans are finally placed in the freezing chambers at a temperature of about 14° F for about two days (Fig. 24). Formerly 300-pound ice cans were used, which were found to be too thick for the agar gel to be thoroughly frozen.

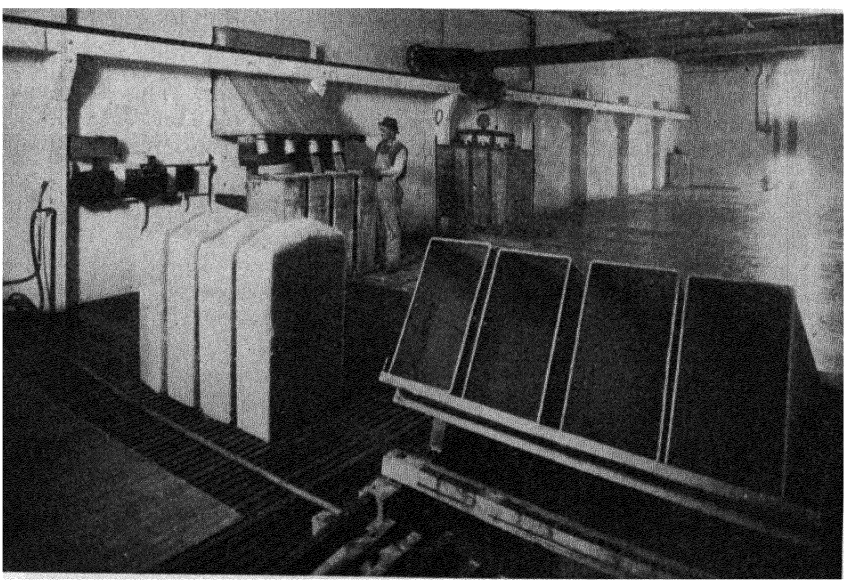


FIGURE 24. Manufacture of agar. Room in which partially purified agar-gel is frozen. (*Courtesy of "The Scientific Monthly."*)

Thawing. The frozen agar cakes weighing about 100 pounds each are cut up finely in a rotary ice crusher, and the crushed granular mass thawed out in a large tank, the temperature of which is maintained below 50° F.

Vacuum Filtration. From the thawing-washing tank the mixture of ice water and agar particles goes to a "dewaterer." This is a rotary vacuum filter which retains the wet agar flakes on the screen and draws away the water containing the

soluble impurities (Fig. 25). The refined agar flakes at this stage carry about 90 per cent moisture.

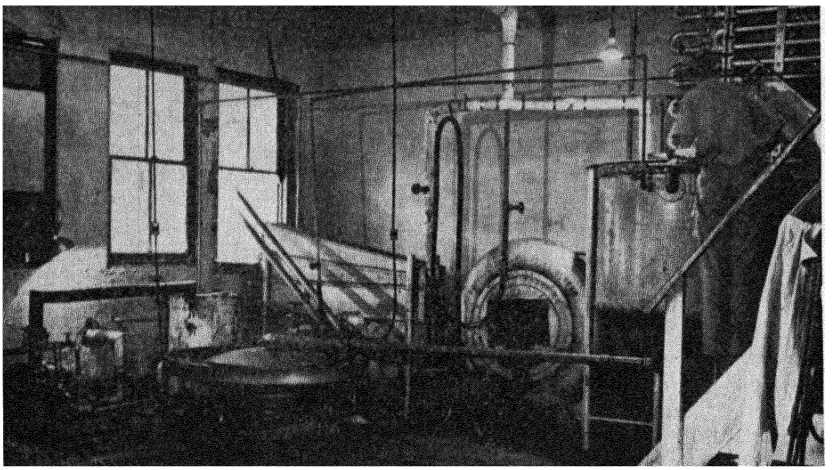


FIGURE 25. Manufacture of agar. Thawing tank on the right and rotating vacuum filter on the left. (*Courtesy of the United States Fish and Wildlife Service.*)

Dehydration

The drying of agar is carried out in a special dehydrator. This is a modified stack drier, consisting of two aluminum cylinders, 35 feet high and 3 feet in diameter (Fig. 26). The wet agar flakes are delivered by a screw conveyor to the first

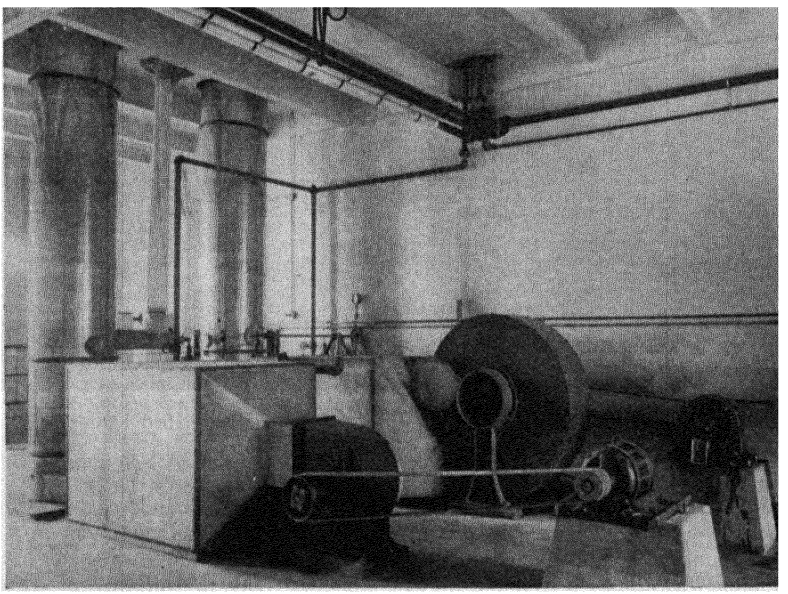


FIGURE 26. Manufacture of agar. The stack driers. (*Courtesy of the American Agar and Chemical Company.*)

cylinder, where an upward hot air blast of about 215° F agitates them constantly. When they are sufficiently dry and thus light enough, they rise over the top of the first column through a fabric pipe to the second cylinder by another screw conveyor. The dried but unbleached agar flakes have a moisture content of 20 per cent in accordance with the U.S.P. requirement, and may now be packed in waterproof paper bags.

Bleaching

Bleaching is carried out when the flakes have passed through the first drying cylinder, and are partially dried, with a moisture content of about 35 per cent. It is effected by the usual hypochlorite method at room temperature. After the excess sodium hypochlorite is reduced by sodium sulfite solution, the bleached agar is washed repeatedly with water, and finally dehydrated in the stack drier.

Grinding

The coarsely flaked agar is satisfactory for most purposes. In certain cases, especially in food industries, a finely ground product is preferred. This is prepared by passage through a swing-hammer mill equipped with suction fan and cyclone collector. The finely ground agar averages 35 per cent 100 mesh and the remainder 60 mesh. Powdering agar is said to involve an average loss of about 10 per cent.

Other Processes. The American process described above is based on the method currently used in making gelidium-agar in California. On the east coast the gracilaria-agar is made by a similar but modified process. Fresh or dry thalli of *Gracilaria confervoides* are washed in long wooden troughs provided with revolving paddles. The agarophyte is digested for about two hours in boiling water in a large open air, wooden cooker. The hot liquid passes through precoat filter presses. The filtered solution is drawn to regular ice cans and frozen for several days. The frozen gel is crushed, thawed, and washed with cold water. The washed flakes are spread on trays, which are then carried to a large hot air room to be dried. Finally the agar flakes are ground to fine powder with a hammer mill.

The New Zealand process for making pterocladia-agar has been outlined by Moore (1944). The dry agarophyte is washed with cold water in wooden vats until the salt, sand, and other foreign materials are removed. It is then digested by hot water in a specially designed pressure cooker. The extracted liquor is drawn off while hot into a mixing vat, where it is treated with bleaching agents and filtered. The filtered liquor is run into open enameled pans. The solidified gel is then cut and dialyzed in a series of operations and the majority of the impurities therein removed by freezing. After thawing, the wet gel is spread on wire-gauze trays and dried in a hot air chamber, until the moisture content is under 18 per cent in accordance with the requirements of the British Pharmacopoeia. Finally, the dry agar is ground in a hammer mill to a fine powder, which is sifted and blended as desired.

The commercial process used in making gracilaria-agar in Australia and South Africa has not yet been published. Wood (1941) has outlined a pilot-plant process, which might have been adopted by the Australian manufacturers. The method used appears to be based on the American process, and, like that formerly used in California and described by MacKinnon (1930), employs activated carbon for decolorizing the liquor before it is subjected to the filter press.

In Japan, besides the traditional method described above, there are several other patented processes, some of which may already be in use. A patent was granted to Utsuki (1922) for a modified process. The seaweed is washed and treated for one to two hours in warm water containing 0.2 to 0.5 per cent Na_2CO_3 or Na_2SO_4. It is then bleached with chlorine or sodium peroxide and boiled in water. The filtrate is concentrated under reduced pressure and left to solidify. The gel is frozen, the frozen gel crushed, thawed, separated, dried and the purified agar powdered.

The process is therefore very similar to the present American process. Oki and Imōo (1933) patented a process for making powdered agar. The seaweed is extracted with hot water as usual, but the agar is separated from the solution by the addition of Na_2SO_4. The precipitated agar is then washed with cold water and dried at a low temperature.

The Russian process is presumably similar to the American, excepting that drum-drying is practiced instead of stack-drying. Several Russian patents have been issued on agar manufacture. Among these is one granted to Smuskovich (1939). Agar is extracted from the agarophyte by boiling in water as usual; the extract is beaten to a froth to obtain a porous gel, which is then cooled and dried in the usual manner.

Kizevetter (1940) was granted a patent for another process. The seaweed *Ahnfeltia* is boiled in water, and the extract stirred at low temperature until it acquires a grease-like consistency. Two to three volumes of cold water are then added. The agar, insoluble in cold water, is precipitated in the form of flakes, which are washed with cold water and dried.

Purification of Commercial Agar. The commercial agar, even that made in a modern factory, contains as much as 3.20 per cent ash and 1.12 per cent crude protein (cf. Table 8). Undoubtedly, a certain portion of the ash and all the proteinaceous matter are present as impurities. Since the two major uses of agar in science are as bacteriological culture media and in colloid research, the presence of these impurities is highly objectionable. Therefore, commercial agar, especially that made by the traditional Japanese method, in which natural means are employed in the freezing, thawing, and drying processes, has to undergo a process of purification before it can be used in critical scientific research.

In the latter part of the last century Marpmann (1887) and a few others employed diluted acids to assist in the purification of agar. The disadvantage of using acid for this purpose lies in its hydrolytic action if present in large enough amounts, resulting in the partial destruction of the jellying properties of agar. Dominikiciewz (1909) appears to have been the first to utilize alcohol for this purpose. To the agar solution he added a large volume of alcohol, weakly acidified with acetic acid. The precipitated agar was then filtered, washed and dried. By simply soaking commercial agar in distilled water for a few days, changing the water several times, and finally filtering the agar solution through cotton gauze, Whittaker (1911) obtained a purified agar having an ash content reduced from 4.03 to 1.67 per cent, crude protein from 2.06 to 1.67 per cent, and crude fiber from 4.27 per cent to none. Feller (1916) purified agar by a method similar to that employed by Dominikiciewz. He washed shredded agar first in ether and alcohol, then in a 3 to 4 per cent acetic acid solution, and finally in water. The washed agar is dissolved in hot water and precipitated therefrom by a large volume of alcohol or acetone. This procedure removes as much as 93 per cent of the nitrogenous matter originally present in the agar. The gels prepared from the purified substance are transparent, and the jellying power is not impaired.

The first commercial processes of agar purification were patented by Steinitzer (1912) and Merck (1913). Steinitzer's process, utilizing acids or salts, affects the quality of the resulting agar unfavorably. Merck's process consists essentially in dissolving commercial agar in hot water, filtering and freezing the solution. The frozen gel is thawed by warming, whereupon water containing most of the impurities separates and drains off. The moist agar is then washed repeatedly with cold water until the washings contain no solid matter in solution. This procedure removes the impurities soluble in cold water. It is fundamentally the same in principle as the Japanese processes of manufacture, and appears to be the forerunner of the American process.

Samec and Isajevič (1921) found that ordinary dialysis failed to remove all the

ash. Several investigators therefore resorted to electrodialysis in the purification of agar for special uses. Harvey (1925b) washed shredded U.S.P. agar twice in 0.5 per cent acetic acid and then with six changes of distilled water; 100 gm of the washed agar was dissolved in 3 liters of water. Electrodialysis of the hot agar sol was conducted in a water-bath kept at 50° for 12 hours, by which time the sol had separated into a flocculent bottom layer and a clear supernatant layer. The latter was siphoned off, filtered through filter paper and supercentrifuged at 40,000 rpm. The clear transparent liquor, which quickly set at room temperature, was rapidly dried at 40°, and the resulting agar had an ash content of 0.81 per cent as compared with the original value of 3.75 per cent. The residue from the centrifuge consisted of diatoms, silica spicules and nondescript debris.

That a hot 1 per cent solution of Harvey's purified agar solution had a pH of 4.9 seems to indicate the incompleteness of the electrodialysis, since Hoffman and Gortner (1925) by a similar process obtained a free agar-acid, a 1 per cent solution of which had a pH of 2.475. These investigators used a Foster-Schmidt apparatus for effecting the electrodialysis. This is a box having three compartments, each of 1,250 ml capacity, separated by heavy sheets of collodion supported by double layers of light canvas. Instead of using a hot agar solution, Hoffman and Gortner merely suspended 50 gm of coarsely ground, air-dried agar in 1,250 ml distilled water in the middle compartment. The 1,250 ml of water in the end compartments was replaced hourly. Electrodialysis progressed for 18 hours, when the granules of agar became very swollen and translucent. The liquid in which the agar granules were suspended gave a pH value of 2.0 and contained 0.7 per cent of dry matter. It showed no appreciable viscosity and no tendency to gelatinize on cooling. It proved a remarkably effective protective colloid for the preparation of metal hydrosols. Ash analysis showed that the calcium and other metallic ions were virtually quantitatively removed.

Hoffman and Gortner therefore suggested that the resulting liquid from the middle compartment was an agar-acid. They further showed that neutralization of this acid with a base results in the formation of a rigid gel which is evidently the metallic salt of the agar-acid. While there is as yet no commercial production of agar by electrodialysis or a similar method in which the free agar acid is first prepared, and then neutralized to obtain the desired metallic agar, it is not improbable that such a process may eventually be conducted on a large scale to produce different metallic agars for special uses.

Reclamation of Used Agar. Because of the recent agar shortage much attention has been given to the reclamation of agar used in making bacteriological culture media. Among the first attempts to recover used agar were those of Mohoričič (1915) and Serger (1916) during World War I. Serger's method is an improvement on Mohoricic's; 0.1 per cent $HgCl_2$ solution was added to the hot solution of the used agar. After 20 minutes, 6 to 8 per cent of a mixture of 2 parts animal charcoal and one part infusorial earth was introduced. The mixture was heated on a steam bath for 10 minutes with frequent stirring, and the resulting mixture filtered through a heated funnel. The filtrate was cooled, and the gel rubbed through a sieve of 0.5-cm meshes. Prolonged washing in cold water with frequent changes subsequently produced a pure agar.

This war has again brought forth several notes on agar reclamation (Brodie and Stiren, 1942; Edward, 1942; MacMorine, 1942; Roe, 1942; Thaller, 1942; Anderson, 1943; Blundell, 1943). While the various proposed methods differ in minor details, they are similar to either Serger's method, purifying by continuous washing in water and with the help of activated carbon, or the commercial method of preparation of agar. In Blundell's method (1943), the purification is effected by the freezing method and the agar is precipitated by alcohol. Anderson (1943) proposed a simple method, consisting of drying the discarded agar media, grinding them in a

Wiley mill containing a 1-mm sieve, washing continuously in running water for 36 hours, filtering and drying the resulting agar. Purification is later effected by using activated carbon in the preparation of the agar media.

Carrageenin

Although there are two extracts from *Chondrus crispus,* differing in their relative solubility in cold water (Haas and Hill, 1921), they are not separated in the commercial processes of preparation. Since both extracts are salts of carrageenin, they are considered together under the same general term.

Washing Method. The "washing" method is the simplest process of manufacture. Chopped carrageen is placed in a basket-type of centrifuge equipped with a fine wire filter screen and is thoroughly wetted with water. More water is added during the centrifuging. The *Chondrus,* now having been leached of a part of its impurities, is spread on the screen and dried. Cleaning is effected by vigorously agitating the dried and leached seaweed over a 100-mesh wire screen. By this procedure the seaweed particles remain on the screen while sand, salt, and other impurities sift through and are discarded. The cleaned carrageen is finally milled to a 100-mesh powder. This process gives a yield of about 70 to 75 per cent (Seltzer, 1935).

Ethyl or isopropyl alcohol is used in another washing process; 125 pounds of carrageen powder are soaked in a mixture of 220 pounds of 91 per cent isopropyl alcohol and 58 pounds of water for two to four hours. The carrageen is separated from the liquor by centrifuging or filtration. The process is repeated once more and the product dried. This gives a yield of 80 per cent (Seltzer, 1935).

By the "washing" process, only crude products containing fibers can ordinarily be prepared, although the majority of the water- and alcohol-soluble salts and impurities have been removed.

Hot Water Extraction Method. The *Chondrus* received by the factory is generally cleaned, sun-dried, and partially bleached. Hence no further washing is necessary, as in agar manufacture. Extraction of carrageenin by this method is effected by hot water, generally about 180° F, for about 40 minutes to an hour. Open kettles are used. Two to four parts of the seaweed are added to 100 parts of water. The actual quantity used depends both upon the quality of the raw material and upon the equipment used in pumping the resulting viscous liquor. The liquor is pumped to a clarifying tank to which filter-aid is added. The treated extract is next passed through an ordinary filter-press. The filtered solution is finally dried on atmospheric roller drums similar to those used by the dairy industry in drying powders. Spray-drying is sometimes used.

Léon (1930) was granted a French patent for a hot-water extraction process in which he used activated carbon for purification. His process is unique in the addition of 1 per cent potassium salt which increases the gelatinizing power of the resulting extract.

Most of the carrageen extracts are prepared by this general method. The product has higher ash content and makes less viscous solutions than that made by the alcohol process, to be described below. Since the majority of this extract is used as a suspending agent for cocoa fibers in chocolate milk, the product made by this cheaper process is quite satisfactory. When a more refined product with high viscosity is required, the alcohol precipitation method is generally employed.

Alcohol Precipitation Method. The first alcohol process was patented by Bourgade in 1871. Although many modifications and improvements have subsequently been made, the general principle involved remains the same. Carrageenin is more or less soluble in cold water, and therefore cannot be purified by the freezing method, as is agar. It can be precipitated, however, by the voluminous addition of alcohol, which acts as a dehydrating agent. The water-soluble impurities remain in the alcohol solution, and the precipitated carrageenin can be separated and dried. A typical

modern process is that patented by Pfister (1941), illustrated in Fig. 27 and described as follows:

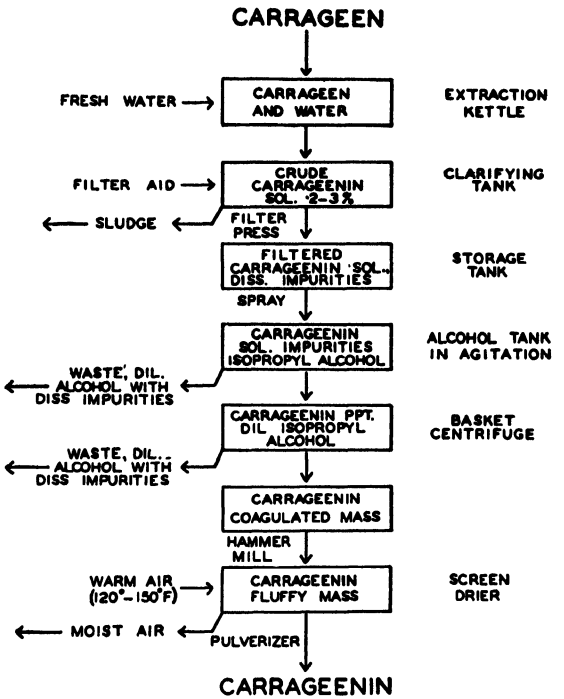


FIGURE 27. Carrageenin manufacture by alcohol precipitation method. Plant flow sheet diagram.

Extraction, clarification and filtration. The extraction of carrageenin, clarification of the liquor, and filtration of the clarified sol are effected in the same way as in the hot water-extraction method.

Alcohol precipitation. The filtered liquor may be subjected to the alcohol treatment or may be evaporated to contain about 10 per cent of the extract in order to conserve alcohol. The concentrated sol is sprayed into a tank containing 91 per cent isopropyl alcohol, which is under vigorous agitation. Upon contact with the latter, carrageenin is precipitated as a coagulated mass. The amount of alcohol used depends upon the volume of the colloid solution, the ultimate mixture of the two being preferably about 50 per cent alcohol by weight. Thus, when a 2 per cent carrageen solution is added, the mixing tank should have about 50 volumes of 91 per cent isopropyl alcohol for each 36 volumes of the liquor.

Pfister recommended another method of precipitation by spraying the liquor into the agitated alcohol. The liquor is introduced below the surface of the alcohol through a fine spinnerette-like nozzle. The resulting precipitate will consist of particles in the form of segments of fine thread. The waste alcohol is reclaimed for later use.

Dehydration. The coagulated precipitate is then mechanically treated to separate it from salts, pigments and other water- and alcohol-soluble impurities. For this purpose, the precipitate is introduced into a basket centrifuge which will remove water and alcohol within 15 minutes. Sometimes a hydraulic press is used in addition to express the liquid from the mass. In all cases heat is avoided, since it is be-

lieved to have an adverse effect on the viscosity of the resulting colloid. To obtain a very fine product, the centrifuged mass is usually subjected to another similar alcohol treatment in order to remove any soluble impurities adhering to the precipitate.

When alcohol and water have been thus mechanically removed, the resulting mass will contain only about 10 to 15 per cent of alcohol and 5 to 8 per cent of moisture by weight. It may be passed through a hammer mill. The resulting fluffy mass is next spread on screens and dried by a blast of air at 120° to 150° F. Within 2 to 6 hours, the product will be thoroughly dried. The dried carrageenin may now be pulverized if desired, or may be sacked directly.

Blihovde's Modified Alcohol Method. Blihovde (1941) was granted a United States patent for an improved process of manufacture, which is similar to the Pfister process save for the introduction of a special mixing spray nozzle. The hot filtered carrageenin solution from the storage tank and alcohol heated to about 185° F are introduced separately into the mixing nozzle. While hot alcohol is preferred, cold treatment also gives satisfactory results. The resulting mixture, containing aqueous alcohol and carrageenin, some as a precipitate and some remaining in solution, is discharged through a funnel into an attrition mill. Precipitation of the colloid continues in the grinding mill, and the precipitate is shredded or pulverized, as fast as it is formed. Dehydration of the colloid is the same as in the Pfister process.

In the same patent, Blihovde described a modification of his process, being an improvement over, and preferred to, the above-mentioned procedure. The filtered carrageenin solution is introduced into a pre-mixing tank and is vigorously agitated; 91 per cent isopropyl alcohol is then added to the tank. As a result of the dehydrating effect of the alcohol, the colloid is thrown down as a fine precipitate. It is to be noted that this is a reversal of the ordinary procedure, in which the carrageenin solution is generally added to the alcohol. The resulting mixture containing about 50 per cent alcohol and carrageenin is then passed through the mixing spray nozzle to the alcohol tank in which precipitation of all the carrageen is completed. The openings leading to the nozzle for this particular process are less than $\frac{3}{16}$ inch in diameter. Since the resulting precipitate is very fine and powdery, the attrition mill used in the previous process is unnecessary. The alcohol solution with the colloidal precipitate is collected in a suitable tank and passed through a filter press. The precipitate is thus separated from the alcohol solution, and is further washed by a final treatment with 91 per cent isopropyl alcohol to remove the last traces of water- and alcohol-soluble impurities. If a hot solution of alcohol is used, the mixture is preferably cooled to room temperature prior to filtration, so as to minimize the evaporation of alcohol. The alcohol from the filter press may be recirculated through the mixing nozzle until its strength drops to 55 per cent. The waste alcohol is reclaimed and gathered in a storage tank. The precipitated colloid in the frames of the filter press is next subjected to a basket centrifuge. This is not always necessary, however, since the fine precipitate at this stage is usually so thoroughly dehydrated that the mildest heat will be sufficient to complete its drying in a very short time.

Blihovde claimed that the colloid prepared by his process makes much more viscous solutions than that from the ordinary process. While a 1 per cent solution of carrageenin prepared by the ordinary cooking, filtering and drying process has a viscosity of not more than 1.5 to 5 centipoises, a similar solution of his product has a viscosity of several hundred to a thousand centipoises. He also claimed that his carrageenin has no crude fiber and practically no ash, or merely traces of it, and that the protein content (N x 6.25) is only 1.5 to 2.7 per cent. In view of the fact that carrageenin is a metallic salt, it is questionable whether an ash-free product can be prepared, as claimed, without drastically changing the properties of the colloid.

Lund's Modified Washing Process. Lund (1943) believes that heating carrageen in water in the presence of salts and other impurities causes partial hydrolysis of

carrageenin to form carrageenin acids and its cleavage compounds, thus resulting in unstable products lacking uniform quality. He found that if the salts, pigments, and other water- and alcohol-soluble impurities were removed first, the seaweed could be safely subjected to hot water-extraction and that the resulting product would be stable and uniform in quality. He further found that dilute alcohol solution, 30 per cent or less, was more effective than stronger solutions in dissolving the salts, pigments and other water- and alcohol-soluble matters. His patented process consists of the following steps.

Washing. Warm isopropanol solution is used in the washing procedure. To 300 pounds of the alcohol in a mixing tank under slow agitation, 100 pounds of chopped *Chondrus* is added. After a few minutes, the solution becomes strongly colored by seaweed pigments. The alcoholic solution is siphoned off and the colored impurities are removed by activated carbon and filtration.

Lixiviation. Cold isopropanol and neutral water are added to the washed seaweed particles. About 300 parts of the alcohol and 700 parts of water are added to 100 parts of the *Chondrus*. Lixiviation is carried out at room temperature and lasts for 15 to 20 hours. At the end of this period, the hydrated particles have undergone a complete dialysis and the water- and alcohol-soluble salts and impurities have almost completely leached out to the weak alcoholic solution.

Extraction. The lixiviated *Chondrus* particles are next subjected to the regular hot water extraction at a temperature of 160° to 200° F. About 50 parts of water are added to one part of the seaweed.

Filtration. The hot carrageenin solution is filtered through an ordinary pressure filter.

Evaporation. The purified carrageenin solution is next concentrated to a 4 per cent solution under reduced pressure.

Bleaching. The vacuum-evaporated extract is then bleached, if so desired, by 2 per cent hydrogen peroxide. Peroxide bleaching is found to have no deteriorating effect on the gelling power and the viscosity of the resulting carrageenin solution. The residual hydrogen peroxide is eliminated from the system during the final stage of drying.

Drying. The final drying is accomplished by means of a vacuum drum drier. The finished product is said to be substantially pure and stable, and possesses a high degree of gelatinizing and stabilizing ability. The process is cheaper to operate than the alcohol method.

Lund also found that, if equivalent amounts of sugars such as sucrose, dextrose, or lactose, are added to the carrageenin solution in the concentrating procedure, the resulting solution may be evaporated to a total solid content of about 12 to 16 per cent. The increase of the amount of carrageenin in the solution will greatly reduce the cost of operation. Besides, the addition of sugars permits the resulting extracts to be dried to a moisture content of 2 to 3 per cent, the sugar apparently exerting a protecting function on the colloid. Ordinarily, the extract can be dried only to 10 to 12 per cent moisture, under which condition, it is alleged, the products are exceedingly susceptible to deterioration in gel strength and viscosity on standing; in fact, a loss of 10 per cent in viscosity in three months is considered as the minimum.

Algin

Since its discovery by Stanford in 1883, algin has been manufactured on the same basic principle in spite of the many processes patented during the last five decades. Alginic acid itself is insoluble in water, but is easily converted by soda solution into the water-soluble sodium salt. Kelp is therefore digested with sodium carbonate or hydroxide solution, and alginic acid subsequently precipitated from the crude sodium alginate solution by the addition of a strong mineral acid. To facilitate purification of the products, several processes involve precipitation of calcium alginate prior to

acid precipitation. The final manufactured product generally takes the form of a soluble alginate, especially sodium and ammonium alginate, since alginic acid itself is very unstable. All the modifications introduced since Stanford's original process have been directed toward making a better product at a cheaper cost. There are very few changes in the fundamentals of the manufacturing method. It is also to be noted that in the earlier process algin was never intended to be the main product of kelp industry, but rather a by-product of the manufacture of iodine and potash, or calcium acetate. It is only in recent years that algin has had a ready and extensive market and has become the principal kelp product.

Stanford's Wet Process. Stanford (1884) originally suggested the manufacture of algin to enable the Scottish iodine factories to utilize kelp as their raw material in competition with the South American iodine industry. He used "driftwood" which consisted chiefly of *Laminaria digitata* and *L. stenophylla.* In his "wet" process, kelp is first treated with cold water to dissolve the water-soluble potash, iodine, and other inorganic salts. The residual kelp is then digested, either cold or warm, for 24 hours with one-tenth its weight of sodium carbonate. The resulting mass is very viscous and glutinous, and is filtered through coarse linen filter bags. Cellulose and foreign matter remain in the bags. To the filtrate, hydrochloric or sulfuric acid is added; alginic acid precipitates in light gray, gelatinous flocks. It is washed and pressed in an ordinary wooden screw press. The alginic acid thus forms a compact cake resembling new cheese. If bleaching is desired, it is carried out during the precipitation. The product may be sold in this condition or as a sodium, potassium, or ammonium salt by dissolving the acid in the respective carbonate. For drying, the alginate may be exposed on trays to a current of air, or on revolving cylinders heated internally by steam. High temperatures are avoided. Sodium alginate thus obtained is in the form of thin, almost colorless sheets, resembling gelatin, but very flexible.

The preliminary water extract obtained is evaporated and ashed, and iodine and potassium salts recovered. The cellulose, or algulose as Stanford called it, which is separated from the alginate solution by filtration, may also be recovered and made to serve various purposes. Thus, Stanford claimed that in his "wet" process, 70 per cent of the air-dried kelp is utilized, whereas in the old "kelp" process and the "destructive distillation" process, the percentages of utilization are only 18 and 36, respectively.

Fermentation Process of Hercules Powder Company. During World War I there was an acute shortage of calcium acetate and its solvent derivatives in the United States. These organic chemicals were in great demand, since large quantities of acetone were used as a solvent in the manufacture of smokeless powders and in preparing dopes for airplanes. A unique process for fermenting kelp to obtain calcium acetate and acetone was developed by the Hercules Powder Company (Higgins, 1918; Anonymous, 1918; Tressler, 1923). It is so far the only process in which organic solvents are the primary products of a seaweed industry—potash, iodine, and algin being merely by-products. The portion of the kelp which was not disintegrated by the fermentation process was utilized for the manufacture of algin. The remaining part of the process is similar to Stanford's original process. The residual kelp is treated with sodium carbonate solution until it is well digested. After filtration, the solution is acidified, and alginic acid is precipitated. Subsequently, sodium alginate is prepared by dissolving the precipitate in sodium carbonate or caustic soda solution.

Green's Cold Process. Stanford's original process has undergone a series of improvements by several investigators in various countries. There seem to be two different developments, judging from the patents issued for algin manufacture. Some inventors have developed processes in which algin is practically the only product concerned, whereas in other processes, algin, potash, iodine and other seaweed prod-

ucts are all dealt with. Since Thornley was one of the founders of the sole algin concern in California, the process originally introduced to the American west coast was the Thornley process which belongs to the former, dealing entirely with algin production. The large algin manufacturer on the east coast, on the other hand, has adopted the latter processes, and as shown by patents issued, seems to be consistently seeking ways and means of utilizing other kelp products which can be manufactured along with the production of algin.

The original Thornley process (Thornley, Tapping and Reynard, 1922; Thornley and Tapping, 1924) has been improved by a few investigators (Reynard, 1928, 1930; Walsh, 1931; Thornley and Walsh, 1931) and finally perfected in the "hot" process of Clark and Green (1936) and the "cold" process of Green (1936). While the two last-mentioned processes differ in the temperature used in the digestion tank and elsewhere, the other important details are quite similar. Green's cold process is characterized by conducting all the different steps of manufacture at the relatively low temperature of 50° F, and on the basis of patent disclosures, may be illustrated in Fig. 28 and described as follows:

Leaching. Freshly harvested kelp (*Macrocystis pyrifera*) is placed in a leaching tank in cold water acidulated with 0.33 per cent HCl. The kelp is left in the acidulated water for one to several hours until the salt content of the kelp is reduced to 5 to 15 per cent. The liquor is then drained off and discarded.

Digestion. The leached kelp is chopped to convenient size and fed to a hammer mill. The milled kelp is added to a digestion tank containing 40 to 50 pounds of soda ash per ton of freshly harvested kelp. The pH is controlled at about 10.0. Digestion will generally be completed in 30 minutes. The digested kelp may be further digested by a similar process for another half hour. The resulting kelp pulp is passed through a hammer mill once again and six volumes of permutited water are added to it; pH is maintained at 9.6 to 11.0.

For certain purposes, crude algin is satisfactory. In this case, the crude sodium alginate solution together with the fibrous materials is dried and sold as such. For most uses, however, a highly purified product free from cellulose and other substances is required. The crude solution will then be subjected to the following steps:

Clarification. The crude liquor is pumped into a clarification tank and filter-aid such as diatomaceous silica added. The supernatant liquor is filtered through an ordinary mechanical filter-press. Other methods of clarification may be employed, such as centrifuging, vacuum filtering, sand filtering or simple settling of the cellulose material upon standing. Before filtration the temperature may be temporarily raised to about 120° F to facilitate the process.

Calcium alginate precipitation. The filtered liquor is slowly added to a calcium chloride solution under constant agitation. Calcium chloride is employed in the proportions of about 100 to 800 pounds (or about 100 gallons) of water per 8 tons of the liquor. When agitation stops, the precipitated calcium alginate gradually rises to the top. The remaining liquor containing water-soluble salts and organic matter is drained off.

Bleaching. In the same tank, more water is added to the precipitate and a suitable bleaching agent such as sodium hypochlorite is introduced. The amount of hypochlorite to be added depends on the color of the crude product; generally 1 per cent is sufficient. Excessive bleaching will have an adverse effect on the resulting product.

Acid precipitation. The bleached precipitate is separated from the water, and introduced into a dilute hydrochloric acid solution (about 5 per cent). About 42 parts of the acid solution are used for each part of the alginate. The acid acts on calcium alginate, converting it into fibrous alginic acid. The mixture is passed through a suitable screen to remove the excess acid and calcium chloride solution resulting from the chemical reaction. The drained precipitate is introduced into a second tank

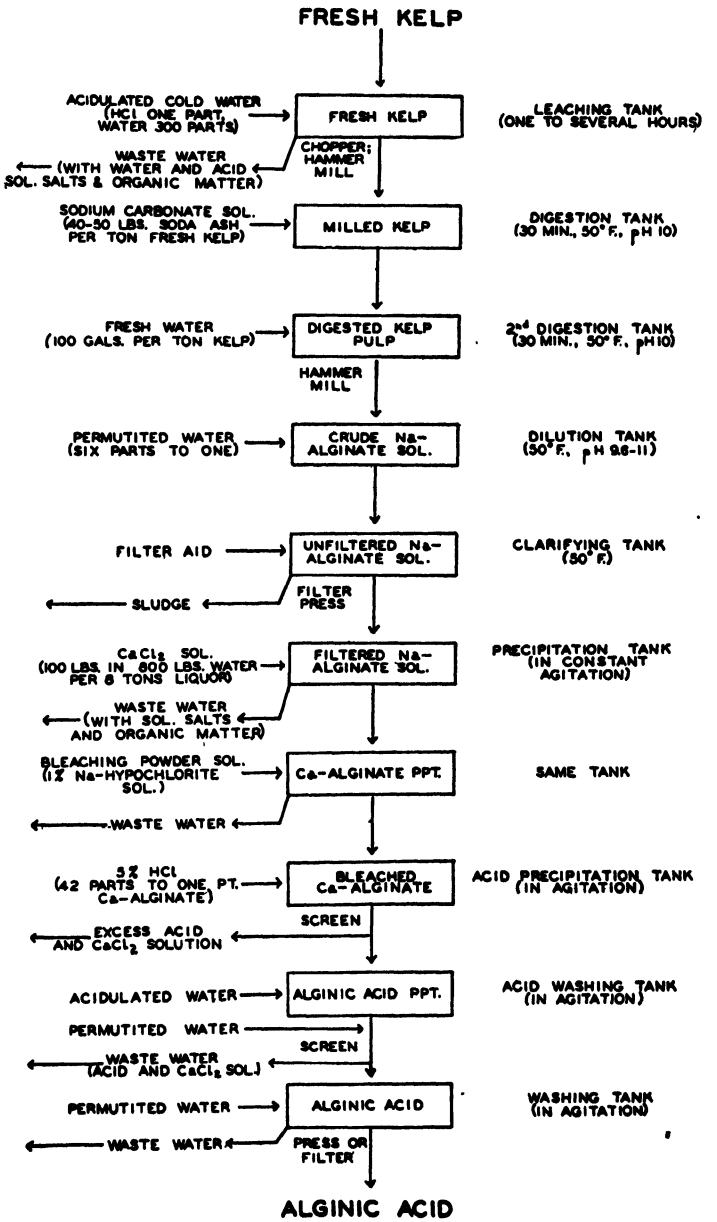


FIGURE 28. Green's cold process of algin manufacture. Plant flow sheet diagram.

of acidulated water, agitated for a while, and then pumped over another screen. This treatment is repeated until the precipitate is washed free of calcium salts. Enough permutited water is used in the washing to render the pH higher than 1.9 and simultaneously to reduce the amount of calcium in the product.

The purified alginic acid is pressed or filtered. The resulting product may be

stored in a refrigerated room, or may be converted into the sodium or other metallic salt by treating it with the corresponding carbonate, oxides, or hydroxide (cf. Thornley and Walsh, 1931). Sodium or other soluble alginates thus formed are dried by one of the various standard methods, ground, screened, and packed or mixed with other ingredients to form one of the several commercial products. The British product is known as "Manucol" which is designated numerically according to specific uses. The California algin is known under several trade names of which the best known are "Dariloid" and "Cocoloid."

Clark and Green's "hot" process (1936) is based on the same principle, except that heat is applied in several of the steps of the process. For instance, in the digesting procedure, the tank is maintained at 180° F. Green (1936) claims that his "cold" process produces algin, a 1 per cent solution of which may have a viscosity ranging from 400 to 2000 seconds, measured by the Woolwich method; whereas alginates prepared by the old conventional methods have viscosities of only 5 to 10 seconds on a 2 per cent solution.

Le Gloahec-Herter's Process. The large algin concern on the east coast of the United States uses the Le Gloahec-Herter process (1938), which, on the basis of its patent disclosures, may be illustrated diagrammatically by Fig. 29 and described as follows:

Lixiviation. This process takes advantage of the fact that a dilute solution of alkaline-earth salts such as calcium chloride will dissolve laminarin, mannitol and various salts in the kelp without any unfavorable effect on algin. The kelp used in the process may be freshly harvested or air-dried. To one volume of the dried kelp, three volumes of 0.8 to 1 per cent $CaCl_2$ solution are added. Lixiviation may be carried out in the hot or cold state, although the latter is preferred. The leached kelp is then washed with soft water, which removes the calcium chloride as well as the remainder of the laminarin, mannitol and salts. Washing is suspended when the exhaust water contains about 0.5 per cent soluble matter. The lixiviated kelp may be additionally subjected to a treatment with dilute acid solution (5 per cent HCl) to dissolve any residual alkaline-earth salts. It is then washed with soft water before the next process.

Digestion. To one volume of the well lixiviated kelp, two volumes of 4 per cent Na_2CO_3 solution are added. The digestion process may be performed in any suitable container, and the mixing may be substantially helped by beaters such as those commonly employed in the paper-making industry. Maceration is continued until the cellulose is reduced to fine particles, and a homogeneous paste obtained. This will take about two hours at 104° F and about 3 hours at ordinary room temperature.

Clarification. The kelp paste is diluted with water in the ratio of 3:7. The mixture is beaten to a homogeneous suspension, and air is introduced through fine apertures. It is claimed that the oxygen present in the air helps to make a product of high viscosity. By the introduction of compressed air, the whole mass is vigorously stirred. If another oxygenating agent, such as ozone or hydrogen peroxide is introduced, agitation is effected by means of mechanical agitators. The oxygenated liquor is then passed through a centrifuge rotating at high speed, which charges the continuously flowing liquor with air bubbles. The resulting emulsion is conveyed to a clarification tank. Upon standing for six to ten hours, the cellulose particles agglomerate to become a rather compact cake floating on the liquor. The clarified liquor can then be removed without any difficulty. Several alternate devices to effect clarification of the liquor are described by Le Gloahec and Herter.

Decolorization. The clarified crude liquor remains colored by seaweed pigments, which must be removed in order to yield a white product. For this purpose an absorbent jelly made of hydrated alumina, gelatinous silica, and aluminum alginate is preferred, although others of similar nature may be used. The jelly is added to the colored liquor in about 20 to 25 per cent of the weight of dry alginous material

therein. The mixture is stirred and the pigments soon adhere to the jelly. The colored jelly is separated from the liquor by centrifuging. This jelly is reclaimed in various ways, for instance by washing it with an organic solvent such as alcohol, which can also be reclaimed.

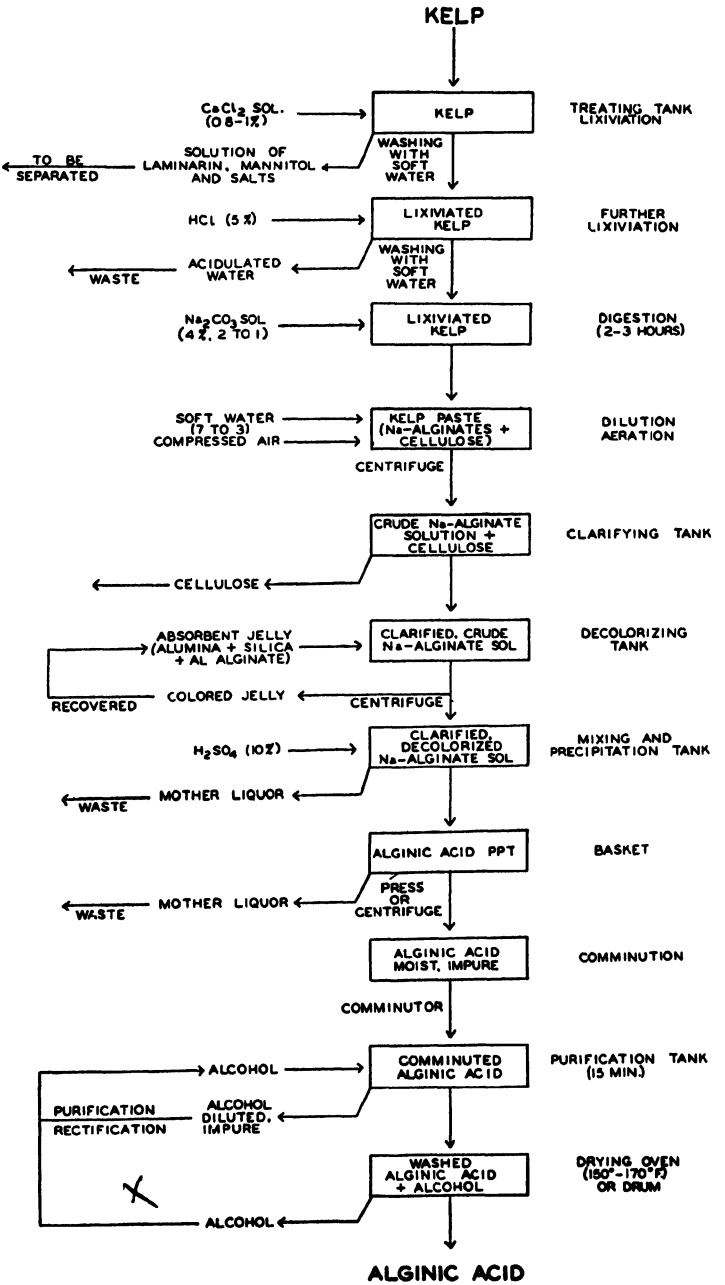


FIGURE 29. Le Gloahec-Herter's process of algin manufacture. Plant flow sheet diagram.

Acid precipitation. The liquor in this stage is clarified and freed from the pigments and other impurities. Addition of a strong acid such as HCl maintained at a pH of 2.8 to 3.2 will cause precipitation of the alginic acid. The mineral acid and the alginous liquor are preferably introduced separately to meet at a mixing baffle, slightly inclined in a tank. The precipitate flows to the adjoining tank as soon as it is formed, thus minimizing its contact with fresh mineral acid. The latter tends to hydrolyze the alginic acid just formed, thus having an adverse effect on the resulting product. Carbon dioxide evolved from the reaction between sodium carbonate and hydrochloric acid helps to cause the precipitate to float on the liquor, and the outflow of the product to the next tank is thereby facilitated.

Purification. The precipitate is removed to baskets and allowed to drain. Freed from the remaining liquor by pressing or centrifuging, it is comminuted and further purified by a solvent, such as ethanol, in vessels provided with a filtering plate. Another washing with alcohol should remove remaining impurities. The alcohol is reclaimed for further use. Methods of purification of the precipitated alginic acid by means of ordinary dialysis or electrodialysis have also been suggested.

Dehydration. The purified alginic acid, together with some adhering alcohol, is finally dried in a specially constructed oven maintained between 140° and 160° F. A method of purifying and drying the alginic acid in special rotating drums has also been suggested. In all cases, the used alcohol may be either employed again or subjected to reclamation.

The alginic acid is converted into its sodium or other metallic salts by the regular methods. Methods for the recovery of laminarin (1940) and iodine (1941) are also patented by Le Gloahec and Herter.

A patent was granted to Le Gloahec and Herter (1939) for a process of improving the decolorization of the alginous materials. These investigators found that by adding formaldehyde (or other protein coagulants such as tannic acid) to the soda-digested kelp, the proteinaceous material present in the mixture becomes coagulated, and that the seaweed pigments readily become fixed to the resulting coagulated mass of protein adhering to the cellulose. Chlorophyll and other plant pigments thus fixed on the protein-cellulose mass can be recovered if so desired. In the decolorizing process, 22 pounds of commercial formaldehyde is added to 2½ tons of water for each ton of demineralized kelp. The mixture is allowed to stand for about an hour. The formaldehyde-treated kelp is then taken out and stored. A period of 15 days' to three weeks' storage is found to cause substantial fixation of the colored matter on the protein-cellulose mixture. When sodium carbonate solution is added to the kelp, it dissolves only the alginous matter, which can thus be separated from both the cellulose and the plant pigments. The process from here on is the same as the one described above, except that decolorization by means of the alumina-silica-alginate jelly is omitted.

It is to be noted that the Le Gloahec-Herter process differ from those of the Green process in the following three main points: (1) dilute $CaCl_2$ solution is used in the leaching or lixiviation process; (2) clarification is effected by means of a special aeration and centrifuge system instead of filter-aid and filter-press; (3) precipitation of calcium alginate is omitted, and to decolorize the product, either a pigment-absorbing jelly or a protein coagulent is used.

Laminarin

Although there is as yet no market for laminarin, the "phaeophycean starch," the commercial possibilities of such a substance, which may comprise as much as 50 per cent of the total dry weight of some kelps, cannot be overlooked. A patent was granted to Le Gloahec and Herter (1940) for a process of recovering laminarin in algin manufacture. In the Le Gloahec-Herter process, kelp is first treated with a dilute solution of calcium chloride, which dissolves the laminarin, mannitol and vari-

ous salts. To recover laminarin, the lixiviation liquor is concentrated and alcohol added in a large enough amount to make up 85 per cent of the solution, so that complete precipitation of the laminarin may be insured. The laminarin is further purified by redissolving it in calcium chloride solution and reprecipitating it in alcohol. The used alcohol may be subsequently recovered.

Precipitation of laminarin by means of an alkaline lead subacetate solution containing about 5 to 10 per cent sodium hydroxide has also been suggested. About one part of lead subacetate is enough to precipitate 10 parts of laminarin. The precipitate is separated from the mother liquor and dried by one of the conventional methods.

Detection and Determination of Phycocolloids

Agar and Carrageenin

When agar was first introduced to the European countries it was used principally in jelly-making, and was regarded in certain places as an adulterant and hence illegal. Methods were therefore devised to detect its presence. Ménier (1879) found that the presence of agar could be established if diatom frustules were found when the substance in question was examined microscopically. This is due to the fact that in the Japanese process of manufacture, agar is never entirely freed from diatoms commonly epiphytic on the agarphytes. On the same principle, Tunmann (1909) devised an improved method by boiling the material in a 5 per cent sulfuric acid solution containing crystals of $KMnO_4$. This treatment thins the material and causes the diatoms to settle. If microscopic examination reveals the presence of diatoms, especially species of *Arachnoidiscus,* the presence of agar is presumed. This has been accepted as a tentative method of detection of agar by the Association of Official Agricultural Chemists (A.O.A.C.) (1940).

Agar and gelatin serve many similar purposes in food industries and can be differentiated by their color reactions with thionin solution, the former being colored violet and the latter dark blue (Straub, 1914). Parkes (1921) devised a method of agar detection based on the fact that agar solution ordinarily does not show sulfate reactions, but does so upon acid hydrolysis; the presence of the sulfate radical is easily shown by precipitating it with a barium salt. King (1925) used the same principle for quantitative determination of agar. From the amounts of sulfate before and after hydrolysis, the percentage of agar in the sample may be calculated.

The enormous gelling ability of agar is utilized in detecting its presence. One of the general methods is to treat the sample first with alcohol to remove fat and other alcohol-soluble substances. The residue is next boiled in water to precipitate the proteins. The mixture is filtered. If starch is found to be present, the filtrate is treated with malt extract until starch is completely hydrolyzed. Alcohol is added to precipitate the agar if present. The precipitate is boiled with a large volume of water to make a very dilute solution of about 0.2 per cent, and if the resulting solution solidifies to a firm gel upon cooling, the presence of agar is indicated.

For the detection of agar in jams or jellies the procedure can be simplified, and the following has been accepted as a tentative method by the Association of Official Agricultural Chemists (1940):

"Cover 30 g of the jam or jelly with 270 ml of hot H_2O, stir until thoroughly disintegrated, and boil 3 minutes. Filter solution while boiling hot thru rapid qualitative filter paper. In presence of agar agar a precipitate will form upon standing not longer than 24 hours. Filter, wash with cold H_2O, and dissolve from paper by means of very small quantity of boiling H_2O. Upon chilling this solution a firm jelly that can be examined by the touch will be formed. This method will

detect 0.2 per cent of agar agar with certainty if proportions of jam or jelly and H_2O specified are strictly followed."

The gel or alcohol precipitates from other tests may be further treated by one or several methods for confirmation. For instance, agar when hydrolyzed shows positive reactions with Benedict, Molisch, Seliwanoff and Tollen tests (Hart, 1939).

Certain protein precipitants used in general food detection also precipitate agar in whole or in part from its aqueous solutions (Table 27, Hart, 1937).

Table 27. Effect of Various Protein Precipitants on 15 ml of a 33 per cent Agar Solution (Hart)

Precipitant	Reaction
Trichloroacetic acid	No precipitate, cold or hot
Potassium ferrocyanide and acetic acid	Precipitate
Dialyzed iron	Precipitate
Picric acid	No precipitate, cold or hot
Phosphotungstic acid	Precipitate cold; dissolved on heating
Tannic acid	Precipitate
Mercuric nitrate	No precipitate cold; precipitate hot

Frehden and Goldschmidt (1937) by using *o*-dianisidine were able to detect the presence of 0.05 mg of agar in the "drop" test. Pirie (1937) successfully applied three color reactions to the detection of agar in the presence of certain other substances: the orcin reaction, the carbazol reaction, and the diphenylamine reaction. These have been adapted from some well known reactions by the use of lower temperatures, a shorter time of heating, or more dilute acid during the development of the color. Under these mild conditions the constituents of agar give a color, whereas most of the other carbohydrates studied are inert. Since the derivatives of the aldehydo sugars behave similarly, these tests are not specific for agar. They are useful, however, because of the rarity in nature of this type of sugar in the open chain or aldehydo form. Carrageenin resembles agar in these reactions.

Jacobs (1938) summarizes and compares some of the characteristic reactions of agar and carrageenin found by various authors (Table 28). Agar is also charac-

Table 28. Characteristic Reactions of Agar and Carrageenin (Jacobs)

	Agar	Carrageenin
Stokes' acid mercuric nitrate reagent	Gelatinizes	Gelatinizes
Neutral lead acetate, 20% soln.	Flocculent ppt., gels	Flocculent ppt., gels
Basic lead acetate (A.O.A.C.)	Voluminous ppt.	Voluminous flocculent ppt., gels
Potassium hydroxide, 10%	Clarifies soln.	Gels
Neutral ferric chloride, 5% soln.	Gelatinizes, heat + excess → ppt.	Voluminous stringy ppt., gels
Alcohol precipitate	Heavy flocculent, adhering to beaker, 20 ml.	Coagulated, translucent, stringy, adherent, 20 ml.
Borax, 4% soln.	Negative	Negative
Millon's reagent	Fine ppt.	Fine ppt.
Addition of 2 vols. acetic acid	Ppt.	Negative

terized by the fact that if a drop each of sulfuric acid and congo red are added to 5 ml of a 0.1 per cent solution and centrifuged, a flocculent precipitate results, and carrageenin by its precipitation by a saturated solution of barium chloride (Jacobs, 1938).

For the detection of agar and carrageenin in drugs the following has been accepted by the Association of Official Agricultural Chemists (1940) as a tentative method: Stir the sample and add water if necessary to produce a fluid mass. Treat a portion of the sample with alcohol to precipitate the colloid. If fatty or oil material is present, remove it by washing the precipitated colloid with ether; then redissolve the colloid in water and re-precipitate it in alcohol. Smear a small lump of the alcohol precipitate on a glass slide. Note the character of the resulting film. Put a drop of chlorzinciodide solution on the film and observe with naked eye and

with a microscope. Carrageenin preparations if not too old will show definite structure and color change within one to two minutes. If no characteristic color is developed, prepare another smear on a slide and add a drop of tincture of iodine, U.S.P., to it. Agar or carrageenin, if present, should show definite color reactions. For confirmatory tests, ruthenium red in 10 per cent lead acetate solution and alcoholic methylene blue are used. (Table 29).

Table 29. Characteristics of Test for Agar and Carrageenin

Phyco-colloid	Original Alcohol Precipitate	Film on Glass Slide	Reaction with Chlorzinc-iodide	Reaction with Iodine Tincture	Confirmatory Test	Remark
Agar	White opaque	White opaque	None	Opaque blue black	Stains with ruthenium red	Does not dissolve or lose shape when covered with water
Carrageenin	Stringy	Thin translucent	Brown (small blue particles); characteristic nodular structure	Brown or lilac	Characteristic blue stain with alcoholic methylene blue	With chlorzinciodide, old preparations may fail to show characteristic structure; with iodine tincture both old and new preparations show reactions

Bryant (1941) used thorium nitrate to distinguish pectin from other gum-like substances, such as agar and carrageenin. The latter do not give any precipitate with 50 per cent alcohol, whereas pectin gives good precipitates. On the other hand, pectin and carrageenin yield precipitates with thorium nitrate, and agar does not. With 10 per cent thorium nitrate solution, carrageenin gives a stringy, white precipitate; agar gives only a slight hazy appearance. With 10 per cent thorium nitrate solution and 5*N* acetic acid, carrageenin gives a white granular precipitate, but agar does not show any apparent reaction.

A method for the quantitative determination of carrageenin was reported by Haas and Russell-Wells (1927), who found that a solution of benzidine chloride precipitated not only the free sulfate but the ethereal sulfate of carrageenin as well. Furthermore, it was found that this reaction is peculiar to carrageenin, since the same solution does not precipitate agar, gelatin, gum arabic, or pectin. The value of benzidine chloride solution as a specific test for carrageenin is further enhanced by its ability to precipitate quantitatively all the carbohydrate in the carrageenin, whether from the hot or the cold water-extract, leaving the resulting solution free from carbohydrate. These investigators found that, on washing the precipitate free from chloride with a saturated solution of benzidine sulfate, heating it with water at 80°, and titrating the resulting solution with sodium hydroxide, 1 ml of 0.1*N* sodium hydroxide was equivalent to 0.0324 gm of carrageenin. This method has been tried with success in the presence of agar, gum arabic, pectin and gelatin. It was found that these colloids do not interfere with the determination of carrageenin. The method has also been applied successfully to determine the amount of carrageenin used in commercial cod-liver oil emulsions.

Algin

The widespread use of algin in food industries is very recent; hence there are very few published methods for the detection and determination of algin. A method was published by Schroeder and Racicot (1941) by which 0.2 per cent of sodium alginate can be detected in dairy products. Concentrated HCl is added to the ice cream or the dairy product under examination; the resulting precipitate is washed

with alcohol and ether and dissolved in 0.1*N* sodium hydroxide, and to the filtrate an equal volume of 95 per cent ethanol is added. The precipitate is dissolved in water, and 0.1*N* sodium hydroxide is added dropwise until the system becomes alkaline. Saturated magnesium nitrate solution is then added, the precipitate discarded and the filtrate acidified with a drop of concentrated HCl; 75 per cent alcohol is added and the precipitate dissolved in 0.1*N* sodium hydroxide. Upon the addition of a sulfuric acid reagent saturated with ferric oxide, the solution will develop a pink color in a few minutes if algin is present.

Egami (1941) used the carbazole method to detect the presence of algin, glucose and other sugars, and estimated the quantity by examination of the subsequent light absorption with a Pulfrich photometer. All these substances were colored red to brown and gave the maximum absorption with filter S_{53}. The absorption band was most marked in the uronic acids and decreased progressively in the ketohexoses, aldohexoses and pentoses in that order.

A method is proposed by Hart (1943) to detect algin and other stabilizers in frozen desserts. This is based on (1) a differential treatment with trichloroacetic acid to remove proteins and sodium alginate and treatment with tannic acid to remove proteins; (2) the addition of alcohol to both filtrates to precipitate gums and the remaining alginates; and (3) certain specific reactions for confirmation. To the filtrates from both the trichloroacetic acid and the tannic acid precipitation are added 4 to 5 volumes of 95 per cent alcohol. If precipitates are obtained from both filtrates, algin may or may not be present. A voluminous precipitate in the filtrate from the trichloroacetic acid treatment, responding positively to Benedict's test and to Tollen's test, and none from the tannic acid treatment indicates the presence of vegetable gums, but not algin. If no or very little precipitate is obtained in the filtrate from the trichloroacetic acid treatment and a voluminous precipitate in that from the tannic acid treatment, and if this precipitate reacts positively with both Benedict's and Tollen's tests, the presence of algin is established. If sugar tests are negative in both cases, gum and algin are absent (Table 30).

Table 30. Differentiation between Gum and Algin by Hart's Method

Colloid	Sugar Test of Hydrolyzed Alcohol Ppt. from Filtrate Previously Treated with Trichloroacetic acid	Tannic acid
Gum with or without alginate	+	+
Gum only	+	–
Alginate only	–	+
Absence of both	–	–

Uses of Phycocolloids

Uses of phycocolloids in general have been discussed by various authors, among whom are Smith (1905), Davidson (1906), Holmes (1906), Sauvageau (1920), Tressler (1923, 1927), Vincent (1924), Clayton (1932), Hoffman (1939), Kimura (1939), Chase (1942), Delf (1943), Dillon (1943), Scheffer (1943) and Tseng (1944b). The uses of agar have been treated by Feller (1917), MacKinnon (1930), Tondo (1931), Horiguchi (1939) and Tseng (1944a, c, 1945). Bates (1867), Ausman (1942) and Fraser (1942) have discussed the uses of carrageenin, and Stanford (1883, 1884), Steiner (1941) and Wohnus (1942) those of algin. Generally, phycocolloids serve as gelling, suspending, emulsifying, thickening and body-producing agents.

In Food Industries

The extensive use of the phycocolloids in various food industries has naturally raised the question of their actual value as a food article and as a food adjunct. In the early days when agar was first introduced to the American markets it was

thought to be a highly nutritious foodstuff. In fact, it was alleged by some agar manufacturers that "Its food value is more than double that of an equal weight of eggs or beef-steak." (cf. Saiki, 1906, p. 264, footnote.) In Europe, even now, carrageen is regarded as "highly nutritious" and "very nourishing." Saiki (1906) made a thorough investigation of the utilization of agar, carrageen, and other seaweed-foods by animals and man. He found that the digestibility and availability of these products in the alimentary tract were very imperfect in both man and animals. He showed that agar, boiled one hour with 2 per cent HCl, gave an average of over 50 per cent reducing sugars calculated as dextrose; but that, when agar jelly was fed to a normal man the reducing sugars found in the agar separated from the feces amounted to only 18 per cent. This indicates that the utilization of agar by humans is very incomplete. Lohrisch (1908) fed dogs and rabbits agar in its usual form and also a specially prepared "soluble" agar. It was found that agar was digestible to a very small extent and even when changed to an easily hydrolyzed form, only about 50 per cent was digested. In her extensive investigations on the digestibility of the various carbohydrates found in algae, Swartz (1911) found that the galactan of *Chondrus crispus* was entirely unaffected by common microörganisms, and only little affected by the digestive enzymes. The coefficient of digestibility of carrageen by dogs is about 33 per cent and by man only 6 per cent, from the average of two experiments in each case.

The only reports in recent years on the nutritive value of these phycocolloids were those of Nilson and his co-workers, using male albino rats as the test animals. The apparent digestibility coefficient of the nitrogen-free extract of agar is about 28 per cent and that of Irish moss about 50 per cent (Nilson and Schaller, 1941). The most significant observation is that animals fed upon basal diets supplemented by 10 per cent of agar grew faster than those of the control. At the end of a year, the rats receiving agar supplement in their diet had a mean weight of 737 grams as compared with 529 grams for the controls. Since the coefficient of digestibility of agar is very low, the beneficial effect of agar-feeding cannot be due to actual nutritional value of the agar, and may possibly be a matter of influencing beneficially the functioning of the intestinal tract, probably through the supply of bulk. Animals fed with the other levels of agar and carrageen grow quite uniformly, and their growth is slightly inferior to that of controls.

Nilson and Lemon (1942) investigated the relative nutritive values of algin and gelatin, both of which are extensively used as stabilizing agents in the manufacture of ice cream and in other dairy products. The apparent digestibility of algin increases with higher level of it in the diet. At a 30 per cent level, 88.3 per cent of the algin was digested and at a 5 per cent level, only 3 per cent. Rats fed the 5 and 10 per cent levels of algin grew as well as the control. It is also interesting that none of the rats fed with algin required more food per gram gain in weight than did the controls. These authors concluded, "Apparently the algin has considerable nutritive value and can be efficiently utilized when properly digested."

From our knowledge to date it may be presumed that among the three important phycocolloids, agar has the least food value and algin has the most, with carrageenin occupying an intermediate position. It should be noted, however, that the real value of phycocolloids does not lie in their actual nutritive value, but rather in their ability to serve as a jellifying, suspending, stabilizing and body-producing agent. In other words, phycocolloids are useful as food adjuncts rather than as food articles. In most cases, they are added in relatively small amounts, and it is immaterial whether they are nourishing to human systems. In fact, an important value of agar in human diet is rather its unavailability as a nutritive food. This feature will be treated in detail in a later section.

As Food Articles. Agar has been and is still used as a food article in a great variety of ways in China and Japan. A "food" in an Oriental sense may not neces-

sarily be nourishing. Only the principal foods, such as rice and meat, need have nutritive value. The "complementary" foods, such as agar and lettuce, may be merely appetizing. Up to the early part of this century China annually imported from Japan over a million pounds of this phycocolloid entirely for food. It is frequently served as a substitute for the expensive "birds' nests." For this purpose the best grade of agar, which will not dissolve too readily in the hot soups, is employed. It is also used in a special kind of "cold dish"; the agar strips are cut into smaller pieces, washed by soaking in cold water, placed in hot water, taken out before they show any signs of going into solution, and then mixed with some good grade of soy sauce, some black vinegar and sometimes a few other ingredients such as red pepper. In Japan agar is served in numerous ways as an article of food, such as agar-rice and agar-cakes.

An important use of agar is in making jellies. For ages, sweetened and flavored agar-gel has been a favorite "cool diet" in the summer in the Orient, especially in the hot tropical and subtropical countries. In Japan, agar jellies are mixed with bean paste and some coloring matter, and made in various shapes. Because of the relative scarcity of animal gelatin in the Oriental countries, many preparations which would normally require gelatin in the Occidental type of food are made with agar as the jellifying agent.

When agar was introduced to America and the European countries sometime in the middle part of the last century, it was originally intended to serve as a gelatin substitute in making fruit and vegetable jellies. In this respect agar has certain advantages over gelatin. Having a much higher gelatinizing power—about eight to ten times that of ordinary gelatin—it is a more economical gelling agent. Unlike gelatin, it does not require special refrigeration to form a firm jelly, even in tropical countries. The time required to make an agar-based jelly is also much shorter. For persons of the Orthodox Jewish faith jellies made of agar are preferred over those made of gelatin, which is of animal origin. Moreover, gelatin is decomposed by many bacteria, whereas agar is quite inert toward most of them. Gelatin, however, has one advantage over agar; it is relatively easy to melt in the mouth. Unlike pectin, agar does not require a sugar in order to form a jelly.

Carrageenin is best known as a food article in the typically Occidental preparation of the delectable blancmange, and may therefore be called the "Occidental agar." Because of its high gelose content the whole seaweed *Chondrus* is generally used for this purpose. Smith (1905) gave the following direction for preparing blancmange from the plant, which is popularly but erroneously called "moss": "Soak half a cup of dry moss in cold water for five minutes, tie in a cheese-cloth bag, place in a double boiler with a quart of milk and cook for half an hour; add half a teaspoonful of salt or less, according to taste, strain, flavor with a teaspoonful of lemon or vanilla extract if desired, and pour into a mold or small cups, which have been wet with cold water; after hardening, eat with sugar and cream."

As a gel-forming substance, carrageenin appears to be an excellent material for making jelly desserts. Since a 3 per cent carrageenin gel is fairly stiff and has a low melting temperature of 27° to 30°, dessert thus made will easily melt in the mouth like that made of gelatin, thus eliminating the sole disadvantage of using agar for this purpose. That carrageenin is not widely used in this way is undoubtedly due to the rather strong seaweed odor accompanying the commonly marketed crude *Chondrus* preparation. With highly purified, odorless extracts now prepared by some carrageen concerns, there is little doubt that the use of carrageenin in this type of food preparation will gain favor. It may be interesting to note here that carrageen jelly and skimmed milk yield excellent results in the dietary of calves (Haas and Hill, 1921).

In Japan, algin is sold in thin slices for food (Kimura, 1939). Elsewhere, it is not commonly used as a food article by itself. Recently, it has been quite extensively

used in the preparation of jams and jellies in the United States for the "lend-lease" exports (Wohnus, 1942). For making jellies, the addition of gelose or gelatin, or admixture with lemon juice or similar substances is necessary (Stanford, 1884).

As Roughage. While Orientals take agar preparations for food and enjoy it, Occidentals take agar more or less unwillingly in a somewhat different way, principally as a bulk-producer. In many kinds of breakfast and "health" foods, as well as bakery products, agar has been incorporated merely to supply the necessary bulk for a wholesome diet. The problem of bulk supply is one that only civilized men, accustomed to highly refined food, have to consider. It is in this particular service that the non-nutritious agar has its most logical and valuable place in the human diet.

Uncivilized man eats mostly coarse food containing a great deal of fiber and other indigestible materials, such as the outer covering of grain, and the skin or woody fiber of fruit. With the advance of civilization comes an increased consumption of more refined food with fewer indigestible portions. For example, wheat is ground to a fine powder with all of its branny covering removed. The hard coverings of rice, corn and other grains are thrown away, and the skin of the fruits peeled off. Unfortunately, while man's mouth is nowadays highly "civilized" in taking only refined food, his intestinal tract still remains rather primitive and "uncivilized." It is still adapted to the rough food of the savages, and requires bulky substances to stimulate the wave-like contraction of its muscular walls. The intestinal tract suffers in the absence of sufficient bulk. Hence there is created a temptation to eat more than the system can assimilate. While the flow in the small intestine is not greatly retarded, it becomes more sluggish in the large intestine. Consequently there is a gradual accumulation of waste material in the colon. The longer such material stays there the more its fluid portions are absorbed, and the drier the resulting mass becomes, leading ultimately to constipation.

It is therefore evident that to prevent constipation a more bulky food should be taken. The substance which increases the bulk of the food without increasing its calorie value is called a "roughage." Because of its cheapness, bran is ordinarily used for daily administration to prevent constipation. To most people, bran is not pleasant to take; moreover, in chronic cases of intestinal disorder bran will cause irritation. Agar is therefore preferred by most victims of constipation. It has the added advantage of possessing great water-absorbing capacity, and on its way to the colon becomes more or less gelatinous. The resulting moist, soft, viscous, bulky mass formed in the intestines greatly stimulates peristaltic action and is easily eliminated. For the type of constipation which results from complete digestion of the food and from extensive absorption of the water from the intestinal tract, thus leaving small and dry stools, treatment with agar is especially recommended (Schmidt, 1905; Mendel, 1908; Gompertz, 1909).

While agar is generally recommended to adults, Morse (1910) obtained very satisfactory results with children between 2½ and 8 years of age by giving them agar in broth or soup. He found that this treatment gave "much better results than the administration of fruit, vegetables, coarse foods and preparations of bran, or the ingestion of large amounts of water." For children, Morse recommended two teaspoonfuls, or about one dram, of the dry agar flakes daily. For adults, one teaspoonful per meal is generally recommended.

Brown and Sweek (1917) recommended a daily dose of two heaping tablespoonfuls in a quart of water, boiled till dissolved, seasoned and flavored to taste, and preferably taken hot. Agar, however, is considered to be more effective as a preventive against constipation if taken in the dried, flaked or shredded form, or mixed with cream and sugar. A United States patent was granted to Rullman (1915) for a special cereal containing 75 parts of germinated barley and wheat, 4 parts of bran and 21 parts of agar. In recent years there are many kinds of breakfast and "health" foods in which dry, ungelatinized agar is incorporated.

Carrageenin and algin have higher coefficient of digestion, and are therefore not so useful as roughage.

Bakery Products. Agar is incorporated in certain bakery products to serve the purpose of a roughage. There are the so-called low-calorie bread and biscuits especially made for obese patients who are in need of reducing, and yet wish to satisfy their desire for food. A United States patent was granted to Keyser (1916) for making crackers, wafers, cookies and other forms of biscuits containing agar for constipation victims. The agar was incorporated in a "dry" dough, and the resulting baked product contained ungelatinized agar. For the same purpose, a special "Agar and Oil Wafer" was made by a Cincinnati, Ohio, company. These were chocolate wafers containing a teaspoonful of mineral oil and agar each, and were recommended to be taken with meals. The oil and agar, released during digestion, mixed with the waste materials in the lower intestine, thus helping in their elimination. An analysis of "Agar-Bran Biscuits" was made by Bailey (1929), who found that these were relatively low in protein and that their carbohydrate was very largely unassimilable. There are also special breads for diabetics in which the starch is replaced by agar. Because of its moisture-holding ability, agar is also extensively used in making fruit cakes. Algin is employed in cakes in which the smoothness of their texture is an important quality.

An important use of phycocolloids in the baking industry is as a stabilizer in icings. One of the chief problems in making icings for layer cakes and sweet yeast dough products such as buns is to prevent the adhesion of the sugar coatings to wrappers, especially on hot, humid summer days. Adhesion is primarily due to the presence of excessive moisture, causing dissolution of a considerable quantity of sugar. Therefore, by the addition of substances which have similar or greater affinity for water than sugar, and which are able to form gels, thus holding large amounts of water and making it inaccessible to the sugar crystals, the adhesion of icings to wrappers may often be prevented. Because of their enormous water-absorbing power and their ability to form gels at very low concentrations, agar and algin are used, along with a number of other vegetable colloids, in stabilizing both the water or flat type and the fat-bearing type of icings. Used as such, these phycocolloids also keep the icings soft and mellow. Glabau (1943-44) conducted a series of experiments on the merits of stabilizers such as agar, algin and cereal in stabilizing various types of icings. He concluded that stabilizers have a definite advantage in improving the keeping quality and in eliminating the adhesion of icings to wrappers, and that there is a definite level at which a particular colloid is most effective. About 0.5 per cent of the phycocolloid is generally sufficient. In the United States the recent agar shortage has compelled manufacturers of icings to try carrageenin; the results are said to be very encouraging.

Agar and algin are also used in making meringues and fillings. While they differ appreciably in their respective colloidal properties, both phycocolloids seem to serve the purpose very well. Where a rigid gel is desired, agar is generally used; algin is preferred if a softer product is wanted. There are occasions when a combination of both colloids gives the best results. For example, in the manufacture of certain types of fillings and custards, it is desirable to produce a gel possessing a moderate degree of fluidity and at the same time able to stand up so that it can be handled. In this instance, a mixture of agar and algin is used. Carrageenin also serves similar purposes.

Dairy Products. One of the most important uses of phycocolloids is as a stabilizing agent in dairy products such as ice cream, sherbets, ices, chocolate milk, and cheese.

Ice cream. One of the most amazing recent developments in the dairy industry is the unusually rapid acceptance of sodium alginate as an ice-cream stabilizer. About ten years ago, algin was practically unknown to ice-cream manufacturers. At

present, about one-half[11] of the ice cream made in the United States is stabilized by this seaweed product.

To serve as an ice-cream stabilizer, a colloid must be able to impart smooth body and texture to the frozen product and to prevent coarsening during storage due to the formation of large ice crystals. An efficient stabilizer, therefore, should have a great affinity for water; it should be able to limit the growth of ice crystals during the freezing process and to hold the free water as water of hydration during the later "heat shock" in the retailer's cabinet. Furthermore, the stabilizer should be convenient to use and should not hinder the normal process of mixing or freezing the ice cream. Its presence should not be evident when the ice cream is eaten. Mixes made with efficient stabilizers should whip fast with sufficient overrun, and the resulting ice cream must show a smooth, clean melt-down without any serum drainage or wheying off.

Previously gelatin was the sole ice-cream stabilizer[12] possessing the good points mentioned above. Stabilizers from plant sources, such as starch, agar, and various gums, have been suggested. Starch swells and absorbs large quantities of water, making a smooth ice cream; it gives, however, an undesirable filmy after-taste to the resulting product and is thus less suitable for this purpose. The plant gums likewise improve the texture and body of ice cream, but in using them, it is very difficult to homogenize the mix, as it is likely to be "stringy" or "livery" when coming from the homogenizer, and is therefore difficult to handle. Ice cream made of gums tends to be "sticky" or "soggy" and hence very objectionable. The chief disadvantage of using agar in ice cream is its low whipping ability, thus resulting in very low overrun; the necessity of dissolving agar at 90°-100° is another serious handicap. Algin is a plant product; nevertheless, it does not have any of these disadvantages. Besides, it possesses certain advantages over gelatin, formerly the standard ice-cream stabilizer.

Goodman (1935) was among the first to study experimentally the value of sodium alginate as an ice-cream stabilizer. He found that only about 60 per cent as much sodium alginate is necessary as compared to amounts required of other stabilizers, 0.15 to 0.25 per cent of algin being sufficient to give satisfactory stabilization. He compared critically ice creams made with 0.25 per cent sodium alginate as the stabilizer with those containing 0.3 per cent gelatin (250 Bloom strength). By means of photomicrographs, Goodman showed that algin has a somewhat greater stabilizing ability than gelatin, as indicated by the smaller size of the ice crystals in the algin-stabilized products. Besides, sodium alginate retards more efficiently the coarsening during distribution, when a large fluctuation of temperature is encountered. This ability to retard coarsening is due to the enormous hydration capacity of the alginate, which is not affected to any appreciable extent by temperature changes. Moreover, the whipping ability of mixes containing algin as the stabilizer is 35 per cent more than that of similar mixes containing gelatin. Goodman believes that this improvement of whipping ability is due to the reaction of sodium alginate with the calcium in the mix, resulting in the formation of undissociated, though highly hydrated, calcium alginate. The amount of calcium caseinate originally present is thus reduced and the shipping quality of the mix improved. The decrease in calcium ion concentration improves whipping by decreasing the fat clumping of the mix.

Sodium alginate is not gel-forming as is agar. It stabilizes the ice cream by virtue of its extreme degree of hydration. Therefore the amount of algin to be used is not limited by the melting characteristics of the resulting product. Gelatin, on the other hand, can be used up to a definite concentration, which sometimes proves in-

[11] Estimate of Dr. H. H. Sommer, University of Wisconsin; personal communication.

[12] Karaya or "Indian gum" was largely used too. The use of protective colloids in infant's milk, ice cream, etc., has been discussed in earlier volumes of this series. J. A.

adequate to effect stabilization, and above which the finished product will be gummy and elastic, retaining its shape instead of melting. Finally, aging is not required of algin-stabilized mixes, while those containing gelatin require a certain aging period in order to obtain the full efficiency of the stabilizing ability of the gelatin (Goodman, 1935).

Mack (1936) conducted a number of trials on the value of algin as an ice-cream stabilizer. His findings were in perfect agreement with those of Goodman. He found that sodium alginate-stabilized mixes whip faster, and produce ice cream with an improved texture and a more desirable melting appearance than that stabilized with gelatin of average strength. The algin-stabilized product melts somewhat more freely than the gelatin-stabilized one, and appears smooth and creamy. Aging of the mix stabilized with sodium alginate is not necessary, but to secure satisfactory results the mix must reach 160° F before adding the stabilizer.

Tracy (1936) found that when sodium alginate was used in the same amounts as 225 Bloom gelatin the two ice creams had approximately the same body scores, but that the algin-stabilized product melted more rapidly. Mixes made with sodium alginate had a lower titratable acidity and a higher pH and showed slightly more color than gelatin mixes.

That sodium alginate has most of the desirable properties of gelatin as an ice-cream stabilizer has been confirmed by the studies of Buell and Bendixen (Briggs, 1936), Stebnitz and Sommer (1937, 1938), Anderson, Dowd and Helmboldt (1937) and Mack (1938). Stebnitz and Sommer reported the uniformity of the viscosity of algin-stabilized mixes during aging, as a distinct advantage to the mix manufacturers in producing uniform products.

Thus, within a few years, the value of sodium alginate as an ice-cream stabilizer has been firmly established. The particular alginous product used by all these investigators was a commercial preparation under the trade name of "Dariloid." Earlier, a similar product called "Kelco-Gel" was tried without much success. According to Green, Clark, Mann and Preble (1937), "Dariloid" contains trisodium phosphate, sugar, and dextrin in addition to the high-viscosity sodium alginate. This product is still undergoing constant improvement in its efficacy as an ice-cream stabilizer. Even in its present form "Dariloid" has been threatening to replace gelatin entirely.

Sommer (1938) summarizes the advantages of sodium alginate over gelatin as an ice-cream stabilizer by the following merits: (1) less amount required, (2) uniform viscosity of the mix during aging, (3) similar or better whipping quality of the mix, (4) lighter color of the ice cream (although the mix is slightly more colored), (5) smoother and cleaner melt-down of the ice cream without any serum drainage or wheying off, and (6) "cleaner" flavor of the ice cream. The disadvantage of algin-stabilizer lies in its failure to dissolve when added to the cold mix. Because of the formation of insoluble calcium alginate before the completion of solution, the algin particles become coated with an insoluble layer. Therefore sodium alginate should be added to the mix at 150° to 160° F.

In a series of experiments comparing the relative merits of sodium alginate and gelatin as ice cream stabilizers, Tracy and Tucker (1939) found no detectable differences in flavor, and concluded that there was no decided preference for either stabilizer so far as the body of the ice cream or whipping time is concerned. In the matter of melt-down and aging, the alginate has some advantage over gelatin.

Commenting on the relative merits of sodium alginate and gelatin as an ice-cream stabilizer, Professor H. H. Sommer made the following remark in a recent communication:

"The question as to whether sodium alginate is a better stabilizer than gelatin cannot be answered unequivocally. Personal judgment, rather than precise measurements, is involved in reaching a conclusion on this subject. . . . From the stand-

point of texture and melt-down characteristics there is no important reason to prefer one over the other except on a cost basis. However, there are differences with respect to their effect on the whipping ability of the mix, and on mix viscosity and the rate at which it develops.

"Sodium alginate *may* produce a mix with a higher whipping ability than gelatin. This is true only where mix composition and homogenizing conditions are such as to be conducive to fat clumping. Sodium alginate tends to prevent fat clumping and thereby produces a better-whipping mix. This fact may be of little consequence where the mix is frozen by continuous freezers, but may be an important factor where batch freezers are used.

"Mixes stabilized with sodium alginate increase in viscosity quite rapidly on cooling and on aging in a cooled condition. Sodium alginate mixes reach their final viscosity practically within one hour after cooling, whereas gelatin mixes develop viscosity more slowly and the viscosity increase up to 24 or even 48 hours after cooling. These facts may be advantageous to one or the other stabilizer according to plant conditions and requirements. Where a plant sells mix to smaller ice-cream manufacturers the quick attainment of its final viscosity in sodium alginate mixes is usually considered quite an advantage, since the mix can be shipped out freshly made or several days old without any difference in viscosity. On the other hand, the rapid increase in viscosity on cooling sodium alginate mixes may be a serious drawback in plants where the surface cooler (aerator) capacity is limited. Due to the increase in viscosity in cooling the mix flows over the cooler in a heavier layer, heat exchange is not as rapid and the mix may not be cooled properly when it leaves the cooler. In some cases this has been the deciding factor against the use of sodium alginate."

As mentioned previously, agar has very poor whipping properties, and is therefore not suitable as an ice-cream stabilizer, although it has been reported to be used as such. Carrageenin has been gaining favor for this purpose in recent years, although there is as yet no scientific records of its merit in this respect. In earlier years, the strong seaweed odor accompanying the crude product prevented manufacturers from using it in making ice cream. To improve the body of the ice cream and to give it a slower melting, a mixture of equal amounts of "Irish moss" and sodium alginate has been suggested as an ice-cream stabilizer, to be added in about 0.3 per cent (Green, Clark, Mann and Preble, 1937). Products containing this mixed stabilizer are reported to be superior to those containing gelatin, because they have both the advantages of an algin-stabilized product, and the body and slower melting of gelatin-stabilized ones.

Sherbets and ices. Since sherbets and ices are characterized by the tartness of their flavor, sodium alginate, being a neutralizing stabilizer, cannot be used.[18] These products contain greater amounts of water and lower content of fat and serum solids than does ice cream; stabilizers are therefore more important in their manufacture. Agar has been used to some extent in stabilizing these frozen products. It makes them smooth and non-crumbly, and holds down the overrun by preventing the drainage of unfrozen syrup in the hardening room. Unlike gelatin, agar acts quickly, and aging of the resulting products is unnecessary. Since agar has low whipping ability, thus producing low overrun, gums are added to improve the whipping quality. Dahlberg (1926) recommended 0.2 per cent agar together with 0.4 per cent gum tragacanth or high-grade India gum for ices, and with 0.2 per cent gum for sherbets. The high cost of agar in recent years has prevented agar from coming into more general use. Lately carrageenin has come into more general use as a stabilizer in making sherbets and ices.

Chocolate milk. Another amazing recent development in the dairy industry is the

[18] A Philadelphia manufacturer has, however, succeeded in using the commercial algin, "Dariloid," in stabilizing ices, and has made about two million quarts of algin-stabilized ices in 1944.

rapid and general adoption of carrageenin in stabilizing chocolate milk. Most, if not all, of its major producers in the United States are now using the "Irish moss" extract as their stabilizer.

Previous to the introduction of a stabilizer, the chocolate-flavored milk on the market always had a sediment of cocoa particles at the bottom of the bottle. The bottle therefore had to be shaken vigorously before the drink was poured. The sediment usually adhered so firmly to the containers that great difficulty was encountered in washing them. Now, with the addition of a small amount of carrageenin, usually to the extent of only 0.04 per cent, these difficulties are largely eliminated.

While gelatin is excellent as an ice-cream stabilizer, it is not suitable for suspending cocoa fibers in chocolate milk. This is primarily due to the necessity of aging for gelatin-stabilized products, and settlement of the fibers will take place in the interim. Other vegetable stabilizers have been tried. For one reason or another, none is comparable to carrageenin in efficacy as a chocolate milk stabilizer.

To make chocolate milk, a chocolate syrup is first prepared. The syrup is made by adding a mixture of cocoa, salt and carrageenin to invert sugar solution at about 190° F, and should contain about 0.4 per cent carrageenin. One gallon of this chocolate-flavored syrup is then mixed with 11 gallons of milk, and the mixture pasteurized and finally bottled. The finished product thus contains only 0.04 per cent of the seaweed extract; yet the cocoa fibers are effectively held in a homogeneous suspension and the butter fat does not rise to the top.

A United States patent was granted to Green, Clark, Mann and Preble (1937) for a process of stabilizing chocolate milk with a mixture of carrageenin and a special algin preparation called "Cocoloid." Algin by itself is not a suitable stabilizer for chocolate milk, although Mack (1938) believed that it could be used as such. The chief objection to the use of alginate is that the resulting preparation tends to develop a "mottled" appearance. Moreover, the amounts of algin used alone are very critical, and too much or too little of it will give a poor product. These investigators alleged that chocolate milk stabilized by carrageenin alone is generally too thick and has an objectionable seaweed flavor. They therefore proposed to use a dry mixture of 0.8 pound "Cocoloid" and 0.7 pound carrageen to stabilize 100 gallons of the product. It should be noted, however, that present-day preparations of carrageenin have no seaweed flavor or odor, and that carrageenin in the concentration conventionally used does not produce a thick drink, as reported by these investigators. Since the amount of carrageen added in their patent should be sufficient by itself to stabilize the resulting suspension, it is doubtful whether Cocoloid has any additional value as a suspending agent.

Cheese. Agar has been used in making cream cheese of the Neufchatel type to reduce the tendency of this dairy product to exude whey at warm temperatures, to improve slicing qualities, and to produce a firmer body (Dahlberg, 1927). While the use of agar has the disadvantage of requiring a higher temperature to dissolve it than if gelatin is used, agar has a decided advantage over the latter in improving the texture of the cream (Marquardt, 1930). For this purpose powdered agar of the highest grade is recommended, and the quantity used varies from 0.2 to 1 per cent.

Mack (1938) suggested the use of 0.1 to 0.2 per cent sodium alginate in making soft cheeses such as cream cheese, whole milk cheese of the Neufchatel type, and cheese spreads. The algin is first dissolved in hot water, and then added to the cream before pasteurization. Except for this modification, the cheese is to be made in the usual manner. For making soft cheese and cheese spreads to be packed in glass containers by Dahlberg's "hot pack process," Mack recommended 0.8 per cent sodium alginate as the stabilizer. Carrageenin recently has been used in making cream and cottage cheese and processed cheese spreads.

Miscellaneous products. Agar is also used in such drinks as malted milk and acidophilus milk, as a stabilizer and thickener. A patent was granted to Lecomte

(1911) for using agar to prevent the separation of fat in cream or milk. In preparing the so-called "Imperishable Milk," North (1924b) separated the solids from the cream, which was then emulsified with agar. This process allegedly took away the "foods" for the growth of putrefying bacteria, thus helping to keep milk fresh. On the same principle, North (1924a) prepared an "Imperishable Butter." For these products, 0.5 per cent agar was used.

Algin has been suggested as a stabilizer in whipping cream used in decorating fancy molds, cakes and other products, in order to reduce serum drainage (Mack, 1938). The addition of 0.4 per cent sodium alginate increases the viscosity of the cream and eliminates serum drainage. Algin is also used as a gelling agent in milk puddings. It is employed in the manufacture of certain types of milk powder, which forms reconstituted milk upon the mere addition of water (Delf, 1943). The presence of the alginate prevents sedimentation. In the manufacture of oleomargarine, the addition of sodium alginate makes a better product, approaching more closely the texture of butter (Wilt, 1939).

In Confectionery. Agar finds an important use in confectionery. It is chiefly used in making jelly candies and marshmallows. The confectioner can make a nice jelly candy with as little as ¾ to 1 per cent agar. In making marshmallows agar has an additional value in that it renders the final product easier to cut. As much as 100,000 pounds of agar have been estimated to be consumed annually in the United States by the confectionery industry (Tseng, 1944a). It may be said that, wherever agar is known, one of its chief uses is in making candies. In recent years, algin and carrageenin have also been extensively used as fillers in confectionery to give body to candy bars and similar confections.

In Meat Canning and Preservation. In the canning industry agar serves both as a thickening and as a gelling agent, especially for the softer types of meat and fish, which might otherwise fall apart in subsequent handling. Furthermore, certain constituents of such fish as herring will attack the metal of the can, and produce a detinning action, thus blackening the contents of the can and rendering the resulting product unsalable. By the use of agar such troubles are eliminated (Gamage, 1922). The ability of agar to retain its gelatinizing power to a greater extent than animal gelatin, after subjection to the high temperature and pressure necessary in processing these foods, makes it superb for this particular purpose. Agar and carrageenin are also widely used in canning pickled tongue and poultry.

Matsuoka (1924) was granted a United States patent for preparing dehydrated and powdered fish extract with agar. This was recommended for use in soups, gravies, or food-flavoring preparations. Another patent was granted to Nishio (1924) for a similar process, except that the solidified mass of fish extract and agar was subjected to the action of molds until a hard product was obtained. While such products might appeal to Oriental taste, they certainly did not seem successful among Americans.

Agar provides a rather simple but effective way of temporarily preserving easily spoiled foodstuffs such as meat and fish. It is especially recommended for hot countries where refrigeration facilities are not generally available. The meat to be preserved is cooked with agar and the resulting meat-gel will remain wholesome for a long time. Agar is not attacked by most putrefying bacteria, and helps to prevent the entrance of bacteria which will otherwise spoil the meat.

Other Uses in Food Industries. Agar, algin and carrageenin are used in preparing various kinds of salad dressings, aspic salads and desserts, and in assisting emulsification in mayonnaise. Agar has also been used as a sausage casing. Carrageenin serves as a base for soda-fountain syrup. A United States patent was granted to Washburn (1932) for a process utilizing agar, alginate and pectin as a stabilizer and bulk producer in making fruit-juice powder. These colloids are also used as thickeners in soups, sauces and gravies, and in fruit butters and preserves.

In Medicinal and Pharmaceutical Preparations

The phycocolloids serve in medicinal and pharmaceutical preparations in various capacities, such as mechanical laxatives, emulsifiers, thickeners and gel-formers.

Mechanical Laxative Preparations. The value of agar as a roughage in the prevention of constipation has already been discussed above. Administered in larger portions agar becomes a natural mechanical laxative. This type of laxative merely accentuates physiological processes concerned in the elimination of the intestinal waste without involving irritation of the intestinal wall as chemical laxatives do. There are two groups of mechanical laxatives. The first is represented by liquid paraffin which acts by softening the intestinal contents, thereby facilitating waste elimination without evoking any peristaltic reflex. Agar belongs to the second group consisting of hygroscopic substances which absorb water, expand considerably, thus increasing the bulk and stimulating peristalsis.

The petrolatum-agar emulsions on the markets are preparations containing both kinds of mechanical laxatives, although it is generally the petrolatum which acts as the laxative while agar, being present in amounts of less than 1.5 per cent, serves as an emulsifier and helps to make it easier to take. Such preparations are generally sweetened and flavored by various substances (Wilson, 1930; Nitardy, 1931). Some contain gums as additional emulsifiers (Nitardy, 1933). Miller (1926, 1930) added lactic acid to thin the solutions so that he could use a great bulk of agar in his preparations. As much as 10 per cent agar was used together with 37.5 per cent petrolatum. The agar used in the Miller preparations has definite laxative value.

Some emulsions of liquid paraffin contain carrageenin as the emulsifier. MacAdie (1942) gave the following direction for the preparation of such an emulsion, using "Gelozone," the trade name of an "Irish moss" extract by a British firm: "To make a pint of a 25 per cent emulsion, place 180 grains of Gelozone in a dry mortar and rub down with 5 fl oz of liquid paraffin. Add all at once 5 fl oz of nearly boiling water and triturate rapidly until a smooth cream results. . . . Triturate at intervals until cold, and then dilute gradually to a pint. As a preservative, benzoic acid ¼ grain to 1 fl oz of emulsion is added and for flavoring, vanillin spirit is used. The preparation creams very slightly on standing 24 hours, but this can be remedied by the addition of a trace of tragacanth. Homogenization gives a superior product." A similar liquid paraffin-carrageenin emulsion has been suggested by Wing (1942), who used sodium benzoate and chloroform as preservatives, vanillin for flavoring and soluble saccharin for sweetening the product.

Pharmaceutical Emulsions. Besides their use in petrolatum emulsions, phycocolloids serve also as emulsifying agents in various pharmaceutical preparations. They have additional values as demulcents. The best known among phycocolloid emulsifiers is probably the "decoction chondri" which is prepared from carrageen. The National Formulary recommends a 3 per cent *Chondrus* solution for the *Mucilago Chondri,* which is prepared merely by boiling the seaweed in water and straining the solution through muslin. This preparation is used by itself as a demulcent and frequently as a vehicle for other medicaments. Wing (1942) devised a simple strainer for small-scale preparation of the *Chondrus* decoction. Two such preparations were made with either chloroform or sodium benzoate as preservative. The following were successfully prepared by using this decoction: syrup substitute, modified Gee's linctus, Barium cream, and cod-liver oil emulsion. The last mentioned is prepared by the following constituents passing through an emulsifier, and contains the following constituents: 10 fl oz cod-liver oil, 10 minims oil of bitter almonds, 1 grain soluble saccharin 550, 20 minims chloroform, and 20 fl oz *Chondrus* decoction preserved with sodium benzoate. Osborn and DeKay (1941) also obtained good results with the use of carrageen in homogenized cod-liver oil. Several commercial cod-liver oil emulsions are stabilized with carrageen.

Sodium alginate is not generally used as an emulsifier, partly because of its chemical reactivity. It can be used, however, as an auxiliary emulsifying agent. Thus, mineral oil emulsions can be prepared by using gelatin, whose isoelectric point lies between pH 4 and 5 and incorporating 0.5 per cent sodium alginate to aid emulsification and to increase viscosity without causing gelation (Shackelford and Cordero, 1943). Agar and carrageen have also been used as stabilizers in emulsions to carry medicinals such as vitamins and sulfa-drug compounds.

Pills and Tablets. Phycocolloids find extensive uses as constituents of pills and tablets. A United States patent was granted to Miller (1935) covering the preparation of a special "seal-ins" coating for pills. This has the ability of regulating the rate of solution of the capsule and consequently, the timing of its opening. This invention is regarded by many as one of the important contributions to pharmaceutical preparation in recent years. Agar is added in tiny particles and distributed in the waxy material, and by virtue of its water absorption, it assists in the release of the coated medicinal preparation in the right place. Agar is used in the coatings of certain gentian violet capsules which are useful in the treatment of infection with *Oxyuris vermicularis;* it is also employed as a constituent in a preparation for the treatment of *Coccidioides* infection in chickens (Dr. E. M. McKay, personal communication).

As granulating agents in the preparation of tablets, such as aspirin tablets, carrageen was found to be satisfactory and sodium alginate quite good (Osborn and DeKay, 1941). Carrageen is also used as a binding agent in the preparation of certain pills.

Ointments and Jellies. Many pharmaceutical ointments and jellies have been prepared with phycocolloids as the bases. A United States patent was granted to McCarthy (1918) on a formaldehyde preparation using 5 per cent agar gel as the base. This formaldehyde-gel was able to release formaldehyde vapor constantly and thus to sterilize or disinfect the surrounding atmosphere.

Sodium alginate is used as a base in the manufacture of greaseless, water-soluble ointment and lubricating jellies replacing tragacanth and other gums; 5.0 to 7.5 per cent of the algin is necessary to produce bases of the consistency of ointments (Osborn and DeKay, 1941). Algin bases are very useful because they are compatible with most of the ingredients which are used in the official ointments. Agar and carrageen are used similarly.

Algin is used in making sulfanilamide ointments, which are valuable on surface wounds and can also be employed on mucous-membrane surfaces such as the conjunctiva. Ordinarily, when sulfanilamide powder is used for surface wounds, the powder, serum, blood and pus soon form a crust. On removing the crust, some of the epithelium may be removed also. When petrolatum is used as a base and emulsified by sodium alginate, this trouble can be eliminated. The following formula has been recommended: Dissolve 10 parts of sulfanilamide in 25 parts hot water, mix it with 5 per cent sodium alginate solution, and to the sulfanilamide-alginate mixture, add 16 parts of anhydrous wool fat, 1 part of sodium chloride dissolved in 4 parts of water, and 78 parts white petrolatum base, and mix until smooth and homogeneous (Anonymous, 1941).

Other Pharmaceutical and Medicinal Uses. Agar is used as a vehicle for lactic acid to combat toxicogenic bacteria in the intestines (Miller, Kurka and Chase, 1928). Agar and carrageenin serve as vehicles for glycerin suppositories. They are also used in glycerin jellies for chapped hands. Agar has been reported to be useful in wound dressing on account of its rapid absorption of bacteria and leucocytes in the pus (Loeper, Barbarin and Vesper, 1916). A highly active anti-coagulant is found in agar and carrageen (Elsner, Broser and Bürgel, 1937). A German patent was granted covering the extraction of the blood-coagulation retarding principle from these substances (Elsner, 1938).

Years ago, "Irish moss" was used as a remedy for consumption, and was sold principally for invalid food. It was recommended in stomach ulcer cases. It is reported to be used in cough medicine, which usually consists of a soothing principle dissolved in sugar syrup. Carrageenin gives body to the medicine and also produces a slight soothing effect. A kind of poultice has dry carrageenin as an important ingredient (Chase, 1942). Iron alginate is useful as a hematinic (Stanford, 1898).

In Cosmetics

In the cosmetic industry agar, algin, and carrageen all find extensive use in shaving creams, toothpastes and other preparations requiring a water-soluble colloid. "Irish moss" is among the ingredients listed in the United States F. D. A. toothpaste specification for use as a binder. A thick mucilage of carrageen is also used in deodorant pastes.

Carrageen and sodium alginate are excellent vehicles for the saponified type of hand lotions. The almond oil and free stearic acid are saponified with triethanolamine, and the colloid then added as a vehicle for the resulting soap (Osborn and DeKay, 1941). A pineapple juice hand lotion containing carrageen is recommended by Chilson (1938). Algin is recommended in preparation of hair lotions and mouth washes (Frydlender, 1939). For stearic acid hand lotions, 0.3 per cent sodium alginate is sufficient to provide the necessary slip (Musick, 1942). Algin is employed in cosmetic preparations having an aqueous or glycerin base, such as glycerin hand jellies, transparent setting lotions, and beauty milks. It is also used in sunburn lotions and creams.

Another important use of sodium alginate in the cosmetic industry is in the manufacture of cosmetic jellies and creams with algin bases, in which a certain amount of a slightly soluble calcium salt, *e.g.*, calcium citrate, is usually added to the sodium alginate solution. By the controlled release of calcium ions, solutions may either be thickened to cream or converted into jelly. It is also possible, merely by altering the proportion of the calcium or other ion-producing insoluble alginates, to vary the viscosity of the resulting solution over a wide range. Since alginate preparations are of controllable consistency and density, the therapeutic efficacy of many dermatologic compounds can be vastly improved. Algin preparations are generally water-white and transparent, and are therefore superior to those prepared with other gums.

By using sodium alginate and calcium citrate in different proportions together with perfume, glycerin and other chemicals, Bergy (1939) has prepared greaseless hair pomade, hair lacquers, and glycerinated hand jelly. They are made by preparing separately a solution of sodium alginate with the necessary ingredients and another of calcium citrate, and subsequently mixing the two solutions. Bergy also suggested formulas for the so-called "bubble bath," in which sodium alginate is used as a foam stabilizer, and for "brushless shave" and hand cream.

Milne (1941) alleged that previously vanishing creams and other skin cosmetics always included an alkali soap or mixture of alkali soaps as the emulsifying agent, and the preparations were therefore alkaline and often irritating to the skin. By using sodium alginate, greatly improved preparations can be made. He proposed the following formula for making a hand jelly: Dissolve 1.5 parts by weight of "Manucol" V (sodium alginate) and 49 parts of glycerin in 35 parts of water, add 0.2 part calcium citrate rubbed up with 13 parts of water, mix and add 1.5 parts of perfume and allow the mixture to stand for about 2 days, with occasional stirring.

As a Microbiological Culture Medium

The most important service that agar renders to mankind, in war or in peace, is as a bacteriological culture medium, although the amount actually employed as such is relatively small. In the United States about one-sixth of the agar is normally used

for this purpose. Nevertheless, agar claims more respect in this particular service than in all the others combined.

Cultures of pathogenic and non-pathogenic bacteria must be prepared for the identification of these microörganisms, the standard analysis of milk[14] or water supplies,[15] and the preparation of certain vaccines and anti-toxins for protection against diseases. In penicillin production the first step is the cultivation of *Penicillium notatum*. In practically all cases of bacteriological and microbiological culture, the medium used is almost invariably agar gel to which are added various chemicals to encourage the growth of these microörganisms. Thus, agar is an indispensable weapon against disease.

Because of certain unique characteristics, agar is still the irreplaceable material used in making bacteriological culture media. Although various agar substitutes have been suggested, they are useful only in limited cases, and none of them has yet proved to be as satisfactory as agar. There are several reasons why agar is preferred to all other gel-forming substances for this purpose.

First of all, a 1 to 2% agar gel is a solid at 37°, at which temperature most pathogenic bacteria must be cultivated. Gelatin, for example, may be a fluid at this temperature. Secondly, agar is relatively inert and is not digested by most bacteria. Although there are now known several species of agar-digesting bacteria, their numbers are almost negligible. None of the pathogenic forms is known to digest agar. On the other hand, there are numerous bacteria, pathogenic and otherwise, which liquefy gelatin. In the third place, while agar "sweats," as do all hydrophilic colloids, the degree of syneresis is not so great as to interfere with the enumeration of colonies on the plate and with the isolation of pure cultures. With certain agar substitutes there is so much water of syneresis that the different bacterial colonies may merge into a large one. Fourth, agar is a reversible colloid, illustrating a striking example of hysteresis. It can be alternately warmed to a solution and cooled to a gel. At about 40° it forms a gel, which will not melt until the temperature reaches about 95°. Silica gel possesses some of these good points, but has the disadvantage of being irreversible. Fifth, the firm and rubbery surface of the agar gel is not easily ruptured by an inoculating loop or needle. Pure agar gel is nearly transparent, and almost neutral in reaction. Having a strong gel strength, and a ten times greater jellifying power than gelatin, agar becomes a much cheaper material.

For ordinary culture media 1.2 to 1.5 per cent agar solution is used. This produces a solid, firm gel. With dilute agar solution, for example, 0.1 to 0.5 per cent, a rather fluidic semi-solid medium is obtained. This is very useful in studying the motility of certain bacteria, *e.g., B. coli communis* (Tittsler and Sandholzer, 1936). Falk, Bucca and Simmonds (1939) demonstrated the value of using a medium containing small percentages of agar (0.06 to 0.25 per cent) for the detection of bacterial growth. They confirmed the earlier findings of Hitchens (1921) and Spray (1936), and recommended the adoption of a semifluid medium as a standard means for the detection and estimation of the extent of bacterial growth in biologic products. For certain purposes, semi-solid agar medium has the combined advantages of liquid and solid media (Berlin, 1930), and recently has been more extensively employed in culture studies.

Since Pringsheim (1912) introduced the use of agar in culturing chlorophyll-containing plants, culture methods similar to that used by the bacteriologists are now in general use in culturing unicellular and even simple multicellular algae.

Owing to the shortage of agar during the war various substances have been introduced to serve as substitutes in the preparation of culture media. Unfortunately

[14] American Public Health Association. 1934. Standard methods of milk analysis. 6th Ed. xiii + 105 pp.

[15] American Public Health Association. 1936. Standard methods for the examination of water and sewage. 8th Ed. xiv + 309 pp.

none has yet proved to be a satisfactory substitute for agar in standard techniques. In specific cases, however, a few substitutes have shown promise, especially carrageenin.

Carrageenin, as mentioned previously, forms a weaker gel and has a lower melting temperature than agar. Léon (1930) found that by the addition of a potassium salt, a product was obtained which made firmer gel than ordinary extracts; a French patent was granted for his process. This investigator suggested its use as an agar substitute in a general way. Apparently, this matter has not received sufficient attention, because no such necessity existed before the war cut off the supply of the rather inexpensive Japanese agar. The outbreak of the war has aroused interest in using carrageenin as an agar substitute, and recently a special product has appeared on the market under the trade name "Carragar."

Walker and Day (1943) conducted a series of experiments to determine the merit of Carragar as an agar substitute. They found that certain disadvantages in using it could be overcome. For most purposes, a 3 per cent gel is found to be firm enough. Where a firmer gel is needed, *e.g.*, for surface inoculation, the addition of 0.5 to 0.75 per cent agar is necessary. This raises the melting point of the mixed gel so that incubation at high temperatures is made possible; a 3 per cent gel of Carragar by itself melts at 45°. In order to prevent hydrolysis the Carragar medium must be neutralized before the application of heat. Walker and Day found that Carragar, used under the above conditions, served well in all the different culture media tried. There were no observed changes in the biochemical or antigenic properties of any of the organisms grown on Carragar or in colony characteristics or morphology, with a single exception.

Some workers found that the excessive syneresis of Carragar media eventually interfered with the counting of colonies on plates. While the gelling properties of carrageenin can be improved by the addition of various salts, this is objectionable in some bacteriological procedures. The resulting gels are still opaque, and the warm solutions viscous (Stoloff, 1943). The general reaction of bacteriologists seems to be that while carrageenin may be used for various special purposes in the culture of microörganisms, it is not a satisfactory substitute for agar in standard techniques.

In Scientific Research and Agriculture

In Scientific Research. Besides serving as a culture medium for microbiological studies, agar has a place in various other fields of scientific research. In studies of the physical properties of hydrophilic colloids agar is undoubtedly one of the most commonly used materials. Numerous scientific papers have been published on this subject. Because of its hygroscopic properties, agar is particularly suited to the measurement of humidity. Placed in a band in the hygrograph it gives a much greater response than human hair, particularly in the range of average to higher humidities (Schultze, 1932). In biological technique, agar is used in embedding small or slender objects for microtome sectioning. It is especially recommended with plant materials to be sectioned with the freezing microtome. In this respect a 5 per cent agar solution instead of water is used to embed the plant parts (Evenden and Schuster, 1938).

It is well known among plant physiologists that in the standard *Avena* test method for determining growth hormones quantitatively, agar is used as the vehicle for the test solution or hormone. A small rectangular block of agar about 4 cm in volume containing the extract is placed unilaterally on the decapitated coleoptile. The resulting curvature of the coleoptile eventually indicates the quantity of hormone in the solution tested. This technique was first introduced by Stark (1921).

In the measurement of pH of soil samples, a system employing a calomel-saturated quinhydrone cell with an agar and potassium chloride bridge gives a relatively high current, and is quick, accurate and convenient (Robertson, 1936). In the ana-

lytical laboratory agar serves as a coagulant for barium sulfate. The addition of mere traces of agar (about 0.1 per cent solution) will cause the flocculation of an ordinary analytical precipitate of barium sulfate in a very short time. The precipitate thus formed does not tend to creep up the sides of the funnel or filtering crucible (Bogan and Moyer, 1942).

Stimmel (1943) obtained a satisfactory aqueous suspension of the urinary female sex hormone residue by using 0.1 to 0.2 gm of sodium alginate in 30 ml of water. The resulting suspension having the viscosity of a heavy oil is stable. The algin is completely absorbed and well tolerated by the spayed rat, and no unfavorable reactions have been observed.

In Agriculture. While studying the effects of various supplements in nicotine sprays, Sharp (1939) discovered that agar activated the insecticide to a noteworthy degree. Inclusion of agar in such a spray reduced to one-third the amount of nicotine required to produce toxic effects. Agar was used at a dilution of 1:500 by weight. Because of the high cost of agar at present, however, utilization of agar in insecticides on a large scale is probably not yet economically feasible.

Sazonov (1940) found a considerable increase in the stability, dispersion and toxicity of a 5 per cent calcium arsenate suspension by the addition of ammonium alginate. The minimum lethal dose for larvae of *Pieris brassicae* was reduced, and the mortality increased from 50.9 to 69 per cent with 7.5 per cent control mortality. The presence of the alginate also reduced injury to bean foliage by the arsenate.

In a United States patent granted to Earp-Thomas (1918) agar was used to protect and coat the granules of humus or peat inoculated with a mixed culture of nitrogen bacteria. These were to be mixed with chemical fertilizers and introduced into the soil, to provide a good supply of these valuable microörganisms. In recent years there have been placed on the market several commercial cultures stated to contain superior strains of beneficial soil bacteria such as *Rhizobium spp.* for promoting crop production. They are generally humus or agar cultures. To determine the value of some of these marketed cultures Spaulding (1940) conducted several experiments, using soybean and peanut plants in the tests. He concluded that there were definitely increased yields of these plants grown in poor land in Alabama, and that, for unknown reasons, the crop yield with the agar cultures was consistently greater than that with the humus cultures. He suggested that probably agar culture was better adapted to maintain the nitrogen-fixing efficiency of the nodule organisms.

As Impression Mold Materials

Dental Impression Materials with Agar Base. The idea of using agar in the art of prosthesis for taking impressions of living tissues was first conceived by a Viennese scientist, Alphons Poller, who was granted a British patent (1925), and later a United States patent (1928) on his invention. The first material was called "Negocoll." Later the De Trey Brothers of Zurich, Switzerland, to whom the Poller patent was sold, manufactured a modified material under the trade name "Dentocoll." As the names imply, they are primarily intended for making dental impression molds.

The greatest development of such hydrocolloid impression materials in dentistry, however, took place in the United States. Within a few years materials of a similar nature have appeared. Paffenbarger (1940) studied critically the relative merits of eight different types found on the market. He found that invariably the essential and important ingredient was agar. Before the issuance of the agar-freezing order by the War Production Board, it was estimated that as much as 75,000 pounds of agar was used annually for dental impression materials (Tseng, 1944a).

Previously, several materials had been used to make castings from the oral cavity. They all have their specific defects. For instance, it takes gypsum four or five minutes to solidify. Since it sets to a stone-like mass, it has to be broken away in order to remove it from the mouth. Such a procedure naturally endangers the teeth

and bridges of the patient. Finally, the broken pieces must be laboriously and carefully reassembled. Materials containing resin and wax have also been used. They displace the soft parts of the gum and do not mold undercut portions, resulting often in quite faulty impressions. Gutta-percha is another material used. It has the drawback of becoming distorted when withdrawn from the mouth of the patient. Most hydrocolloids cannot be used either because they do not solidify sufficiently to yield accurate negatives, or because attainment of the requisite degree of solidification is too slow.

The agar molding materials invented by Poller and later modified by various manufacturers have been very successfully applied in dental work because they are without the above-mentioned disadvantages, and have several additional good points. The special merit of these agar-based materials "lies in their elasticity, and, consequently, their ability to reproduce undercuts and dovetails, which may be very troublesome in the withdrawal of an impression which is made with any of the ordinary materials." (Skinner and Kern, 1938).

That agar is so useful a material for taking molds of living tissue is due to several unique characteristics, which have already been presented. Agar is well known for its extraordinary gelling power. By using a very concentrated solution of agar to which are added certain chemicals and fillers, satisfactory impression materials are made having the necessary toughness, hardness, resistence to permanent set, body development and plaster-effect required in dental work. Because of their extraordinary hysteresis agar compositions can be heated and cooled to nearly body temperature and then introduced properly into the oral cavity. It takes only about a minute for them to solidify. Such compositions are therefore easy and convenient to use.

The original Poller formulas (1925, 1928) contain about 6 per cent agar and some filler materials such as rubber, fatty and fibrous substances together with some powdered chemicals and small amounts of resins. Harrison (1935, 1937) improved the material by adding potassium sulfate, which serves as a plaster-hardening agent. The strength of the mixture, however, still depends on filler materials. Preble (1941) introduced borate compounds, such as borax, together with plaster-hardening agents, such as potassium sulfate used by Harrison. The resulting material not only behaves well toward dental plaster, but also has the necessary high breaking strength and resistance to plastic deformation afforded by the addition of borax. It was found that the incorporation of as little as 0.025 per cent borax in the agar gel showed an increase in strength of roughly 25 per cent over a corresponding plain agar gel. To obtain the best result, borax and potassium sulfate are used in the ratio of about 1:4, and the pH is maintained between 7.9 and 8.2. Preble used about 12.5 per cent agar in his material.

Further improvement was made by van Rossem (1941) who introduced an oxide or hydroxide of an amphoteric metal, and buffered the mixture to the slightly basic side, from pH 8 to 9. By using this together with a borate compound and potassium hydroxide he prepared a much improved hydrocolloid impression material showing a high degree of toughness, hardness, and resistance to permanent set, a significant body development on cooling, and a minimum adverse effect upon the plaster setting. As an example, he first dissolved 10 gm of tin sulfate and 1 gm of calcium metaborate in about 50 ml of water and slowly added 18 ml of 50 per cent KOH. The resulting pH was about 9.0. Separately he had 150 ml of 20 per cent agar solution. The resulting physical properties of the final composition depended upon the relative amount of the chemical mixture to be added to the agar solution. When only one-fourth of the mixture was used, the resulting material was suitable for general full-mouth impression. When one-half was used the composition became tougher, and was most suitable for inlay and fixed bridge work. If the full amount of the mixture was added the final material was very tough, and was particularly recommended in immediate dental restorations where a good deal of tissue compression was desired.

Investigations by Skinner and Kern (1938) on six commercial hydrocolloid impression materials showed that these materials are very sensitive to changes in humidity, and that the accuracy of mouth reproduction can be obtained only by pouring the cast or model as soon as possible after obtaining the impression. Soaking of the impression in water before pouring the cast or model, as recommended by some manufacturers, causes expansion beyond their original dimensions in some of the materials. The presence of fibers in these materials helps to prevent dimensional changes due to fluctuations in humidity, but does not enhance their mechanical properties.

Paffenbarger (1940) studied eight commercial materials and a laboratory sample, and found great differences among them with respect to strength, deformation, set, and stiffness. The gelling temperature varies from 36° to 44°. He suggested, as did Skinner and Kern, that the gypsum model should be prepared immediately after withdrawal of the impression. He recommended the immersion of the impression in water pending the pouring of the cast. The material should be poured or used at the lowest temperature at which it is of suitable plasticity. Paffenbarger formulated a specification for hydrocolloidal impression materials.

Dental Impression Materials with Algin Base. During the effective period of the United States War Production Board agar-freezing order, preparation of dental impression materials from agar was not permitted. Among necessary substitutes algin materials have shown the most promise. Other proposed substitutes made of resin, wax, rubber and agar-like substances have various defects. All these materials are decidedly inferior in elasticity. As a result, while they can be withdrawn from undercuts, they do not resume the exact contour of the parts being molded.

The basic ingredients of the algin-based impression materials are a soluble alginate (sodium, potassium or ammonium alginate), a calcium compound having a low solubility (anhydrous calcium sulfate), a small amount of a soluble salt forming a very insoluble calcium compound (trisodium or tripotassium phosphate, ammonium citrate, or sodium oxalate), and inert fillers. The sodium alginate is acted upon by the calcium ions slowly released by the rather insoluble calcium sulfate or citrate. The resulting calcium alginate formed is insoluble but highly hydrated, and forms an insoluble gel. The gelation of the algin-based material involves a chemical reaction and is thus different from that with agar as the base. The small amount of trisodium phosphate is added as a retarder to prevent premature setting of the gel. This forms calcium phosphate, which is even more insoluble than calcium alginate, and by the formation of which the calcium ions formed during the mixing period are effectively removed. The timing of the gelation can therefore be regulated by the amount of the soluble phosphate added in the mixture, since after the phosphate is used up, any further calcium ions released will react with the alginate to form the slightly less insoluble calcium alginate, and thus the elastic gel. This principle was made use of by Wilding in his method of preparing oral impression materials, for which a British patent (1940) and later a United States patent (1941) were granted.

Paffenbarger (1943) reported that these algin-based materials had very short shelf life, which was attributed to the absorption of moisture by the powder. It was found by the scientists of the National Bureau of Standards that the addition of some trisodium phosphate to the water prior to mixing restores the usefulness of the deteriorated compounds.

In their investigations of impression materials employing soluble alginates, Schoonover and Dickson (1943) found that although they gave excellent results, the following difficulties[16] have been encountered in their manufacture and use: (1) absorption of moisture during storage, resulting in the premature removal of the

[16] Recently some manufacturers of dental impression materials of the soluble alginate type claimed to have solved these problems by using water-proof packages and by changing the formulation of the compounds.

soluble phosphate and formation of an insoluble gel before mixing; (2) shrinkage of the gels; and (3) poor surfaces of the resulting stone models. The three trade brands of these materials under investigation compared favorably in their physical properties with agar-based compounds, except in the value for permanent set under heavy loads (see Table 31).

Table 31. Physical Properties of Impression Materials Employing Agar, Soluble Alginate, and Insoluble Alginate as Bases (Schoonover and Dickson)

Lot	Breaking Load Gm. per Cm ^{2}	Strain [17] (%)	Set [18] (%)
	Agar Type		
A	2,100	18.6	2.4
B	2,800	17.0	0.6
C	3,500	13.9	0.8
	Soluble Alginate Type		
A	2,400	19.0	5.9
B	3,500	14.1	3.8
C	2,000	14.5	4.5
	Insoluble Alginate Type		
A	3,500	13.6	3.8
B	3,500	12.9	3.4
	Federal Specification Requirements		
	2,000 or more	4 to 20	0 to 3

A new type of impression compound was developed by Schoonover and Dickson in which insoluble alginic compounds are employed instead of the soluble ones. Calcium alginate or alginic acid is used and is converted to the soluble form by a soluble phosphate at the time of mixing. It was found that best results were obtained with alginate previously treated with an acid so that the individual alginate particles were coated with a layer of alginic acid. The following formula was recommended: 4 gm of the acid-treated alginate with 5 gm of calcium sulfate ($CaSO_4 \cdot 2H_2O$), 2 gm of magnesium oxide, 0.5 gm of borax ($Na_2B_4O_7 \cdot 10H_2O$) and 5 gm of powdered wax. The wax aids complete mixing, decreases the tendency of the mixture to absorb moisture, and improves the surface of the finished impression. This is to be mixed with 40 to 60 ml of water at 65 to 75° F to make one full dental impression. The resulting paste should be placed in the mouth within three minutes after mixing is started, and left therein for three to four minutes to form an elastic gel. Soaking the impression in a 10 to 20 per cent manganese sulfate solution for ten to fifteen minutes is a prerequisite if smooth, hard stone surfaces are desired. To obtain the best results, the mold or cast should be made as soon as possible. The material is also recommended for making duplicate models.

Schoonover and Dickson found that their product compared favorably with the ordinary agar impression materials in strength, permanent set and ability to withstand strain under compression (see Table 31).

Comparison of Agar and Algin-type Materials. Algin-based impression materials seem to have passed the substitute stage, and probably will be permanent additions to dental supplies. With the agar-freezing order recently revoked in the United States, agar impression materials are again manufactured. It remains to be seen whether agar can win back its former dental market.

Agar is a reversible hydrocolloid and materials made with it must be warmed to a solution and cooled to a gel. In using algin-based materials, however, a chemical reaction is involved, resulting in the formation of calcium alginate. Thus, no heating

[17] "Strain" is the amount of stretching or compression.

[18] "Set" is the actual permanent deformation after the material has been stretched or compressed.

is required; but the temperature of the mixing water should be about 70° F or more to accelerate the chemical reaction and to obtain the best results. Alginate materials are therefore slightly more convenient to use. On the other hand, agar has a distinct advantage over alginate in being a more strongly hydrophilic colloid, and hence able to hold its absorbed water more tenaciously. Alginate compounds lose water more rapidly upon standing. Some dentists have found that impressions taken with the alginate materials cannot be stored or shipped, and the models should be poured promptly.

Both agar and algin compounds are valuable impression materials, and each has its strong and weak points. A good many dentists have said that they would prefer to use the agar type, simply because they have been using it for years and because it involves less precaution and complication.

Carrageenin has been reported to be used in dental impression materials. There are, however, no published data concerning its merits and demerits. From the nature of the carrageenin gel, it seems doubtful whether materials using it as a base can ever compete with those based on agar or algin.

Prosthetic Works. Besides serving as dental impression molds, agar is also used in prosthetic works in general, as well as in sculpture and similar arts. Von Brandt (1936) was granted a United States patent for a preparation using a highly concentrated agar solution as the binder with clay and similar substances to supply the necessary body.

An important use of agar as a result of the war will perhaps be in taking molds for making artificial fingers, hands, ears, etc. Painter (1944) has reported on the amazing work of Captain C. D. Clarke on artificial hands, etc. To make an artificial hand, for example, a human hand is first put in an agar composition which coats it like a glove. The resulting negative mold is hardened in ice water, and from it a rubber outside is made, complete with pores and fingerprints. A microcrystalline wax is then put in it, giving both body and flexibility to the hand. The patient may set the artificial fingers in any desired position.

Other Molding Materials. Ammonium alginate powder, when mixed with a suitable filler, transferred to a mold of any desired shape and subjected to a pressure of several tons for a few minutes, produces a hard mold (Loomis and Kennedy, 1926). Hydrocarbon-treated alginic acid may be plasticized by the addition of ammonium hydroxide and oxide of calcium, zinc or copper. A very water-resistant, hard and tough material may be obtained, if a finely divided metal such as copper is added (Burgess, 1930). When treated with sulfur dichloride and vulcanizing agents such as carbon disulfide or carbon tetrachloride, algin becomes an elastic flaky dough, "sea caoutchouc," which may be molded into variously shaped substances (Houques-Fourcade, 1930). Such a material has been used to make rollers for typewriters, among various other articles (Delf, 1943).

In the Textile Industry

As Sizing Materials. In the manufacture of cotton and other textiles, sizing is required to stiffen the longitudinal thread of warp preparatory to weaving. The warp threads must be made much stronger than the weft, as they have to withstand more wear and tear. They are therefore sized to lay all the loose fibers, to produce a smooth surface, and to give strength to the yarn. In the finishing of cloths, sizing is also employed to give weight and smoothness to the product. In sizing both threads and cloths, phycocolloids are extensively used.

Funorin is undoubtedly the most important phycocolloid sizing material. Annually over ten million pounds of the seaweed funori are produced in Japan, and one or two million pounds in China; these are used almost entirely in sizing textiles and paper and as a starch substitute in laundries. It is especially useful in sizing silk

yarn. One advantage of using funori is that it readily dissolves in hot water in a very short time. Before being made into the paste, funori is steeped briefly in cold water to leach out contained salts. The following is a description of its application in sizing silk yarn in China (Tseng, 1933):

"The device for applying the size to the silk yarn . . . consists of two rollers, supported at waist height at a distance of from 30 to 40 feet from each other, and capable of being revolved at will or fastened rigidly. Strands of yarn of standard number and of the desired length, usually 70 chang (about 280 yards), are wound upon one of these rollers and then attached by one end to the other roller after passing singly between the teeth of a movable comb-like instrument made of bamboo. The size is applied to the comb and distributed by moving the comb along the suspended span of yarn. When the size is dry on a given span, the yarn is wound from one roll to the other until a fresh unsized span is exposed. The effect of the size is to envelop and smooth down the numerous tiny fibres, the ends of which radiate from each strand of unsized silk thread or yarn."

The amount of the sizing material used is very small. For a batch of yarn one yard in width and 280 yards in length, only 4 catties, or a little more than 5 pounds, are needed. For sizing finished cloths, powdered funori mixed with wax, starch and wetting oil is used (Kosaka, 1939).

In Japan two other seaweeds, "tsunomata" (*Chondrus occelatus*) and "ginnanso" (*Iridophycus sp.*) are used in a similar way. Although a small quantity of funori has been imported by France and other European countries for sizing textiles, carrageenin is generally the phycocolloid used. To make a carrageenin size, the seaweed carrageen is boiled for some minutes in water. Stocks and White (1903) reported that there were some sizing materials on the market made of carrageen. They mentioned as the main drawback the presence of salt in the product, which imparted harshness to the yarn. In modern preparations of carrageen extract, extraneous salts are no longer present.

Agar is used as a sizing material for the more expensive type of textiles such as silk. It is especially useful for fine tissues where suppleness is more desired than weight and stiffness. Agar also strengthens and compresses the cloth while other gums, which might also give suppleness to the product, leave it shallow and without sufficient body. Carrageen, used as a size at a concentration of 3 per cent, gives the resulting cloth a rich and "unctuous" touch, quite different from that sized by agar.

Algin is also a valuable sizing material. This was, in fact, one of the uses originally proposed for algin by its discoverer (Stanford, 1884). It is said to be superior to starch as a finish, since it fills the cloth better and makes a tougher and more elastic product without the stiffness imparted by starch. Algin has the added advantage of being transparent and inert to acids. It makes a very viscous solution, about 14 times more so than ordinary starch, and 37 times more than gum arabic; therefore, it goes further than other commonly used sizing materials. When a stiff dressing is required, aluminum alginate in caustic soda is used. For dark materials the crude unbleached alginate may be employed. Ammonium aluminum alginate serves to give a glossy surface to the fabric, and is quite insoluble in water after drying.

Textile Fibers. In recent years great development has taken place in the European countries, in Russia and in Japan on the use of alginic fibers for textiles. The manufacture of alginic textiles is based on the fact that if a sodium alginate solution is extruded into an acid coagulating bath or one containing a metallic salt solution producing an insoluble alginate, valuable textile fibers are produced (Bonniksen, 1934a, b; Mori, 1939; Ohasi and Narita, 1939; Takahasi, 1939; Gohda, 1934, 1937a, b; Rose, 1940). The fiber may then be variously treated or washed to produce a pure and strong product. In Carlier's process (1939a, b) a solution of a polymerized

vinyl acetate in an organic solvent is treated with an alginic compound, the mixture maintained at a uniform temperature between 24 to 40° and subsequently spun through nozzles.

Alginic fibers prepared by the general methods are subject to a serious disadvantage because of the relative ease with which they are swollen and dissolved by an alkaline solution, such as that of soap or soda. The resulting fibers are not suitable for normal textile usage. In such a treatment, the cross-linkages formed from the acid side chains of alginic acid and the metals are readily decomposed by alkali, and alginic acid is regenerated and subsequently dissolved. Speakman (1940, 1943) overcame this difficulty by using salts of metals such as chromium, possessing high coördinating power. The salts employed are preferably of the polymerized form, so that a large number of acid side chains of alginic acid can be combined with a molecule of the polymer. The alginic acid or calcium alginate fibers are prepared in the regular way. These are then immersed for 30 minutes in a basic chromium acetate solution. The resulting yarn is highly resistant to alkali, and has the added advantage of possessing an affinity for chrome mordant dyes.

Chromium alginate fibers, however, have the disadvantage of being colored grayish to greenish and purplish, according to the nature of the heat treatment involved during and after conversion. Speakman and Chamberlain (1943) found that colorless and alkali-resistant yarns may be obtained by treating algin fibers with beryllium compounds such as basic beryllium acetate, involving a partial or complete conversion of the alginic compound into beryllium alginate. Sodium alginate solution may also be spun directly into a beryllium sulfate bath at 25°, whence beryllium alginate fibers of good quality are produced. Similarly, mixed beryllium and other metallic alginate fibers may be obtained.

Beryllium alginate fibers have another advantage in being fireproof, which points naturally to their use in curtains and hangings in public buildings in order to reduce fire risk. They wet-out easily, and their crease-resisting properties are fairly good (Tsimehc, 1940; Whittaker, 1944). Chromium and beryllium alginates may be dyed with mordant dyestuffs, but they have no affinity for cotton or acid dyestuffs. Wilcock showed that a pretreatment of such rayon with "Fibrofix" gives the fibers a very good affinity for direct cotton dyestuffs, and an improved affinity for some mordant dyestuffs (Whittaker, 1944).

Because they are soluble in alkaline solution, sodium and calcium alginate fibers are used by Speakman as binding threads during weaving, and are subsequently removed by a simple soap treatment. By this procedure, there are produced fabrics of a net-like structure, the manufacture of which normally required a tedious and dangerous method of carbonizing the cellulose fibers subsequent to weaving (Whittaker, 1944).

Kringstad and Lunde (1938) investigated algin fibers by x-ray, and found that they show a definite structure analogous to that of cellulose. Wall (1940) studied the properties of fibers and found that alginic chains fulfill all conditions for a basic chain, since by condensing the carboxyl group with a diamine, in which one group is protected, and afterward condensing with a fresh set of chains by means of a second group, a complete mesh system is obtained with all the variables under control.

Miscellaneous Uses in Textile Industry. *Water-proof cloth.* By treating cloths with a paste containing funori, glue, wax and other substances, Sakao (1939) obtained a soft, water-proof cloth. Algin has been successfully used as a rubber dispersing agent in preparing compounds for rubberizing textile goods (Kolesov, 1933). Erdahl (1935) used a mixture of 20 to 60 per cent of rubber latex dispersed in ammonium hydroxide and the balance, an algin, such as copper ammonium alginate, to impregnate canvas and textiles which may then be manufactured into raincoats and similar articles. Ammoniated aluminum alginate becomes insoluble after drying and hence may be used for preparing waterproof fabrics.

Dyes. By nitrating alginic acid, Nettlefold (1888) prepared a brown dye suitable for dyeing unmordanted cotton a fine Bismarck brown, which is more fast to soap than many alkaline colors and is as good as chrysoidine. The depth of the shade was considerable and could be worked to a great intensity. In an acid solution the dye could not be fastened to the fiber. The brown dye had little affinity for wool and mordanting did not increase its depth.

Algin can be used as a fixer for mordants in fabrics and to some extent as a mordant and as a dunging substitute (Stanford, 1884).

As a Thickener in Printing Pastes. In recent years both carrageenin and sodium alginate have been quite extensively used as thickeners in printing pastes. Agar has also been used similarly in a more limited way.

Algin may be used partly or completely as a substitute for gum tragacanth for the preparation of printing inks with basic dyes in combination with dextrin, and other constituents (Rakhlina and German, 1940). Cate (1938) stated, however, that basic colors precipitate sodium alginate, which therefore cannot be used in print pastes with basic dyes or with the naphthol salt color. Algin may be used partly as a substitute for starch in making printing paste except in cases where a color or special density is desired (Blutin and Tavrovskaya, 1939).

In Manufacture of Paper and Coating Materials

Agar is utilized to some extent as a paper coating to impart resistance to the penetration of resin, wax, and grease. Funori is also used as a sizing material in manufacturing paper. It is used in China in making a peculiar type of paper money for the dead, and as a "varnish" on paper lanterns and the like (Tseng, 1933).

By adding a cold ammonia emulsion of wax to a gel of a double alginate of ammonium and iron, aluminum, or copper, and a small amount of formaldehyde, Erdahl (1922) made a mixture for impregnating paper pulp and the like to produce weather boards, roofing papers, and similar fabricated articles. In another process Erdahl (1927) prepared an ammonium alginate gel fortified with beeswax; the resulting preparation is suitable for coating and impregnating all types of paper materials as well as paper containers. Electrical articles, when impregnated with such a colloidal mixture, possess excellent insulating qualities. Kennedy (1931) was granted a United States patent on his alginate-asbestos paper, which is claimed to have a greater strength and to be smoother and much more flexible than ordinary asbestos paper.

On the same basic principle as is applied to the preparation of algin textile fibers, various alginate films and coatings have been prepared. Swett (1920) wetted a porous support of a desired shape with calcium chloride solution or any other algin-precipitating agent, and then immersed it in a sodium alginate solution. The coating thus formed may be used as sausage casing, and in making capsules and containers for non-aqueous fluids.

Algin films, in general, are rather inexpensive, almost nonflammable and less influenced by light than is ordinary Cellophane. Recently algin has been reported to be used as a transparent wrapping for various kinds of articles. By treating an alginate solution with an ammonium salt followed by dilute HCl containing HNO_3, a viscous solution is obtained. When the resulting substance is diluted, poured upon a polished surface and evaporated to dryness, a transparent film is formed. This may also be obtained by the action of a coagulant containing NaOH and furfural (Gohda, 1934).

By quickly drying a clear and sterile aqueous solution of sodium and ammonium alginate containing 10 per cent or less alginic acid, Bonniksen (1934a, b, 1936) prepared transparent films and threads convertible into insoluble calcium alginate by treatment with a calcium chloride solution. The resulting films are similar in appearance to the well-known gelatin and cellulose films and may be used for wrapping and decorative purposes. The threads may be spun into silk substitutes.

Preble (1939a, b, c) found that triethanolamine reacts quickly with alginic acid to form triethanolamine alginate. The resulting stiff and heavy paste, unlike that made of gums, gelatin and casein, does not spoil easily since it retards the growth of mold and microörganisms. When a film of triethanolamine alginate is dried it is smooth, soft, flexible, strong and readily soluble in water but insoluble in oils and greases. It should be noted that unplasticized sodium or ammonium alginate films are relatively brittle and hard, and will crack when bent sharply. Triethanolamine alginate is strongly adhesive and can therefore be used for coating practically all solid surfaces such as cheese, meat, glass, metals, wood, plastics and various other articles.

In dentistry tinfoil is ordinarily used to cover and protect dentures made of acrylic resin. It is, however, difficult to apply evenly. Recently a material using ammonium alginate has been perfected by dental research workers at the National Bureau of Standards (1943). For its preparation, 15 gm of ammonium alginate and 5 gm of trisodium phosphate are dissolved in 100 ml of water. The resulting viscous solution can be easily applied with a brush to the gypsum molds when these are still warm from the wax removal. Two coatings are necessary in processing clear acrylic. When dry, these are immersed in calcium chloride solution, and thus converted *in situ* into insoluble calcium alginate coatings.

In Varnishes and Paints

Both carrageenin and algin are extensively employed in making water paints. Annually about 25,000 pounds of carrageen are used in the United States for this purpose (Chase, 1942).[19] Casein paints stabilized with carrageenin are easily applied and hold to the surface while drying. "Irish moss" has been suggested as a substitute for fish glue in the preparation of bichromated enamel. It has never been popular in this respect because of the lesser uniformity which it gives to the product (Mertle, 1937).

Sodium alginate solution dissolves shellac to form a lacquer which dries to a tough, tenacious film. Treatment with dilute acids or calcium chloride solution renders this film insoluble and hence useful as a water-proof varnish (Tressler, 1923). Sodium alginate is coated on asphalt paints for steel plates and insulated wires to prevent the painted surfaces from adhering. It is also used as a stabilizer for camouflage paints. Copper alginate serves as a dressing for canvas and burlaps to prevent mildew (Wohnus, 1942).

Recently sodium alginate has been extensively used in the preparation of vehicles for resin emulsion paints. Such vehicles consist of two phases, the water and the oil phases, which must be thoroughly mixed. The alginate is first added to enough hot water to make an approximately 1.4 per cent solution. The alginate solution is added under agitation to a mixture of an antifoaming agent, pine oil, "Dowicides" and casein, according to one formula. To the water phase thus prepared is gradually added the oil phase containing a hot-water solution of gum, oil, wetting agents, linoleate and ammonium hydroxide. More water is added, and stirring is continued, until the emulsion is thoroughly uniform. The resulting emulsion contains approximately 0.15 per cent of the alginate.

Phycocolloids are all reported to be used as an ingredient in calcimine. In Japan funori, *Chondrus* and *Iridophycus* are mixed with plaster to make wall paints and similar substances.

Fire-retarding coatings help to stop or retard the spread of flame along the surface, and as such are very valuable paints. A new type of such coating, recently developed at the United States Forest Products Laboratory, consists of finely ground

[19] A reliable informant states that American Indians in Maine used to make a long-lasting "white-wash" by adding slaked lime to a boiled solution of Irish moss. J. A.

fire-retarding chemicals dissolved and suspended in an aqueous sodium or ammonium alginate gel (van Kleeck, 1943). The alginates are employed at 0.75 to 1.5 per cent of the suspension as thickening agents. Their use makes it possible to incorporate in the preparation a quantity of fire-retarding compounds considerably in excess of that required to saturate the solution, since the undissolved particles can be held in suspension. Pigments may be introduced if desired. Best results are obtained with mono-ammonium phosphate as the fire-retardant, although satisfactory preparations are made from a mixture of borax and boric acid.

Creaming of Latex

Traube (1924) discovered that hydrophilic colloids, such as carrageen "moss," Iceland moss, and other vegetable mucilages are effective in causing a separation of rubber latex dispersions into two layers: an upper rubber-rich layer and a lower rubber-free layer, generally called "serum." The latex is said to be "creamed." McGavack (1927) heated the concentrated latex, creamed by the addition of carrageen extract, pectin or karaya gum, at 80° for two hours to reduce its viscosity, since he believed concentrated latex with a low viscosity to be of considerable value for certain purposes. In a later process McGavack (1935) used ammonium alginate as the creaming agent. He subjected the alginate-treated latex to a violent agitation for a short time, to accelerate the rate of creaming. In recent years the alginate has become the most important latex creaming agent in the manufacture of rubber.

The mechanism of latex creaming has recently been the subject of investigation by several authors. Baker (1937, 1938) was the first to establish the fact that the action of a creaming agent is to promote the formation of loose, easily reversible agglomerates of the dispersed rubber particles. Because of their size, these agglomerates exhibit none of the Brownian movement characteristics of the individual particles of normal latex, and being lighter than the dispersion medium, they rise freely to form a concentrated upper layer.

Bondy (1939) made a study of sodium alginate as a creaming agent. He found that proteins, soaps, lecithin and other emulsifying agents are precipitated by the added algin. The rate of creaming and the rubber content of the cream are found to depend on the concentration of the creaming agent and on the initial rubber content of the latex. Bondy advanced the view that creaming agents exert a dehydrating influence on the latex protein, the denaturation of which permits the individual protein-protected rubber particles to approach each other closely and eventually to cohere.

In their study of the creaming action of locust bean gum and ammonium alginate, Hauser and Dewey (1941) found that a maximum in the rubber content of the cream occurs at that concentration of creaming agent (0.254 per cent of locust bean gum or 0.042 per cent of ammonium alginate) just sufficient to bring the rubber content of the serum very close to its minimum. With lower concentration of the creaming agent, the loosely formed clusters are prevented from becoming compactly arranged by the action of molecular bombardment. With higher concentrations, the increase in cohesive forces prevents ready rearrangement of the preformed clusters into a denser structure.

Hauser and Dewey agreed with Bondy in the explanation of the creaming mechanism. Small amounts of creaming agent exert a desolvating effect on the latex protein, thus destabilizing the latex dispersion. A somewhat greater concentration of creaming agent so completely dehydrates the protein that this constituent itself is destabilized, thus resulting in the sludge formation observed by Bondy and confirmed by them. When the concentration of creaming agent is further increased, the protein exerts a desolvation effect on the gum instead, resulting in the formation of the ropy, weak gel. Thus, the conclusion was reached that the primary action of creaming

agents in separating the rubber from the serum is in their dehydrating action on the stabilizing protein constituents of the latex.

In Various Industries

Photographic Film. Utilization of agar in making photographic film was suggested in the latter part of the past century. Several patents were granted in various countries for making them. It is claimed that agar is superior to gelatin for certain types of photographic film because an agar film need be only one-eighth the thickness of a gelatin film, is less soluble in water, does not melt in tropical heat, and, because of its high gel strength, is cheaper (Cooper, Nuttall and Freak, 1910). According to Chase (1942), one firm asserts that, as a reagent in sensitized emulsion agar is better than any similar material now on the market.

That up to the present agar has not been used on a large scale in making photographic film is due to various reasons. The fluctuation of the quality of agar on the market, even now, probably accounts to some extent for the failure to develop its use in this direction. A more important reason is that manufacturers of photographic film are satisfied with gelatin as the emulsion base, and there is therefore no need for developing a new material such as agar. Besides, there is an important practical difficulty in using agar for films or plates. Because of syneresis of agar gel, the resulting layer of water expressed between the base and the jelly causes the latter to slide off the former rather easily.

Agar is unsuitable for use in certain photographic materials because of its tendency to stick to gelatin and its insolubility in solvents or in an alkaline solution. The esters of agar, however, are soluble in a number of organic solvents and can therefore be employed as a coating or backing for photographic film from which they may later be removed by means of alkaline solutions (Malm and Emerson, 1940). These backings are necessary to keep the film flat and, to some extent, to carry colored material which will diminish halation.

Wire-drawing Lubricant. Agar is used as a lubricant in the hot-drawing of tungsten wires for electric lamps. Formerly there was used in this process a lubricant composed of deflocculated graphite held in suspension, known in the trade as "aqua-dag." This is rather expensive and is procurable only from limited sources. Brann (1922) found that an agar gel holding powdered graphite mechanically in suspension made an even better lubricant. It is not only cheaper and much easier to procure; it is also able to hold somewhat larger graphite particles, which, within certain ranges of sizes, provide more complete protective covering on the exterior of the wire. Suspending the powdered graphite in this way also prevents precipitation of the particles, and makes a more uniform lubricating coating than does the expensive aqua-dag. Several thousand pounds of agar are used annually in the United States for this purpose.

Iredell (1929) was granted a patent for improving this lubricant by adding 0.75 to 1.0 per cent of Turkey red oil. The agar used is the *Gelidium*-agar made on the American west coast or in Japan. Recently agar made from *Gracilaria confervoides* from the American Atlantic coast has been tried. It is found that while for ordinary process it is satisfactory, in the hottest process, the higher ash content of the *Gracilaria*-agar has an adverse effect on the wire.

In Liquor Clarification. Agar has been extensively used in the clarification of liquors. In the manufacture of sake in Japan, schnapps in Holland, and liquors in general, agar is employed and is said to sharpen the flavor.

Before liquor prohibition in the United States the fining of beers and ales was one of the most important uses of carrageen (Chase, 1942). In the early stages of beer brewing, the cloudy solution of malt extract contains insoluble and undesirable proteins. These can be removed by natural slow settling or rapid "fining" with the help of a clarifying agent. Upon boiling, the carrageen releases its gelose, which com-

bines with the tannin of the hops to form a flocculent mass. The gelatinous mass attracts the suspended impurities, which are then removed, together with the flocculent mass, as a scum. While carrageenin is still extensively used in the liquor industry, it has been partially replaced by other chemical finings.

To use carrageen as copper finings, it should not be washed with water preliminary to use (Rankin, 1929). The clarification is practically uninfluenced by dextrin, concentrated glucose, tannin or hop infusions. When added in too large an amount, carrageen will cause the production of a haze during fermentation due to the production of acid. "Irish moss" is also reported to be used in the fining of coffee, for which purposes it is more economical than eggs (Chase, 1942).

Acidification of liquors containing sodium alginate results in the formation of alginic acid which forms a coagulating mass able to clarify the liquor by adsorbing impurities. This method has been applied to the purification of beet juices in sugar manufacture (Ricard, 1925).

In Boiler-water Compounds. The use of algin in making boiler-water compounds dates back to Stanford (1884), who reported that his friend Spiller "found it to precipitate the lime in a state in which it could be easily blown off." The virtue of alginate lies in its reaction with calcium in hard water. The precipitated calcium alginate forms globular flocculent masses and envelops other sediments to give a soft pasty sludge, most of which can be blown out of the boiler at regular intervals. Being flocculent and hydrated, the calcium alginate precipitates are less likely to adhere to heating surfaces of the boilers. Alginate also appears to interfere with crystal growth, which in itself is a long step toward scale prevention (Bannister, 1944; Pinnington, 1944).

Glues and Mucilages. With the exception of agar, phycocolloids are useful in preparing glues and mucilages. Funori has long served as hair glue in Japan. It is used in China as a special mucilage for Chinese paintings, which are generally made on thin paper and have to be pasted on thick, tough paper. A mucilage may be made with carrageen, starch, and a preservative (Figgis, 1906).

Leather Finishing. Carrageenin is used in finishing leathers, as it imparts to certain types of leather a desirable gloss and stiffness. Its principal use is in the finishing of straight grains and grain upper leathers. The gelose solution from carrageen is brushed on the leather, which is then glazed by rubbing with glass cylinders. Mucilage made of carrageen is able to smooth and hold down the tiny, rough projections on the surface of unfinished leather. In the case of the inner soles, carrageen is used as a filler to impart stiffness and body to them. The use of "Irish moss" also helps in the waterproofing of very heavy leather. When used in shoe polish and leather dressing, carrageen serves to restore the finish to worn, scuffed leather. According to Chase (1942), one shoe manufacturer in New England alone used to import annually about 12,000 pounds of *Chondrus crispus* from Ireland solely for leather finishing.

Agar and algin have also been reported to serve similarly to impart a gloss and stiffness to leather in the finishing process.

Miscellaneous Uses. Agar is used in Japan in making electric lamp shades. In the electroplating of lead, addition of 2 gm of agar per liter renders the deposit of lead most satisfactory. Shredded agar is reported to be used in tobacco to retard excessive evaporation of moisture. In hectograph duplicators, agar is used to make the gelatinous rolls. Recently it has been used in the manufacture of marine storage batteries.

Algin may serve as a binder to make a seaweed charcoal product under the name "carbon cement," useful as a boiler covering for heat insulation (Stanford, 1884). A mixture of alginic compound with an inert siliceous material and concentrated sulfuric acid, after heating and washing free from acid, makes an efficient color-absorbing product (Boyd, 1941). In the United States, algin is used as a binder in

cartridge primers (Chase, 1942). It is employed in oil-well drilling muds to seal off porous formations, in can-sealing compounds, as a medium for separating plates in the manufacture of batteries, and as a binder for printer's ink.

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Luminescent Paints, Pigments, and Inks *

ALEXANDER STROBL

Stroblite Co., New York

Luminescence is a phenomenon of light emission which does not involve noticeable rise in the temperature of the light-emitting body, that is, without any overall increase in the kinetic energy of the molecules. There are various types of luminescence: photoluminescence, chemi-luminescence, electro-, thermo-, bio-, tribo-, crystallo-luminescence, etc. Here we consider only photoluminescent substances, which have found most important practical applications.

Light consists of electromagnetic waves; consequently, energy must be supplied to the body emitting the light. In photoluminescence this is done by activating the material with light. The irradiated material first absorbs the light energy and then re-emits it in the form of electromagnetic radiation of waves which are longer than those of the absorbed light. This follows the law of conservation of energy; since the light energy emitted cannot be greater than that absorbed, the luminescent light cannot have a greater frequency (shorter wave length) than the exciting radiation.

If the light emission of the excited material ceases simultaneously with cessation of the radiation, it is termed *fluorescence*. If, however, the re-emission continues after the activating light is cut off, it is termed *phosphorescence*. In phosphorescence the light emission may last from a fraction of a second to many hours, and is popularly called afterglow.

Theoretically, photoluminescence can be explained as a function of the atomic and molecular structure of a substance. The electrons in every atom normally occupy a certain level in relation to the nucleus, and according to the Bohr theory, they can exist only in certain electronic energy states. The lowest state is the "ground state"; higher energy levels are called "excited states." When the molecule absorbs light energy, electrons are raised to a higher energy level (excited state); then as they fall back to the lower energy level (ground state) the absorbed energy is emitted as light waves. In fluorescence this transition of the electrons from the excited higher energy level to the lower level is instantaneous; in phosphorescence some electrons pass first into an intermediate metastable state, from which they subsequently are released, with simultaneous light emission, by the heat energy supplied by the surrounding medium.

The internal energy of a mono-atomic molecule is defined exclusively by the configuration of its electrons. In polyatomic molecules the vibration of atomic nuclei and the rotation of the molecule also define their internal energy. The various energy states of the molecule can correspond either to different states of electronic excitation, or to superposition of different vibrational energies on one and the same electronic state. Owing to the more complex energy transitions of polyatomic molecules, many of their luminescence manifestations are not clearly understood.

The first luminescent material was made about 1604 by Vincencio Casciarola of Bologna, who produced a phosphorescent barium sulfide during his alchemistic ex-

* See also paper on "Luciferin and Luciferinase" by E. N. Harvey in Vol. II of this series, pp. 395-402. J. A.

periments. About sixty years later Christoph Baldewein made phosphorescent calcium sulfide. The first phosphorescent zinc sulfide was made in 1866 by Sidot. Balmain in 1870 made the first commercial phosphorescent calcium sulfide.

The scientific groundwork of luminescence was established by Becquerel in the middle of the nineteenth century, and in 1904 Lenard published his electromagnetic theory of luminescence which, though since elaborated in many ways, is still valid.

The useful application of luminescent materials started only at the beginning of the twentieth century. The first products were fluorescent x-ray screens which were made with barium platinocyanide, later with calcium tungstate and subsequently with cadmium tungstate.

When radioactive materials became commercially available, the self-luminous "radium luminous pigments" made their appearance during the first decade of this century, and found wide application in watches and instrument dials. These luminous pigments consist of a phosphorescent zinc sulfide mixed with a small amount of a radioactive salt of radium, mesothorium, radiothorium, etc.

More recently fluorescent screens have come to have wide application in cathode-ray tubes used in television receivers, oscillographs, electron microscopes, photography, etc. In photography fluorescent calcium tungstate or zinc sulfide are employed as x-ray intensification screens. The electron microscope uses a fluorescent screen for image viewing. Another interesting application of luminescence in photography is Vanino's process called luminography, in which an activated phosphorescent screen is used as illuminant for making contact prints on photographic paper of a drawing or print.

The photomechanical reproduction industry utilizes fluorescence in a process developed by B. Berry, for eliminating half-tone dots on the white parts of the reproduced designs. One of the latest achievements of fluorescence is the modern fluorescent lamp, presenting great progress in the technique of producing light for general illumination. The efficiency of conversion of producing light with electricity is so much higher in fluorescent than in incandescent-filament lamps that it can be predicted that in the not too distant future, fluorescent lamps will probably be in general use. Today fluorescent and phosphorescent materials are commercial products and are finding ever-increasing industrial applications.

Luminescent materials are used in form of paints, pigments, and inks, which are prepared with fluorescent and phosphorescent substances called phosphors. Fluorescent phosphors are organic and inorganic compounds; phosphorescent phosphors are mainly inorganic. For practical applications it is necessary that the fluorescence yield should be as high as possible, and also that the fluorescent material be in a form easily applied to various industrial needs.

There are many fluorescent organic salts, some of which have sufficient fluorescence for industrial use; but more important are the fluorescent synthetic dyes, which offer a wide range of colors and are therefore most useful in preparing fluorescent products. The fluorescent dyes have various degrees of fluorescence when dissolved in liquids or in solids or adsorbed on fibers. Their fluorescence yield is greatly influenced by the chemical composition and the physical nature of the surrounding medium; but very little is known of the connection between chemical constitution and the fluorescence of organic compounds.

Many dyes believed to be non-fluorescent are strongly fluorescent when dispersed in a solid solvent like gelatin, sugar, benzoic acid, etc., or adsorbed on wool, and even become phosphorescent under certain conditions. Dyestuffs and many other organic compounds give strong phosphorescence when dissolved in solid anhydrous boric acid. Certain groups of "non-fluorescent" dyes become fluorescent when dyed on textile fibers or when adsorbed on activated alumina. P. Cooper-Hewitt (U. S. P. No. 1,188,655, June 27, 1916) describes how a strong fluorescence is obtained with Rhodamine dispersed in nitrocellulose. Rhodamine B has hardly any fluorescence in

the dry state, but in liquid solution it shows considerable red fluorescence. When it is dispersed in gelatin, the fluorescence yield is about 21 per cent; in cellulose acetate it is 62 per cent.

The writer in 1927 discovered that fluorescent dyes like Rhodamine B, Auramine, etc., will show a very brilliant fluorescence if dispersed in solid white shellac. The highly fluorescent shellac phosphor is obtained either by absorbing the fluorescent dye in dry shellac from an alcohol-water solution; by adding the dye to an alcoholic solution of shellac and evaporating the alcohol; or by preparing a water emulsion of shellac with borax or an alkali salt, adding the dyestuff to the emulsion and precipitating the fluorescent shellac with a metal salt. In each case the shellac phosphor will show a very high fluorescence yield.

No satisfactory explanation has been found for the influence of external conditions on the fluorescence yield; but the fact that many compounds show increased fluorescence when dispersed in solid media is of greatest practical importance. Since we are dealing here with a colloidal state in which the fluorescent dye is the dispersed phase and the solid substance the dispersion medium, it is quite possible that by applying the colloid theory to these manifestations, some new light may be thrown on the subject. The size of the micelles of the dispersion medium and the colloidal state of aggregation of the dye probably are the factors which determine the fluorescence yield of those phosphors.

Among inorganic substances which have found the widest application are the synthetic inorganic phosphors, both the fluorescent and phosphorescent pigments. These are various types of Ca, Sr, Zn and Cd sulfides, tungstates, molybdates, silicates, and borates. They are prepared by mixing the carefully purified ingredients with a very small quantity of an activating metal impurity (*e.g.*, less than 0.01 per cent of Mn, Cu, Ag, Bi, As, Sb, etc.). The dry mixtures are heated for a period of ten minutes to one hour to a temperature of 900°; they are then allowed to cool, and finally are ground to crystalline powders. In preparing the sulfide phosphors, 10 to 20 per cent of a flux, consisting of the chloride, fluoride and sulfate salts of K, Na, Ca or Mg, is added, which greatly facilitates formation of the phosphor. The properties and the wave length of the light emitted from these phosphors depend upon the basic material and the activator used in preparing them.

The size of particles to which the phosphors are ground is of great importance. The sulfide phosphors are ground into particles not less than 0.1 mm in diameter. Tungstate and silicate phosphors can be ground as fine as 0.001 mm, without impairing their fluorescent qualities. Fine grinding destroys phosphorescence, probably because of structural differences between the surface layers and the deeper layers of the crystalline grains.

The physical structure of the inorganic phosphors is not clearly understood. When the compounds are precipitated as amorphous powders they do not fluoresce, and only their crystalline modifications, obtained by heating them to sintering temperatures, are luminescent. It seems likely that during the heating process the atoms of the activating material diffuse into the molecular structure of the basic material, *e.g.*, an ion or atom of the activator, having a smaller radius than the cation of the basic material, enters its crystal lattice, thus supplying the electrons responsible for the luminescent properties of the phosphor. However, very little is known about the location of the activating atoms in the phosphor lattice.

Since in preparing a phosphor, the material passes from an amorphous state to a crystalline modification, it seems desirable that the factors influencing the transition from the amorphous or colloidal state to the macroscopic, or crystalline state, should be considered here, as they may give valuable information regarding the formation and nature of inorganic phosphors.

The luminescence spectrum and duration of light emission of the phosphors depends on the basic material, the activating impurity and its concentration, the method

of preparation, the temperature and duration of heating and also on the flux. These factors are varied according to the product desired. Thus we can obtain phosphors emitting different colors during and after activation; fluorescent phosphors with no afterglow; phosphorescent phosphors with shorter or longer periods of afterglow, and phosphors responding to various wave lengths of activating radiation. There is an optimum concentration of activators for fluorescent and for phosphorescent phosphors. Increased concentration may heighten the intensity of fluorescence relative to the intensity of phosphorescence; but in too high a concentration they frequently act as quenchers. Other impurities also may act in this manner, particularly in the case of phosphorescence, but very often of fluorescence as well.

In the preparation of luminescent materials several factors must be considered. What light should be used for activation? What quality of luminescence is desired? What is the method of application?

Luminescent paints, pigments and inks can be prepared in various ways, but the colloidal state of the preparation exerts a great influence on the final product. Fluorescent dyes, for instance, can be precipitated as pigments, giving lakes with various degrees of fluorescence. If in the preparation of these lakes other organic substances such as gelatin, nitrocellulose, etc. are also incorporated, the intensity of fluorescence of the pigment is greatly increased. If the precipitation takes place in the presence of protective colloids, very fine pigments are obtained. After filtering and drying the pigments, they are dispersed in proper vehicles to make paints and inks. Since the particles of the pigment are very fine, there is little difficulty in keeping them in suspension. Often finely dispersed inert pigments are added, which must also be kept in suspension by a deflocculant.

The inorganic luminescent compounds present greater difficulty as far as suspension is concerned. Fluorescent inorganic pigments, such as zinc sulfide, cadmium sulfide, and their various combinations, consist of very fine particles; and since grinding does not affect their fluorescent quality, they can be ground into the vehicles. However, their specific gravity being rather high (4.1-4.5), a suspending agent must be used, *e.g.*, such as sodium silicate for water vehicles and zinc stearate for vehicles containing oils and solvents. Owing to the fineness of the particles, they can be used in paints and even in printing inks in the same way as ordinary pigments.

The preparation of paints and inks with phosphorescent pigments presents greater difficulty. As the particles of these pigments are rather large, and are crystalline in structure, they cannot be ground without destroying the luminous quality. The specific gravity of CaS and SrS phosphors is between 3.0 and 3.5, that of ZnS and CdS phosphors between 4.1 to 4.5. They are dispersed in vehicles by thorough mixing without grinding. The problem of preventing settling and packing of ready-mixed paints is quite serious and has not as yet been solved. The addition of suspending materials to the dispersed pigment helps considerably, but does not eliminate the difficulty. This condition is quite a handicap, particularly if the paints are applied with an air-spray where additional thinning is required, and mechanical stirring during application becomes necessary. In distributing the ready-mixed paints commercially in containers, the pigments pack in a very solid mass on the bottom of the container. When phosphorescent materials are applied by the silk-screen process for paper-coating and textile printing, it is possible to use more viscous mediums and thereby partly eliminate these difficulties. Due to the coarseness of the pigment particles, phosphorescent pigments cannot be used in printing inks.

Photo-luminescence can be excited by electromagnetic radiations of visible light, or by invisible ultraviolet, x-rays, or the very short radiations of radioactive substances. The radiation emitted may be invisible, or may be visible light of a wave

length characteristic of the particular luminescent material, but longer than the exciting radiation.

In most of the common applications of luminescence, both visible (electric light and daylight for phosphorescent materials) and invisible light (ultraviolet radiation for fluorescent materials) are used. X-rays are the activating radiation in fluoroscopic work; and γ rays (in addition to α and β rays) furnish the necessary energy for the light-emitting property of radioactive luminous materials.

The ultraviolet radiations, which extend from the near ultraviolet (longer waves between 3000 and 4000 Å) to the far ultraviolet (short waves between 2000 and 3000 Å) find the most extended practical applications. The short wave ultraviolet of about 2537 Å (obtained with mercury vapor) is utilized in the recently introduced fluorescent lamps. The lamp is made of a glass tube which is coated on the inside with a fluorescent pigment to be activated by the ultraviolet radiation generated by electric discharge. The fluorescent pigment absorbs the invisible short-wave radiation and emits a longer wave of visible light. By selecting the proper phosphor, light of various colors is obtained.

The most significant activating light in fluorescent work is radiation of about 3650 Å, popularly called *blacklight,* and is used for illuminating objects made with the luminescent paints, inks and pigments, discussed in this article.

Any light source that radiates near ultraviolet can be used as an activating light. Since all light sources also emit more or less visible light, this is reduced or practically eliminated by employing filters which transmit ultraviolet but absorb visible light. The best blacklight filter is Ni-Co glass (Wood filter), which has a high transmission in 3650 Å but which absorbs most of the visible light.

The smallest ultraviolet light generators are discharge bulbs filled with argon and having a negative pole glow; these are available in from ¼ watt to 3 watt sizes. The most intense ultraviolet light sources are carbon arc and high-intensity mercury-arc lamps, which are made in 100 to 1,000 watt sizes. The simplest source for ultraviolet light is incandescent lamps, but they have a very low efficiency.

The newest and very efficient light sources for ultraviolet illumination are fluorescent lamps coated inside with a special phosphor which, when activated with ultraviolet radiation or the 2537 Å mercury line, emits the longer wave ultraviolet radiation of 3650 Å. By using a dark ultraviolet filter glass to absorb all visible light, we have an excellent blacklight lamp.

A fluorescent effect produced with a fluorescent blacklight lamp presents an interesting phenomenon. Short-wave ultraviolet radiation is generated from the fluorescent lamp; this activates the fluorescent pigment inside the glass tube and is converted to long-wave ultraviolet; the still invisible long-wave ultraviolet emitted is used to activate a fluorescent material which in turn converts it to a longer-wave, visible light.

Luminescent paints, pigments and inks are used in many branches of the industries, arts, and sciences. Their applications are so manifold that it would not be possible to cover the subject in detail in the space available here. May it suffice, therefore, to mention only the most important and the newest developments.

To determine whether the use of a luminescent material for a given task or product will serve the purpose, it should be kept in mind that photoluminescence does not function without some outside source of light, that is, the luminescent material does not replace light. Furthermore, the brightness of luminescent materials is of a relatively low value, and therefore can be seen only if the surrounding medium has a still lower brightness.

The brightness of phosphorescent materials activated with light varies between 10 and 50 microlamberts, and after one hour, the afterglow decays to 0.1 to 0.5 microlambert. Phosphorescent paints will be effective therefore only in complete darkness. Some luminous paints have a useful afterglow even after 8 to 10 hours,

but only a dark-adapted eye can see the low light emission of about 0.01 microlambert. Under the above conditions phosphorescent products render invaluable service. They are used on ships, landing boats, tanks, etc. During blackouts they are employed as safety markings in streets and shelters, and are worn by pedestrians. In factories, hospitals, and public places they serve as emergency measures during power failure. In the home, luminous markings give great comfort by enabling people to find various objects in the dark. Commercially, they have wide applications in making luminous paints, inks, chalks, fabrics, papers, plastics, etc., used in the manufacture of luminous novelties, art objects, printings, decorations and other products.

Fluorescent products are used where continuous luminosity is required and electric power is available for obtaining blacklight. Besides its intrinsic light conversion efficiency factor, the brightness of a fluorescent material depends upon the intensity of the ultraviolet light used for illumination. By varying this intensity it is possible to obtain wide degrees of fluorescent brightnesses from 3,000 microlamberts down to zero. If we consider that one of the fundamental factors controlling vision is the contrast in brightness between the object and its background, and that the ultraviolet radiation increases only the brightness of the fluorescent object and not that of the background, we have the basic principle for successful applications of fluorescence produced with blacklight. In completely dark surroundings, a moderately low intensity of blacklight will sufficiently increase the brilliance of the fluorescent object to make it visible. This condition exists in the application of fluorescence on dials (in airplanes, battleships, military instruments, home radios) military maps, carpets in theater aisles, etc. By increasing the brilliance of fluorescence with more intense ultraviolet radiation, the brightness contrast can be increased to a very high level in dark or even in dim surroundings. This condition exists when fluorescence is used for producing spectacular and brilliant color effects on the stage, or in displays, decorations, etc.

The fact that some fluorescent inks are invisible in ordinary light but can be seen under blacklight illumination is utilized in the invisible marking system for secret identification of checks, money, documents, stamps, books, merchandise, etc., and in the new invisible laundry marks.

Increasing the brilliance of contrast between the object and background enables one to see otherwise invisible particles in the fluorescence microscope, by either staining the specimen with a fluorescent dye or viewing it against a brightly fluorescent background.

In fluorescence analysis advantage is taken of the selective brightness contrast obtained between fluorescent and non-fluorescent substances in the specimen, when it is irradiated with blacklight. The fluorescent color or intensity changes of certain compounds, caused by their state of ionization, is utilized in the application of fluorescent indicators.

The fact that many colorless substances exhibit marked fluorescence in ultraviolet light (*e.g.*, the quartz mercury lamp) was applied to chromatograms by Winterstein and Schön and by Karrer and Schöpp, who termed it "ultrachromatography." Grassmann and Lang use the expression "fluorescence chromatogram." Traces of impurity may exert surprising effects on fluorescence. Thus Winterstein, Schön and Vetter [*Z. physiol. Chem.*, **230**, 158 (1934)] found that 0.00033 per cent of naphthalene completely suppresses the fluorescence of anthracene, and even one-third of this tiny amount is nearly as effective. Zechmeister and Polgár [*Science*, **100**, 317 (1944)] describe a fluorescent polyene having a characteristic spectrum, in a hexane extract from tomatoes.

Progress in the isolation of the cancer-producing substance from tar was slow until Mayneord and Hieger (1927-30) made use of fluorescence spectrography. Hieger observed [*Biochem. J.*, **24**, 505 (1930)] that tars and oils having carcino-

genetic activity showed characteristic fluorescence spectra with bands at 4000, 4180, and 4400 Å. Finally Cook, Hewett, and Hieger [*J. Chem. Soc.*, **1933**, p. 395], making use of fluorescence spectrography, were able to isolate and identify 3,4-benzpyrene, a then unknown hydrocarbon, as the active agent in tar, where it was present to the extent of about 0.003 per cent (see L. F. Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., 1936). Najjar and Emmett Holt [*Science*, **93**, 20 (1941)] report that in pellagra there is an excretion of specific fluorescent substances in the urine, which can be measured quantitatively and are criteria of nicotinic acid deficiency.

Spectro-chromatography has been dealt with by Almasy [*Biochem. Z.*, **291**, 421 (1937)], and chromatography in general is covered in books by Zechmeister and Cholnoky (English translation by Bacharach and Robinson, J. Wiley & Son, New York, 1941), by Strain (Interscience Publishers, Inc., New York, 1942), and by Clarke in his paper in Vol. V of this series, pp. 457-471.

In a new method for determining small amounts of zinc [L. Merritt Jr., *Ind. Eng. Chem.*, (Anal. Ed.), **16**, 758 (1944)] fluorescent turbidities are measured by producing a colloidal suspension of highly fluorescent Zn 8-hydrozyquinolinate. The range is 0.05-0.6 mg and the accuracy 0.02 mg.

Among the many other uses of fluorescent materials, we can only mention a few: observing the blood circulation by injecting fluorescein into the blood stream (useful in surgery, diagnosing heart diseases, establishing extinction of life, state of physical death); adjusting contact lenses to the eye with the aid of a fluorescent dye; detecting surface flaws in metals and plastics; reading theater programs in the dark; detecting the flow of water underground; signaling in the dark; completely changing the decorative effect of a room by change in illumination.

An interesting use of fluorescent colors is in painting pictures in which contrast of brilliance is greater than the range of colors in the regular palette of the artist. New fluorescent ultraviolet artist's colors have been developed by the author, which increase the range of brilliance of the colors in the palette, thereby enabling the artist to reproduce scenes true to nature, as far as brilliancy contrasts are concerned. Of course, for illumination, a source of light must be used which is very rich in ultraviolet radiation.

In this new ultraviolet color system we have to consider besides the three basic concepts of colors, *i.e.*, hue, value and chroma, a new fourth characteristic, namely, the fluorescent intensity which we may call ultraviolet brilliancy. The ultraviolet color system will define a color by four concepts, instead of the three used in the Munsell color system; and instead of the I. C. I. (International Commission on Illumination) Tristimulus coordinate system (see U. S. Dept. of Agriculture, Report by Dorothy Nickerson, May, 1938), four stimulus values in a new system must be used in ultraviolet colorimetry.

While most of the industrial uses of luminescent products have been developed in the past 20 years, the great demand for these materials during the war has stimulated production on a large scale and the cost of luminescent paints, pigments and inks was greatly reduced. The next few decades therefore, will most likely show great developments in the application of luminescence in the various fields of art, science and industry. Thus again, what was once a laboratory curiosity will serve to add more safety, entertainment, comfort and beauty to our everyday life.

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The Skin and Its Technological Hazards

FRANK C. COMBES, M.D.

New York University

Statistics show that 60 to 90 per cent of industrial injuries result from contact with the skin of noxious substances which produce physicochemical changes therein, requiring in some instances many months of treatment to dispel. Furthermore, the environmental hazards to which man is exposed contribute to over two-thirds of the dermatoses for which he seeks relief. Thus, a careful consideration of industrial contactants and the nature of the skin's response to injury therefrom is necessary, not only in treatment but in prevention of occupational dermatoses.

In order better to appreciate the abnormal, it is essential that the normal structure and function of the skin be known. A brief review of these subjects follows.

Structure of the Skin

The covering of our bodies known as the skin, integument or dermis, and in lower animals as the hide or pelt, is a rather complex organ of ectodermal and mesenchymal origin. Structurally it is an elastofibrous sheath, enveloping the entire body and at the natural orifices is continuous with the mucous membranes. It consists of two layers: the surface epithelium, or epidermis, and the corium, or cutis vera. The subcutaneous tissue or hypoderm, which is situated immediately beneath and merges with the corium, and which is considered by some to be an integral part of the skin, is really a distinct structure. It is composed of fat cells and interlacing bands of connective tissue, which afford the skin intimate attachment to the underlying fascia, periostium, aponeurosis, etc.

Minor differences exist in the skin's anatomic and chemical structure in either sex, different races, and individuals. These variations may contribute to differences in response to environmental influences and contact substances. The oily skin is less sensitive to cold, acids, alkalies and aqueous solutions; but is more sensitive to some dyes, halogens, and substances readily soluble in oils, as tetryl and trinitrotoluol. It also seems to be more sensitive to some of the complex organic sulfur compounds.

As a rule the skin of children and the aged is hypersensitive to contactants, the former because of the thinness of the horny layer and underdevelopment of the pilosebaceous glands and pigment; the latter because of atrophic changes and dryness. Women are, in general, more susceptible than men. The skin richly supplied with hair also possesses greater resistance, and the defense mechanism is more highly developed therein. The blond skin offers a greater technological hazard than that of the brunet. The tolerance of the negroid skin for mechanical, thermal and chemical contactants, because of its pigment and copious secretion of sweat and sebum, is so well known that this race is employed exclusively in some chemical industries.

A few dermatoses show sexual preferences. Lupus erythematosus, lichen simplex, chloasma, the vitiligoid syphilide, Paget's disease, cosmetic dermatitis and the cutaneous complications of pregnancy and the climacteric are encountered more (or exclusively) in women; whereas carbuncles, alopecia, leukoplakia, industrial diseases, epithelioma and chancroid are met with more in men.

In the full-blooded negro, psoriasis, basal-cell carcinoma, leukoplakia and pedicu-

losis are uncommon; while the skin of this race shows a predilection to develop keloids, tinea capitis, granuloma inguinale, the annular and pustular syphilids. Jews and to a less degree other Mediterranean races are especially subject to pemphigus, Kaposi's sarcoma, glomus tumor and dermatoses of nervous or emotional origin. The American Indian seldom shaves, rarely has psoriasis and is rarely bald-headed. The Scandinavian shows a propensity to cutaneous tuberculosis. In the tropics many diseases attack the new arrival or visitor. Natural hyposensitization of the New Jerseyite to the bite of his proverbial mosquito, which makes life miserable for the summer vacationist from other States, is well known.

Many qualitative and quantitative differences exist in the skin of the individual. For instance, its thickness may vary from 5 mm on the soles to 0.5 mm on the eyelids. It is thinnest in the latter location, and on the forehead and flexures of the extremities.

The color and texture vary in different persons and even in the same person. Those portions exposed to sun and wind become "weathered," tanned by the actinic rays, and may develop "liver spots," areas of parakeratosis due to the irritating effect of the rays upon the germinative layer. The brown to black color of these lesions is due to oxykeratin and not to normal cutaneous pigment. Color in the normal skin is the result of several factors: first, thickness of the epidermis tends to produce a yellow hue (carotene); secondly, the amount of capillary circulation, its depth beneath the surface and the relative amount of hemoglobin and oxyhemoglobin tends to produce varying shades of red; thirdly, the amount of melanin in the basal-cell layer is responsible for variations from blond to black. The pinkish skin of the albino is due to the capillary circulation shining through the yellow epidermis in the total absence of melanin. The pink eyes of this affliction are due to retinal vessels whose color is transmitted through a chorioid and iris devoid of pigment.

In the brown races and negro, increased amounts of pigment (melanin) may be seen in the basal layer and even in the superficial part of the corium and in the prickle cells of the epidermis.

The Epidermis

The epidermis or scarf skin is the external layer of the integument. It is this layer that absorbs the first shock of environmental injury. Its lower border is in contact with the corium or cutis vera from which it is separated by the basal membrane. It varies considerably in depth. On the palms and soles it may be as much as 3 mm in thickness, while on the eyelids this is less than 0.05 mm. Like all epithelium it is devoid of blood vessels and nerves, receiving its nourishment from lymph which circulates freely in the intercellular spaces.

The epidermis is divided into four layers:

(1) Stratum mucosum
(2) Stratum granulosum
(3) Stratum lucidum
(4) Stratum corneum.

(1) The *stratum mucosum* from a functional standpoint is the most important. Sometimes designated as the germinative layer since it represents the matrix of the entire epidermis, it is capable of complete regeneration; and injuries to the skin which do not penetrate below this layer are followed by complete restoration without scarring. It is composed basically of two types of cell: the cuboidal cells, arranged in a single row, resting on the basal membrane and known as the basal layer; and several layers of polyhedral cells, connected by spinous processes (prickle cells). In contact dermatitis this layer seems to exhibit the initial structural changes.

In this layer also are situated those elements responsible for the formation of melanin, the most important cutaneous pigment. It is also important in the production of fixed tissue and circulating antibodies.

(2) The *stratum granulosum* consists of two to five layers of flattened cells. These are diamond-shaped or rhomboidal with their long axes parallel to the surface. These cells are studded with irregular, coarse granules of kerato-hyalin, the precursor of keratin.

(3) The *stratum lucidum* is a clear layer of flattened, refractile cells, devoid of nuclei, which contain a colloid known as eleidin, an intermediate in the production of keratin.

(4) The *stratum corneum* is the most superficial layer. It is composed of flattened or fusiform, horny cells, devoid of nuclei. It varies considerably in thickness. On the prepuce and eyelids it consists of only a few layers of cells, while on the soles it may constitute as much as half the entire depth of skin. The cells are so densely packed that their margins are obliterated. The cell structure is homogeneous and filled with a substance known as keratin, the nature of which will be discussed later. This corneous layer constitutes the first line of defense against physical and chemical industrial hazards.

The Corium

The corium or true skin, which is the wider layer, contains most of the anatomic structures and cutaneous appendages, including the glands, muscles, nerves, lymphatics, blood vessels, etc. Its average thickness is about 2 mm, slightly more on the buttocks, and less in women. Its reticulum consists of a dense network of connective-tissue fibers (collagen) arranged in bundles, running in all directions and interspersed with fibers of elastic tissue (elastin). The latter are more abundant around the glandular elements, on the face and in the region of movable joints, in order to afford greater elasticity and freedom of movement and expression.

The Hypoderm

The hypoderm or subcutaneous layer is composed essentially of fat cells in a connective-tissue reticulum. It carries the larger blood vessels, nerve trunks and lymphatics. It also acts as a buffer, and because of its presence our bodies have a certain roundness or shapeliness. It is usually better-developed in women. This layer is an important reservoir of lipid and constitutes one of the first depots to be depleted in febrile diseases and chronic illness. The distribution of subcutaneous fat varies in either sex and to some degree is determined by the secretion of the anterior lobe of the pituitary gland. In Froelich's syndrome, acromegaly and Cushing's basophilic degeneration of the pituitary, abnormalities of the hypoderm are seen.

Functions of the Skin

The fundamental purpose of the skin is protection of the organism, and the great majority of its activities contribute to this function. These include sensation, temperature regulation, secretion, excretion and the ability to repel or neutralize various chemicals, bacteria, fungi and other harmful agents.

One other property of the skin, which does not contribute toward its defense but which may constitute a danger to the health and life of the individual, is its ability to absorb certain substances.

Protection. The epidermis, corium and hypoderm shield the underlying tissues against injury, infection, and against loss of liquids and body heat. The epidermis, due to its physicochemical pattern and coating of fatty sebum, protects the deeper layers from injury by heat, cold, caustics, poisonous liquids and pathogenic organisms. The varying amount of melanin and the ability of the skin to mobilize it when and where needed, protect the underlying structures from the destructive influence of the sun's rays.

The looseness of the subcutaneous tissue and the elasticity and firmness of the

corium afford protection to the internal organs against physical trauma, blows, etc.

Both sebum and sweat protect against microorganisms. The former keeps the corneous layer soft and supple, so that it does not crack and fissure, thus opening avenues to infection; the latter possesses definite fungicidal properties, and it is probable that the epidermis itself is capable of some degree of autosterilization. The unbroken epidermis is impermeable to bacteria although they may penetrate through the pilosebaceous orifices. Fungi, yeasts and moulds thrive on the keratin of the corneous layer.

Sensation. The skin is richly supplied with sensory nerves which may afford the individual a pleasing sensation, warn him of danger or harmful pathologic changes, enable him to judge the size and shape of objects, variations in environmental temperature, etc. In lower animals this function is developed to a much greater degree than in man, as witness the "cat's whiskers." In the blind, cutaneous sensation is also particularly acute.

The perception of cutaneous sensation arises in certain specific receptors, each designed so as to respond to some particular kind of physical or chemical stimulus, *i.e.*, caloreceptors (heat and cold), tangoreceptors (touch), chemoceptors (taste and smell); the latter responding to chemical stimuli. These specific designations do not mean that a receptor is incapable of response to other than one type of stimulus, but rather that the threshold for those stimuli is lower than for others.

The ability of the skin to perceive environmental hazards, and through its nerve terminals and synapses to initiate impulses which may be translated by the brain into motor impulses of such nature as to protect the body from injury, is one of its most important functions.

As previously mentioned, these sensory nerve endings are specialized for the perception of heat, cold, touch and pain. Their distribution is not uniform but limited to small discrete areas. Many of them having been "mapped," we find tactile sensibility, which depends for its perception on "touch spots," greatest on the fingertips, tongue, lips and nose. Over the shins and shoulders, "touch spots" are sparse. Tactile corpuscles are frequently arranged in close proximity to hair follicles, the slightest pressure on the hair shaft acting as a lever to activate the sensory impulse. The perfect development of this pilar sensibility in lower animals to serve as a warning of approaching danger, bespeaks its vestigial nature in man.

Thermal sensibility consists of the ability of the skin to distinguish slight and extreme differences in temperature. Areas most sensitive to heat and cold are the tip of the tongue, lips, cheeks and eyelids. The hands are the least sensitive, although the distribution of these end organs varies greatly in different individuals. Caloreceptors, as they are called, while not responding to mechanical stimulation, are capable of giving a sensation of pain to temperatures in excess of 50 C.

The pain sense, like that of temperature and pressure, has a similar punctiform distribution. The impulses are capable of evoking reflex muscular contractions for the purpose of protection and defense. By means of the cathode-ray oscillograph it is possible to measure electrically the speed of the nerve impulse. This differs; the nerves with the thinnest fibers conducting their impulses at the slowest speed, three to six feet per second; while the fastest nerve impulses travel approximately 380 feet per second.

The cutireceptors for pain are more numerous than those perceiving other sensations and have never been successfully mapped on the cutaneous surface. Some physiologists believe that this sensation may be elicited from any area of skin. Goldsheider asserted that any of the nonmedullated nerve fibers might serve as pain receptors. It is true that excessive pressure or extreme degrees of heat and cold, or trauma sufficient to cause a solution in continuity of the skin of such depth as to reach the basal layer of the epidermis, are capable of producing painful sensations. However, the majority of observers agree that specific end organs for pain exist in

the skin and that they serve no other purpose. Experimental evidence to this effect may be demonstrated by the cocainization of a nerve trunk, when loss of sensation to pain, cold, heat and touch occur in the order mentioned.

The sensation of itching which is so common a subjective symptom in many dermatoses has never been successfully explained. For many years it was generally accepted to be due to pressure on the epidermis from beneath. This is readily disproved experimentally since the intracutaneous injection of physiologic saline solution does not evoke the sensation, and in simple idiopathic pruritus there is histologically no edema which could exert such pressure. The theory that itching is a sublethal stimulation of the receptors which perceive pain has some basis in fact, since the injection of certain drugs may abolish pain and pruritus without disturbing the receptors of other sensations. Sir Thomas Lewis denied that itching was due to edema or stretching of the nerve ends and believed it due to histamine, since injections of the latter always itch, even if wheal formation and localized edema are prevented by stopping the circulation.

Temperature Regulation. The temperature of normal skin varies from 33.5 to 36.9° depending on environmental and body temperatures. It decreases with advancing age.

Through the involuntary response of nerves, muscles, blood vessels and glands the skin plays a major part in adjusting the body to changes in internal and external temperature by regulating the amount of heat liberated from the body surface. Body heat is emitted by conduction, radiation, convection and vaporization. The corneous layer of the epidermis is a poor conductor and thus prevents its too rapid dispersal. Both the epidermis and unstriated muscles exert a constant pressure on the cutaneous blood vessels, preventing their overfilling, with an associated heat loss. When the body or portions of it are exposed to excessive cold, a reflex action occurs through the vasomotor and heat-control centers in the medulla, evoking contraction of the arrectores pilorum muscles. This compresses the capillaries, blanches the skin, and simultaneously squeezes sebaceous material onto the surface as an added defense and insulation. This involuntary contraction is objectively evident not only by blanching, but also by prominence of the pilosebaceous orifices ("goose-flesh"), shivering and involuntary chattering of the teeth.

In febrile patients the opposite conditions exist. The skin is flushed, the integumentary muscles relaxed and the surface bathed with perspiration. Not only is a large amount of heat removed by sweat but in the process of its evaporation, heat is consumed. (Evaporation of one gram of water causes a heat loss of 0.54 calories.) This enables us to endure temperatures of 38° C (100 F) or higher, providing the humidity is low enough to allow evaporation of sweat. Conversely, one may feel uncomfortably cool in winter in a room whose temperature is 27° C (80° F) if the humidity is so low as to cause excessive loss of heat from the skin by vaporization.

In health, the skin is constantly active as a heat-regulating factor. In the newborn, this function is not fully developed so that the infant must be artificially protected from sudden changes in environmental temperature; and everyone is acquainted with the extreme degrees of hyperthermia with which it responds to inconsequential gastrointestinal upsets, dentition, coryza, etc.

The average rectal temperature of man is 37° C (98.6° F); this may vary normally as much as one degree in either direction during the day, the lowest being observed during the early morning hours. The author has observed the unusual temperature of 34.4° C (94° F) in a patient suffering a severe grade of malnutrition. In the therapy of malignancy, temperatures of 26.2° C (80° F) have been maintained for as long as 8 days.

Secretion and Excretion. Both the sweat and sebaceous glands perform secretory and excretory functions.

The sudoriferous or sweat glands secrete a clear, odorless watery solution which

is normally neutral or slightly acid in reaction and has a salty taste. It is composed essentially of water which comprises about 99 per cent of its volume. In addition to an appreciable quantity of sodium chloride (about 0.3 per cent), sweat contains traces of alkaline sulfates, phosphates, urea, uric acid, glycogen, glucose, skatol, lactic acid, creatinin, indican, ammonia, various fatty acids, albumin and fats derived from sebum.

The amount of sweat excreted in health varies in different individuals and under various conditions of atmospheric humidity, water ingestion, temperature, muscular activity, etc., the average at rest being about one quart in 24 hours.

The relative importance of the skin as an emunctory organ may be appreciated by the fact that in individuals doing strenuous exercise at high temperatures, the nitrogen excretion through the sweat amounts to as high as 12 per cent of the total nitrogen excretion.

Many chemicals introduced into the body by various means, both intentionally and accidentally are excreted in appreciable quantities in sweat. These include tars, turpentine, iodides, bromides, chlorides, sulfur compounds, arsenic, phosphorus, ether, and volatile oils.

Excessive loss of sodium chloride through the skin, in those industries where the individual is exposed to intense heat, such as smelting, glass blowing, mining, etc., is important from both a health and economic standpoint. Although vitamin C may be demonstrated in sweat, it is present in such small amounts (0.6 mgms per 100 cc) that a deficiency due to its loss through this avenue would seem highly improbable.

Increased perspiration also predisposes to cutaneous irritation by silica, feldspar, quartz and metallic dusts, especially arsenic where the most common and troublesome effect is the production of various skin lesions, especially scrotal edema with ulceration, dermatitis of the face, hands, feet, axillas and groins. Hyperhidrosis also predisposes to cutaneous absorption of metallic dusts with systemic intoxication.

Disturbances in the sweat function are associated with some metallic poisonings. Chronic tellurium poisoning is associated with a suppression of sweating; while selenium, which resembles tellurium chemically and in its physiologic effects, causes night sweats. Chronic poisoning by lead, antimony, arsenic and mercury is frequently associated with hyperhidrosis of the palms and soles.

The *sebaceous glands* secrete sebum, a lipid, composed chiefly of the esters of fatty acids and higher alcohols, with traces of the triglycerids. Inspissated sebum and keratin, collecting in the orifice of a gland as a small tallowlike plug, is called a *comedo*. It is frequently black ("blackhead") over its exposed surface due to oxidation (oxykeratin).

Physiologically, the sweat and sebaceous glands have much in common, and act in concert, seborrhea and hyperhidrosis frequently occurring simultaneously. Sebum tends to lubricate the integument, maintain its softness, prevent the development of fissures and consequent entrance of pathogens into the skin. In addition it is impermeable to substances dissolved in aqueous fluids, rendering the skin less permeable. It also impedes the too rapid evaporation of sweat and thus aids in conservation of heat.

Sebaceous glands are most numerous and best developed where the subcutaneous fat is least abundant, and on exposed surfaces such as the chin, nose, forehead, scalp, sternal and upper vertebral regions. The amount of sebum secreted by an individual varies from 1-2 grams to a maximum of 180 grams daily. Glandular activity is usually greater in slender individuals and in brunets and Negroes.

Absorption. The ability of the skin to absorb certain substances, while affording an avenue for the administration of various types of medication whose administration by mouth is for some reason contraindicated, at the same time may result in unexpected toxicity from absorption of substances applied for topical effect or the accidental absorption of industrial poisons.

The epidermis is absolutely impermeable to aqueous fluids but less resistant to gaseous and volatile substances. It is also improbable that any substance in its dry state is ever absorbed through the intact integument. This resistance is due to the corneous layer which is normally impregnated with sebum. Even when saturated, this layer may swell and become "water-logged," but not permit the penetration of water.

Many substances, if suspended or dissolved in an oil of fatty material and applied with friction, are absorbed into the general circulation. By far the greatest amount of absorption takes place through the sebaceous glands and along the hair follicles. Volatile and sublimable substances, turpentine, ether, alcohol, menthol, camphor, etc., are slightly absorbed if the skin is previously washed with soap and water or if it is very dry. Tars, phenols, naphthols, chrysarobin, arsenic, sulfur, iodine and mercury readily penetrate the unbroken skin when applied with friction in a fatty base; and in some instances, *i.e.*, liquid phenol, absorption occurs rapidly and with fatal results when the pure substance is simply applied to rather restricted areas.

In industry, lead absorption through the skin is apparently possible, especially when it is incorporated in oil or turpentine, as in paint. Some investigators believe attempts to remove paint from the hands and forearms with turpentine, naphtha or benzine may favor its absorption.

The skin is the most important mode of entrance into the body of benzene and its derivatives, especially dinitrobenzene, tetryl, trinitrotoluene, aniline and other compounds found in the dye industry; all of which may cause systemic poisoning.

It is probable that many gaseous substances may be absorbed, especially those that are soluble in fats. Carbon dioxide is absorbed in insignificant quantities, proportionate to its concentration in the atmosphere. Ammonia behaves in a similar fashion. Hydrogen sulfide acts similarly up to a concentration of 0.2 per cent when it causes a dermatitis which curtails its absorption. The absorption of elemental sulfur by the skin probably occurs after its conversion to hydrogen sulfide in the horny epidermis. Carbon monoxide is not absorbed at all.

Of the various fats, those that are fluid and of animal origin seem to have the greatest absorptive capacity. Next come the oleates and vegetable oils. So-called mineral fats are not readily absorbed but will frequently readily release dissolved ingredients for absorption.

Chemical Structure of the Skin

Compared with other organs, comparatively little is known of cutaneous chemistry. However, microchemical examination of freshly removed skin has shown that the normal value of chlorides, non-protein nitrogen, sugar, uric acid, etc. is markedly different from that of the blood.

Each layer shows distinct differences in chemical structure; in fact, each stratum of cells in the epidermis differs chemically from the one immediately adjacent thereto.

The "Acid Mantle." Studies of the hydrogen ion concentration of the epidermis have been made by many investigators with varying results. There are many reasons for this divergence, two of the principal ones being the impossibility of removing sweat as an interfering factor, and the presence on the surface and in the epidermis of various aerosols absorbed from the atmosphere. Including these sources of error, and sebum which also affects the pH values, it has been determined that the healthy epidermis varies from pH 4.2 to 5.6. This "acid mantle" is maintained by the residue of fatty acids remaining after the evaporation of sweat and is an important factor in protection of the organism against invasion by bacteria and fungi. Because of minor physiologic differences in the sweat glands in certain locations, there is a difference in the chemical composition of the secretion, resulting in pH values in these areas approaching neutrality or even alkalinity. These areas are the axillas in adults, the

anogenital folds, the nipple areolas, the interdigital spaces (especially the fourth interspace on either foot) and certain portions of the soles.*

Irvin H. Blank after studies made on 200 subjects, aged 19 to 27, came to the following conclusions:

(1) The pH of the exposed areas varies from 4.0 to 7.0, but most of the potentiometer readings are between 4.2 and 5.6.
(2) The average pH of females is about 0.5 higher than that of males.
(3) The extensor surfaces of the arms are slightly more alkaline than the corresponding flexor surfaces.
(4) The cubital fossa is the most acid area on the skin.

Pillsbury and Shaffer have shown that the intact epidermis is particularly tolerant to acids, withstanding solutions ranging to pH minus 2 (three times normal hydrochloric acid). They also showed that keratolysis of the stratum corneum occurs at a pH in excess of 12.6; being particularly rapid and severe at 12.8. (Laundry soap varies from 10.5 to 12.0.)

In industrial dermatitis of the hands the most common contributory factor seems to be soap or one of the strongly alkaline detergents used for cleansing purposes.

As previously stated the epidermis is not chemically homogeneous. The outer layer, or stratum corneum, is composed essentially of keratin, an albuminoid of varying composition, rich in cystine, histidine, tyrosine, argenine, and tryptophane. Its elemental composition is: C 48.7 per cent, H 6.5 per cent, N 16.5 per cent and S 3.9 per cent. In hair, a product of the epidermis, the S content is high due to the high cystine content (10-15 per cent). The normal sulfur content of nails is about 3.2 per cent. Traces of fluorine also have been found in the epidermis and its appendages.

There are different keratins, which accounts for variations in the epidermis of different individuals and in nails, hair, feathers and horns.

Keratinization. The chemistry of keratinization is described briefly by Markowitz as follows:

"The epithelial cells of the skin in their continuous change outward in their life cycle, depending essentially on a loss of water of hydration and a deficiency of oxygen, results in keratinization. The slow and moderate oxidation of the horny substance produces a brown oxykeratin; the reaction explains the blackish color of ichthyosis, the dark color of keratomas, and comedo heads. . . . During hydrolysis of keratin a part of the organic sulfur is eliminated by the squamae of the epithelium, the hair and the nails. This is also a route of elimination for arsenic, silica and other elements."

The albumins and globulins of the epidermis do not differ from those of blood serum; those of the corium consist principally of collagen and elastin. The latter is derived from the former and they are similar in chemical composition (C 50 per cent, H 7 per cent, N 17 per cent, O 22 per cent, with traces of S and P), except that elastin contains about 25 per cent of glycine, and its leucine content (21 per cent) is ten times greater than that of collagen. Both differ from keratin in that they do not contain tyrosine, cystine, or tryptophane, and are rich in glycocol.

Nitrogen being such an important part of the protein molecule, it is appropriate that the part played by the skin in its excretion be mentioned here. The importance of this function is not generally appreciated. The skin accounts for approximately 10 per cent of the total urea output, both through the medium of sweat and horny scales.

The normal total nitrogen excretion through the skin by an adult, at rest, is from 0.16 to 0.71 gram per day.

* The fungus causing athlete's foot commonly grows between the smaller toes, probably because it finds there a favorable pH. In his "Natural History," Liber XXV, Par. 185, Pliny states that alumen (alum), the basis of most of our modern "deodorants," diminishes offensive odors of the axillae, and reduces sweating in general (Bailey's translation). Older books on pharmacy give formulas for "toilet vinegar," which enhanced skin acidity. J. A.

Fats in the Skin. The epidermis is normally saturated with lipids which are absorbed from the blood stream and are brought to the surface during the process of keratinization. They include the true fats (palmitates, stearates and oleates), waxes, phospholipids, glycolipids and cholesterol. Of the latter, about 90 per cent is uncombined.

The fat of the hypoderm is similar to that found in other parts of the organism, and although it contains only traces of cholesterol the total amount of this substance present in the hypoderm exceeds that found in any other tissue or organ.

Carbohydrates in the Skin. Glycogen and glucose are important constituents of the epidermis, and are quantitatively present in amounts greater than in the corium. Experimental work in animals indicates that the skin acts as a depot for glucose when it is ingested in excessive amounts; and conversely it is a source of supply, when ingestion is below optimum requirements.

The normal glucose content is only about half that of blood. Besides its role in normal cellular oxidative processes, glucose is active in controlling the water content of the skin, an excess causing water retention. Increased lactic acid values due to oxidation of carbohydrate ingestion also favors the secretion of sebum and increases the sugar content of sweat where it is found to vary normally from 3-40 per cent.

Inorganic Salts and Water Metabolism. The non-combustible residue of the skin contains sodium, magnesium, potassium and calcium, as chlorides, phosphates, sulfates, and carbonates; iron, sulfur and aluminum, with traces of silicon, arsenic and copper. Sodium chloride is the most important since the skin is the principal depot for chlorides, which are indispensable for the regulation of water metabolism. The latter is by far the largest single constituent of the body and approximately 72 per cent of normal skin consists of water. It differs from other organs in that it is an actual depot. While other tissues may contain more abundant water, what they have is essential for their economy; whereas the skin can at any time liberate large quantities when the occasion arises. This ability of the skin to store both water and salt is dependent upon its richness in connective tissue. Following the intravenous injection of a salt solution, as much as 77 per cent of the amount retained will be found in the skin. An excessive amount of sodium chloride in the cutis and hypoderm attracts water, and causes edema if large amounts of the latter are subsequently ingested.*

Catalysts and Enzymes. There exist in the skin, in very minute quantities, certain metals and metalloids which are necessary for the maintenance of health and act as catalysts, since they are not themselves expended in metabolism. These have been studied by Bertrand of the Pasteur Institute and include arsenic, which is present in amounts up to 0.026 per cent; iron in amounts of 1 mgm per cent; copper, zinc, cobalt, nickel, lead, aluminum, gold, fluorine, iodine, tin and titanium. They are obtained from ingested food and are shed through the horny scales. Copper apparently plays a role as catalyst in oxidation of dehydroxyphenylalanine ("dopa") in the formation of pigment. Gorter in 1935 showed that a reduction in pigmentation of the hair occurred in cats, rabbits and rats by reducing the intake of copper and vice versa.

Enzymes functionally are similar to the inorganic catalysts and have been designated as "biochemical catalysts." † They take an active part in facilitating cutaneous metabolism and while the identity of many is unknown, the more important fall in the general classes of amylases, glycolases, proteases and demolases.

Vitamin C also functions as an enzyme and exists in the stratum mucosum in appreciable amounts where it is active in oxidation-reduction processes and in the

* H. Schade (see his paper in Vol. II of this series, p. 635) considers the great colloidal mass of connective tissue, much of which lies under the skin, to be an important "organ" whose swelling and shrinking are of great importance for the physiology and pathology of the human body. J. A.

† See paper in Vol. V of this series by J. Alexander on "Catalysis as a Biological Factor." J. A.

formation of melanin. The part played by biotin, inositol, pantothenic acid, pyridoxine, para-aminobenzoic acid and other filtrate factors of the B complex is obscure.

Hormones. Hormones, which are usually simple chemical substances of remarkable potency (one gram of thyroid hormone is sufficient for an average individual for a period of five years), affect the skin in three ways: first, directly; secondly, through their influence on the vegetative nervous system; and lastly through their effect on the mind. Our knowledge of their action on the skin is pitifully defective and far inferior to our knowledge of cutaneous anatomy and physiology. As in the instance of vitamins we learn of their activity chiefly through clinical manifestations of deficiency.

Thyroid. Hypothyroidism results in the deposition of subcutaneous fat and simultaneously a lessening of sebaceous secretion, with dryness and thickening of the skin, and subnormal surface temperature. The hair is coarse, sparse, dry and lusterless. An associated nitrogen retention causes an accumulation of water in the skin, producing myxedema. This type of individual is prone to contact dermatitis. There is also a hypersensitivity to systemic intoxications and depression of the cellular and humoral defense mechanism. However, the administration of thyroid hormone by mouth usually results in prompt restoration of normal function. The small amount necessary to produce the desired effect suggests the action of a catalyst.

In hyperthyroidism there is often hyperhidrosis and diffuse pigmentation, particularly on the trunk.

Parathyroids. The parathyroid glands are of little known significance dermatologically. Their extirpation, besides being followed by tetany, is accompanied in addition by hypotrichosis, and atrophy and loss of the finger nails. It has been suggested that the alopecia accompanying thallium intoxication may be a result of its effect on the parathyroids. Hyperparathyroidism is seen in calcinosis cutis and in some cases of scleroderma.

Adrenals. Adrenal cortical hormone, which is under reciprocal relationship with the anterior pituitary gland, possesses multiple functions, especially as regards electrolytes and glucose metabolism, few of which are clearly understood. Overactivity in the female is productive of hirsutism, especially on the face; a coarse, dry skin, loss of libido and development of virilism.

The hormone, in conjunction with the pineal body, gonads, anterior pituitary hormone and thyroid, control the growth and distribution of hair. Besides overactivity of the adrenal cortex, hirsutism occurs in hypopinealism, hyperpituitarism and hypergenitalism.

Pituitary. The most significant cutaneous changes are encountered following dystrophies of the anterior lobe. Hypofunction produces the familiar Froelich's syndrome * or dystrophia adiposo-genitalis, in which the skin is thin, dry, subnormal in temperature, pale and slightly scaly. Hyperhidrosis and urticaria are frequent. Striae atrophicae are often seen, due to the rapid deposition of subcutaneous fat. Hyperfunction produces the syndrome of acromegaly with thickening and coarseness of the skin, pigmentation and multiple papillomata. The nails are hypertrophic, thickened and brittle. There is seborrhea and hypertrichosis; the hair shafts themselves being coarse and heavy, the eyebrows thick and bushy. This change in the hair is the most constant objective sign of acromegaly, occurring in a quarter of the cases.

Cooper has said that "hypopituitarism causes the male to assume the female type of distribution of hair, but it does not cause the female to assume the male type of

* Froelich's syndrome (*dystrophia adiposogenitalis*) is a disease complex consisting of hyposecretion of gonadotrophic hormone of the anterior lobe of the pituitary gland and failure of development or regression of development of the sex glands. Some few instances are due to a chromophobic adenoma of the pituitary gland rather than simple hypoplasia. The syndrome is readily recognized by the familiar clinical triad consisting of obesity, genital hypoplasia and faulty skeletal development.

distribution. Hyperpituitarism on the other hand, causes the male to become more masculine in type, and the female to become male in type."

Gonads. Following castration of males the skin becomes dry, thin, and there is atrophy of the sebaceous glands, sweat glands and lanugo hair. The scalp hair, on the contrary, becomes more luxuriant, although dry and lusterless. (Eunuchs are never bald.) Some observers feel that the absence of testicular hormone predisposes to epithelial carcinoma.

Estrogenic hormone secretion bears a definite but obscure relationship to pigmentation and hirsutism. Presumably it acts by activating the epidermal melanoblasts, especially in the areola of the nipples.

The Skin as an Emulsion

Herman Goodman in recent papers and discussions has proposed a unique theory in an attempt to explain cutaneous irritation following the application of soaps for toilet, household cleanliness and industrial utilization. He advances the idea that it is not the soap or the substitute which is at fault, but rather the skin. In other words, it is the wrong kind of soil for the soap.

Skins are classified as of two major types, the first of which is the oil-in-water emulsion type. Normal soap is this type of emulsion. If the individual's skin is of this oil-in-water type and the soap is of the oil-in-water type, then the skin can tolerate the soap emulsion. However, it should be appreciated that there are two subvarieties of oil-in-water emulsion soap: one soluble, formed from fatty acid and univalent basic salts (Na, K, and NH_3); the other, insoluble and formed from fatty acid and polyvalent salts (Ca and Mg). Many persons who can tolerate the soluble oil-in-water emulsion type soap cannot tolerate the insoluble form. The latter is an irritant, the noxa being either the physical nature of the insoluble soap, or its chemical form, or both. The first reason may be responsible for the lack of confirmative conventional patch tests.

The second type of skin is the water-in-oil emulsion type. It does not tolerate the oil-in-water type emulsion soap. Every grandmother knew this, for they substituted oil for soap when the child's skin was irritated after a soap and water ablution. Substitution of one oil-in-water emulsion phase soap for another of the same physical nature does not help the irritated skin. Certain superfatted soaps were once available, the manufacturers of which claimed that they were in effect of the water-in-oil emulsion type. Many creams offered as substitutes for oil-in-water emulsion type soaps are in effect the same soap in cream form. They are oil-in-water emulsions with water rather than partially dehydrated oil-in-water emulsions in soap cake form.

In prescribing for the skin one must therefore take into consideration the phase of skin. Goodman believes that the vehicle used for topical medication may be of equal or greater importance than the active ingredients. An effort should be made, therefore, to have the base in the same phase as the skin at the time of application, in order to avoid further injury. If it should happen that the vehicle prescribed is in the opposite phase, irritation may result. In all instances of acute contact dermatitis it is customary to preclude the use of soap and water. This, in effect, is an admission of the incompatibility of this lesion with emulsions in the oil-in-water phase. To be consistent, applications to this type of dermatitis should be in a water-in-oil emulsion type vehicle. Lanolin emulsions are of the water-in-oil type. The individual who does badly with lanolin water-in-oil emulsion type vehicles should be placed on starch water gels or mucilages. These are equivalent to the opposite phase finished emulsions when in contact with the sebum of the injured cutaneous surface.

Until recently, only trial and error have determined whether the skin in health or disease is of one type or the other. It is by consideration of these factors that Goodman believes the type of base used for topical applications used in medicine and cosmetics should be determined.

Types of Technological Attack

Response of the Skin to Injury

Space does not permit a comprehensive discussion of the part played by enzymes and catalysts in the response of the skin to injury, but it is important that we be familiar with *what* happens when various noxae attack the skin, even though we are not acquainted with the theories as to *why*.

Injuries may be broadly classed etiologically as due to mechanical, thermal or chemical agents. Certain agents such as electrical impulses and radiant energy may be capable of more than one variety of effect. The cellular response of the tissues varies and it is therefore advisable that the types of injury be considered separately as they affect different layers of the skin. The action of all harmful agents is, of course, to produce degenerative changes, although there is always a defensive response on the part of the tissue attacked.

An interesting fact regarding various types of cutaneous injury is the difference in the time element between trauma and its effect. For instance, the results of mechanical trauma are almost immediately apparent; for burns, this time is slightly delayed; in freezing it is still further delayed; actinic-ray burns may require several hours; and roentgen and gamma-ray reactions and sequelae require weeks to months before they are apparent.

It is of further interest that those injuries to which the human race has been exposed for the longest time and which are most often repeated and common, are quickest in showing their effects; while the more unusual types of injury require some time to develop. Lewis believed that the reaction involved in all instances is fundamentally the same to slowly acting stimuli as to the more quickly acting ones, the longer latency merely being indicative of a difference in manner in which the stimulus acts; representing the time required for certain hypothetical substances (H-substances) released by the tissues to accumulate.

Mechanical Injury. Acute mechanical injury of the epidermis may be caused either by incision from a sharp instrument or blow, or a bruise from a blunt instrument. Incised injuries of the epidermis do not cause bleeding and heal without scar formation, regeneration being complete. Acute bruises are followed by the circumscribed exudation of serum and blister formation; this being an effort on the part of nature to render the noxae inert by dilution, or perhaps for neutralization by antibodies.

Long-continued friction or repeated mild pressure leads to formation of a callosity or clavus, which lesions show thickening of the horny layer. In old calluses and corns there is in addition hypertrophy of the prickle-cell layer.

Acute injuries of the corium of a mild nature are followed only by vasomotor disturbances (redness, edema, etc.) which disappear without trace. Following more severe trauma there is a varying degree of necrosis which is followed by escape of serum and phagocytes from the capillaries. Suppose, however, that the necrosis takes place, not in one area, but in several, and in a skin which is, for some reason, hypersensitized or the site of a preëxisting hyperemia, vasomotor disturbance, or circulatory stagnation; then the recuperative process is delayed, repair more difficult, requiring weeks or months to be completed. We then have an inflammation of the skin, dermatitis or eczema. This trauma may afford favorable soil for infectious microorganisms; so in addition we have infection.

Thermal Injury. Here may be included changes due to extreme degrees of heat and cold. While it includes electric burns, it excludes sunburn and changes produced by x-rays, radium and other sources of radiant energy.

Burns of the skin are popularly divided into three degrees: first, redness (erythema ab igne); second, formation of bullae (dermatitis ambustionis); and third, destruction of the corium or hypoderm with the formation of an eschar (necrosis).

Cutaneous injuries due to cold may be similarly classified (erythema pernio, dermatitis congelationis and necrosis). Clinically they resemble those due to heat.

Chemical Injury. The many chemical agents capable of injuring the skin may be included as animal, mineral or vegetable in origin; but in addition should include radiant energy, since this produces chemical changes in the skin which are degenerative in nature.

Lesions precipitated by chemical causes may be classified as follows:

(1) Erythematous and urticarial dermatoses—those caused by the stinging nettle, the sting of a mosquito or other insect, caterpillar hairs, animal furs, jelly fish, and most sensitizing and non-sensitizing contactants of industry. These are basically angioneurotic in nature.

(2) Vesicular dermatitis, etiologically identical with the foregoing; but either the noxa is more potent, present in greater quantity, or the individual or certain areas of his skin are in a state of hypersensitivity.

(3) The hyperkeratoses, including arsenical keratoses, comedos, the folliculitis of cutting oil, croton oil, tar, pitch, petroleum, chlorinated hydrocarbons and other acneform eruptions.

(4) The superficial necroses following the weaker caustics, such as silver nitrate, phenol, etc.; and the more penetrating caustics, as mineral acids, caustic soda and potash, glacial acetic acid, etc. Few of these caustics cause any inflammation, only simple necrosis, ulceration and granulation.

The Biochemical Requirements of Tissue Repair

It is only within recent years since the demonstration of the biologic significance of vitamins, catalysts and enzymes, and the importance of proteins and electrolytes in maintenance of cellular osmosis, that medicine has appreciated the importance of these biochemical factors in the healing of wounds. Bruger has recently reviewed this subject in a brief but thorough fashion. In the healing of cutaneous injuries, there are three biochemical requisites, namely (1) ascorbic acid, (2) equilibrium of serum proteins and (3) normal carbohydrate metabolism. According to Holden and Crile, Jr., there is little evidence that a good "over-all" physical condition and vitamins other than ascorbic acid are necessary.

Ascorbic Acid. A deficiency of this vitamin in the tissues resulting from an inadequate intake, an inability to absorb or store it, results in improper maturation of precollagen to collagen. Not only does it retard the reparative process but the cicatricized skin and fascia lack tensile strength. According to Bartlett, Jones and Ryan a fasting plasma ascorbic acid level above 0.2 mg per 100 cc is necessary to insure proper wound healing. (Normal fasting ascorbic acid varies from 0.7 to 1.4 mg per 100 cc of plasma.)

Plasma Proteins. In order to maintain a normal balance of tissue proteins, essential for tissue repair, it is necessary that plasma proteins exist in equilibrium. Deficiencies of both tissue and plasma proteins may result from inadequate intake, an inability on the part of the liver to synthesize protein from amino-acids absorbed from the portal vein or excessive loss of protein in instances of extensive suppuration, nephrosis, paracentesis, extensive burns and hemorrhage. As previously mentioned in the paragraph on ascorbic acid, hypoproteinemia causes not only delayed healing and poor growth of fibroblasts, but according to Hartzell, Winfield and Irvin scars of poor tensile strength with a tendency to disruption.

Carbohydrate Metabolism. It has for years been the general impression of the laity and many of the medical profession that hyperglycemia, *per se*, predisposed to infection and was a contributing factor toward delayed wound healing. Bacteriologic studies reported by Bayne-Jones show that blood containing a high concentration of sugar is no better culture medium than that of lower sugar content. The tendency to infection in uncontrolled diabetes mellitus and the abnormally slow healing of

wounds is due rather to edema of the skin, vascular thrombosis and tardy and incomplete deposition of fibrin. In controlled diabetes healing proceeds normally (Bennett). Bruger in summarizing the significance of hyperglycemia says "*per se* it does not retard wound healing nor predispose to infection provided that (1) insulin is acting and the metabolism of the tissue cells is not disturbed; (2) the peripheral circulation is adequate; and (3) the resulting glycosuria and concomitant polyuria do not produce excessive dehydration."

Response of the Skin to Infection

All eruptions, particularly those of an infectious nature must be regarded as defensive efforts against injury, each element of skin reacting in its own way. The several ways in which the integument is capable of reacting is the product of many complex factors. One element determining the site and nature of cellular response is whether the pathogen reaches the skin through the circulation or directly from the environment. In the latter instance the primary reaction is in the epidermis; in the former, it is vascular, appearing in the capillary network of the corium. In addition, as Sabouraud has so tersely expressed it, "each cell reacts in its defense against microbic invasion by pursuit of its own special function."

The mechanism by which bacteria became established in the skin and the factors determining their pathogenicity are far too complicated and problematic to consider here. However, it may be stated that their survival, proliferation and dissemination depend upon certain definite factors, chief of which are the following:

(1) The physical properties of the tissues into which the bacteria are introduced.

(2) The physical, chemical and antigenic properties of the invading organisms including morphology, capsule formation, pleomorphism, sporulation, antigenic activity, anti-enzyme formation, etc.

(3) The motility of the bacteria, including the presence of flagellae, surface tension differentials, etc.

(4) The physical and biologic relationship between the invading bacteria and the environmental cellular tissues, vascularization, immunologic status, moisture, temperature, aeration, CO_2 tension, hydrogen ion concentration and the presence of metabolic requirements.

Most epidermal infections encountered in industry are due to streptococci, staphylococci, moulds and fungi. In those due to streptococci, the eruption consists of superficial vesicles and bullae (impetigo contagiosa). These bullae are situated just beneath the horny layer. There is only the mildest edema of the prickle-cell layer and corium, with a very sparse polynuclear leukocytic infiltration. The main reaction therefore is in the superficial layers of the epidermis and consists of serous exudation which is attracted to the surface by some chemotactic principle, probably similar to Lewis' H-substance or the E-substance of the Germans.

In staphylococcal infections of the epidermis the invading microbes enter the pilosebaceous follicles. The type of cell partaking in this defense effort is the polynuclear leukocyte. These collect in and around the staphylococcus laden follicle, forming a pustule containing white or creamy pus.

Pathogenic fungi and moulds invading the skin attack the horny layer, hair and nails. Typical of this is tinea versicolor, a most superficial infection due to invasion of the horny layer by a fungus (*malassezia* or *microsporon furfur*). Here the defensive response is non-inflammatory, confined to the epidermis and consists in the formation of an abundance of defectively keratinized cells, which are spontaneously cast off as thin furfuraceous scales. Most of the fungi are thus disposed of, but some few which manage to penetrate the prickle layer always remain. Some other individual species of fungi are capable of provoking erythema, vesicles, papules and crusts, but this intense reaction in the prickle-cell layer and corium is due to toxins of the fungi rather than the organisms themselves.

Streptococcal inflammation of the corium and hypoderm involving the lymphatics is best illustrated by erysipelas. The streptococci, inoculated through a wound, grow and disseminate through the lymph channels of the cutis, the limits of their extension depending on mechanical external pressure by compression of the lymphatic sinuses, or artificial interference with the medium by the injection of drugs. Although today, therapy is directed against the invader itself (with sulfanilamid), these indirect methods of checking spread of the disease were popular for many years.

Hematogenous infections and toxemias produce initially a vascular response, but many cause changes in the epidermis with papules, nodules and bullae. For years these eruptions were explained solely on the basis of an angioneurosis, and Unna classed them with the "neurotic inflammations," due either to central or peripheral vasomotor disturbances; but later it was found that they were inflammatory and therefore could *not* be produced by simple vasomotor disturbances.

In this category are included the toxic erythemas. All members of this group show, in addition to a sharply localized edema of the corium, an inflammatory infiltrate of perivascular distribution. The whole vascular network of the papillary body is dilated and surrounded by closely packed cells; there is edematous swelling of the epidermis and dilatation of its lymph spaces. Macroscopically, papules, vesicles and bullae are present.

Hematogenous toxins are common. Besides those of microbic origin we have toxic products of metabolism and various noxae from the environment which have gained access to the circulation, as arsenic, lead, mercury, gold, volatile oils, sulfuric ether, aldehydes, benzols, coal-tar dyes and many other substances. Dermatitis medicamentosa and stomatitis medicamentosa, idiocratic reactions of an eczematoid nature caused by medicaments administered internally for the relief of disease, are also included in this group.

Vascular Responses of the Skin

The distribution of the cutaneous capillary network and its response to trauma have been studied by many investigators, none of whom have added more to our knowledge than Sir Thomas Lewis.*

When the skin is stroked lightly with a blunt instrument, there immediately occurs a pallor, due to the mechanical emptying of the terminal capillaries in the papillary body. This is merely momentary, and disappears, to reappear in 15-20 seconds. It reaches its maximum in about 50 seconds, gradually fading in a few minutes until indistinguishable. This response to light trauma is due to contraction of the minute superficial capillaries and terminal arterioles responsible for skin color. It is independent of any central or local nerve reflex and occurs in any area of skin even if the nerve supply has been intentionally destroyed or has previously undergone degeneration.

However, when the skin is *firmly* stroked with a blunt instrument, another series of responses may be observed which have been designated by Lewis and his coworkers as the "triple response." This consists of the following:

(1) **Local Capillary Dilatation.** This begins within 20 seconds, is confined to the area stimulated, and reaches its maximum intensity in about 3 minutes, gradually fading. It is due to active dilatation of the superficial minute vessels previously mentioned and is observed equally well in skin in which the nerve supply has been removed. It must, therefore, depend for its production on a direct response of the capillaries to trauma or to some substance liberated as a result of the stimulus. Adjacent to this red area, if the stimulus has been sufficient there is a narrow blanched zone.

* Many years ago Dr. Fenton B. Turck (see his book entitled "The Action of the Living Cell," Macmillan Co., 1933) demonstrated the fact that trauma set free something which he called "cytost," which could enter the circulation and produce symptoms of shock. J. A.

(2) **The Flare.** When the stimulus is sufficient or when the skin is particularly susceptible, in 15 to 30 seconds subsequent to the initial local capillary dilatation, a flushing of the neighboring skin appears, which increases in intensity and spreads over an area several times wider than the "red line" and assumes a brighter color. At this period, the original red line may be bluish. This flare is due to arteriolar dilatation and is dependent on the presence of nerves, as it is a short axon reflex, initiated by some substance liberated locally. It is the only element of the "triple response" elicited through nerve channels.

(3) **The Wheal.** In some individuals (those with urticaria factitia or dermographism), after firm stroking of the skin, in addition to the local capillary dilatation and flare, there appears a localized edema, forming an urticarial wheal. The pressure of this edema occludes the terminal capillaries, producing a central blanched zone.

This entire triple response is explained by Lewis as due to H-substance, similar to histamine, but probably not histamine, which is released locally as the result of some trauma. It can be produced by a great variety of stimuli;—mechanical, thermal, electrical, chemical, etc. Its duration depends upon the quantity of H-substance liberated and the time required for its absorption. The response may also be produced by pricking a little histamine into the skin. The flare, depending upon the integrity of the peripheral sensory nerve fibers, is utilized to determine the integrity of the axon reflex.

Reactive Hyperemia. When the arterial and venous circulation in a limb are entirely occluded by a tourniquet, cyanosis develops, its onset being directly related to the temperature of the limb. After release of the tourniquet, the area previously deprived of blood immediately becomes bright red due to active dilatation of the minute vessels, the walls of which are essentially endothelial. There is in addition to this hyperemia an increase in velocity of blood flow. This response is known as *reactive hyperemia* and is attributed by Lewis to H-substance accumulated during the stasis; but is in all probability due rather to an accumulation of normal metabolites, in the skin deprived of blood, which are capable of producing vasodilatation. Reactive hyperemia is independent of ennervation. Its significance resides in the fact that it suggests that these metabolites may be identical with the hypothetical H-substance. Lewis admits this possibility by inferring that the latter probably embraces more than one substance.

Variations in skin temperature resulting from changes in capillary tone have also been attributed by Lewis to variations in the production of H-substance.

Biologic Mechanism of Inflammation

When the skin or any tissue of higher animals is invaded by viable pathogenic organisms or is exposed to injury by non-viable irritants, it reacts locally in a specific manner which has been designated as "inflammation." This is a basic or elemental reaction to injury and constitutes the physical basis of all infectious processes.

The anatomic elements concerned in the phenomenon of inflammation are the vascular capillaries, blood, lymph, the local cellular structures and so-called intercellular fluid.

Inflammation may be divided into the following stages:

(1) **Edema.** The initial change consists of edema following the passage of plasma from the capillaries. The factors responsible for edema are

(a) Localized vasodilatation and increased capillary pressure.

(b) Numerical increase in functioning capillary channels.

(c) Increased permeability of capillary endothelium.

Krogh was of the opinion that the increased capillary permeability was a direct result of vasodilatation stretching the endothelium. The precise mechanism responsible for this capillary and arteriolar dilatation and augmentation of capillary permeability has been a subject for postulation by many investigators. The hypothesis

offered by Lewis and Grant and based on the liberation of a histamine-like substance by the injured cells is generally accepted. That the substance is not histamine and lacks the properties and characteristics of histamine has been proved by Menkin,* who believed it to be a diffusible, crystalline material, probably a simple polypeptid, which he termed "leukotaxine." It is found in all types of inflammatory exudates, and its subcutaneous injection will produce an immediate vasodilatation and increased capillary permeability.

(2) **Fixation of Irritant.** While one result of the passage of plasma into the tissue is dilution of toxins and the introduction of immune bodies into the area, the essential result is fixation or "walling off" of the noxa by fibrinogen, and thrombosis of the lymphatic channels of the corium, thus effecting a veritable blockade, localizing the inflammatory process.

(3) **Cellular Sequences.** To Cohnheim (1867) and Metchnikoff (1892) is attributed the credit for stressing the significance of leukocytosis in the disposal of various vital and non-vital tissue irritants and their products. Liberation of leukotaxine by cells of the stratum spinosum is responsible for local leukocytosis but not for elevation of the level of circulating leukocytes.

The cytologic sequence in all inflammation caused by living pathogens and chemical irritants consists initially of an active migration of polymorphonuclear leukocytes, followed by an infiltration of mononuclear phagocytes or microphages. The source of the latter is not definitely known, but Maximow and Bloom believe they originate in the blood and are really transformed lymphocytes and monocytes. The biologic force responsible for this cellular migration is obscure but is probably a product of the activity of proteolytic enzymes, present in the leukocytes (leukoprotease, lymphoprotease), in addition to leukotaxine.

Action on the Skin of Industrial Irritants

Having previously discussed the divers ways in which tissues respond to contact irritants, let us now consider briefly the ways in which these substances are capable of acting on the skin.

(1) **Oxidants and Reductants.** Examples of these are chlorine and the chlorates, chlorites, chromates, permanganates, nitrates; bromine, iodine and their salts and compounds; phosphorus, pyrogallol, sulfur compounds and the oxalates. These act by interfering with the normal process of keratinization, resulting either in formation of a parakeratotic scale or denudation of the horny layer.

(2) **Desiccants.** While oxidizing and reducing agents in high concentration are capable of desiccation, most desiccants are concentrated organic and inorganic acids, and the stronger alkalies.

(3) **Protein Precipitants.** These are the true astringents and consist principally of the salts of heavy metals.

(4) **Keratolytics.** These are substances capable of dissolving keratin, mostly alkalies; and those substances capable of emulsifying the lipids of the keratin layer, consisting chiefly of the degreasing agents such as soap, turpentine, benzene, benzine, acetone, toluol, xylol, carbon disulfide, trichlorethylene and the alcoholic esters.

(5) **Mitotic Stimulants.** Certain few substances are capable, either mechanically or because of their chemical structure, of irritating the cells of the germinative layer of the epidermis, augmenting proliferation and causing new growths, benign or malignant. The principal substances exhibiting this action are arsenic, chlorphenyl compounds, chlornaphthalenes, petroleum products, (dibenzanthracene, benzpyrene) waxes, oils, coal tar, carbon, pitch, etc.

(6) **Sensitizers.** A large group, particularly the nitro- and nitroso- compounds are capable of allergenization.

* See paper on Inflammation by Valy Menkin in Vol. V of this series. J. A.

Cutaneous Sensitization

The Mechanism of Allergy *

Many years ago it was observed that certain persons were so susceptible to particular foods that immediately after eating them they experienced an attack of urticaria. The explanation was that the individual had become highly sensitized to certain foreign proteins, which, owing to a gastrointestinal disturbance, had been absorbed at some previous time as "toxic albumin," unconverted by proper digestion.

At present it is generally recognized that this phenomenon is an antigen-antibody reaction, taking place in the tissues. Von Pirquet designated it as "allergy," from the Greek, "allos" (other) and "ergon" (work); and it is defined by Sulzberger as "any acquired specific alteration in the capacity to react, which occurs in living organisms or tissues upon exposure to certain living or inanimate agents or substances." The "specific" refers to the fact that the alteration which is produced by a certain agent can manifest itself following reexposure to only that same agent or to an immunologically related agent.

In the case of cutaneous allergy, the shock tissue is the skin. However, the cutaneous parenchyma does not behave immunologically as a single shock tissue, but actually contains three primary shock tissues; viz., the epidermis, in which the clinical manifestation of allergy is allergic contact dermatitis; the blood vessels of the cutis, responsible for neurodermatitis, infantile eczema, urticaria and prurigo; and the blood vessels of the hypoderm, sensitization of which produces angioneurotic edema. It is essential that these differences be appreciated when testing for the suspected allergen.

There is a tendency to use the terms allergy and sensitivity interchangeably. Strictly speaking this is improper since allergy is a subdivision of sensitivity, the latter term referring to a pathologic increase in sensitivity of tissue to all types of stimuli; whereas, the former is based specifically on an antigen-antibody mechanism.

There is an additional tendency to confuse the site of an allergic manifestation with the portal of entry of the allergen and vice versa. For example, it is not uncommon to see patients with urticaria who have had all manner of patch tests, when actually the primary shock tissue in this instance is not the epidermis but the blood vessels of the cutis or subcutis. The epidermis is involved only secondarily. It is important to know this, both for purposes of testing and of therapy. Skin tests of various types performed in urticaria are of little value.

How does the skin become allergized? Simply by exogenous or endogenous exposures, plus predisposing factors, especially individual constitution or idiocrasy. The time required for allergization varies and is influenced by many predisposing factors besides the nature of the excitant. Ordinarily it is from 10-15 days, but under certain conditions may require months or even years. The greater the influence of the excitant the shorter the period of allergization and the less the influence of predisposition. Conversely in the presence of greater predisposition, weaker allergizing contactants may in time produce hypersensitization. These predisposing factors are numerous, the influence of many being obscure. They include age, sex, race, complexion, climate, season, food, vitamins, environmental temperature, etc.

Duke proposed the designation "physical allergy" to describe hypersensitiveness to various physical agents such as heat, cold, actinic rays, trauma, etc. He recognized two types; the contact type, in which the manifestations were local and confined to the area of contact; and a reflex type, in which the manifestations, in addition to a local urticarial type of reaction in the skin, were general and affected remote organs, such as the heart (tachycardia), intestinal tract (diarrhea), meninges (migraine), and other organs.

* See paper on Allergy and Anaphylaxis by Carl A. Dragstedt in Vol. V of this series. J. A.

The Pathologic Mechanism of Physical Hypersensitivity

Primary physical allergies are not common. Few are definite antigen-antibody reactions in which passive transfer by the Prausnitz-Küstner technique * may be accomplished. In contradistinction to true allergy, this phenomenon has been designated as "pathergy." Its exact mechanism is unknown.

Secondary physical allergies, on the contrary, are invariably allergic, but by a mechanism differing from that due to chemical substances and infectious organisms in that the individual is sensitized to a histamine-like substance produced in his skin by the physical agent. Therefore the antigens must be interpreted as autogenous, created by a method similar, if not identical, to autosensitization to blood serum and keratin.

This histamine theory of physical allergy is supported by the benefit derived in this type of sensitivity from the administration of histaminase (Roth and Horton), and from desensitization by means of histamine injections (Bray, Saylor and Wright).

The ability of infectious organisms to previously sensitize the skin, rendering it susceptible to physical influences, has been demonstrated experimentally by Burky, who prepared rats with staphylococcus toxin, cultured in broth made from rat-muscle tissue. Subsequently the rats reacted anaphylactically to trauma. This bacterial sensitization due to remote foci of infection is the basic cause of many bacterids and microbids † which, when precipitated by industrial contacts, offer a problem in diagnosis and therapy, especially when situated on the hands and forearms.

While endogenous allergies and pathergies due to pressure and physical trauma are occasionally observed, those due to light rays, heat and cold are more common. In the case of the latter, the great majority are localized pathergies and not really allergic. The origin of this sensitiveness has been variously attributed to liver disease, intestinal infection, endamebas, etc. Exogenous causes include principally drugs, (sulfonamides, gold, acridine dyes, porphyrins, eosin, sulfonal, barbiturates) administered by mouth or by injection. Local sensitization to light may be produced by oils of bergamot, lavender, cedar, vanillin; eosin, sulfonamides, coal tar, pitch and some coal-tar dyes.

Many intractable, chronic urticarias are due to sensitivity to cold. Furthermore, it is probable that many instances of sudden drowning in good swimmers are due to this phenomenon, rather than to cramps or coronary thrombosis. In some instances, the mere dipping of the hand into cold water is sufficient to precipitate an attack of syncope, tachycardia, nausea and vomiting. Illustrations of the pathergic type of cold sensitiveness are quite common in the literature, being provocative of

* The Prausnitz-Küstner Technique of passive transfer is an ingenious idea by which blood serum from a hypersensitive patient is tested in the skin of a known non-sensitive patient. Briefly the technique is as follows: One-tenth cubic centimeter of the allergic blood serum is injected intracutaneously in a normal individual (previously proved non-allergic to the substances being tested). Twenty-four hours later 0.1 cc of the allergen is injected into the same site and the reaction read in the usual way. False positive reactions may usually be eliminated by observing several recommended precautions and limitations. The primary purpose of the technic is to eliminate non-specific reactions.

† "Microbid" is a term used to designate the allergic response of the skin because of previous sensitization by some microscopic organism or its toxin, which has reached it from some remote infectious focus. While some allergists prefer the term "id" to designate this immunologic state, restricting the term "microbid" to the sensitization mechanism as it refers to bacteria, the author prefers to refer to these latter states collectively as bacterids and specifically as staphylococcids, streptococcids, etc. This group of microbids thus includes tuberculids, trichophytids, epidermophytids, microsporids, favids, moniliids, etc. Syphilids and leprids should not be included in this group as they do not represent sensitization reactions but are actually themselves infectious lesions. The term "id" and "microbid" cover the mechanism and *not* the morphologic clinical picture. Leukamids are not related to this phenomenon, nor are they sensitization reactions.

localized whealing at the site of exposure. This is usually apparent within a few minutes but may be delayed for as long as 48 hours (Freund).

The mechanism of heat allergy and pathergy is identical with that due to cold. Overheating from exertion is sufficient in some instances; and patients presenting the "effort syndrome" are often sensitive to heat. It is also possible that many patients supposedly photosensitive are acutally sensitive to solar heat rays.

Contactants

The allergens responsible for allergic diseases include ingestants, inhalants, injectants, infectants, physical agents and contactants. Of these the latter are, by far, most important in industrial medicine.

A contactant, from the standpoint of the immunologist, may be defined as a substance, usually allergenic in nature, capable of eliciting evidences of hypersensitiveness when brought in contact with the skin or mucosa.

The most harmful contactants encountered in industry, in their order of frequency, in the opinion of the author are:

Petroleum products
Alkalis and their compounds
Fat solvents and degreasing agents
Metals and metal plating compounds
Lubricants (soluble and insoluble)
Paints and paint solvents
Chromates and chromic acid
Dyes
Synthetic resins
Rubber and its compounds

Occupations with high cutaneous hazards as listed by Lane are:

Bakers
Building cleaners
Cement workers
Chemical workers
Dishwashers
Dye handlers
Electroplaters
Gardeners
Lithographers
Machinists
Painters
Photographers
Shoe treers
Soda-fountain workers
Tanners

Contactants for purposes of study may be classified as follows:

(1) Animal and vegetable parasites
(2) Plants and their products
(3) Animals and their products
(4) Chemicals

While most contactants are true allergens, some are protoplasmic poisons and produce cutaneous inflammation because of primary irritation. These are consequently termed "primary irritants" and include the stronger acids and alkalis, metallic salts, soaps, etc. The allergic type of contactant produces a specific cutaneous hypersensitivity (sensitization or allergic dermatitis). In this latter type a certain period of sensitization occurs after the exposure responsible for allergization, during which time the contactant may be handled with impunity, unless it is applied in such concentration or in such quantity as to act as a primary irritant. After the development of this hypersensitization, the individual becomes susceptible to the specific allergen, or to one immunologically related to it, in dilutions far greater than that necessary to produce a dermatitis in the non-allergized skin. Many substances which are usually considered primary irritants, such as soaps, formaldehyde, xylol, turpentine, kerosene, etc., may actually become sensitizers when applied in dilution over a long period of time. It is of utmost importance that sensitization dermatitis be recognized early and if possible, its spread prevented. It is a common

observation that an allergic contact dermatitis which was originally restricted to a fairly well-restricted area, spreads by continuity or contiguity to other areas. The identical eruption may even appear on remote portions of the skin, far removed from the original area of contact with the offending allergen. This is due to three factors: first, the escaping serum is irritating to the hyperemic epidermis surrounding the lesion; secondly, autosensitization, the cutaneous proteins acting as foreign substances; thirdly, the development of polyvalent hypersensitivity, in that mechanical trauma of any type elicits a cutaneous reaction more intense than that observed in the non-sensitized skin. This explains the appearance of linear vesiculation in patients with ivy-poisoning, on areas of skin never exposed to toxicodendrol, after excoriation or grattage. Schwartz is of the opinion that the possibility of allergization is overemphasized, having found that only 18 per cent of over 10,000 instances of occupational dermatitis were strictly allergic in origin.

The criteria distinguishing a primary irritant from an allergen as proposed by the Committee on Occupational Dermatoses of the American Medical Association are as follows:

(1) When a substance in a given concentration, in a given vehicle and after a given manner and length of exposure produces a clinically manifested irritation on the skin of a majority of persons not previously sensitized to that substance, then that substance is a primary irritant under the specified conditions.

(2) The irritation may be redness, papulation, vesiculation, ulceration or other sign of damage at the site to which the irritant has been applied.

(3) By contrast, substances which produce reactions only on the skin of persons who are hypersensitive to that substance are not primary irritants.

(4) A sensitizing agent is one that increases the tissue capacity to react to subsequent exposure.

(5) Hypersensitivity means having a greater capacity to react than the normal.

A critical review of these distinguishing characteristics discloses that while the authors defined a sensitizing agent they failed adequately to differentiate between hypersensitivity and allergy. As previously stated allergy is a type of hypersensitivity; the latter actually exists as a product of many unrelated predisposing factors, such as the amount of skin exposed to the irritant, the degree of pigmentation, dryness, oiliness, perspiration, thickness of the horny layer, general health, environmental temperature, humidity, season, diet, bacterial and virus synergism, autosensitization (lens, muscle, serum, keratin), etc. All these may make the individual hyper- or hyposensitive. On the other hand, allergy is the product of an antigen-antibody mechanism, and when it occurs the individual is said to be sensitized or allergized. Almost any substance may be a sensitizing agent but it is not designated as such until it has sensitized the individual, and is then so designated only when referring to it in connection with the individual so sensitized. However, there are certain substances that are prone to sensitize many individuals. Every industrial physician should be acquainted with these and take appropriate measures to prevent sensitization of workers. Furthermore, extreme care must be exercised in performance of patch tests with these substances as one may, by this procedure, sensitize a previously normal skin by applying the substance in too great a concentration or for too long an interval of time.

An illustration of extreme hypersensitivity due to allergization is an instance of facial dermatitis following contact with dinitrochlorbenzol, in which the victim subsequent to his recovery could not enter a building in which it was in use without developing facial erythema.

The more common substances, noted for their ability to sensitize readily are:

Dichlorbenzene
1, 2, 4 dinitrochlorbenzene
Methyl salicylate (natural and synthetic)

Nitroso-dimethyl aniline
Orthoform
Para-nitroso-dimethyl aniline
Picryl chloride
All plants (fresh or dry, leaf or sap)
Resins
Dinitrochlorbenzol
Phenylhydrazine

Skin Tests

These include the scratch test, intracutaneous test, passive-transfer test, percutaneous, patch and scratch-patch tests. The latter two, especially the patch test are the only ones applicable in cases of contact dermatitis, since in these instances the epidermis is the shock organ.

The patch test, introduced by J. Jadassohn in 1894 and subsequently popularized by Bloch, Peck and Sulzberger, when properly performed and interpreted, is of great value in the diagnosis of industrial dermatitis. The purpose of the test is to determine hypersensitivity of the area tested to specific contact substances. In other words it determines the part played by the epidermis as an allergic shock organ, but is almost valueless as a decisive factor in determining allergization of the papillary capillary plexus or the vascular network of the corium and subcutis in patients with urticaria, chronic lichenified eczema, seborrheic eczema, noneczematous drug eruptions, neurodermatitis and angioneurotic edema.

The detailed technique of its application may be found in any standard textbook on dermatology or allergy. Briefly, the object is to reproduce, as far as possible, the actual contact conditions existing in the occupation of the individual by applying to a small area of skin the substance suspected responsible for this dermatitis. The concentration in which these contactants are applied is previously determined by tests on the skin of nonsensitized individuals. Tables of these dilutions are available. Insoluble substances should be dissolved in appropriate solvents, and primary irritants applied in dilutions found to be innocuous to the nonsensitized epidermis. Volatile substances may be tested by having the individual apply his forearm to the aperture of a test tube or bottle containing the solution. Miller has suggested a "fume test," in which the suspected allergen is poured on some cotton which is subsequently placed in a fenestrated pillbox attached to the patient so that only the vapor comes in immediate contact with the skin.

Sometimes it is desired that the suspected substance be dissolved in sweat before its application, since there are from time to time variations in the pH of the perspiration of the worker which may make him hypersensitive to an exogenous allergen at one time and not at another. An artificial sweat prepared as follows should serve to simplify this procedure:

Sodium chloride	3.
Sodium sulfate	0.1
Urea	2.
Lactic acid	2.
Olein	2.
Stearin	2.
Distilled water	1000.

The skin at the site of the patch test or the material tested is moistened with this solution.

Since the actual diagnostic value of the test depends upon how and where it is done, a few words on the latter seem indicated. First, a patch test should not be done in the presence of an acute dermatitis but rather after its disappearance or at least during the stage of resolution. The site selected should be at the border of the involved skin or actually on the area previously inflamed. By such procedure one is less likely to miss topical sensitivities wherein the entire integument is not

hyperergic. Experience has shown that the back is the poorest site for patch testing, many more negative reactions resulting there than from tests done on the flexor or inner surface of the arm, or on the sides of the chest between the axillary lines. In dermatitis of the face the V of the neck is a very satisfactory site. This location and behind the ear are frequently used for testing cosmetics, hair dyes, etc.

Interpretation of the Patch Test. Downing has said, "Patch tests have no diagnostic value. They have their fallacies and limitations, but with a carefully taken history showing definite exposure to the test material, and with a characteristic test eruption, a positive finding followed by the prevention of further exposures should result in a cure."

Experience in reading and interpreting the tests add proportionately to their actual value. A positive reaction usually appears within 24 to 48 hours. A response appearing after the patch has been in contact with the skin for a period longer than 72 hours should be regarded with caution because of the possibility of allergization having been caused by the test itself.

The following arbitrary grades may be used to designate the degrees of reaction:

1 plus: sharply defined erythema
2 plus: erythema, edema, papules
3 plus: erythema, edema, papules, vesicles
4 plus: single large confluent bulla

In addition to the local reaction there may be an acute focal flare at the site of the healed or chronic dermatitis, an extremely interesting and important immunologic phenomenon.

False positive reactions may result from using the allergen in too small a dilution, causing a "toxic reaction" or "primary irritation." Furthermore, tests should never be done during the acute stages of a dermatitis, as false positives may result. Sulzberger has shown that diphenyl compounds, tars, greases and oils may cause an acneform reaction to epidermic tests, especially in persons with acne vulgaris. Ingram in making patch tests found that 4 per cent of individuals are sensitive to initial tests with paraphenylendiamine.

False negatives may result from testing with an allergen in too great dilution; the area tested may not be properly chosen or the patient may be in a temporary period of hypoergy. Sometimes the area tested may be so oily and greasy that substances in aqueous solution may not come in sufficient contact with the epidermis. Powders should be tested both in their dried state and in appropriate solution. Sometimes patch tests fail to indict the contactant responsible for an industrial dermatitis because the actual conditions are not faithfully reproduced. These include hyperhidrosis, attending work under high temperatures, excessive humidity, friction, maceration of the epidermis, trauma, etc.; all of which are factors effecting allergization. Sometimes, in such cases, scratch-patch tests are more significant, especially when there is a negative patch test or a response of the delayed type.

Plants and Their Products as Contactants

In certain occupations such as horticulture, gardening, farming; and in florists, road workers and housewives, the individual is exposed to various plants which may, depending upon the degree of exposure and immunologic status cause a toxicoderma. Well over a hundred plants are capable of producing a harmful effect on the human skin causing inflammatory responses of varying intensity.

As in the case of other contactants there are two types of reaction, *viz.*, that of primary irritation and that of allergy. Let us, for example, consider urushiol, an oleoresin, the chemical principle of *Rhus vernicifera,* the dried sap of which is used to finish lacquered articles, such as toys, games, earphones, wooden ornaments, etc.

It is the cause of "lacquer dermatitis." The pure chemical painted on a restricted area of skin of the non-sensitized human or any lower animal will immediately produce a white area, similar to that following phenol or one of the caustic organic acids, with subsequent necrosis, sloughing and ulceration requiring two to three weeks to cicatrize. This is a toxic dermatitis due to primary irritation. In contradistinction is the allergic dermatitis, occurring on subsequent exposures and which is peculiar to humans and a few other species. In this instance dilutions of urushiol as great as 0.0000015 cc in a drop of oil are capable of producing a dermatitis which, however, is not evident for several hours and which will spread beyond the area of initial contact, requiring three to six weeks to disappear (Toyama).*

Common plants, flowers, vegetables and fruits responsible for contact dermatitis include:

Rhus toxicodendron radicans (poison ivy).
Rhus toxicodendron diversiloba (poison oak).
Rhus toxicodendron vernix (poison sumach).
Rhus vernicifera (Japanese or Chinese lacquer).
(The noxae in the above four plants appear to be chemically identical).
Iridea (orris root).
Primulacea (primrose).
Liliacea (tulip).
Carduacea (chrysanthemum).
Narcissus jonquilla (jonquil).
Carduacea coccineum (pyrethrum).

The more common vegetables and fruits causing allergization are asparagus, tomatoes, tobacco, oranges, lemons, limes and mangoes. The chief irritant of the citrous fruits is a terpene called Limonene.

It is not uncommon for wood cutters, lumbermen, carpenters, cabinet makers, joiners and others who handle wood to develop an allergy to one or more varieties. In these instances the allergen may be contained in the bark, leaves, sap, freshly cut wood or any part of the tree. Occasionally, according to Urbach, the allergization is not to the wood *per se* but rather to the fungi or mites living as parasites in the wood. Not infrequently the painter who has developed an hyperergy to turpentine and turns to carpentry for his livelihood, experiences a relapse due to exposure to turpentine in pine wood. Perspiration and an oily skin predispose to allergization of the skin to woods, suggesting the possibility that the allergen is volatile, a fact which is supported by the observation that many of these allergized individuals experience manifestations of sensitivity when merely in the environment of the cut wood. It is not, however, an instance of allergization by inhalation since the epidermis is the shock organ and the chemical manifestation is an erythemato-vesicular dermatitis.

Animals and Their Products

Allergization to animal products other than inhalants is uncommon. Sheep wool, lanolin and silk are the most common allergens of this type, particularly in cases of eczema confined to the face, neck, shoulders and arms. Hypersensitivity to the

* In *Science* of May 18th, 1945 (101, 517-8) I. W. Sizer and C. E. Prokesch report that the action of mushroom tyrosinase on the oxidation of the irritant principles of poison ivy and on related toxic compounds is demonstrated by measurements of oxygen consumption (in Barcroft respirometer), color change (darkening) decrease in phenolic groups ($FeCl_3$ test), and reduction in dermatitis-producing properties of these compounds on human and on guinea-pig skin. Since the action of tyrosinase occurs on the human skin as well as *in vitro,* this enzyme may offer a new method of treating poison ivy dermatitis, providing it is effective when applied some time after the toxicant has reacted with the skin (even after erythema has been produced).

High molecular weight alkylamines have an effect on the skin somewhat like that of poison ivy. Details may be found in the trade literature. J. A.

leather of gloves, cuffs, jackets, shoes, hatbands, hoods, etc. is not so uncommon. Fur gloves rarely cause any difficulty attributable to the fur itself, most allergizations being due to the dye, especially paraphenylenediamine. Norwood and Evans felt that the dermatitis in workers wearing leather gloves is caused by the macerating effects of the leather on a perspiring skin which has been made hyperergic by the presence of dermatophytosis elsewhere on the skin. They designated these lesions "leather phytids." This synergistic action of fungi and contactants, if pursued, reveals the practical impossibility of differentiating compensible industrial dermatoses from dermophytids. Kammer and Callahan reported 22 instances of contact dermatitis due to crude kerosene on the hands of men sensitized by a superficial mycotic infection.

Chemicals

There is no doubt that chemical agents constitute the predominating cause of industrial dermatoses. As is the case with other contactants they act either as primary irritants or allergens. Schwartz and Tulipan classify these chemical agents as follows:—

Principal Primary Irritants

Inorganic:

(1) Acids (including some of their salts).
- Sulfuric
- Nitric
- Hydrochloric
- Arsenious
- Phosphoric
- Hydrofluoric
- Chromic

(2) Alkalies
- Alkaline sulfides
- Sodium hydrate and carbonate
- Potassium hydrate and carbonate
- Ammonium hydrate and carbonate
- Barium hydrate and carbonate
- Calcium oxide hydrate and carbonate
- Sodium silicate and metasilicate
- Tri-sodium phosphate
- Calcium cyanamide

(3) Irritant Elements and Salts
- Sulfur and sulfides
- Mercuric iodide, bichloride, nitrate
- Chromates and bichromates
- Nickel chloride and sulfate
- Zinc chloride
- Arsenic and arsenates
- Antimony chloride and sulfide
- Sodium
- Potassium
- Phosphorus *

* Over thirty years ago phosphorus necrosis ("phossy jaw") was eliminated from the U. S. match industry by the Esch bill, which placed a prohibitive tax on the "strike-anywhere" matches made with white phosphorus. In order to make passage of the Esch bill feasible, an important match manufacturing company surrendered for cancellation its patents on the available substitute (phosphorus sesquisulfide), and furthermore furnished without charge to each of its competitors the working formulae and "know-how" it had spent much time and money in perfecting. For this wise action in the public interest the Company and its President, William Archer Fairburn, were awarded the Louis Livingston Seaman Medal of the American Museum of Safety. Very soon thereafter, a well-known and well-meaning preacher publicly attacked the Company for maintaining this occupational disease; but when the facts were drawn to his attention by the writer, he immediately published a retraction and apology. Only a few years ago, however, a well-known health authority republished the charge that the beneficent corporation had foisted "phossy jaw" on the match industry, but admitted the error when the writer drew attention to the facts. Nevertheless, the Editors of the magazine which had published this ancient falsehood, refused to print a retraction, on the plea that notice of it had come too late. J. A.

Organic:

(1) Acids, Anhydrides (and some salts).

Oxalic	Lactic
Carbolic	Maleic
Cresylic	Phthalic
Formic	Hydrocyanic
Acetic	Abietic

(2) Solvents

Turpentine	Alcohols
Petroleum distillates	Carbon tetrachloride
Carbon bisulfide	Trichlorethylene
Benzol	Amyl acetate
Toluol	Liquid chlorinated phenols
	Liquid chlorinated benzols

(3) Essential Oils

(4) Some Dye Intermediates

Dinitrochlorobenzol
Phenyl hydrazine
Sulfonic acids

(5) Acne Producers

Petroleum oils	Solid chloronaphthalenes
Pitch	Solid chlorobenzols
Tar	Solid chlorodiphenyls
Paraffin	Solid chlorophenols

Principal Specific Irritants (Allergens)

These affect only hypersensitive persons. The hypersensitivity may be congenital or acquired by contact with the chemical. Certain chemicals are powerful sensitizers: of these, dinitrochlorobenzol and paraphenylenediamine are notable examples.

Hypersensitive persons readily become sensitized to the primary skin irritants. Such persons will develop a dermatitis from dilutions of these substances too weak to affect normal individuals, or will be burnt by them on shorter exposure than would affect normal skins.

(1) Dye Intermediates

Aniline and compounds	Naphthalene and compounds
Chlor compounds	Benzidine and compounds
Nitro compounds	Benzanthrone and compounds
Acridine and compounds	Naphthylamines
Anthracene and compounds	

(2) Dyes

Fur and Hair	Paraphenylendiamine
	Aniline Black
	Paramidophenol
Leather	Chrysoidine
	Bismarck Brown
	Nigrosine
	Amido-azo-toluene
	Amido-azo-benzene
Fabric	Crystal and Methyl Violet
	Malachite Green
	Auramine
	Metanil Yellow
	Brilliant Indigo, 4 G
	Erio Black
	Hydron Blue
	Indanthrene Violet, R.R.
	Ionamine, A.S.
	Pyrogene Violet Brown
	Orange Y
	Safranine
	Sulfanthrene Pink
	Rosaniline

(3) Photo Developers
- Metol
- Paraphenylendiamine
- Hydroquinone
- Para-amidophenol
- Pyrogallol
- Bichromates

(4) Rubber Accelerators and Antioxidants
- Hexamethylenetetramine
- Guanidines
- Mercaptobenzothiazole
- Tetramethylthiuram monosulfide and disulfide
- Paratoluidine
- Orthotoluidine
- Triethyl-trimethyl triamine
- Phenylbetanaphthylamine

(5) Soaps
- Containing excess of free alkali
- Containing perfumes
- Containing antiseptics

(6) Insecticides
- * Creosote
- Nicotine
- * Tar
- Pyrethrum
- * Mercury compounds
- * Phenol compounds
- * Petroleum distillates
- Arsenic compounds
- * Fluorides
- * Lime

(7) Cosmetics
Those containing irritant or photosensitizing dyes, essential oils, and perfumes.

(8) Oils
- Cutting oils
- Coning oils
- Sulfonated oils
- Linseed Oil
- Mustard oil
- Coconut oil
- Castor oil
- Cashew nut oil
- Tung oil

(9) Resins

Natural	*Synthetic*
Pine resin	Phenolformaldehyde
Wood resin	Ureaformaldehyde
Burgundy pitch	Chlorinated waxes
Japanese lacquer	Chloro-naphthalenes
Dammar	Chloro-benzols
Copal	Chloro-diphenyls
	Cumarone

(10) Coal Tar and Its Derivatives
- Acridine
- Anthracene
- Phenanthrene
- Carbazole
- Pyridine
- Fluorene

(11) Explosives
- Trinitrotoluol
- Tetranitro-methylaniline
- Fulminate of mercury
- Nitroglycerine
- Dinitrophenol
- Lead styphnate
- Ammonium nitrate
- Picric acid and picrates
- Sensol
- Dinitrotoluol
- Sodium nitrate
- Potassium nitrate

(* also primary irritants).

Acids. Cutaneous injuries from inorganic acids comprise about 3% of all occupational dermatoses occurring in the United States. While concentrated inorganic acids may inflict extensive ulcerations they are, in general, not as penetrating as alkalies.

Organic acids are not as penetrating as the inorganic, but their fumes may be irritating, especially acetic and formic acids; and carbolic acid may be absorbed through the skin causing severe nephritic damage. Oxalic acid may cause gangrene. In dilution it causes dryness and brittleness of the nails. Picric acid is absorbed and is capable, in dilution, of causing extensive contact dermatitis. It and its salts are used extensively in the therapy of burns. Allergization is not uncommon.

Alkalies. It is probable that alkalies constitute the most frequent cause of all occupational dermatitis since they are the chief ingredient of cleansing powders, detergents and soaps. The principal alkalies are compounds of sodium, potassium, calcium and ammonium. Only the soaps of sodium, potassium and ammonium are soluble in water.

Soaps. Soap is basically an alkaline salt of a fatty acid. All soap requires alkali and the usual ones used are sodium and potassium hydroxide. The fatty acids are derived from vegetable or animal fats, or a combination of both. Coconut oil, added to soaps, makes a profuse lather but at the same time renders them more irritating.

Liquid soaps are usually neutral coconut-oil soaps, containing varying amounts of sugar, glycerin or alcohol, and diluted with water. They are often irritating.

Soap powders consist of finely comminuted hard soap with added sodium or potassium carbonate and sodium silicate. Some powders, especially those recommended for bleaching purposes, contain trisodium phosphate and sodium hypochlorite. Abrasive soaps contain ground silica or pumice.

Dermatitis from detergents is one of the most common the dermatologist encounters. Besides soaps, in this group are included other cleansing agents such as abrasives (feldspar, silica, pumice), sodium carbonate, degreasing agents, (naphtha, gasoline, acetone, turpentine, alcohol, etc.) and oils (kerosene, machine and paraffin oil).

While Osborne considers fatty acids responsible for most cases of irritation by soaps, there are other ingredients which are capable of primary irritation or allergization. These are the alkalies liberated when the soap dissociates after solution in water, the degreasing action caused by emulsification of sebum, the perfume and perfume fixatives, or other ingredients added for their so-called medicinal effect (phenol, cresol, salicylic acid, tar, sulfur, bichloride of mercury, etc.).

Biologic Agents Causing or Complicating Industrial Dermatoses

Although one does not usually associate infections and infestations with occupational pursuits, such are not uncommon and are caused by many animal, vegetable and bacterial parasites.

These biologic agents are classified by Schwartz and Tulipan as follows:

(1) Bacterial Infections
- Infected occupational wounds
- Folliculitis, caused by staphylococci and streptococci
- Anthrax of hide handlers
- Glanders of cattle handlers
- Vaccinia of cattle handlers
- Impetigo of cattle handlers
- Erysipeloid of animal product handlers
- Verruca Necrogenica of cadaver handlers
- Butcher's Pemphigus

(2) Fungi
- Monilia (Kitchen workers)
- Yeast (Bakers and fruit handlers)
- Dermatophytes — Animal caretakers, Fur handlers, Hide handlers, Wool sorters, Barbers, Bath attendants
- Sporotrichosis, Blastomycosis — (Horticulturists)

(3) Parasites
- Ground Itch (Uncinariasis) — Miners, Farmers, Laborers
- Mange (Acarus Sarcoptes and Demodex) — Dog handlers

Grain Itch (Pediculoides)	Wheat handlers
	Straw handlers
	Linseed handlers
	Corn handlers
	Handlers of other grains

Carpoglyphus passularum (Dried fruit handlers)
Caterpillar dermatitis, caused by urticant hairs (Horticulturists)

Industrial Dermatitis

While systemic intoxication by industrial poisons is usually chronic, most of the cutaneous reactions encountered are acute in nature; or chronic, only in the sense that proliferative changes are produced from repeated acute attacks.

Predisposing factors, independent of the responsible contactant, are many and varied, often exerting an influence difficult to understand and determine. It is not sufficient to know what substance a worker handles; one must know what substances are present in his environment, what methods and materials are used for cleansing the skin, and the nature of his domestic contacts. Detergents are responsible for many instances of dermatitis of the hands, incorrectly attributed to industrial contactants.

There exist several other etiologic factors, not always appreciated, but nevertheless exerting considerable influence on the incidence of industrial dermatitis. These consist of the following:

Age. Both extremes of age as a rule are more susceptible to contact dermatitis. In the elderly this is due to dryness of the skin and senile atrophic changes in the epidermis. Although, because of child-labor laws, little data is available regarding occupational dermatoses in children, we do know that in England and in Germany during World War I, children were definitely more susceptible to trinitrotoluene. Aplastic anemia and purpura hemorrhagica from benzol is much more common in adolescents, and in menstruating girls and young pregnant women.

Another reason for the prevalence of dermatitis in younger workers is that they are careless and not experienced in methods of prevention.

The chronic eczematoid type of industrial dermatitis and malignancies developing in scars of old burns and in follicular keratoses are naturally more common in the middle-aged worker and beyond.

Race. As previously mentioned, the negroid skin is less prone to contact dermatitis than that of the Mongol or Caucasian. In the manufacture of dye intermediates, coal-tar dyes, and in those processes requiring the handling of aniline, paranitraniline, dinitrobenzene, nitrobenzene, etc., the negro can work with less danger of cutaneous irritation. Negroes also show a certain degree of resistance to the vesicant action of mustard gas. On the other hand, they are liable to develop keloids and areas of depigmentation following cuts, abrasions, burns and other cutaneous injuries. The Chinese and Japanese, because of their tendency to dry skin, are particularly prone to palmar and plantar keratoses, intertrigo, eczematous lesions, friction burns, etc.

Sex. Because of its tendency to greater dryness, statistics show the skin of women more susceptible than that of men, exclusive of their inherent tendency to notice minor irritations which a man might ignore. Schwartz and Tulipan believe that menstruation and gestation, because of an associated increase in perspiration, increase susceptibility.

Perspiration. Excessive sweating while acting to dilute many contactants, also serves as a solvent for many solid contactants, such as calcium oxide, sodium carbonate, sodium hydrate and others which become irritants when moist or in solution. Another action of perspiration is that, if excessive, it will macerate the epidermis, rendering the skin less resistant.

Excessive heat and humidity likewise increase cutaneous sensitivity, accelerate

the action of poisons and facilitate their absorption through the skin which is flushed and bathed in sweat.

Diet. There being no acute inflammatory dermatosis which is not influenced to some degree by foodstuffs and their metabolism, it is natural to suppose that dietary habits might exert some influence on susceptibility. Through their effect on perspiration, acidic diets tend to decrease cutaneous irritability. T. Saito has suggested the possibility of nonspecific desensitization by the rapid reversal of a disturbed acid-base equilibrium in the skin by means of diet.

The influence of alcohol on all industrial poisonings, although overemphasized is nevertheless important, particularly in contact dermatitis. Because of its tendency to flush the skin, it increases cutaneous irritability.

Of course a nourishing, well-balanced diet is essential for optimum efficiency. During World War I, the food blockade of Germany demonstrated conclusively that the lowering of nutritional standards results in a marked decrease in resistance to industrial poisons.

Individual Susceptibility. This rather ambiguous expression includes, besides hereditary neurovascular disturbances, skin types, idiosyncrasies, atopies, allergies, temperament variations and certain other factors concerning which we are totally ignorant.

There is probably no problem as troubling to the industrial physician as this variation in individual susceptibility. Suppose he initially surveys a group of employees, all of whom will be assigned identical tasks and exposed to identical contactants. Some of them will develop a dermatitis. Which ones and why, he cannot foretell. It is especially difficult to explain this to employers, as they argue that what is safe for one is safe for all, and what is dangerous for one should be dangerous to all. We know, however, that in epidemics of infectious diseases, although all members of a given community may be equally exposed, a large proportion do not become ill. Sometimes, in determining the causal relationship of a dermatitis, the examiner denies its industrial nature because no other employees exposed to identical contactants are affected, totally disregarding the possibility of an inherent individual susceptibility.

The Diagnosis of Industrial Dermatitis

For obvious reasons early recognition of a dermatitis of occupational origin is essential. In some instances the relationship is quite obvious; in others it is extremely difficult to determine.

The following criteria comprise the fundamental requisites for differentiation of occupational from non-occupational dermatitis as defined by the Committee of Industrial Dermatoses of the Section on Dermatology and Syphilology of the American Medical Association.

(1) The dermatologic diagnosis is a dermatosis in which the role of an occupational causal factor (major or contributory) has at some previous time been established beyond reasonable doubt.

(2) The individual has been working in contact with an agent known to have produced similar changes in the skin.

(3) The time relationship between exposure to the agent and the onset of the dermatitis is correct for that particular agent and that particular abnormality of the skin.

(4) The site of the onset of the skin disease is the site of maximum exposure.

(5) The lesions present are consistent with those known to have followed the reputed exposure or trauma.

(6) The individual is employed in an occupation in which similar cases have previously occurred.

(7) Some of the individual's fellow workers using the same agent are known by the examiner to have similar manifestations due to the same cause.

(8) So far as the examiner can ascertain there has been no exposure outside occupation which could be implicated.

(9) If the diagnosis is dermatitis, the following items are important:—

(a) The evidence of previous attacks, coming after exposure to an agent followed by improvement and clearing after cessation of exposure, constitutes most convincing evidence of the occupational factor as a cause.

(b) The results of patch tests performed and interpreted by competent dermatologists corroborate the findings of the history and examination in the majority of cases.

Industrial Dermatoses Other Than Contact Dermatitis

The most frequent manifestations on the skin of occupational disease other than contact dermatitis and those dermatoses due to biologic agents are:

Burns: acid and alkali burns, molten metals, resins, rosins, pitch; hot water, fats and oils; steam, hot air, flash burns, fire and explosions. Electric and acute actinic-ray burns may also be included here.

Callosities: basket makers, cloth cutters, leather stakers, metal burnishers, engravers, carpenters, painters, shoemakers and stagehands.

Chilblains: ivory cutters, woodcutters, soldiers, gardeners, farmers, road workers, night watchmen, policemen, linemen, etc.

Epithelioma (Carcinoma): post-cicatricial, shoemakers, farmers, sailors, fishermen, radium workers, x-ray technicians, mesothorium and uranium workers, chimney sweeps, arsenic workers, petroleum and aniline workers, mule spinners and workers with coal tar. While crude coal tar is capable of causing folliculitis and because of its keratoplastic action may cause follicular keratoses, only the products of distillation are primarily carcinogenic. These include 3, 4-benzopyrene; 1,2,5,6-dibenzanthracene; methylcholanthrene and pyridine. Other carcinogenic substances are arsenic, chromates, nickel carbonyl, asbestos, creosote, benzidine and naphthylamine.

Keloids: post-traumatic, heat and severe sunburns, acid burns. Negroes are particularly susceptible.

Keratoses: paraffin, wax, pitch and arsenic workers. Workers with lampblack, animal charcoal and boneblack. Graphite miners and coal-tar workers.

Radiodermatitis: physicians, x-ray technicians, radium handlers, etc.

Tattoos: coal miners, stone cutters, silver, steel and gunpowder industries.

Lupus erythematosus: sunburn, heat, smelters.

Angiokeratoma: follows chilblains.

Depigmentation: post-dermatitic. Edward A. Oliver *et al.* reported on the development of leukoderma in 20 men employed at a tannery from wearing a heavy gauntlet type of rubber glove. Investigation showed the antioxidant, which was the monobenzyl ether of hydroquinone, to be the causative agent. There was no effect on the general health of the individuals and biopsies showed no cutaneous changes except depigmentation, the dopa reaction being negative in the vitiliginous areas and positive in those in which pigmentation had returned to normal. Repigmentation occurred after discontinuance of contact with the gloves containing this antioxidant. Other antioxidants are without this toxic effect. The action of the methyl ether of hydroquinone on cutaneous pigment formation is obscure, but it apparently prevents formation of melanin by exerting some effect on one of the intermediate products between tyrosine and mature melanin, perhaps inhibiting a catalyst.

Folliculitis: the most common cause of folliculitis is contact with cutting oils, their compounds, and lubricants, all of which are used by machinists and metal-workers. Cutting oils are of two general types,—the soluble and the insoluble. The former usually consists of a mixture of sulfonated oils, soap oils and phenolated

amines, diluted with water; the latter, of various animal, vegetable and mineral oils. The addition of chlorine or sulfur to vegetable and animal oils is thought by some to strengthen the film and to increase the lubrication value. This sulfur and chlorine, (the latter ranging from 0.15 to 7.0 per cent by weight) was formerly considered responsible for the follicle-irritating properties of the insoluble oils containing them, although the cause may be the inhibitors (phenolic amines) or some other unidentified substance. The folliculitis is definitely not due to infection contracted from the oils, as the insoluble type, which is responsible for most cases, is always sterile; and while the soluble type may occasionally be contaminated, it rarely causes folliculitis. The addition of various antiseptics and sterilization by heat have not succeeded in cutting the incidence of either folliculitis or dermatitis from cutting oils; in fact, in some instances it seems to have augmented the frequency of dermatitis.

Workers handling oils, greases, pitch, tars, chlorinated hydrocarbons, sugar and hypertonic salt solutions may also develop conditions varying from a mild folliculitis to nodules. These are located on the face and extensor surfaces of the forearms and thighs, although in severe cases they may be more extensively distributed. Paraffin pressmen develop large follicular keratoses on the forearms and hands which may become malignant. These are due to the mechanical irritation of the wax which becomes imbedded in the ostia of the pilosebaceous follicles and even in the sweat ducts. The lesions of "oil acne" are invariably sterile.

Another important source of chloro-compounds causing folliculitis is the manufacture of various dielectrics used for insulation of wires, cables and electrical apparatus. It is also observed in those workers handling the finished materials, especially insulated cables ("cable rash"). The substances responsible are the solid or highly viscous chlorinated hydrocarbons, *i.e.,* dichloroethylene, trichloroethylene, perchloroethylene, tetrachloroethane, monochlorobenzene, dichlorobenzene, trichloronaphthalene, chlorodiphenoloxide and other chlorinated waxes. The commercial preparation known as "Halowax" consists generally of a mixture of chloronaphthalenes and chlorodiphenyls. Its role in production of folliculitis was first described in this country by Schwartz, who observed the folliculitis in shipyards in those workers who were exposed in close quarters, for long periods, to cables coated with halowax as an insulating material, and which on drying, flaked off and adhered to the worker's skin and clothing.

The designation of the folliculitis following exposure to these chlorinated hydrocarbons as "chloracne" is unfortunate since there is no evidence that chlorine is responsible; and furthermore chlorine, phenol, diphenyl, naphthalene and benzene do not themselves cause acneform eruptions. Basically the lesions resemble those following plugging of the follicles with simple paraffin waxes, and consist of foreign-body reactions. Peck found the content of these lesions to be invariably sterile.

Cable rash or chloracne is not uncommon and must be differentiated from ordinary acne vulgaris. It differs from the latter in several respects; first, it occurs at any age and is dependent upon exposure, whereas acne vulgaris is generally confined to puberty. While the skin in acne vulgaris is usually oily, in chloracne it is invariably dry. Secondly, the lesions of the latter develop around a hair follicle and not necessarily around a pilosebaceous gland; thirdly, while occurring on the face, chloracne as previously noted, is more common on the extremities. Lastly, the plugging of the glandular orifices, *i.e.,* the comedos, are more keratotic than in acne vulgaris. These in turn cause large cysts, especially on the face and ears, on the nape of the neck, shoulders, abdomen and thighs.

The acneform lesions caused by coal tar, pitch and vegetable tars may be distinguished from the chloracnes by the presence of a greater number of comedos and the absence of cysts.

Prevention of all these folliculoses is simple and consists in *cleanliness,* both

of skin and clothing. The former should be cleansed with one of the sulfonated oils, sulfoacetates, or aliphatic alcohols containing one of the surface-active or synthetic wetting agents.

Prevention of Industrial Dermatoses

The task of prevention is a problem for the industrial engineer; the physician acting as consultant and adviser, assisted by the Dermatoses Investigation Section of the United States Public Health Service and auxiliary services provided by the individual States.

The first requisite is selection of the proper personnel for employment depending upon the nature of the work and the contactants to which the employee is likely to be exposed. State legislatures should enact such laws as insure appropriate preplacement physical examinations and enable the removal of an employee from a job, unsuitable for him from a health standpoint.

Patch tests are almost valueless as part of a preemployment examination. However, the individual with a dry, ichthyotic skin should be excluded from occupations where he is exposed to fat solvents and degreasers. Likewise, blonds should not be exposed to photosensitizing contactants. Patients with a previous history of various allergies, hay fever, asthma, eczema, etc. should receive a particularly detailed investigation.

All personnel should receive appropriate instruction regarding the particular hazards to which they are exposed and given detailed directions as to protection, and prevention of personal injury. Frequent inspections by foremen or safety engineers should be encouraged. Furthermore, all nonoccupational skin diseases should be regarded as potential hazards and treatment recommended. Patients with sycosis vulgaris, severe acne or ostiofolliculitis are potential subjects for furunculosis if employed handling greases, oils, chlorophenyl compounds and chlorinated hydrocarbons. Seborrheic eczema frequently precedes the development of industrial contact dermatitis. Fungous infections of the feet are undoubtedly the most important predisposing factor sensitizing the entire integument to contactants.

The prevention of sensitization dermatitis is sometimes complicated as it is not uncommon for a simple dermatitis due to a primary irritant, if neglected, to eventuate in one of this type, offering a serious economic problem as well as a medical one. Furthermore, the worker, following a monovalent contact dermatitis, may occasionally develop polysensitivity, reacting to many contactants, found not only at his place of employment but also in his home.

Osborne and Jordon in outlining the prevention of this type of dermatitis have designated four phases, *viz.*:

(1) The proper selection of workers.
(2) The elimination of unnecesssary hazards.
(3) Prevention of exposure to sensitizing substances.
    (a) Use of closed methods of manufacture.
    (b) Employment of suitable exhaust hoods.
    (c) Proper general plant ventilation.
    (d) General plant cleanliness.
    (e) Proper workclothing.
    (f) Proper cleansing facilities.
    (g) Instruction to workers regarding the dangers of their occupation.
(4) Early recognition of sensitization dermatitis.

Besides those protective measures which are the responsibility of the sanitary engineer, such as adequate ventilation, light, heat, mechanical protective devices, etc., certain other measures of a more personal nature are useful in preventing contact dermatitis.

Most industrial physicians are opposed to gloves as a protection since they make the hands sweat, the skin soft and macerated, in excellent condition for contact dermatitis following a rip or tear in the glove, which when saturated with sweat acts as a poultice of poison encasing the hand. Furthermore, gloves often constitute a potential machinery hazard having been responsible for many mutilating injuries following their accidental entrapment in moving machine parts. Protective clothing, headshields, goggles, respirators and other devices are also effective in reducing the incidence of injury.

Protective creams and ointments offer a partial solution to the problem. Unfortunately they rub off easily, are difficult to keep on when handling fluid substances, and are of questionable value if exposures are massive or continuous, or the contactants very irritating. In order to be effective, a protective application must be appropriate for the contactant which it is supposed to protect against. For instance, greasy or oily substances such as lanolin and castor oil would be appropriate as a protective application against industrial organic solvents and degreasing agents. Conversely a cream containing boric acid, aluminum acetate or sodium hexametaphosphate would counteract the irritating effects following exposure to alkalies that macerate the epidermis.

Louis Schwartz has recently reviewed the problem of protective applications, describing the following six classes:

(1) A simple vanishing cream which, when rubbed into the skin, fills the pores with soap and facilitates the removal of dirt when washing after work: Stearic acid 20, sodium carbonate 2, glycerin 6, water 78.

(2) Ointments, emulsions or solutions of "invisible glove" type, either water-soluble or water-insoluble, that leave a thin protective film of resin or wax on the skin. Because of the tendency of perspiration to loosen or remove the water soluble type, fats or oils may be added. The water-insoluble resins or waxes require a solvent for application and a special cleanser for removal, either of which may irritate the skin after frequent use. Possible irritant effect may be minimized by the application of a hydrous wool fat cream after work. This type of protection may be used on the face, especially when masks or respirators are worn. A: Acacia 5, tragacanth 5, borax 2, water 88 (water-soluble glove). B: Gum benzoin 5, beeswax 2, anhydrous wool fat 5, ethyl alcohol 88 (water-insoluble glove).

(3) Ointments that fill the pores with a harmless fat protect against water-soluble irritants and petroleum oils and to some extent against greases; anhydrous wool fat 70, castor oil 30, with sufficient perfume. To facilitate the removal of this type of protective ointment, wetting agents may be added.

(4) Protective ointments containing nonirritant chemicals to neutralize industrial irritants. Boric and benzoic acids are recommended to neutralize industrial alkalies and soaps; magnesium hydroxide to neutralize industrial acids; and nonirritant oxidizers such as dichloramine T to detoxify vesicant gases; magnesium carbonate 5, talc 5, soap 30, hydrous wool fat 30, castor oil 28, Duponol 2, with sufficient perfume.

(5) Protective ointments which permit inert powders to adhere to the skin and thus form a protective covering. This type of protection is recommended for exposure to allergenic substances such as the chemicals used in the manufacture of explosives, and for protection against mechanical irritation of abrasives, particles of steel and glass and so on: Zinc oxide 5, talc 5, iron oxide 1, Irish moss 2, gum benzoin 2, water 10, alcohol 15, vanishing cream 60.

(6) Protective applications against photosensitizing agents such as the heavy coal-tar and oil distillates: hydrous wool fat 58, castor oil 30, titanium dioxide 5, menthyl salicylate 5, Duponol 2, with sufficient perfume.

Cleansing Agents

Inefficient cleansing of the skin and the use of improper detergents are responsible for many instances of industrial dermatitis. The importance of this procedure is seldom appreciated and understood by many workers. Frequently the dermatitis suffered by him is due not to industrial contactants but rather the detergents used for their removal. Painters remove paint with turpentine; machinists use gasoline; printers, kerosene; others, strongly alkaline soaps, soap powders, pumice, etc.

Schwartz feels that "a normal industrial cleanser for general use should consist of a superfatted neutral toilet soap, containing a wetting agent or synthetic detergent. It should contain a minimum of free alkali and have a pH of 10 or less, in 1 per cent solution. It should not contain silica, quartz, pumice, feldspar, rosin fillers nor organic solvents." The following soap is recommended by the Committee on Industrial Dermatoses; neutral toilet soap 30, bentonite 30, Santomerse 10, hydrous wool fat 5, perfume 1.

The specific industrial hazards to which the skin is exposed in the more common occupations and their prevention are listed by Schwartz as follows:

Occupation	Hazard	Prevention
Abattoirs and butchers	Anthrax, glanders, actinomycosis, dermatomycosis, erysipeloid, pemphigus, verruca necrogenica, hog itch (ascaris).	Long rubber gauntlets. Covering of all breaks in the skin to prevent infection. Immediate disinfection of all cuts and abrasions and covering to prevent infection. No scratching of any part of face or body before disinfecting hands and part to be scratched.
Actors	Dermatitis from cosmetics.	Use of cosmetics containing nonsensitizing perfumes and dyes.
Agricultural workers	Anthrax, glanders, actinomycosis, sporotrichosis, blastomycosis, poisonous plants, sunlight causing melanosis and epithelial proliferation, parasites from grain, uncinariasis, cowpox, ("orf").	Disinfection of all cuts and abrasions as soon as received. Wearing of gloves or avoid known poisonous plants. Wearing of protection against sunlight glare.
Asphalt and pitch workers	Acne, comedones, photosensitivity, epithelioma, melanosis.	Protective clothing. Cleanliness of body and clothes. Protective ointment containing lightblocking chemicals to be applied on face. Proper exhaust ventilation over fumes and dusty processes.
Bakers	Flour, persulphates, acid phosphates, bleaches, cinnamon, flour parasites.	Cleanliness and wearing of rubber gloves.
Brewers	Yeasts, hops.	Cleanliness and wearing of rubber gloves.
Building trades	Sun, lime, cement, paint.	Cleanliness. Daily change of work clothes. Wearing of rubber gloves and dust-proof coveralls. Rubbing lanolin into hands after work.
Button makers	Dust, erysipeloid from bone, boils.	Cleanliness. Disinfect all cuts and scratches.
Cabinet makers and carpenters	Volatile solvents in shellac, lacquer; resins in shellac, lacquer, poisonous woods, glue.	Cleanliness. Wearing rubber gloves. Protective clothing.

Occupation	Hazard	Prevention
Canning and food preserving	Paronychia from fruit juices, sugar, mycotic infections, essential oils, tomatoes, citrus fruit, asparagus, acid juices.	Cleanliness. Wearing rubber gloves. Rubbing lanolin into hands after work. Impervious sleeves and aprons.
Celluloid workers	Solvents, pigments, dyes.	Impervious sleeves and aprons. Cleanliness. Wearing rubber gloves. Rubbing lanolin into hands after work. Exhaust ventilation over processes where fumes are given off.
Cement makers (building)	Dust, lime, silica.	Cleanliness. Dust-proof work clothes changed daily. Respirators.
Confectioners and pastry makers	Essential oils, fruit juices, sugar, vanilla, paronychia.	Cleanliness. Wearing rubber gloves.
Dyeing	Soaps, bleaches, alkaline dye liquors, acid dye liquors, aniline dyes, chromates, solvents.	Cleanliness. Wearing rubber gloves, boots and aprons.
Dye manufacture	Intermediates, especially the nitro compounds, hypersensitivity to finished dyes; alkalis; acids.	Cleanliness. Exhaust hoods over dusty fume evolving processes. Protective clothing in the form of impervious gloves, sleeves, aprons and boots. Totally enclosed manufacturing processes.
Electroplating	Solvents and alkalis used in degreasing; acids used in "pickling"; vapors coming off bath which may contain cyanides; chromic acid; nickel sulphate and salts of other metals.	Cleanliness. Rubber gloves, boots, impervious sleeves and aprons. Vaseline in nostrils. Protective ointment on face. Exhaust ventilation of tanks. Lanolin rubbed into hands after work.
Explosive manufacture	Tetryl, TNT, fulminate of mercury, DNT.	Impervious sleeves, aprons and gloves. Protective ointments. Daily change of work clothes, cleanliness.
Felt hat making	Acid and mercuric nitrate solutions used in "starting." Acid and alkali in sizing solutions. Bichromates used in dyeing. Mercury irritants and alkalis used in carroting fur.	Cleanliness. Rubber gloves and boots. Impervious sleeves and aprons over wet processes.
Fertilizer manufacture	Nitrates, calcium cyanamide, fluorides, bone dust, solvents used for fat extraction from animal refuse.	Cleanliness. Daily change of dustproof work clothes. Respirators.
Fishermen	Sun, tar on fish lines, erysipeloid, salt, poisonous fish.	Protection from sunlight. Gloves when handling tarred lines. Disinfection of all cuts and scratches.
Flour mill workers	Parasites of grain; dust; flour bleaches and conditioners.	Cleanliness. Dustproof clothing.
Fur workers	Loss of nails from "fleshing," dermatitis from salts, arsenic and lime used to preserve the hides, alkaline degreasers, mordants such as chromates, alum, lactic acid, formaldehyde, dyes, aniline, paraphenylenediamine, dander, mycosis.	Cleanliness. Wearing of rubber gloves, aprons, boots.

Occupation	Hazard	Prevention
Garage workers	Gasoline. Oil and grease folliculitis.	Impervious sleeves and aprons. Cleanliness. Daily change of work clothes.
Gardeners	Fertilizers, insecticides, poisonous plants, mycosis, sun, uncinariasis, creeping eruption.	Cleanliness. Protection against sunlight. Gloves.
Glass manufacture	Soda ash, lime, arsenic, hydrofluoric acid used for etching. Lesions of lip from blow pipe.	Cleanliness. Daily change of dustproof work clothes. Respirators. Rubber gloves for etchers.
Hairdressers	Mycosis, hair dyes, alkalis used for permanent waving, tonics, perfumes, cosmetics.	Rubber gloves. Cleanliness. Lanolin rubbed into hands after work.
Iron and steel workers	Heat telangiectases; lime; alumina; chromium; pickling acids; drawing compounds like soaps, greases; lubricant oils; nitric fumes and cyanide fumes in tempering; volatile solvents used as degreasers of metal parts.	Cleanliness. Daily change of work clothes. Canvas or leather gloves for handling of steel. Rubber gloves for degreasers and picklers.
Laundry workers	Soaps, alkali cleaners, bleachers, dirty clothes.	Rubber gloves. Lanolin rubbed into hands after work.
Leather manufacturers	Lime; salt; acid and arsenic used to preserve hides; unhairers such as lime, arsenic and sulphides; tanning agents such as sumac, oak, synthetic tannins and bichromates; leather dyes, anthrax.	Cleanliness. Daily change of work clothes. Rubber gloves, aprons and boots. Immediate disinfection of all cuts and abrasions.
Machinists	Folliculitis from oils and greasers, dermatitis from acids, alkalis, cutting compounds and solvents.	Impervious sleeves and aprons. Cleanliness. Daily change of work clothes. Protective ointments.
Match manufacturers	Phosphorus sequisulphide, glue, paraffin, chrome salts.	Cleanliness. Exhaust ventilation over processes evolving fumes and dust.
Miners	Uncinariasis, bacterial infections, furunculosis.	Cleanliness.
Painters	Volatile solvents; dyes; chrome pigments; resins; lime; paint removers; anti-fouling compounds such as arsenic, tar, creosote, zinc chloride.	Impervious sleeves and aprons. Cleanliness. Daily change of work clothes. Rubber gloves when using volatile solvents and irritant chemicals.
Paper manufacturers	Alkalis used in digesting wood pulp and rags, bleaches, dust from sorting old rags.	Cleanliness.
Perfume manufacturers	Essential oils, solvents.	Cleanliness. Rubber gloves.
Petroleum refining	Acne; keratosis; epithelioma and melanosis from crude petroleum, paraffin, and petroleum residue; dermatitis from volatile petroleum distillates.	Cleanliness. Daily change of work clothes.

Occupation	Hazard	Prevention
Photo-engraving and lithographing	Bichromates, dyes, solvents, photo-developers, silver salts, acids, cyanides.	Cleanliness. Rubber gloves when handling bichromates, acids, solvents, etc.
Photographers	Developers, metol, pyrogallol, hydroquinone, platinum salts, bichromates, alkalis, silver salts, mercuric iodide.	Cleanliness. Rubber gloves.
Pitch workers	Photosensitization, melanosis, acne, folliculitis, cancer, tumors.	Cleanliness. Daily change of work clothes. Protective ointment on face to protect from photosensitivity.
Polishing	Abrasives, cyanides, solvents, lime.	Cleanliness. Rubber gloves when using solvents and irritant solutions. Daily change of work clothes.
Printing	Solvents, inks, dyes, alkalis, chromates.	Impervious sleeves and aprons. Cleanliness. Rubber gloves. Daily change of work clothes.
Radium and x-ray technicians	Dermatitis, ulceration, cancer.	Protection against radiation. Semi-annual blood examination.
Rayon manufacturers	*Viscose Process:* Alkalis (NaOH), sulphuric acid, bleaches, formaldehyde (preserving wet cellulose caps), carbon bisulphide, coning oils. *Cellulose Acetate Process:* Acetic acid, solvents. *Cellulose Nitrate Process:* Nitric acid, sulphuric acid, solvents.	Cleanliness. Rubber gloves.
Resin manufacturers	*Phenol Formaldehyde Type:* Formaldehyde, hexamethylene tetramine, phenol, cresol, dyes, dust. *Urea Formaldehyde Type:* Formaldehyde, hexamethylene tetramine, dyes.	Cleanliness. Daily change of work clothes. Impervious sleeves and aprons.
Restaurant workers	Soaps, alkalis, plants, vegetables, erysipeloid, mycosis.	Rubber gloves. Lanolin rubbed into hands after work.
Road workers	Dust, tar, sun, asphalt, plants.	Cleanliness. Protection against sunlight.
Rubber manufacturer	Accelerators, antioxidants, wild rubber, volatile solvents, alkalis (reclaiming rubber).	Cleanliness. Daily change of dustproof work clothes for dusty occupations.
Seamen	Sun, alkali and abrasive scrubbing compounds, tar used in caulking and on ropes, oil and grease in engine rooms.	Cleanliness. Protection against sunlight. Daily change of work clothes for engine room workers.
Shoemakers	Hides, leather, chromates, dyes, solvents, glues.	Cleanliness. Daily change of work clothes.
Silk workers	Hair of silkworm found in wild silk; hot water used to soften cocoons; alkalis and soaps used in silk throwing; acids used in weighting silk; dyes; mechanical injuries to skin on fingers and hands of reelers and winders.	Rubber gloves. Lanolin rubbed into hands after work.

Occupation	Hazard	Prevention
Soap manufacturers	Alkalis, sodium hidroxide, trisodium phosphate, sodium silicate, olive oil "foots," perfume, antiseptics.	Cleanliness. Rubber gloves.
Solderers	Acids, zinc chloride.	Cleanliness. Immediate washing off of acid splashes.
Sugar refining	Ulcers, boils, dermatoses from hot molasses and sugar, mycosis, paronychia, mechanical irritation of skin by sugar crystals.	Cleanliness. Canvas gloves in handling dry sugar. Daily change of work clothes.
Tobacco workers	Dust, fermented tobacco, tobacco juice, glue used on cigar wrappers, stems of tobacco leaves on stemmers, flavoring agents like vanilla.	Cleanliness. Elimination of hand work.
Varnishers and lacquers	Japanese lacquer, rosin, synthetic resins, solvents, dyes.	Cleanliness. Daily change of work clothes. Rubber gloves.
Wax (synthetic) makers	Chlorinated paraffin, chlorinated ceresin, chloro-naphthalene, chloro-benzol, chloro-diphenyls.	Cleanliness. Daily change of work clothes. Exhaust ventilation. Totally enclosed manufacturing processes.
Welders	Melanosis from ultra-violet rays of arc; zinc chloride.	Metal masks with deeply tinted glass over eyes. Rubber gloves.

Conclusion

The brevity of this consideration on the technological hazards to which the skin of man is exposed is no indication of the importance of this subject from a social and economic standpoint. While treatment of industrial dermatoses does not differ essentially from that of dermatoses of other origin, their recognition and prevention is yearly assuming ever greater significance. The physician to the military realizes that the health of the troops is his problem and that as commanding officer of the military hospital he controls the activities of all patients, even those of superior rank. In like fashion must the industrial physician appreciate that his interest is in the health of the worker, his duty to the producer and not to the product nor the owner. He must ever be alert lest he sacrifice necessary safety measures, because of excessive cost or for some other economic reason. Alice Hamilton has succinctly said, "His [the physician's] task is to safeguard the health of the patients who are entrusted to him, often without any volition of their own. The successful production of goods is outside his field. To the physician always, life is more than meat and the body than raiment."

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Solid/Liquid Separations

J. V. N. Dorr, D.Sc. and Franklin P. Lasseter, Ph.D.

The Dorr Company, New York, N. Y.

Introduction

Solid-liquid separations may involve three relatively distinct steps: (1) destabilization, (2) aggregation, and (3) separation.

Some suspensions, as formed, are naturally in a separable condition; the first two steps require only secondary consideration. Others may be sufficiently unstable but may still require special treatment to render the phases separable. Still other suspensions may be of such a nature that aggregation takes place almost instantaneously following destabilization. Separation takes place as a result of destabilization and aggregation, but it is consequent upon the fact that larger particles move through a suspending medium more rapidly than smaller particles according to Stokes' law.

These steps are concerned with systems that separate into two products, a satisfactorily clear liquid and a sludge. This discussion excludes both classification and filtration.

Technical discussions of destabilization and aggregation generally designate the combination of these steps as "flocculation." Each step performs a separate but necessary function; however, flocculation is here interpreted in the usual way.

The first step involves the addition of a suitable reagent. This functions to remove or render negligible the stabilizing forces so that the particles will coalesce upon contact. The aggregation step promotes the grouping of the separate particles and originally small flocs into clumps having sufficient diameter to settle at an economic rate.

Fundamental Considerations

Separation processes utilizing the steps involved in flocculation constitute highly important technical applications of the fundamental concepts evolved to explain the behavior of colloidal substances. Although these applications are by no means confined to true colloidal suspensions, it is believed that a resume of pertinent colloidal phenomena should be included in this discussion.

Colloids are divided into two major classes which may be differentiated by their sensitivity to the action of electrolytes. Various terms have been coined for each class, and these are defined by Hauser.[1] Since separation processes deal, in the majority of cases, with suspensions of solids in water, only the terms "hydrophobic" and "hydrophilic" will be employed. Hydrophobic sols are non-hydrated and are very sensitive to electrolytes, while the reverse is true of hydrophilic sols. However, when the latter are dehydrated they behave as hydrophobic colloids.

The most generally accepted explanation for the behavior of hydrophobic colloids is based on the concept of an electric double-layer theory by Helmholtz [2] and later modifications of this theory by Gouy [3] and Stern.[4] The dispersed particle is conceived as having charge-carrying adsorbed ions distributed at its surface, constituting the inner layer of the particle configuration. The counter ions are conceived

as distributed over a depth of several monomolecular layers, diffusing to a point where the mean electric charge is zero. This diffuse layer of the counter ions constitutes the outer layer of the particle configuration. The adsorbed ions determine the nature of the charge on the particle; in most cases they are negative.

Other concepts have been suggested to explain the behavior of hydrophobic colloids, but no attempt is made to present them. Hauser [1] suggests that the double-layer theory permits the development of the charge by simple adsorption or chemical reaction. A reasonable explanation for economic applications of flocculation can be based on this interpretation of the phenomena.

Hydrophobic sols are most sensitive to destabilization by ions carrying a charge opposite that of the suspended particle, the activity of the ion increasing markedly with its valence. Linder and Picton,[5] Schulze,[6] Hardy [7] and others studied the role of valence in flocculation. They found that as the valence of the flocculating ion increases from 1 to 2 to 3 the flocculating power of the ion increases very roughly as 1:100:1000. There are many exceptions to this rule. Freundlich [8] explained the increased flocculating power of the higher valence ions on the basis of the adsorption isotherm. The rough valency rule developed from these classical investigations is of practical value as a guide in choosing the type of coagulant for a given application.

Another factor of importance is the relation of the destabilizing power of electrolyte to the concentration of the stable sol. Kruyt [9] illustrates the variation in the flocculating power of mono-, di- and tri-valent ions on an arsenic trisulfide sol at varying concentrations. Generally, the coagulating power of a monovalent ion decreases with sol dilution, and that of a trivalent ion increases with dilution. The divalent ion is intermediate between the two, and is substantially independent of sol dilution. There are exceptions to this, but the trend is of practical value to the solution of separation problems.

Classical investigations have dealt with flocculation phenomena primarily as they are related to the isoelectric point, or the point of electrical neutrality. However, two zones of coagulation have been defined.[10] A suspension of particles at the isoelectric point is in the zone of rapid coagulation where each collision between particles results in coalescence. A zone of slow coagulation exists in the range between the isoelectric point and the critical potential at which the particle charge is just sufficient to prevent coalescence. A reduction in potential below the critical permits flocculation, the rate of the latter depending upon the extent of this reduction and the probability of collision. The existence of such a zone is of very considerable technical importance, and almost all economic applications of flocculation are conducted under slow coagulating conditions. Very few of such applications depend entirely upon the factor of isoelectric point adjustment.

The flocculation of dilute suspensions and others carrying relatively large individual particles is best accomplished by subjecting them to the enveloping action of a gel-like substance. This enveloping action supplements the attracting forces between partially or totally discharged particles and increases the probability of coalescence upon collision. Aluminum salts, so widely employed in practice, combine these factors. The application of aluminum sulfate, for example, to the flocculation of suspensions is usually conducted within a pH range permitting the precipitation of aluminum hydrate, but without regard to the isoelectric point of the suspended solids.

Three functions are performed by the salt upon addition to a dispersed suspension: (1) the dissolved aluminum ions reduce the surface charges sufficiently to permit flocculation of the particles; (2) the aluminum hydrate precipitate formed may carry a positive potential and neutralize some of the negatively charged particles, resulting in mutual coagulation; (3) the gel-like precipitate envelops and cements the particles together into clumps. The first and third functions are the predominant factors controlling coalescence. Their relative importance probably depends respectively upon whether the particle charge is nearly completely destroyed or just reduced to a

value permitting some coalescence upon contact. The adjustment of pH is necessarily a part of the first function.

In general, the principles and practice involved in the flocculation of suspended particles by aluminum salts apply in the use of ferric salts.

The development of organic flocculants, or organic substances as aids to flocculation, has resulted in the extension of the envelopment principle to the treatment of a variety of materials. Perhaps the most important of these developments is the use of starch in the flocculation of coal slurries. The Henry process[11] originated the use of starch in the flocculation and clarification of slurries at Belgian coal preparation plants. Similar processes were developed in England. Various factors relating to the principles and application of starch flocculation were studied by Raybold,[12] Samuel,[13] Wilkins,[14] Needham,[15] Holmes,[16] Tomalin.[17]

Assuming a clear liquor is desired, the flocculation of a slurry utilizing starch takes place in two stages. The first stage is the destabilization of the inorganic colloidal component of the slurry, principally clay, and it should be pointed out that the starch reagent has little or no effect on this material in its stable state. The flocculation of the inorganic colloidal component follows the previously outlined mechanism of potential reduction with small quantities of a suitable inorganic reagent. The second stage is that performed by the specially prepared starch reagent in assisting the collection of the small flocs and relatively large coal particles into quite stable clumps. The starch gel is apparently adsorbed as a coherent film on the coal particles. Details for preparing these starch reagents are given by Gardner and Ray.[18] Gelatin and glue may be employed to assist the flocculation of coal slurries, but these have not been used as extensively as the starch.

This enveloping tendency of starches and glues offers some very interesting possibilities in the flocculation and separation of suspended solids in unusual environments. A few examples will suffice. Caustic starch and "Tufjel" are used to flocculate $Mg(OH)_2$ in brine solution. Glue is employed to flocculate the suspended material in strong liquors of aluminum sulfate. The effectiveness of glue in this case probably has some relation to its isoelectric point at a pH of about 4.5. Dry blood and blood albumin have been used in place of glue for the above. "Tin" paste suspended in a 10 per cent solution of sulfuric acid has been flocculated by adding glue. These are interesting applications of a material which ordinarily would be expected to render a suspension more stable.

The use of sodium aluminate in flocculation practice is discussed by Coxe[19] and Evans.[20] Advantages claimed for the salt are a faster settling floc, less causticity and a reduction in after-precipitation. Jackson and Turner[21] review the investigations dealing with sodium aluminate flocculation in water treatment. They list a selected bibliography on the general subject of water purification.

Baylis[22] has obtained some very interesting results using, as an aid to coagulation, a specially prepared solution of sodium silicate. In alum flocculation of water the proper use of the silicate solution developed "enormous" aggregates which settled very rapidly. The material broadens the pH range over which good alum flocculation may be obtained. The mechanism of this aid to flocculation may probably be developed on the basis of the enveloping action suggested for starch and alum.

In the processing of hydrophilic colloids the predominant factor governing the treatment to be applied is the degree of hydration of the suspended substance. The addition of small quantities of a coagulating electrolyte has little or no effect on the stability of such hydrated systems. This class of colloids is, however, least stable at the isoelectric point. The stability is a function both of electric charge and hydration. To be effective, the flocculating electrolytes must serve to dehydrate the suspended material and also to adjust the charge to a point permitting coalescence upon contact. As previously pointed out, after dehydration a hydrophilic substance will respond

to treatment as a hydrophobic colloid. Neutralized hydrophilic substances will flocculate immediately after dehydration.

Relatively concentrated suspensions may be flocculated quite readily by isoelectric point adjustment alone, and the processing of certain metallurgical slimes appears to constitute an example of this practice. Williams [23] found that cyanide slimes respond more readily to treatment at a given lime content than at higher or lower concentrations of the reagent. Free [24] states that there are no specific gelatinous colloidal substances in ore slimes. The colloidal properties of slimes are explained as due to the normal behavior of finely divided minerals in suspension in water. Ralston [25] concludes that the valency rule applies in the flocculation of slimes by electrolytes.

Generally, when suspended solids in a flocculant condition are sufficiently concentrated to settle with a sharp line, a clear supernatant liquid may be expected. However, certain lime-treated metallurgical pulps in an apparently well coagulated state have been observed to settle leaving a relatively turbid overflow liquor. Certain clays may be flocculated by the use of hydrochloric acid alone. These appear to be cases of flocculation primarily by isoelectric point adjustment.

Classic theory states that hydrophobic substances are, after coagulation, brought back to a stable suspension with considerable difficulty, whereas coagulated hydrophilic substances are quite easily redispersed. However, exceptions to these are listed and it is recognized that many materials may display behavior intermediate between the two classes. These findings have been based on results from what may be termed primarily fundamental investigations, and experience in practice does not necessarily follow.

Most commercial suspensions of hydrophobic substances, *i.e.*, those sensitive to small concentrations of a coagulating electrolyte, are quite easily dispersed by chemical or physical methods. Separation process equipment is generally designed so that the system is subjected to as little physical disturbance as possible. Such physical disturbance does not stabilize the suspension against reflocculation, but it may result in quite unsatisfactory separation, due to partial permanent dispersion. This is most probably a characteristic of suspensions in the zone of slow coagulation. So many variables are encountered with the usual commercially processed suspension that it is quite impossible to define and control them as closely as may be done in purely basic investigations. This may account largely for any differences in interpretation of behavior.

It has been found that if a suitable quantity of a hydrophilic substance is mixed with a hydrophobic system, the latter is rendered less sensitive to the action of a coagulating ion. Lottermoser [26] suggested that such substances be called protective colloids. Zsigmondy,[27] Freundlich,[28] Abramson [29] and many others have studied the mechanism of the protective behavior of hydrophilic colloids. Hauser [1] and Alexander [30] discuss in some detail the results of these studies.

The protective action may develop in either of two ways. Hydrophilic particles may be adsorbed on and form a thick film around the hydrophobic particles, the whole system adopting a behavior characteristic of the hydrophilie film. The protecting colloid particle may be so large that it adsorbs on its surface a number of the hydrophobic particles, but not sufficiently so to prevent the predominance of the hydrophilic behavior in the system. It would not be difficult to picture such an accumulation of hydrophobic particles at the surface that the system would become sensitized and easily precipitated. Very small quantities of protective colloids quite often decrease slightly the stability of the system. This effect is most probably due to a mutual coagulation of negatively charged particles by those carrying a positive potential. Alexander also cites examples of plural and cumulative protection, and each condition encountered may influence the separation process.

Previous discussion has dealt with factors determining the stability of disperse

system of colloids or colloid-like materials, primarily in water. However, this does not mean that suspensions in liquids other than water are excluded. The objective was to outline the factors influencing the probability of cohesion between particles and to discuss practical methods by which stable systems may be destabilized.

The first stage of the flocculation process has been assumed as including only those factors relating to stability. These permit the adjustment of the particle charge to some point between that just preventing cohesion and that giving a probability of cohesion of one. The aggregation step is a function of the probability of collision, and is not to be confused with tendency to coalesce.

The probability of collision in a coagulable suspension, so long as no outside energy source is employed, depends primarily upon the sol concentration and the temperature. The latter influences the behavior of the system as a consquence of its effect on the Brownian motion of the particles. Investigations dealing with the influence of Brownian motion on coagulation have resulted in conflicting claims. Ostwald [81] claims that the Brownian movement of the particles is diminished by electrolytes before coagulation begins. Hissink [82] contends that coagulation itself is the cause of the diminution of the movement. Svedberg [83] agrees with the latter, stating that electrolyte addition has no effect on the Brownian movement so long as there is no coalescence.

Smoluchowski [10] was able, by assuming complete discharge of particles and inelastic collisions, to develop a mathematical theory explaining the collision mechanism and the velocity of the coagulation process. Further limiting conditions were that the suspended particles are spheres of uniform size, unaffected by gravity. Kruyt [9] discusses this classic theory in some detail. The equation developed has been proved generally applicable to monodisperse suspensions in the region of rapid coagulation assumed. Smoluchowski also treated the case for the region of slow coagulation, believing the same law applied and that time of coagulation only would vary from the behavior in rapid coagulation. This application of the theory has not been generally confirmed.

Muller [84] developed a mathematical application of the Smoluchowski theory to polydisperse systems in the region of rapid coagulation. Wiegner and Tuorila [85] confirmed this application.

Tuorila [85] suggested, in a very extensive treatment of coagulation and related phenomena, that particles may collide as a result of the Brownian movement, by stirring or by the streaming of a particle in one direction, as in sedimentation. He found that if the initial number of colloid particles is less than 10 per cc, no coagulation due to Brownian motion will result over the usual range of electrolyte concentrations. Contact between particles due to unidirectional motion can occur only in polydisperse systems of relatively dilute sols.

Muller further developed a general theory for rapid coagulation applicable to polydisperse systems and unidirectional motion. His theory involved three assumptions: (a) for the coagulation of two particles, surface contact is essential; (b) the frequency of contact is determined by the temperature movements and streaming of the particles; and (c) the coagulation of a given particle is determined only by the stationary distribution of the particles. Spherical and disc-like particles were found to aggregate at about the same velocity, whereas rod-like particles grouped more rapidly. Polydisperse systems aggregate more rapidly than monodisperse systems.

Recognizing the importance of the theories developed for the coagulation rate as applied to idealized cases, such as a completely discharged monodisperse system, it must be recognized that their direct application to commercial flocculation practice is limited. This is partly because control cannot be maintained over the nature of the whole system, and the treatment will vary accordingly. One factor given perhaps too little emphasis in classic coagulation studies is the effect of shear within the suspension due to the flow currents caused by an outside energy source. Freundlich [86]

and his co-workers concluded that stirring hastens coagulation when the electrolyte concentration is relatively high. Copper oxide sols were coagulated by mechanical stirring alone. Ferric hydroxide coagulation rate by stirring is independent of concentration and proportional to the square of the stirring rate. Ostwald [37] believed that mechanical coagulation was more likely to be caused by potential differences between stirrer and the suspension. Several others have studied the effect of stirring on various systems, and their conclusions naturally vary with the solid phase studied. The majority favor a positive effect. The intensity of the stirring action suitable for the coagulation of one system may tend to disperse other systems; and this probably accounts for some differences of opinion.

In general, for the dilute suspensions encountered in the applications of flocculation to commercial separations, the probability of collision due to Brownian motion and streaming due to sedimentation is not sufficient for the treatment rate desired. As aggregation proceeds, any Brownian activity decreases and finally ceases. Also, any tendency of the aggregates to grow to uniform size will reduce the effect of unidirectional motion. This leaves the factor of shear to promote further contact between suspended particles and flocs in order to reach a desired excellence in flocculation. This has been accomplished in practice by subjecting the system to treatment in a so-called mechanical flocculator.

There are several types of such flocculators available and these will be discussed later. Their primary objective is to increase the probability of collision between the particles and small flocs so that the rate of aggregation is increased. That this can be done to a marked degree on a commercial scale has been demonstrated on a variety of solids suspended in water. One other objective is to control the contact time before separation is permitted to begin. Such control determines the floc size and structure within limits (not readily definable), and permits more effective envelopment or "sweeping out" of entities not easily susceptible to flocculation. Aggregation due to streaming by sedimentation will be eliminated by this treatment.

As previously suggested, most economic applications of flocculation are in the so-called region of slow coagulation. The suspension is only partially discharged, so that the probability of adhesion based on isoelectric point adjustment is somewhere between zero and one. For many dilute systems in practice the dilution factor combined with the low probability of adhesion would prevent efficient flocculation and separation. It is in the processing of such systems that the effect of a gel or gel-forming reagent is combined with the promotion of shear to most economically arrived at a desired excellence in flocculation. The mechanism of the enveloping reaction has already been discussed. The development of a shearing motion within the liquid system increases the probability of collision to such an extent that enough cohesions result to make the process both effective and efficient.

In some cases, such as turbid river water, the relatively large (5 micron and up) size of some of the particles militates against the probability of collision and of cohesion. For such large sizes in dilute suspensions both a sufficiently high rate of shear and an enveloping type of reagent are necessary to a satisfactory excellence in flocculation and separation.

The aggregating rate of a suspension in a flocculable condition will increase as the ratio of water to solids decreases. This is obviously a function of the probability of collision. Finally a ratio will be reached where, with no stirring other than that maintained in a flowing stream, the rate of aggregation will be almost instantaneous. Usually, a system either is quite obviously dilute and relatively slow coagulating, or it coagulates rapidly in one to three minutes. The extent to which the particle charge in a dispersed system is reduced below that just preventing coalescence may have some influence upon the rate of aggregation.

The mechanical flocculation of raw sewage, without reagent addition, to increase the removal of suspended solids before further processing constitutes a relatively

recent development. This is an example of the effect of gentle shear in the region of slow coagulation. However, the process may conceivably be assisted by the presence of a gel-like substance which increase the tendency to coalesce upon contact.

Separation

Destabilization and aggregation are the primary steps in the conditioning-for-separation phase of the separation process in any of its practical applications. These operations are preferably conducted so that little or no separation is permitted, since they are generally carried out in equipment designed specifically for this function. Once the material or pulp is properly conditioned for satisfactory separation, there are several operations which may be utilized for the final step. Sedimentation methods constitute a solution to the problem which is basically sound and economical.

Sedimentation has been defined [38] as the movement of particles (or flocs) through a fluid due to an imposed force. The character of the subsidence from high to low dilutions will vary as the solid phase becomes more consolidated. Three regions have been defined,[39] as follows:

(1) "Independent subsidence" is defined as that condition in sedimentation where each floc or particle settles freely, that is, its movement is not influenced in any way by other flocs or particles in suspension. The condition is characterized by no difinite line of subsidence, a substantially constant rate of clarification equivalent to the settling velocity of the smallest particles or flocs present, and is further controlled by the shape and effective gravity of the particles and the viscosity of the liquid.

(2) "Collective subsidence" is defined as that condition in sedimentation under which the particles and flocs are sufficiently close together to retard the coarse, fast-settling particles while the slow-settling ones are entrapped and carried down with the mass. The condition is characterized by a definite line of subsidence, a substantially constant settling velocity over some distance, and finally a marked decrease at the critical point. The flocs are conceived to be close enough to touch but not sufficiently close to result in compression. The line subsidence rate decreases with decrease in dilution.

(3) "Compression subsidence" is defined as that condition in sedimentation under which the flocs or particles are conceived to be in close contact, further subsidence occurring as a direct effect of compression resulting in the elimination of water from the flocs and interstitial spaces. The settling velocity decreases with time of settling.

Depending upon whether pulps settle according to one of the three methods defined above, they may be classified as in Table 1.

Table 1. Character of Subsidence of Various Types of Pulps

Operation	Type of Pulp	Character of Subsidence	Description
Clarification	Dilute Class 1	Independent Subsidence	Particles or flocs settle independently. No definite line of subsidence. Settling rate dependent upon size and density of particle or floc.
	Concentrated Class 2	Collective Subsidence	Definite line of subsidence. Settling rate decreases with increasing concentration of solids. Settling rate influenced by particle or floc interference.
Thickening	Compact Class 3	Compression Subsidence	Flocs and particles in intimate contact. Subsidence due to compression (pressure of particles or flocs upon those below them).

This table is based upon a classification originally suggested by Deane.[40]

In the region of independent subsidence, or class 1 as outlined, the laws determining the free movement of suspended particles or flocs under the force of gravity are

controlling. By equating the gravitational force causing subsidence to the dynamic resistance opposing it, and solving for V as indicated, a usual form of the law derived by Stokes [41] is obtained.

$$V = \frac{2g(d_s - d_l)r^2}{9s}$$

where V = the velocity,
g = the acceleration due to gravity,
d_s = density of the solid,
d_l = density of the liquid,
r = the radius of the particle,
s = the viscosity of the fluid: all in cgs units.

A well formed floc should be substantially spherical in shape and sufficiently compact to settle as a separate entity in independent subsidence, the fall velocity depending upon its effective size and density. The latter are not easily susceptible of accurate measurement, but such clumps, unless very large or unusually dense, generally will settle independently in the regime defined by the above equation. The rate of separation in independent particle subsidence is dependent upon the settling velocity of the slowest-settling flocs when a clear overflow is desired. For this reason the conditioning-for-separation steps are very important for a variety of commercial systems. Examples of these are water softening and purification, certain trade wastes treatment and raw cane-juice defecation. Such systems do not usually exhibit well defined line settling and hence cannot benefit by the entrapping effect characteristic of the latter.

Dilute systems which do not exhibit line settling are usually analyzed with respect to their overflow rates. Equipment sizes are based primarily on this factor. If the suspended solids settle to give a satisfactorily clear liquor three feet below the surface in one hour, the probable overflow rate is three feet per hour, and clarification equipment is designed accordingly.

An exception to the usual downward settling of solids and upward flow of clear liquor is the method by which the solid phase is floated upward while the clear liquid flows downward. The same forces apply as in the former case, and selective flotation is not a factor in the process. Conditioning for separation involves, in addition to charge neutralization and aggregation, a step which will give the separable solids an effective density less than that of the suspending medium. This is done by causing gas bubbles, usually air, to attach themselves to or be "precipitated" upon the flocs. It is essential that aggregation take place almost instantaneously in this case, and sufficient reagent is usually added to destabilize the suspended solids completely. Generally the reagent or some one of a combination of reagents will serve to promote flotation as well as flocculation.

As the ratio of liquid to solid in a suspension is reduced, a dilution is reached where the solid entities cease to subside independently. A sharp line develops at the clear liquid-pulp interface. The flocs become sufficiently close to influence the individual settling velocities, and collective subsidence begins. The separate flocs maintain substantially their position with respect to others present without appreciable shape distortion or compression. Stokes' law does not apply under these conditions of collective subsidence. The liquid may be pictured as passing upward through the torturous channels between the flocs. Roberts [38] suggests that the flow through these channels may be subject to Poiseuille's law, and that this conception would be more fruitful than Stokes' law in a theoretical study and analysis of the mechanism of collective subsidence. Work and Kohler [42] developed this approach to the problem in a study of the settling characteristics of aged aluminum hydrate and calcium carbonate suspensions in water.

Work states that there are two forces tending to decrease the subsidence rate: a friction drag due to the viscosity of the liquid and a resistance due to particle inter-

ference. The first remains constant and is defined by Stokes' law. The second is negligible in independent subsidence and varies in collective subsidence, its influence increasing with concentration of the solid phase. The differences between a maximum velocity, based on Stokes' law, and the absolute velocities in collective subsidence for various concentrations are plotted on log-log paper against the corresponding solid fractions. A pipe flow analogy is presented, and good agreement is noted between the two cases. Further investigation along this line should be of considerable interest and value.

The most active interest in the settling behavior of metallurgical slimes dates from the discovery by Dr. John V. N. Dorr that the separation process could be conducted using a relatively shallow tank to deliver continuously a clear overflow and discharge a satisfactorily thickened sludge. However, as early as 1851 Scheerer [43] studied the effect of reagents on slime settling. Carrick,[44] Nichols,[45] Ashley,[46] Forbes,[47] Mishler,[48] Free,[24] Ralston [25] and others contributed to the development of the subject. Coe and Clevenger [39] developed the first comprehensive treatment, and methods outlined by them are still employed as a basis for design.

According to Coe, in a continuous machine pulps in collective subsidence may pass through an indeterminate number of concentration zones while settling from initial to final dilution. The rate of subsidence will vary for the different zones, as will the amount of water to pass through any zone. Consequently, the zone displaying the slowest subsidence rate relative to the amount of water to be separated will be the zone which limits the separation process. All the solids must pass through this limiting zone, and it will permit only a certain quantity of liquid to be separated. The formula for determining this zone is usually written as follows:

$$A = \frac{1\,333\ (F - D)}{R\,s}$$

where $A =$ the sq ft of area per ton solids per 24 hours,
$R =$ rate of subsidence in feet per hour,
$F =$ the dilution of the pulp giving the rate of subsidence R,
$D =$ the dilution of final discharge,
$s =$ density of suspending medium.

Settling tests are made at a series of dilutions for a given suspended material, and the data are substituted in the formula. The dilution giving the largest value for A while still in collective subsidence will be the limiting dilution.

Coe defines two types of pulps based on their batch-settling behavior in cylinders. Type I pulps, when permitted to settle quiet in a cylinder in collective subsidence, pass through a constant rate period, but after they enter compression the settling rate gradually decreases. This is shown by plotting unit volume settled as ordinate against unit time. Such a plot generally shows a rather sharp break at the end of the constant-rate period, usually called the critical point. Settling data from tests on Type II pulps, when plotted as suggested above, show that their settling rate gradually decreases after reaching a concentration giving collective subsidence conditions.

Deane [40] outlines a procedure for observing the mechanics of the separation process as the suspended materials are permitted to settle at gradually decreasing dilutions from independent through collective to compression particle subsidence.

When pulps become sufficiently concentrated with respect to the solid phase to exhibit the characteristics of compression subsidence, further separation results from particle distortion and squeezing due to their weight. Special methods may be employed to promote floc distortion to increase separation efficiency, particularly where the sedimentation volume is large and the elastic limit of the separate clumps is not exceeded by the weight of the concentrated mass.

The subsidence rate in compression decreases as the dilution is decreased. Coe [39] concluded that for a given dilution in compression the subsidence rate is proportional to depth. Within limits, if the depth is doubled the settling rate doubles; but the

rate cannot exceed the slowest rate found for the collective subsidence zones. Some pulps give settling test results [49] which do not agree with the above. These data were obtained under slow stirring conditions, and this may account for some of the difference. The slow stirring is employed because the condition simulates practical thickening performance. Moreover, it has been demonstrated that settling rate in compression under slow stirring conditions is usually greater for a typical metallurgical pulp than the rate without stirring, other conditions remaining the same. Generally a lower final dilution is also obtained under slow stirring conditions. Floc structure is destroyed and better packing results. A condition may, however, develop which will prevent further consolidation by stirring. The pulp may tend to set or develop a gel-like behavior and move in mass.

A number of pulps have been observed, in practice, to develop a condition which has been termed "island formation." It is characterized by the formation of a coherent mass of pulp in the thickening zone, the mass usually revolving with the mechanism. The development of this condition has been ascribed to thixotropy, a property of certain pulps characterized by their ability to undergo repeated transformations from gel to sol to gel by alternate shaking and quiescence.

According to Freundlich,[50] the forces essential to thixotropy are identical with those controlling aggregation. Hauser [1] agrees with this, but considers also the influence of the electrolyte in the dispersion medium. The electrolyte activity and related phenomena are summarized by Ostwald.[51]

Thixotropy is pictured as a state intermediate between a dispersed and coagulated system. It is determined [5] by the relation between the energy of attraction and the energy of repulsion of the particles. The concentration of the sol is also a factor, and the solid phase must contain a portion of particles under 5 microns in diameter. A critical ratio of the latter to the total solids present is not given, but it is probably relatively small.

It has been demonstrated that metallurgical slimes subject to "island formation" may undergo the reversible sol-gel transformations defined for a thixotropic substance. The minus 5 micron fraction of these slimes constitutes only a small fraction of the total solids present.

Applications and Equipment

In many applications of separation by sedimentation the suspended material is already in a separable condition. In others, of course, there is very little tendency for any but the coarsest particles to settle. These cases require careful treatment and control to realize the best possible economy in practice. For those cases already in a separable condition it may sometimes be possible, by careful adjustment of certain factors, to develop valuable economies. Each case must be considered separately, and too much emphasis cannot be placed upon care in sampling for test purposes.

Uniformity in flow, both for reagents and the stream to be treated, is essential to the best economy. The reagents may be introduced into the stream in a powdered state or in solution. Either method is susceptible of automatic control. Certain handbooks in addition to manufacturers' publications may be referred to for details.

The objective of reagent addition combined with proper mixing is to destroy the stability of the suspension by obtaining uniform distribution of the flocculant in the shortest possible time. This results in a minimum of local overdosing. When special mixing devices are employed for this purpose their relatively violent agitation effect should not be prolonged after uniform distribution is accomplished. In other words, in a continuous process, the detention time in the mixing device should be no more than is necessary to get the desired reagent distribution in the stream. Violent agitation beyond this point may be harmful.

Several methods and types of equipment may be employed. Turbo-mixers are quite widely used. Early methods employed baffled launders which are still in use.

Paddle-type mixers are in use which may serve the double purpose of mixing and agitation to promote floc growth. Reference sources describe the various types, of which there are many.

Metallurgical slimes and others having relatively high solids concentrations may be fed directly to clarifiers or thickeners, since flocculation may take place in a very short time after entering a relatively quiet zone. With dilute suspensions the treatment may, in many cases, be made economical only by subjecting the system to suitable shear-producing steps between reagent mixing and clarification. Investigations [49] have shown that the increased flocculation rate resulting is proportional to the increased rate of shear, and flocculation time is reduced accordingly.

Earlier practice involving flocculation as one step in a separation process provided for flocculation in separate units ahead of clarification and thickening. Figures 1 and 2 illustrate equipment employed in this type of plant. The most recent develop-

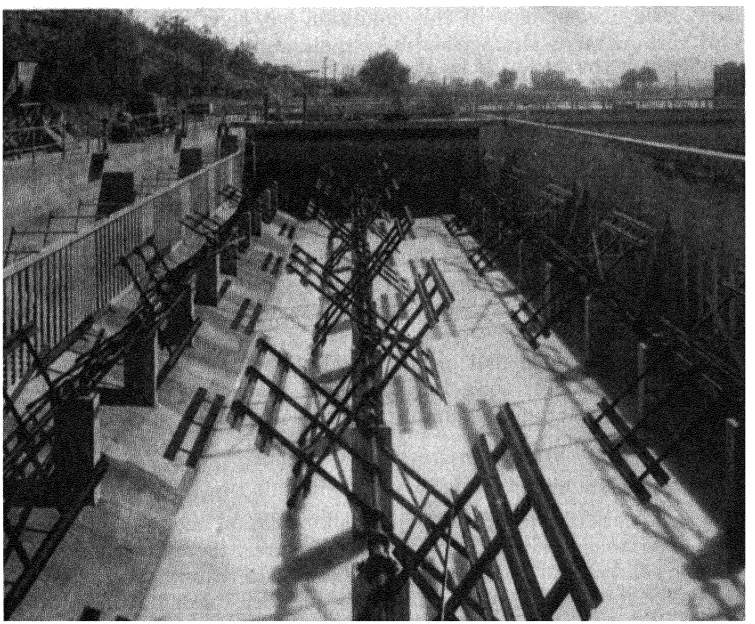
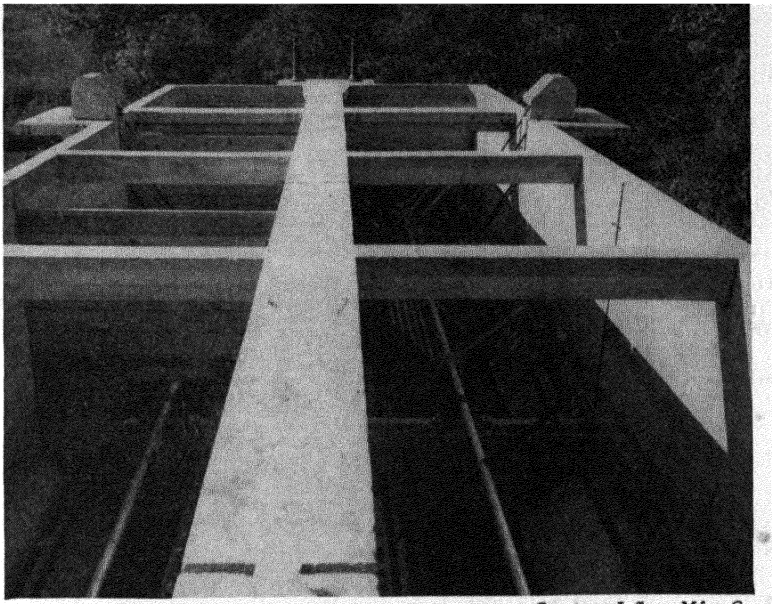


FIGURE 1. Dorrco Flocculator Installation.

ments employ combination units which, in a single tank, provide for flocculation in separate cells preceding the clarification and thickening steps. Figures 3 and 4 illustrate these combination units. Detention time in the flocculation cell, where no separation is desired, will be a function of the time required for aggregate formation necessary to satisfactory excellence in both clarity and separation rate. Separate or combination units may be employed, economy in first cost probably favoring the latter.

No study has been made to define the dilution above which mechanical flocculation is beneficial and below which it is of no value, and may even prove harmful. A number of factors will influence this, and most probably the value, if desired, would have to be determined for each case encountered. Some of these factors are the nature and density of the solid phase, the character of floc formed, and the nature of the suspending medium. The rate of shear developed within the system is also a factor. Within limits the rate of shear is controlling, but this must be adjusted so that the



Courtesy Jeffrey Mfg. Co.

FIGURE 2. Jeffrey Flocculator Installation.

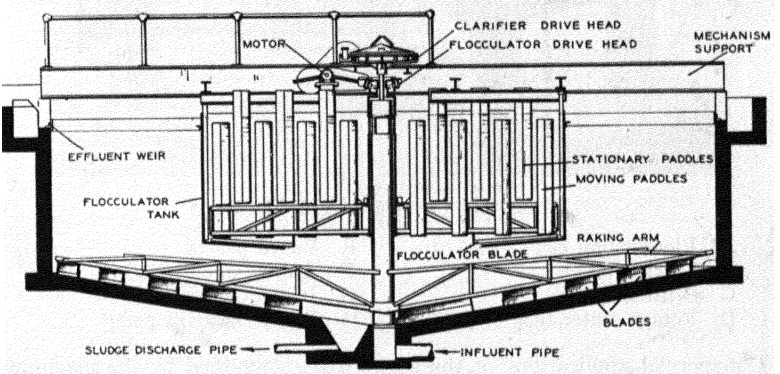


FIGURE 3. Dorrco Clariflocculator.

large, well formed aggregates will not settle or be destroyed. A very important factor, of course, is the probability of adhesion. With relatively low probability of cohesion, mechanical flocculation is probably beneficial in concentrations of the solid phase up to roughly 1000 parts per million.

Recent practice in water softening, for both municipal and industrial use, involves treatment so that the softening reactions take place in a sludge "blanket." Reaction at a solid-liquid interface presumably results in the development of fewer nuclei and promotes the formation of relatively dense, fast-settling particles. Supersaturation is inhibited and stabilization results as a consequence of the intimate contact between the sludge and treated water. Flocculating electrolytes, such as aluminum sulfate or ferric salts, are usually added in very low concentrations to assist the clarification

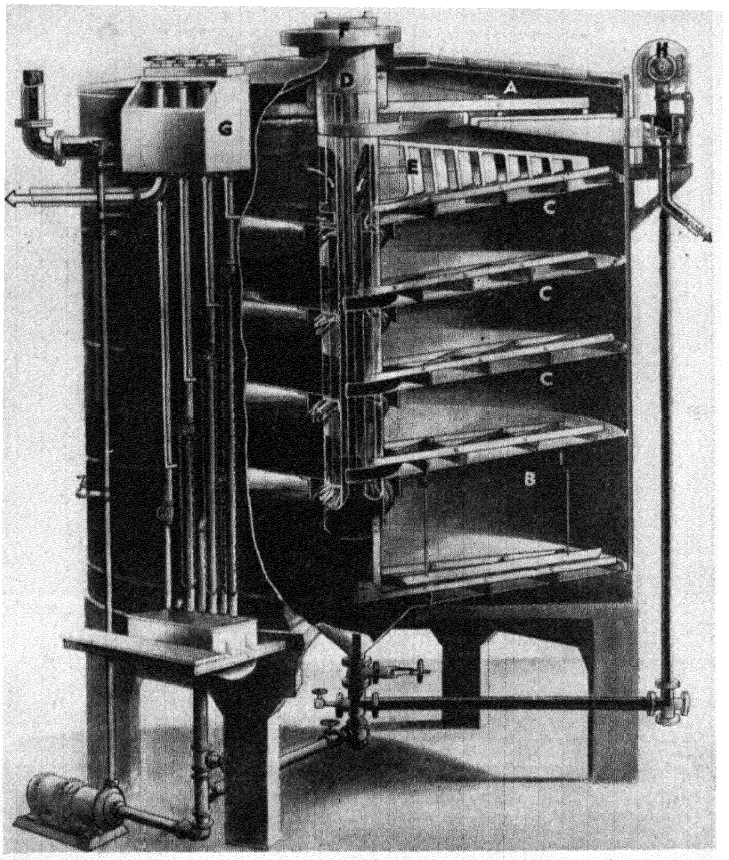


FIGURE 4. Dorr Multifeed Clarifier.

A	Flocculation cell	E	Vaned panels
B	Thickening cell	F	Special speed reducer
C	Settling trays	G	Juice overflow box
D	Rotary center tube	H	Dorrco cachaza pump

step. Commercial applications of the above are exemplified by the machines illustrated in Figures 5, 6 and 7.

Sufficient solid-liquid contact for stabilization may be provided simply by permitting the sludge concentration to build up to a satisfactory figure while maintaining its even distribution over a predetermined volumetric space above the feed entrance level. Figure 5 illustrates how this may be done. The concentration of solids in the reaction zone, permitting maximum overflow velocity with good stabilization will vary from 1 to 2 per cent by weight. Concentrations much above these do not permit the maximum overflow rates possible, whereas lower concentrations may result in poor stabilization.

Following the conditioning-for-separation steps, the solids are most generally permitted to subside in a relatively quiet zone in equipment designed to perform continuously the separation desired. The Clariflocculator, Figure 3, and the Multifeed, Figure 4, are suitable for application to the problem, both for initial conditioning and final clarification and thickening. Depending upon the nature of the suspended solids

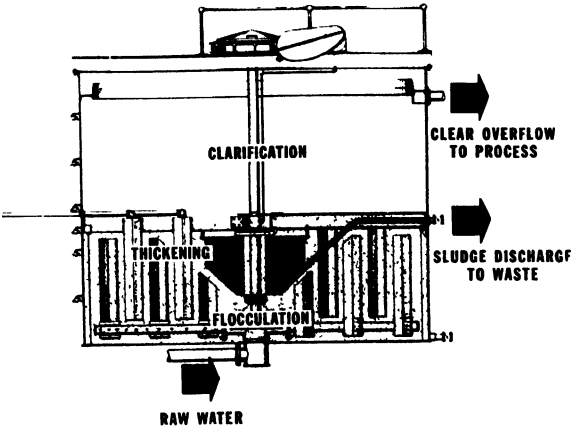
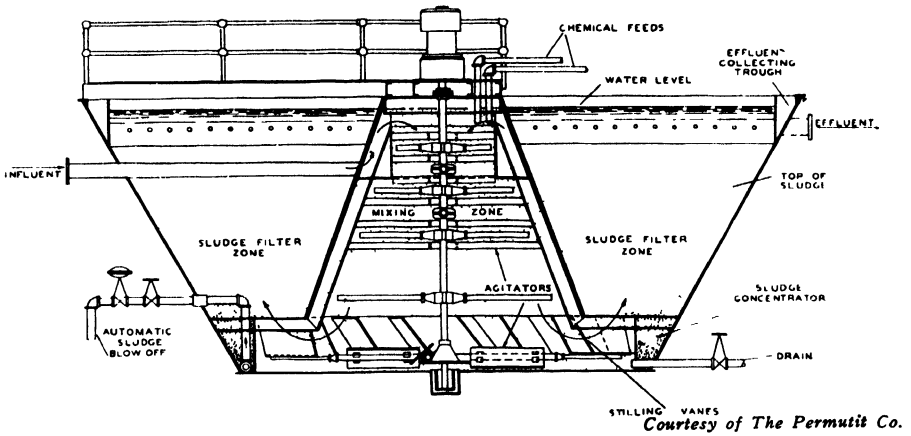


FIGURE 5. Dorrco Hydro-Treator, sectional elevation.



Courtesy of The Permutit Co.

FIGURE 6. Spaulding Precipitator, sectional section.

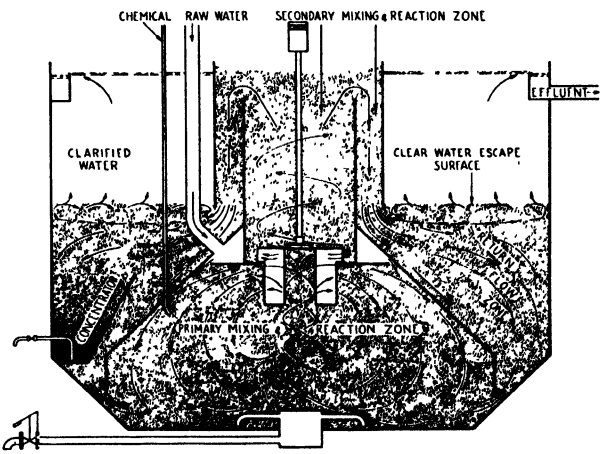


FIGURE 7. Infilco Accelator, flow diagram.

the final thickener discharge may vary in per cent solids by weight from 3 per cent to as much as 70 per cent.

Other types are available and designs for application to any separation problem can be developed from test data. Figures 8, 9 and 10 illustrate some of these. Tray-type units may be employed where relatively large clarification area is needed and little projected area is available. Head room is, of course, an important factor in such cases. Tray units, offering large clarification area with minimum surface for insulation, are particularly adaptable to separations at elevated temperatures. Unit-type clarifiers are employed for treating water, sewage and trade waste at atmospheric temperatures. A typical design is illustrated in Figure 9. The type shown in Figure 4 is widely employed to clarify cane and beet juice in sugar manufacture.

Clarification by flotation is applicable to relatively low-density materials or to a flocculated mixture of these with higher-density materials. A typical example is paper-mill white water carrying suspended solids which may be practically pure cellulose fiber or a mixture of the latter with a filler. High-density substances alone are, however, not excluded from such treatment.

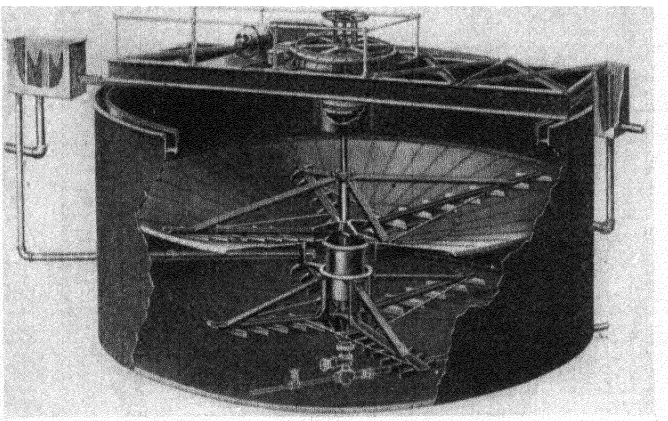


FIGURE 8. Dorr Balanced Tray Thickener.

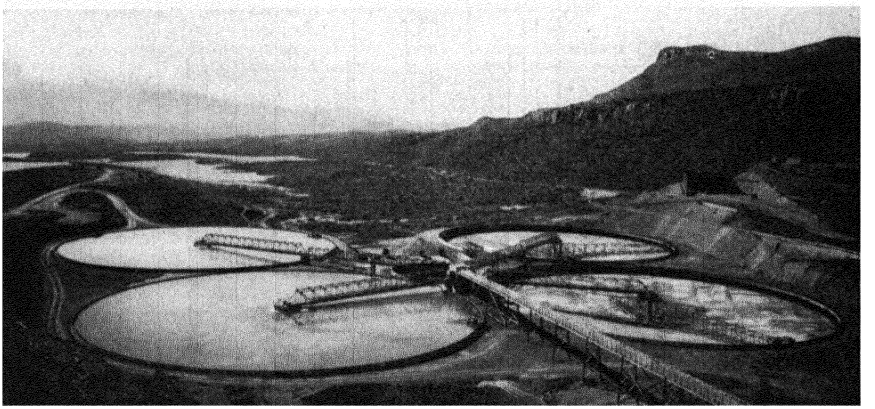
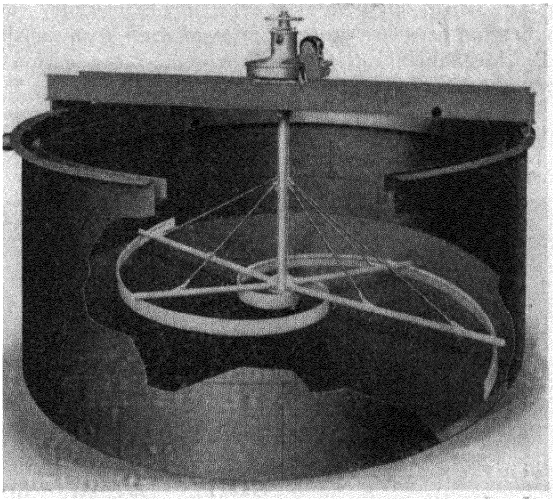


FIGURE 9. Dorr Traction Thickener Installation.



Courtesy Hardinge Co., Inc.

FIGURE 10. The Hardinge Spiral Clarifier.

Reagent addition takes full advantage of the enveloping tendency of compounds formed from alum already present, while at the same time establishing a condition promoting ease of flotation. Saponified substances, such as sodium oleate, are quite effective over a pH range of 5 to 7. The suspended solids vary from 2 or 3 up to 15 pounds per 1000 gallons. Air is injected into the stream. The resulting agitation serves to mix in the reagent, which is usually introduced at the same point. Figure 11

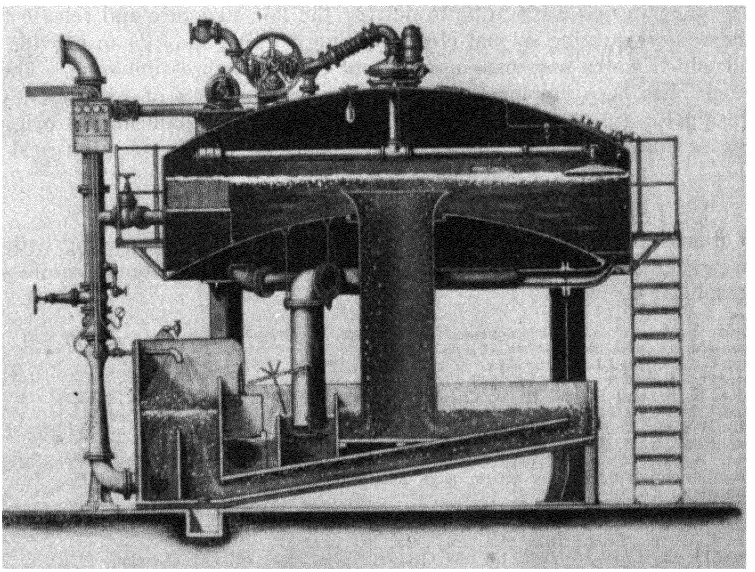


FIGURE 11. The Adka Save-all.

illustrates a machine which operates at about 7 inches mercury vacuum. Capacities for a given clarification area are quite large compared with subsidence methods already discussed. Mechanical stirring to promote aggregation is not essential. Relatively large concentrations of reagent are employed, and floc growth is exceedingly rapid.

Figure 12 illustrates a mechanism developed [52] to promote more efficient separa-

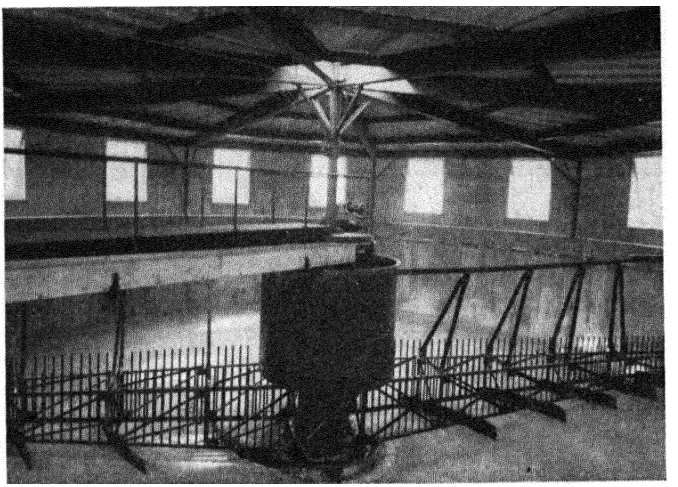


FIGURE 12. A Dorr Picket Thickener Installation.

tion of solids from pulps in compression when the settled volume is large and the floc structure has sufficient strength to support the mass. The pickets have been pictured as functioning in two ways: (1) to destroy the floc structure and release the water not otherwise separating so that closer packing results, and (2) to provide channels through which water may pass upward out of the compression zone. The "Picket Thickener" has been employed to advantage in a variety of separation problems. Some examples are gluten thickening, for which the mechanism was originally developed, sewage thickening, and the treatment of certain metallurgical slimes.

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Centrifugals as Applied to Colloids

L. P. SHARPLES
The Sharples Corporation, Philadelphia, Pa.

There are several million centrifugal separators in daily use throughout the world. A majority of them are used for separating cream from milk, but tens of thousands are used for other industrial and laboratory separations of particles from a liquid.

The highest-speed centrifugal rotor yet developed is 3/16 inch in diameter and has been run at 6,600,000 rpm. The largest rotating body close at hand is the earth, which rotates at 1/1440 rpm. The former generates a centrifugal force over 50 million times the force of gravity, and the latter less than 1/100th of the force of gravity. Nevertheless, the centrifugal force generated by the earth causes the Mississippi to flow uphill, the mouth being some 3 miles higher than its so-called upper waters.[27]

There are several hundred different well-established commercial uses for centrifugals involving the continuous flow of a liquid to and from the centrifugal rotor, whereby colloidal particles are removed from the liquid.

The Ultracentrifuge

This term refers to a centrifuge in which the sedimentation of particles under centrifugal force takes place without disturbance from convection or other currents. Svedberg's definition further limits an ultracentrifuge to "an instrument by means of which sedimentation in a centrifugal field is measured quantitatively." The first ultracentrifuge was built by Svedberg in 1924. Weights of molecules of unknown constitution were determined by Svedberg and his associates. They also investigated the degree of particulate complexity and stability of such complex substances as the proteins. They discovered by centrifugal analysis that under fixed conditions pure proteins usually possess perfect molecular homogeneity and thus have a definite molecular weight.*

Svedberg's results stimulated analytical centrifugal work by many other scientists. It has been found possible to study the aggregation, association, and dissociation of proteins. It has been shown [12] that the molecular weights of the starches depend upon their previous history, and that in general starches are polydisperse. The ultracentrifuge has been applied to the study of many substances made industrially,[19, 11] such as rubber, neoprene, cellulose and its derivatives, because the centrifugal method is perhaps the most satisfactory one for the study of high molecular weight materials of great diffusive mobility. It is possible to study the hydration of molecules in solution and to determine the ratio of the radius of unsolvated to that of solvated particles.[18]

The ultracentrifuge has proved a powerful tool for the concentration, purification, and crystallization of high molecular weight virus proteins and is indispensable in the case of unstable viruses existing in low concentrations in the host.[24]

The formulas applicable to the sedimentation equilibrium method and the sedimentation velocity method used for these determinations may be found in the book "The Ultracentrifuge" by Svedberg and Pedersen (Oxford University Press, 1940).

* See Svedberg's table in Vol. V, pp. 564-7. J. A.

A 19-page bibliography covering the ultracentrifuge will be found at the end of that book.*

Some basic formulas which are useful in centrifugal calculations follow.

Stokes' Law. If w = the resistance offered by a homogeneous fluid of viscosity η toward the motion of a sphere of radius r moving with a velocity v, then

$$w = 6\pi r\eta v \tag{1}$$

When the particles are not held in a state of diffusion by Brownian movement, v will continue to increase until the resistance offered by the fluid balances the downward acceleration, so that for a spherical particle, when v becomes constant,

$$6\pi r\eta v = 4/3\pi r^3(\sigma_1 - \sigma)g \tag{2}$$

when
σ_1 = density of particle
σ = density of fluid medium
g = gravitational acceleration

Solving for v we get

$$v = \frac{2(\sigma_1 - \sigma)gr^2}{9\eta} \tag{3}$$

Osmotic Pressure and Diffusion. The two phenomena we may expect in any colloid system according to the kinetic theory are osmotic pressure ($P = \frac{RT}{N}.n$, where n = the number of particles per unit volume), and diffusion. The diffusion constant, D, is defined by the equation (4)

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{5}$$

where c = concentration, x = distance, t = time, and

$$D = \frac{RT}{N}\frac{1}{f} \tag{6}$$

where f is the frictional force of fluid medium on the suspended particle. In the case of a spherical particle from (1)

$$f = 6\pi\eta r \tag{7}$$

and

$$D = \frac{RT}{N \cdot 6\pi\eta r} \tag{8}$$

In colloidal solutions the diffusion of dispersed particles is in accord with the kinetic theory, and Perrin's Law states that:

$$\log_e \frac{c_o}{c_x} = mgkx \quad (1) \tag{9}$$

where
c_o = concentration of particles at an initial level
c_x = concentration of particles at x height from this level
m = relative mass of one particle (for a sphere = $\frac{4}{3}\pi r^3(\sigma_1 - \sigma)$
g = gravitational acceleration
$k = \frac{N}{RT} = 3.0 \times 10^{13}$ at 20°, in which $N = 6.06 \times 10^{23}$
$R = 5.313 \times 10^7$

* See also Vol. I of this series, pp. 838-54, 855-60, 861-909; and paper by E. Pickels in Vol. V of this series. J. A.

Sedimentation Equilibrium. In the ultracentrifuge an equilibrium between sedimentation and diffusion may be reached for each molecular species.

$$M = \frac{RTs}{D(1 - \bar{V}\sigma)} \tag{10}$$

where

$s = \frac{dx/dt}{\omega^2 x}$ and is the sedimentation in a unit centrifugal field

M = molecular weight

ω = angular velocity

V = partial specific volume of the dispersed phase, which is the incremental volume per unit weight of the solute. It may be determined pycnometrically according to the formula

$$V = \frac{W - (l - h)}{\sigma h} \tag{11}$$

W = weight of solvent the pycnometer will contain

l = weight of solution the pycnometer will contain

h = weight of solute in l

From this we obtain

$$M = \frac{RT \operatorname{eln}(x_2/x_1)}{D(1 - \bar{V}\sigma)(t_2 - t_1)\omega^2} \tag{12}$$

and

$$M = \frac{2RT \operatorname{eln}(c_2/c_1)}{(1 - \bar{V}\sigma)\omega^2(x_2^2 - x_1^2)} \tag{13}$$

Sedimentation Velocity. In an ultracentrifuge each molecular species may be sedimented with measurable velocity from which the sedimentation constant S for the species may be calculated by the formula:

$$S_{20}^\circ = \frac{dx}{dt} \cdot \frac{1}{\omega^2 x} \cdot \frac{\eta}{\eta_0} \cdot \frac{1 - V\sigma_0}{1 - V\sigma} \tag{14}$$

where S_{20}° = the sedimentation velocity of the particle in a unit gravitational field referred to water at 20° as the dispersed phase.

$\frac{dx}{dt}$ = observed velocity

η_0 = viscosity of water

σ_0 = density of water at 20°

If M is found by the sedimentation equilibrium method and s by the sedimentation velocity method, the molar friction constant for the species assuming a dilute solution is

$$f = \frac{M(1 - V\sigma)}{s} \tag{15}$$

The molar frictional constant of a sphere, f_0, according to Stokes' Law, is

$$f_0 = 6\pi\eta N \left(\frac{3MV^{1/3}}{4N}\right) \tag{16}$$

and the ratio f/f_0, the dissymetry constant, indicates the degree of variation of the shape of the molecule from spherical.

Oil-driven Ultracentrifuge

The oil-driven type of ultracentrifuge was designed by Svedberg and his associates. The machines are normally run at speeds to give a maximum centrifugal

force of the order of 400,000*g* and by using a smaller rotor have been run to give 900,000*g*. The lower force in the larger rotor gave greater "resolving power" and more accurate determinations because of the greater depth of sample permitted.

The rotor is fitted with a cell with transparent windows so that light can pass through the cell. Thus the sample of liquid can be photographed while the rotor is spinning at high speed.

A sample of the solution containing the molecules to be analyzed is placed in this cell. A "hydrogen vacuum" is generated in the surrounding casing to minimize both friction on the surface of the rotor, and resulting convection currents in the cell. Some hydrogen may be bled through to carry off such heat as is generated. Photographs of the sample are taken at intervals to record the progress of sedimentation. Measurements of sedimentation velocity are thus obtained and photometric curves plotted.

Air-driven Ultracentrifuge

The suspended air-driven type ultracentrifuge is useful for similar purposes. One form is shown in Figure 1. This type has the advantages of greater simplicity and of lower cost. Beams and his associates were the originators of this type, which is based on the air-spun top of Henriot and Huguenard.[6] An air turbine above provides the power, the air-cushion under the turbine supporting the weight of all revolving parts. The rotor with cell is suspended in a vacuum chamber below by a

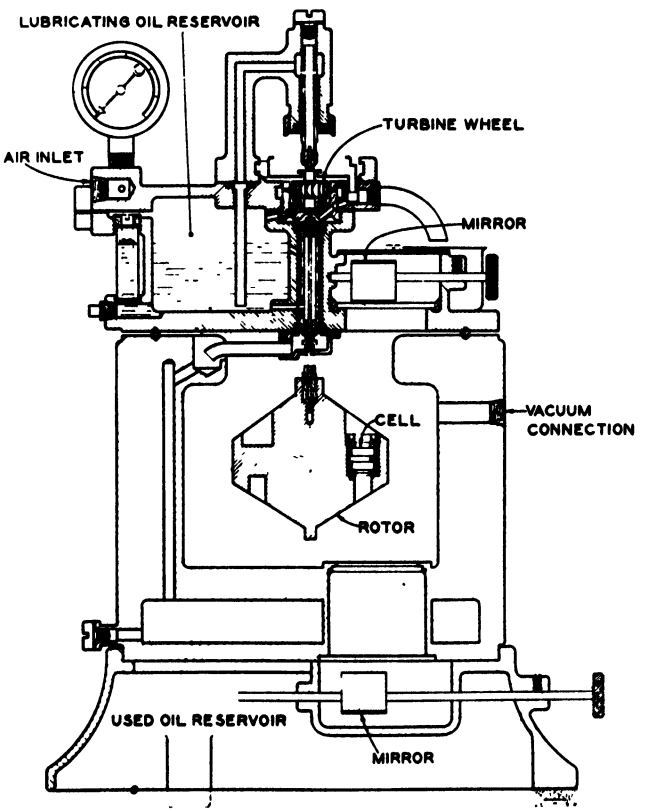

FIGURE 1. Sharples suspended air-driven ultracentrifuge.

spindle of piano wire. A vacuum-tight oil seal is used and presents a minimum of friction due to the small diameter of the wire spindle. All vibration of the rotor is absorbed by the flexibility of the spindle, so that tiny bearings on the spindle suffice.

The ultracentrifuge shown in Figure 1 is operated by 15 lbs per sq in air pressure, and runs at 80,000 rpm, developing a centrifugal force of 250,000*g*. The rotor chamber is evacuated to 0.2 micron of Hg, giving a frictional temperature rise in the sample of less than 1° in two hours' operation.

A stroboscope is used for determining speed. A grid-tube gauge is used to measure the vacuum and a diffusion pump in tandem with a piston pump is used to produce it. Quartz optics are required if ultraviolet light is used. Observations may be made on the basis of differential light absorption or differential light refraction by the different fractions as separated in the cell. In case the absorption bands of the solvent overlap those of the materials being centrifuged, the refraction method may be usable.[25]

It is understood that at least two well-known investigators are using ultracentrifuges for control of commercial production of dye pastes and tobacco mosaic virus.

Quantity Rotor Vacuum Centrifuge

"Quantity rotors" may be used in the air-driven type of ultracentrifuge. The rotor suspended by the piano wire is in this case fitted with a number of test tubes of Celluloid composition placed in drilled cavities (see Figure 2). Such a machine

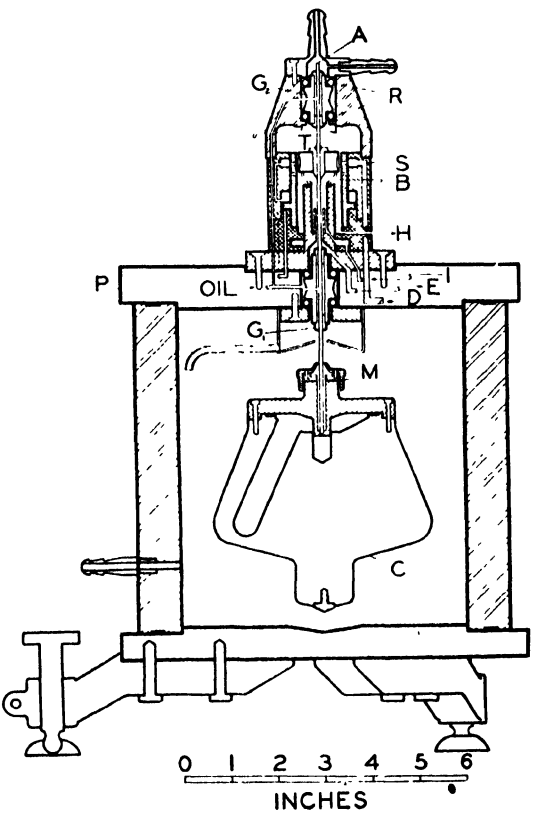

FIGURE 2. Suspended ultracentrifuge with "quantity" rotor, made at University of Virginia.

may be used to concentrate the required principle from a dilute suspension. Some 16 tubes of 7 cc capacity each may be carried by such a rotor. The supernatant liquid is decanted from the tubes after the rotor has stopped. This type has been used by Bauer and Pickels [2] for the concentration of yellow fever virus. Wyckoff and Stanley have concentrated the tobacco mosaic virus which has an estimated molecular weight of about 17,000,000, and a diameter estimated at 33 millimicrons. The ability to study filtrable viruses opens a new field of research into the control of diseases caused by viruses as distinct from diseases caused by bacteria.

Continuous-flow Vacuum Centrifuge

Figure 3 shows Beams' design [3] suitable for separation of gases and vapors. This has an air turbine, T, and an air bearing below the frame. Gas is fed to the rotor R

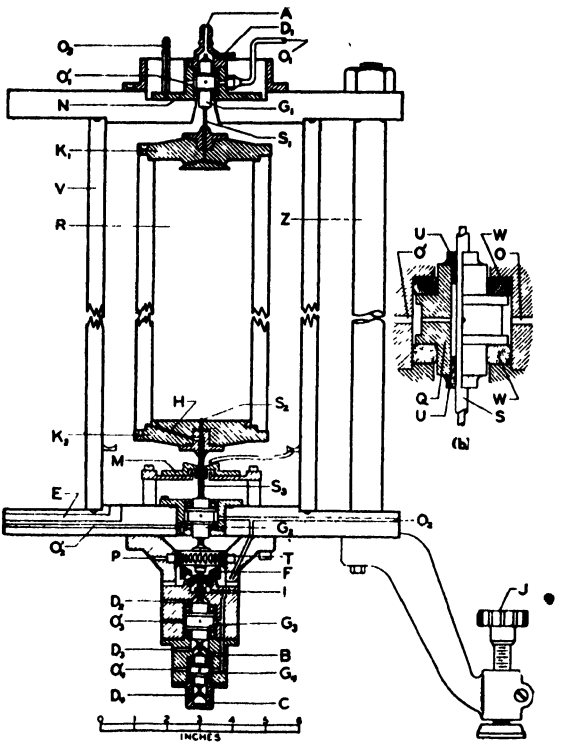

FIGURE 3. Continuous-flow centrifuge for the separation of gases.

through the flexible hollow spindle S_1 (hypodermic needle stock) and the separated fractions leave the bowl through the co-axial hollow spindles, S_2 and S_3. The supporting air is fed at I, the driving air at P. The vacuum chamber surrounding the rotor is evacuated to less than one micron of Hg. A similar machine with 2″-diameter rotor has been run at 66,000 rpm.

When this apparatus is used for centrifuging liquids a somewhat modified rotor is used.

A similar rotor may be suspended magnetically and driven electrically.[10] Figure 4 shows an electrically driven machine. A vertical iron rod, S, is suspended by the co-axial field of a solenoid, L. The centrifuge rotor, C, is supported by the iron

rod. The height of the rod in the field may be controlled by a photoelectric cell. An alternating current in the field F causes the armature, D, to spin.

Ultracentrifuges Not Using Vacuum

McBain and his associates have developed useful variations of the Henriot-Huguenard [6] spinning top. They place the sample to be analyzed in the turbine, or top, itself. Capillary tubes, jellies, or stratifying discs are used to immobilize the sample, and minimize convection currents. The resulting devices are notable for their simplicity.

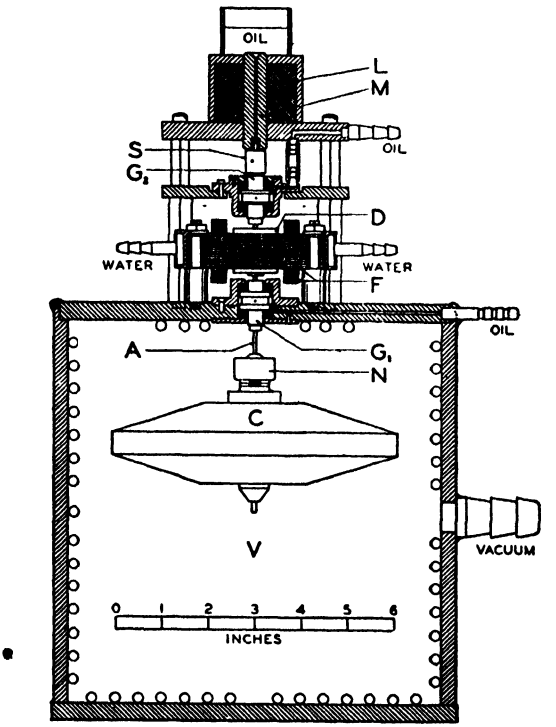

FIGURE 4. Magnetically-suspended, electrically-driven rotor.

In one design, a piece of photographic film is placed under the cell containing the sample. The top is spun in darkness for a desired interval, after which a beam of light is permitted to pass through the sample to the film. Images showing sharp boundaries, measurable with a travelling microscope, were obtained after centrifuging the erythrocruorin of earthworm blood.

A multi-tube rotor, or spinning top, has been developed by Ford.[16] Capillary tubes are inserted in radial holes in the rotor. After the rotor has been run and stopped the tubes are removed and photographed. The tubes, mounted on microscope slides, may be used as the negative in a photographic enlarger. McBain has developed a rotor fitted with a disc stack for immobilizing the sample. One hundred discs, each 0.08 mm thick, were used. The calculated molecular weight of sucrose was determined as 341 (theoretical 342)[17] by using a rotor of this type.

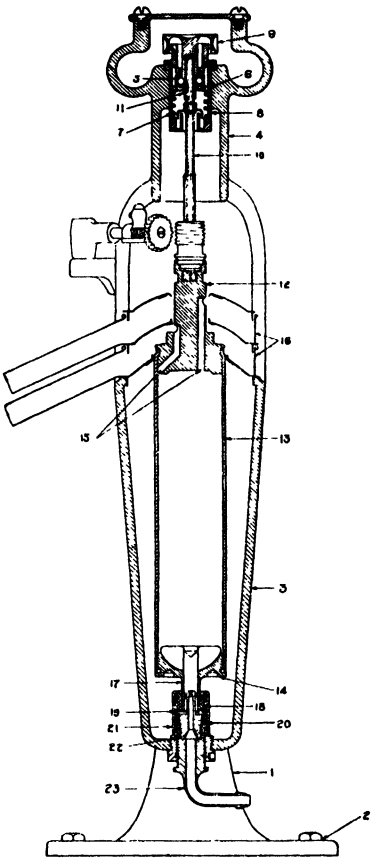

FIGURE 5. 60,000 rpm laboratory size Super-centrifuge for continuously separating two liquids.
1, frame; 3, barrel; 5, ball bearing; 9, turbine; 10, spindle; 13, rotor; 15, heavy and light effluent outlets; 16, effluent covers; 17, liquid inlet; 18, drag bushing; 23, feed tube.

Supercentrifuge, Laboratory Type

Figure 5 shows the Sharples Super-Centrifuge for laboratory work. The rotor is 1¾ inches inside diameter, 8 inches inside length, and holds 275 cc of liquid. It runs at 25,000 to 60,000 rpm, depending on the model used. The latter speed gives a centrifugal force of approximately 100,000*g*. Liquid may be fed in continuously at 23 and the heavy and light fractions discharged through the passages at 15. Batch rotors are supplied if continuous flow is not required. Electric, air, or steam drive is available. Cooling coils may be mounted in the frame 3 so that heat generated by air friction against the bowl 13 is carried away by the air which is kept cooler than the liquid passing through the rotor. Thus the liquid near the walls of the rotor may be slightly cooled to minimize convection currents.

Machines of this type have been used by Hauser [9] to make particle-size fractionations in colloidal systems and measure particle-size distribution in the resulting fractions. A study was made of the thixotropic properties of the resulting suspensions of particles of varying average particle size. Five fractions of bentonite of varying average equivalent spherical diameter of 14.3 to 87 millimicrons were obtained by this method.

Bradfield [4] and others have reported work in this field and a paper by Hauser will be found in this volume.

McIntosh and Selbie,[5] using a modified-feed jet and rotor of the laboratory supercentrifuge were successful in concentrating viruses and bacteriophages by continuously feeding the suspension to the machine at rates varying from 16 to 650 cc per minute. It was noted that the suspending liquid in the rotor at the end of the run could be completely displaced by saline or water, which also served to remove some of the soluble contaminating material from the deposit. Some results of their work are shown in Tables 1, 2, and 3. The supernatant fluid was reduced in infectivity at

Table 1

Suspension	Volume (cc)	Rate of Delivery (cc/min)	Speed (rpm)	Titre		
				Original	Supernatant	Deposit
Staphylococcus aureus	1000	650	21,000	1.3×10^{7}	1.1×10^{5}	1.3×10^{9}
B. prodigiosus	1000	450	21,000	1.5×10^{7}	7.3×10^{5}	3.7×10^{9}
Pleuropneumonia	1000	80	21,000	10^{7}	10^{5}	10^{10}
Vaccinia	1500	20	40,000	10^{3}	nil	10^{6}
Rous sarcoma virus	4000	20	40,000	10^{2}	10^{1}	10^{4}
Staphylococcus bacteriophage	1000	18	40,000	10^{4}	10^{1}	10^{8}
B. coli bacteriophage	9000	16	40,000	10^{10}	10^{5}	10^{14}

Table 2. Comparison of Minimal Infective Dose of Deposit and Theoretical Weight of Particle

	Total dry weight of deposit (mg)	Titre of deposit	Minimal infective dose of deposit (mg)	Weight of particle (mg)
Staphylococcus aureus	465	3×10^{12}	1.6×10^{-10}	3.4×10^{-10}
Vaccinia virus	9.4	10^{6}	3.4×10^{-7}	5.2×10^{-12}
Rous sarcoma virus	14.2	10^{4}	5.1×10^{-5}	2.9×10^{-13}
B. coli bacteriophage	26.9	10^{14}	9.5×10^{-14}	6.0×10^{-14}

Table 3. Chemical Composition of Deposits

	Minimal infective dose (mg)	Extractable lipoid (%)	Non-lipoid fraction (%)			
			Nitrogen	Carbohydrate (as glucose)	Ash	Total P
Staphylococcus aureus	10^{-10}	0.6	12.3	7.9	8.2	2.6
B. coli	10^{-10}	1.6	13.6	15.0	5.1	1.9
Vaccinia	10^{-7}	46.0	15.0	9.6	5.0	1.3
Rous sarcoma No. 1	10^{-5}	39.0	13.3	8.7	2.0	1.03
Tumor 7 *		42.0	13.3	15.7	3.0	1.15
Sheffield dibenzanthracene tumor †		39.0	12.7	8.2	0.7	1.1
B. coli bacteriophage	10^{-13}	10.4	13.4	25.0	6.0	2.9

* Non-filtrable fowl tumor (McIntosh and Selbie, 1939).
† Non-filtrable fowl tumor (Mellanby, 1934).

least 100 times in all experiments, except with Rous sarcoma virus which was reduced only 10 times. Experiments with *staphylococcus aureus* and *B. prodigiosus* showed that all these organisms can be recovered by this method. The report indicates that concentration of an order of 1000:1 was effected by the centrifuge.

The laboratory type supercentrifuge is also being applied to the large-scale continuous concentration and production of tobacco mosaic virus. The direct recovery of antigens from serum has been found practical in the supercentrifuge.

Similar machines have been used for the concentration of *B. acidophilus*. A cultured trypsin digest of skim milk may be fed continuously through the rotor and a practically complete recovery of the *B. acidophilus* obtained. The concentrate collects on the walls of the rotor and may be removed at the end of the run.

Supercentrifuges are used in the fractionation of human blood serum to remove thrombin and various globulins in the process of preparing blood albumen.

Silver salts may be recovered by the supercentrifuge from waste photographic emulsions. Particle sizes range down to 0.5 micron. Recovery is effected at 40,-

000 rpm. Cloudy agar solutions may be continuously clarified centrifugally to yield a brilliant product without the assistance of albumen as a "gathering" agent. Corpuscular matter and fibrin may be removed from blood in the preparation of serum. Pigment may be centrifugally removed from paint or enamel to facilitate analysis. Many gelatinous substances which would tend to clog a filter may be centrifuged without difficulty.

Microscope-Centrifuge

In order to observe the behavior of mitotic figures and other structures under centrifugal force, to determine deformation in a centrifugal field, to observe rate of movement of granules and calculate viscosity of protoplasm, etc., the microscope-centrifuge was devised.[8] Figure 6 shows a usable optical system. The light from *X*

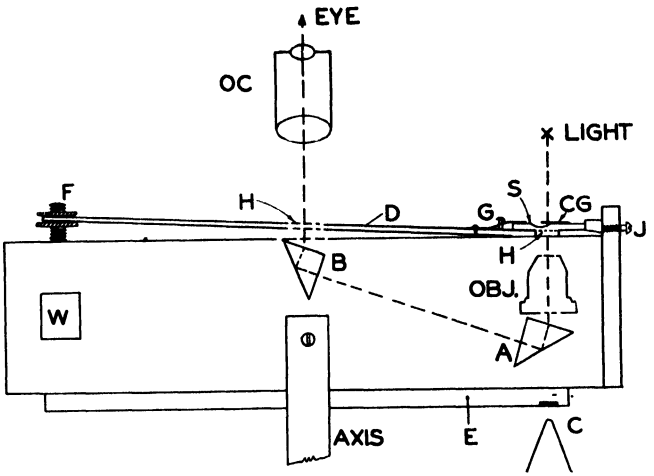

FIGURE 6. Optical system of microscope-centrifuge.

(stationary) passes through the sample, *S*, at one point in each revolution of the rotor. The light beam then passes through the objective (Obj.) and through two prisms (*A, B*) to the axis of rotation and into the stationary eyepiece, *Oc*. Thus the movement of the image of the cell is slow, compared with the movement of the cell itself. Photomicrographs have been obtained, using a synchronized flashing light source and an X62 objective, of bacteria and chromosomes in dividing cells which are hardly distinguishable in clarity from those taken when the cells are at rest. The Harvey-Loomis microscope centrifuge is commercially available. Living cells have been studied [7] in it and from the relative movement of the different parts of the cell estimates were possible of the viscosity and surface tension of the protoplasm, the relative density of the substances in the cell and the elasticity of the cell membrane. Solutions of polystyrenes in different organic solvents have been investigated [28] and the results have been interpreted as showing that free movement of the long molecules could take place only in very dilute solutions, and that movement became less with increasing molecular weight.

Other Laboratory Centrifuges

Machines for whirling glass containers at atmospheric pressure are commercially available in great variety; likewise bucket-type rotors, perforate or imperforate; and special glassware for separation of essential oils, urinary sediments, etc.

Production Centrifugals

For industrial uses, centrifugation is only one of several available methods of separating colloidal solids from liquids or liquids from liquids. Some other methods are: Filtration, distillation, crystallization, solvent extraction, and gravity settling.

However, centrifugation has certain unique advantages which may be summarized as follows. (1) It is quick. From the time the liquid enters the continuous centrifugal until it is separated and discharged is ordinarily a matter of 10 to 30 seconds. If the liquid is unstable and inclined to spoilage, this may avoid harmful changes. If it has been chemically treated immediately before centrifuging, undesirable side reactions may be avoided. (2) Centrifugation is continuous, and fits in as a step of a continuous process without requiring large surge or storage tanks. Elimination of the investment in the liquid in such tanks may be an important item. (3) The centrifugal has but small space requirements, and building overheads may be reduced. (4) The centrifugal will handle many amorphous or gummy materials that would tend to plug filters and some other equipment. (5) Liquid passing through a centrifugal does not intimately contact solids already removed, and thus differs from a filter. (6) The solids removed are usually highly concentrated as compared with gravity settling. (7) Centrifugation usually presents an efficient method of separating oil-water emulsions stabilized by colloids.

Production centrifugals (that is, centrifugals adapted to handling hundreds of gallons of liquids per hour) are commercially available in many types to suit the individual requirements of the hundreds of different industrial uses for centrifugals. Many practical considerations are involved in selecting the proper type for any individual application. Following are the main types and their distinguishing features:

Type I: Supercentrifuge

Figure 7 shows the tubular rotor of the supercentrifuge.[22] The relatively small diameter permits the generation of high centrifugal force without high stress in the metal. The long rotor provides long travel for the liquid in a thin layer. Thus the necessity for laminating plates in the rotor is usually avoided. A robust, easily cleaned, all-purpose machine results, generally suitable for the great majority of industrial applications. A machine of normal size has a 4″ diameter rotor 30″ long and revolving at 15,000 rpm. Such a machine is suitable for the separation of protein particles one micron in diameter and 1.3 specific gravity from aqueous suspension. Frames for operation under pressure or vacuum are available; also triple-discharge rotors for 3-phase systems, and many other variations. The machines are used for fish-oil clarification, citrus fruit-oil separation from the juice, raising the dielectric of insulating oil, clarification of pharmaceuticals, dewatering creosote oil, concentrating rubber latex, clarification of consommé, selective clarification of tomato purée, clarification of pineapple and apple juices, removal of Ca and Mg salts from caustic solution, colloidal silver recovery from photographic solutions, dewaxing lubricating oil, acid-sludge separation from acid-treated petroleum, soap removal from caustic-treated vegetable oils; clarification of solutions containing agar, balata, black leg aggressin, butter color, cascara, cough syrup, pectin, serum, shellac, sizing, etc.; purification of hot chewing gum, continuous purification of diesel engine oil while it is in use, removal of oversize pigment particles from paint, dye clarification, dewatering fuel oil, glue separation from packing house liquors, clarification of mercerizing solutions, and many other uses.

Type II: Stratified Rotor

Commercial centrifugals are frequently fitted with multiple cones (as in Figure 6) in the rotor, so stacked that they stratify the liquid. The stack of concentric cones

stratifies the liquid that is under centrifugal force so that a particle of lower density than the liquid vehicle, when migrating radially toward the axis, will promptly meet a metal surface to speed its contact with other similar particles and provide one-way traffic during their further migration to the inner exit. Stratification is particularly suitable for the concentration or packing of discrete particles of a low density component as, for instance, rubber latex, or cream of high milk-fat content. Cream containing 84 per cent butterfat (standard butter contains 80 per cent butterfat) may be produced centrifugally. Butter oil containing 100 per cent butterfat may be separated centrifugally from cream if the cream is first diluted with hot water to weaken the stabilizing power of the colloids present.

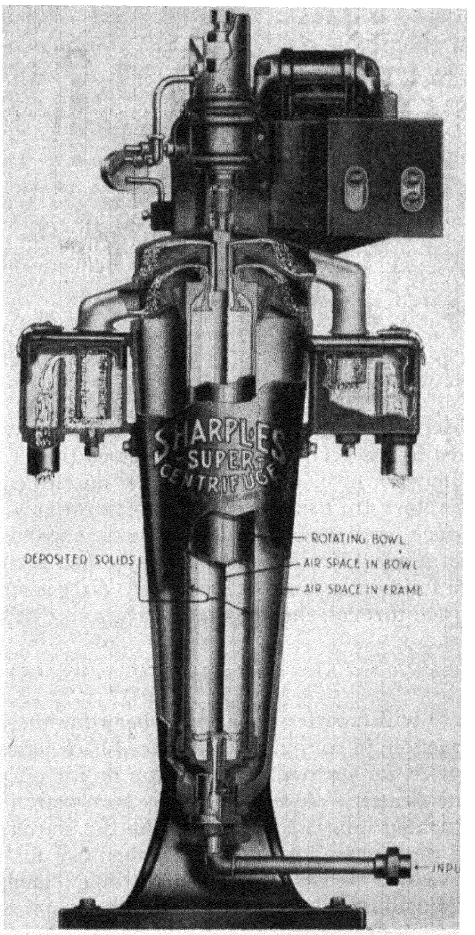

FIGURE 7. Commercial size Super-centrifuge suitable for separating two immiscible liquids.

Type III: Peripheral Discharge Rotor

Figure 8 shows a rotor with stratification and with a peripheral valve [21] or circumferential opening which permits bowl cake to be discharged while the rotor is running. The valve is kept closed until an accumulation of solids has been deposited in the rotor, being normally held tightly closed by springs. Hydraulic pressure under the inner bowl is used to raise it and thus open the valve. By using a timer this

may be done automatically at predetermined intervals. This machine may be used where several per cent of suspended solids are to be centrifugally removed from a liquid. One commercial use is for fish-oil recovery. Particles of solid fish form the bowl cake which is intermittently discharged. A normal-sized rotor is 14″ in diameter and runs at 6,400 rpm.

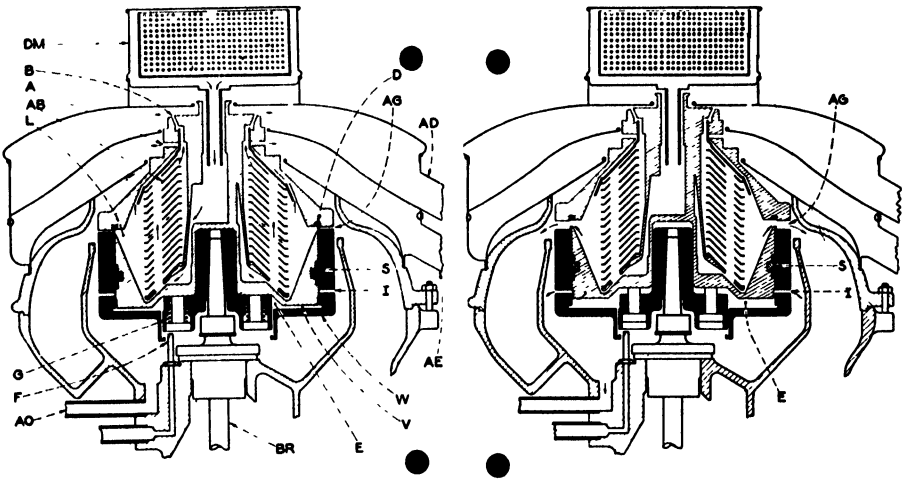

FIGURE 8. Rotojector rotor (discs shown in right half only). The upper half can be raised by hydraulic pressure while the rotor is running.

Variations of this general type of self-cleaning rotor are available. One variation, the "Nozljector," has nozzles fitted in the periphery of the rotor so that a percentage of the liquid passing through the rotor discharges through the nozzles carrying the deposited solids with it. Such rotors are used for yeast concentration. Another variation, the "Autojector," has such nozzles also, but has automatic means for keeping the nozzles closed except when a predetermined depth of cake has accumulated in the rotor. Such rotors are used for wool-grease recovery from dirty scouring liquors. The sand and dirt are discharged through the automatic valves so that they do not clog the rotor.

Type IV: Recirculating Rotor

The Merco centrifugal has a rotor [18] with nozzles at the periphery for the continuous discharge of the high-density fraction, in conjunction with feed-back passages in order that this fraction may be recycled for further concentration or for purging from it a third fraction of intermediate density. A suspension of corn starch and corn protein in water may thus be separated into two fractions, one the starch and some water, the other the protein and the remaining water. Another use for this type of machine is the removal of oversize particles from thixotropic "muds" [14] weighted to prevent gas discharge while drilling oil wells.

Type V: Solids-Conveyor Rotor

The Bird centrifugal has a rotor [20] which runs some 10 rpm slower than the concentric helicoidal conveyor mounted inside the rotor and operated by differential gearing. The helicoidal conveyor discharges the solids after they deposit on the wall of the rotor. The clarified liquid discharges continuously from the large end of the rotor. A normal-sized machine has an 18″ diameter rotor running at 2,000 rpm. One use for these machines is the classification of a suspension of clay in

water. Oversize particles are deposited in the rotor and discharged separately. The smaller colloidal material remains suspended in the effluent water from which it may be recovered by filtration.

Type VI: Periodic Centrifugals

Large diameter (20″ to 80″) batch-type rotors with imperforate walls, available in commercial centrifugals, are sometimes used for the removal of colloidal material suspended in a liquid. The liquor may be fed continuously to the spinning rotor until a load of deposited solids is accumulated in the rotor. Then a knife-like unloading mechanism can be used, without stopping the rotor, to remove the deposited solids. Commercial centrifugals are available in which this operation is entirely automatic. This type of centrifugal has been used for the removal of protein from soybean meal. The meal is first suspended in caustic liquor, thus dispersing the protein. The protein will then be deposited in the rotor of the centrifugal when the liquor is fed through it.

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26. U. S. P. 2,085,538, assigned to Bird Machine Co., South Walpole, Mass.
27. This anomalous statement is based on the following considerations: The earth's surface being largely covered by a continuous body of water free to conform to all the forces acting upon it, the centrifugal force of the earth's rotation enforces a "swell" at the equator of 27 miles in the earth's diameter, that is, a rise of 13½ miles in what otherwise would be the ocean level there. This tapers off as we move toward the poles, and at the mouth of the Mississippi (29° N. L.) it is 10.3 miles, while at the river's source (Little Elk Lake, Minn., 47°.4 N. L.) it is only 6.2. The difference, 4.2 miles, represents the height of the ocean at the mouth *above* the height of the ocean at the source. But the source is at an elevation of 1670 feet (0.32 mile), so that the net "upward flow" of the Mississippi is 3.8 miles.

    It must, of course, be remembered that the river itself is really a long, narrow arm of the ocean, and that the earth's centrifugal force, acting upon its waters, is what makes the river "run uphill."

Adsorption from Solution by Activated Carbon

W. A. HELBIG

Chemical Engineer, Darco Corporation

Activation Methods

Activated carbon may be visualized as a solid foam, *i.e.*, a large surface within a rigid granule or particle structure of relatively small volume.

Such a structure may be achieved by heating or chemically treating organic matter, preferably of cellular structure, such as woody products or bone. Activation by means of heat is essentially a process of destructive distillation, whereby a portion of the material is driven off in the form of volatile products, leaving a carbonaceous residue with a large volume of internal voids. Chemical activation, ordinarily accomplished with zinc chloride or phosphoric acid and usually supplemented by heat treatment, achieves a similar result.

Factors Involved in Activation

The development of a large area per unit weight is, however, only part of the process of activation. Area may be considered the capacity factor of the energy involved in adsorption on carbon. The corresponding intensity factor appears to be of the nature of interfacial tension, as is suggested by the differential form of the simplified Gibbs equation for adsorption from solution.[1, 2]

$$\frac{RT}{C}dC = -\omega d\sigma$$

in which C is concentration of solute, ω is interfacial (wetted) area, and σ is interfacial tension, $-\omega d\sigma$ thus being the differential change in interfacial energy associated with a differential change in solute concentration dC.

Since the nature of the wetted surface plays a large part in interfacial tension, it will be seen that activation of carbon must include conditioning of the developed surface so that first of all it is wettable, and secondly, that it provides an interfacial tension favorable to high adsorption per unit area. If gases adsorbed on carbon are actually in the liquid state, as many investigators believe, these considerations apply to gas adsorption as well as to adsorption from solutions.

If we accept the fundamental premise that adsorption occurs only at the liquid-solid interface, *i.e.*, that the reduction of concentration in the solution is wholly accounted for by transfer of solute to the interface, it follows that the amount of excess solute per unit area of interface is a function of the interfacial tension. This, of course, may in turn be influenced by such surface properties as configuration of surface carbon atoms, free valence bonds, etc., and such properties of the adsorbed solute as molecular orientation, polarity, etc., concerning which so much has been written in the literature on activated carbon.

Surface conditioning is effected by control of activation temperature and time, and of the activation atmosphere, which may be modified by the use of mild oxidants such as steam or carbon dioxide. The raw material used also influences the surface character of the finished product.

Adsorption Selectivity

Within rather broad limits, activated carbon can be given a degree of selectivity toward certain classes of adsorbates. This must, however, be taken in a strictly qualitative sense; selectivity with respect to a specific adsorbate cannot be imparted, because it is not possible to measure quantitatively the surface characteristics involved, nor to correlate these with the physical and chemical properties of the adsorbate.

With regard to selectivity, two broad classes of activated carbon are produced commercially: one, carbons especially suited for gas- and vapor-phase adsorption, and the other, carbons designed for adsorption in liquids and solutions. The gas- and vapor-adsorbent carbons have low capacity for adsorption from solutions, and conversely, the carbons designed for use on liquids usually have low adsorptive capacity for gases and vapors.

This differentiation very possibly arises from the fact that the gases and vapors adsorbed by the first class of carbons are in general of relatively simple physical and chemical composition, and of relatively low molecular weights and dimensions, whereas the second class of carbons must be activated to adsorb bodies of considerable complexity, which are frequently colloidal or semi-colloidal in nature, such as the colors, gums, and colloids encountered in sugar refinery operations. Although direct measurement has not proved possible to date, there is strong circumstantial evidence that the capillary diameters in gas carbons are very much smaller than in carbons used for liquid purification, and that in both cases, these diameters are of a molecular order of dimension, those of the gas carbons being too small to permit entrance of complex molecules or of colloids.

Types of Carbon Suitable for Adsorption from Solutions

Classified as to type of raw material used in their production, carbons suitable for adsorption from solutions may be divided into carbons of animal origin, commonly designated as bone char, and carbons of vegetable origin. The raw materials used in producing vegetable carbons in the United States are lignite, wood charcoal, and the black ash residue which is a by-product of paper manufacture.

Bone Char. Bone char is used primarily for sugar refining, having been in use by that industry since the early part of the nineteenth century. Freshly made char consists of approximately 90 per cent mineral matter, mostly calcium phosphate, and about 10 per cent carbon. It is of granular structure, the mesh distribution being about 16 × 30: *i.e.*, the granules are of such size that they will pass a screen having 16 openings per linear inch, and will be retained on one having 30 openings. Decolorization of sugar liquors is effected by percolating these through filters holding about 1200 cubic feet of the char.[8] The rate of flow usually ranges from 150 to 250 cubic feet per hour.

The installation required is between 25 and 40 such filters per million pounds of sugar melted per day. Each filter is ordinarily used for the treatment of a succession of liquors of diminishing purity: a filter containing new or freshly regenerated carbon is used first on liquor of relatively low color, *i.e.*, high purity; as the char becomes spent to the point where this liquor no longer leaves the filter with a satisfactory color, liquor of lower purity is filtered through it, and so on.

When it is no longer economical to continue, the filter is cut out of service and "sweetened off." The liquor remaining in the char is first displaced by flowing hot water into the filter under pressure; by careful operation, a large fraction can be so displaced without dilution. The diluted liquor following this displacement is reconcentrated, and the water following the diluted liquor is sent to waste, as it contains too little sugar to warrant recovery.

The spent char is revivified by "burning" in char kilns, at a temperature of 1000-1200° F. Dust losses through attrition from mechanical handling and physical

shrinkage of the granules caused by the burning, require fresh char replacement at the rate of 15 to 30 per cent annually.

The size of the bone char installation, the complexity of its operation, and the large volumes of filter wash water containing recoverable sugar to be reworked have led in recent years to extensive use of the powdered activated carbons of vegetable origin. The beet-sugar industry uses this type of carbon almost exclusively; in the cane-sugar industry, the availability of vegetable carbons has led to a sizeable production of "tropical refined" sugar, and in the corn sugar industry, a number of large refineries have abandoned bone char in favor of vegetable carbons.

Vegetable Carbons. These carbons are applied by stirring a small percentage with the liquid to be treated, for a period of ten to thirty minutes, and then removing them by filtration.

The dosage required depends upon the nature and amount of impurity to be removed; on beet-sugar liquors the range is 0.20-0.60 per cent, on cane sugar liquors 0.25-0.50 per cent, and on corn sugar liquors, 0.75-1.25 per cent. These figures are based on solids contents of the liquors; for cane sugar and glucose, they refer to dosages applied in two-stage countercurrent treatment.

Temperature as an Adsorption Factor

Temperature of treatment is determined by the nature of the liquid being treated. In general, it is advantageous to treat at as high a temperature as the nature of the liquid permits. This is apparently a contradiction to theoretical considerations, as the Gibbs equation

$$a = -\frac{C}{RT}\frac{d\sigma}{dC}$$

in which a is mols adsorbed per sq cm of interface, indicates that increase of temperature should result in decreased adsorption. Actually, the governing factor appears to be viscosity; as this is reduced by increase of temperature, penetration of the liquid into the sub-microscopic capillary structure of the carbon is improved, with proportionate effect on development of effective interface and rate of adsorption.

In the case of sugar and many other organic solutions, an upper limit is imposed on treatment temperature by the effect of heat on the solute being purified. Thus sugar solutions, depending upon type, are usually treated at 155-185° F. With solutions in which heating does not cause darkening or decomposition, carbon treatment is frequently carried out at the boiling point.

With waxes and other liquefiable substances, the treatment temperature should be sufficiently above the melting point to insure that solidification does not occur in the treatment tank, pump, and filter. Steam-jacketed filters are frequently used in handling such materials. No general rule can be given; in many cases a temperature 20 to 30° F above the melting point is satisfactory, but higher temperatures may be necessary to reduce viscosity to a point at which satisfactory handling is possible.

Temperature has a definite effect on the adsorption of volatile substances, the adsorption equilibrium being displaced in the direction of desorption with increase of temperature. With volatile adsorbates, especially when the liquid is of relatively low viscosity, carbon treatment is best conducted at room temperature, or even lower if this is feasible. In such cases a somewhat longer contact time than the usual ten to thirty minutes may be necessary.

Time as an Adsorption Factor

It is frequently stated that adsorption is a substantially instantaneous process. When powdered activated carbon is added to a liquid, however, time is required to reach adsorption equilibrium. Even though such carbon has a particle count ex-

pressed in billions per gram, each suspended particle must be considered to have a definite "sphere of adsorption" many times greater in volume than the particle itself, and it must "sweep" this sphere under the impulse of stirring to bring about the full reduction in concentration of which the extent and nature of its area is capable.

Contact time required to reach adsorption equilibrium is therefore inversely proportional to the dosage of carbon used. This is strikingly illustrated in the case of carbons used to remove tastes and odors from water—the dosages employed are on the order of one to five parts per million, and a contact time of 90 to 120 minutes or more, with active agitation, is required to reach equilibrium. For the same reason, a relatively longer contact time is necessary for carbons of high adsorptive capacity than for those of lower capacity. Smaller dosages of the former are required to achieve a given amount of adsorption; hence a relatively longer time must be allowed for the smaller number of particles to sweep the liquid thoroughly and bring about the maximum possible reduction of adsorbate concentration in it.

The effect of viscosity on penetration of the liquid into the capillary structure of the carbon has already been mentioned; this, and the effect of viscosity in retarding motion of the particle during stirring, are also factors affecting contact time necessary to reach equilibrium.

A third factor which is not commonly encountered is suspended matter other than carbon in the liquid. If this is appreciable in amount it will reduce the "mean free path" of the carbon particle in sweeping its "sphere of adsorption" and thereby increase the necessary contact time.

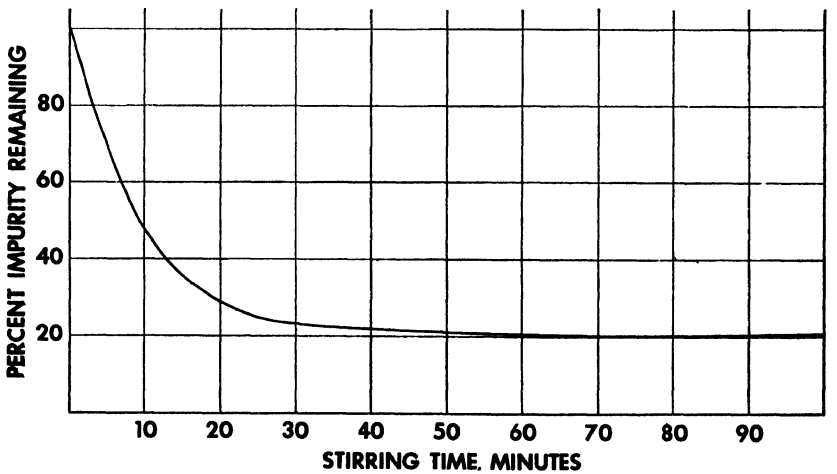

FIGURE 1. Typical contact time curve.

The course of adsorption with time, and the time necessary to reach substantial equilibrium, can be readily shown by plotting a contact time curve. This is done by treating a series of samples of solution each for a different time period before filtering off the constant dosage of carbon. The residual colors or concentrations of adsorbate for the various samples are then plotted against the corresponding contact time periods. In general, the residual concentration falls rapidly within the first ten minutes, and then more slowly; this portion of the curve has the appearance of an asymptote following the time axis. As a practical matter, that contact time is chosen for regular use, beyond which there is insignificant further reduction in adsorbate concentration.

pH as a Factor in Adsorption

It is frequently stated that carbons adsorb more effectively in acid solutions than in alkaline solutions. This generalization happens to be correct for many industrial applications of carbon, but it should not be used as a criterion without qualification. The principal effect of pH on carbon adsorption appears to be indirect, through its influence on the solubility of the adsorbate. As a rule, maximum adsorbability is associated with minimum solubility, and this frequently occurs in the alkaline pH range. Alkaloids, for example, are more strongly adsorbed in this range than in acid solution, where their solubility is usually greater; also, if the adsorbate is colloidal and has an isoelectric point or range on the alkaline side, it will be more strongly adsorbed there than in acid solution.

Metal ions in true solution are not strongly adsorbed by decolorizing carbons, but if pH adjustment in the alkaline direction results in the formation of a colloidal hydroxide or other colloidally dispersed compound, good adsorption is frequently possible.

The impression that carbons adsorb better in acid than in alkaline solutions probably arises from the fact that above pH 9.5-10.0, many adsorbable substances are susceptible to hydrolysis, with consequent simplification of physical and chemical structure and therefore lower adsorbability.

It is conceivable also that in the higher alkalinity ranges, the part played by alkalinity in determining the interfacial tension between carbon surface and solution is dominant: the σ, C curves of alkaline solutions, it will be recalled, ordinarily have a positive slope, whereas for adsorption, the prerequisite is a σ, C curve of negative slope. It is to be expected therefore that in terms of interfacial tension, alkalies having a σ, C curve of positive slope would affect equilibrium in the direction of desorption.

The desorptive effect of alkalinity, both with and without accompanying hydrolysis, is indicated by the fact that it is frequently possible to effect partial regeneration of a carbon that has adsorbed a substance in the lower pH range by subjecting it to an alkaline wash. The adsorbate may be recovered without substantial change at moderate alkalinities, whereas at higher alkalinities, the material recovered from the carbon may be a partially or completely hydrolyzed form of the original; usually it can be described only as a "gooey mess."

Carbon Dosage

The Freundlich Adsorption Isotherm. With treatment temperature and contact time established, the third variable to be fixed in any particular application is minimum carbon dosage. For this, the empirical Freundlich adsorption equation, and its plot on logarithmic paper commonly known as the Freundlich adsorption isotherm, are very useful.

The Freundlich equation is usually written $X/M = KC^{1/n}$. In this, X is units of adsorbate held by the carbon, and M is the carbon weight with which such adsorption was effected. C is concentration of substance remaining unadsorbed at equilibrium. The two constants K and $1/n$ are particular to the system, *i.e.*, to both the carbon used and the nature of the adsorbate. The equation thus correlates adsorptive capacity per unit weight of carbon, X/M, with concentration of adsorbate remaining in solution at equilibrium.

The equation in logarithmic form appears as

$$\log\left(\frac{X}{M}\right) = \log K + 1/n \log C,$$

which is a straight-line equation having a slope of $1/n$ and an intercept of K at $C = 1$. The numerical value of K is of course dependent upon the units employed to express C.

Adsorption data plotted as X/M vs. C on logarithmic paper will in practically all cases give a straight line over a considerable range of concentration. The line will curve at both ends (*i.e.*, K and $1/n$ are no longer constant) at extremes of concentration.

The problem of ascertaining carbon dosage in industrial uses may be stated as follows: What dosage is necessary to reach a given permissible residual concentration of impurity? The laboratory procedure consists in treating a series of samples of the liquid or solution in question with different weights of carbon, along with a blank sample on which no carbon is used, for the length of time and at the temperature indicated by preliminary tests on these two factors. If nothing is known about the response of the impurity to adsorption, a trial test with widely spaced carbon dosages, *e.g.*, 0.5, 1.0, 2.0, and 3.0 per cent, is desirable, to ascertain the correct dosage range that will give the desired residual impurity concentration. A second, more closely spaced series of dosages can then be run, *e.g.*, 0.1, 0.3, 0.5, 0.8 and 1.2 per cent.

Upon completion of the treatment the carbon is filtered out of each sample, and the impurity residual determined for each filtrate, including the blank. The results are tabulated, as shown below, for an isotherm on benzoic acid adsorption and the corresponding X/M values calculated for plotting.

Table 1. Benzoic Acid Adsorption Data

(Tests of 50-cc samples of solution, $C_0^* = 0.1500$ gram)

M (grams) Carbon Dosage	C (grams/50 cc) residual Benzoic Acid	X (grams acid adsorbed) $= C_0 - C$	$\frac{X}{M}$ (grams acid adsorbed from 50 cc per gram of carbon)
0.0	0.1500	....	.....
0.2	0.0900	0.0600	0.3000
0.4	0.0560	0.0940	0.2350
0.7	0.0256	0.1244	0.1791
1.0	0.0136	0.1364	0.1364
1.5	0.0070	0.1430	0.0953
2.0	0.0040	0.1460	0.0730

* C_0 is the concentration of the blank sample.

Let us suppose that the dosage to reach a concentration of 0.01 g/50 cc is sought. From the isotherm plot, read off the X/M for this C value; it is 0.113. The X value is $0.1500 - 0.0100 = 0.1400$; thus $\frac{0.1400}{M} = 0.113$, and the desired M value is 1.24 grams per 50 cc.

It is to be wondered, perhaps, why the apparently simpler procedure of plotting M against C, and reading M directly from this plot, is not preferable to that outlined above. The reason is that in general an M vs. C plot is curvilinear on all ordinary coordinates; the dependable linearity of the X/M vs. C plot on logarithmic coordinates is a very useful check on adsorption abnormalities, which are not detectable in the curvilinear M vs. C plot. Furthermore, the important constant, $1/n$, cannot be given a numerical value from such a plot; as will be discussed in a subsequent section, this constant is necessary for countercurrent dosage calculation, if the single dosage is found to be too high from a cost or operating viewpoint. In the X/M vs. C plot, $1/n$ is numerically equal to the slope of the straight line, and as such is very simply determined.

It is possible to determine both M and $1/n$ graphically from the isotherm plot, and to plot the isotherm itself without computing any X or X/M values, if C is expressed as a percentage of C_0. This is done [4] by using logarithmic paper which has printed on it the locus of X vs. C in percentage units, and a scale rule logarithmically divided, as shown in the illustration. (Fig. 3) The X vs. C locus is used as a guide curve; to plot a particular (M, C) point, the scale rule is laid on the paper with the

M-scale edge on the C line in question; the 1 of the M-scale is set on the printed guide curve. The point is plotted by making a mark on the graph sheet at the M-scale value in question.

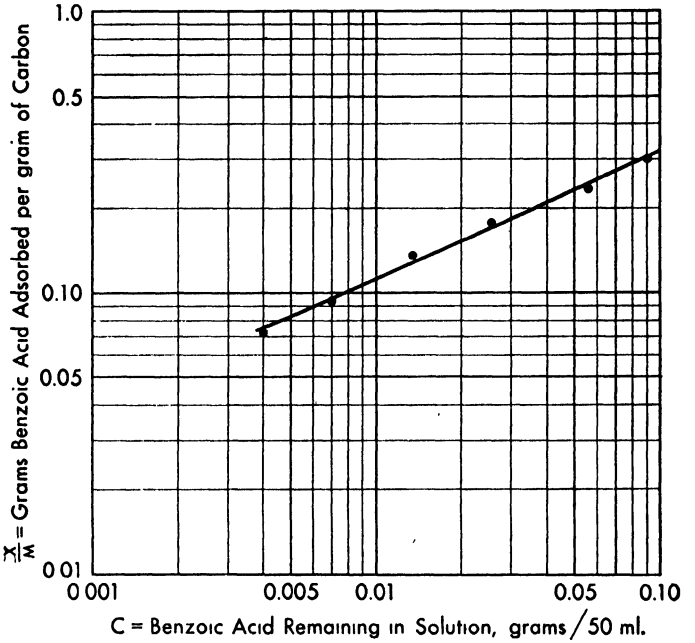

FIGURE 2. Benzoic acid adsorption isotherm.

Mathematically this is a slide-rule operation; the guide curve point at which 1 of the M-scale is set has for its ordinate the value log X. The scale rule operation subtracts log M from log X, thus giving log X/M, the ordinate sought for the corresponding abscissa C. Thus X/M is plotted against C directly from the laboratory data M and C.

The solution for M to reach the desired C_f (permissible residual concentration) is accomplished graphically by laying the M-scale as before with 1 on the guide curve and the M-scale edge on the C_f line; the M value sought is read off at the point where the isotherm line cuts the M-scale.

One great convenience of this method of plotting is that it makes possible the solution of the Freundlich equation for C when M is given; this cannot be done algebraically. Graphically, it is accomplished by using the guide curve as a track for 1 of the M-scale, which is moved across the paper until the plotted isotherm cuts the scale at the given M value. The C line at which this occurs is the value sought.

The reverse side of the M-scale rule carries a $1/n$-scale, arithmetically divided, by means of which the slope of the isotherm is quickly measured.

The specially printed logarithmic paper and the scale rule used with it have been available for some years, and are in widespread use in industrial laboratories. This plotting is particularly useful in calculating countercurrent carbon dosages, a subject discussed in greater detail in a later section.

The Freundlich equation is applicable (*i.e.*, a straight-line plot is obtained on logarithmic paper) when the concentration C is expressed in units of color [5] or odor intensity,[6, 7] providing that the units employed are linearly proportional to the actual concentration of the color or odor substances adsorbed. In fact, it is rarely possible

in industrial work to determine either the composition or the gravimetric concentration of a colored or odor-causing adsorbate. This fact must be clearly borne in mind in considering decolorizing or deodorizing capacities of carbons; color or odor may be adsorbed with relatively smaller carbon dosage from one type of solution than from another, merely because a smaller gravimetric amount of adsorbate is involved, even though this may have a high color or odor per unit weight. Conversely, a faint color or odor may require relatively high carbon dosage because of association with an appreciable gravimetric concentration of adsorbate.

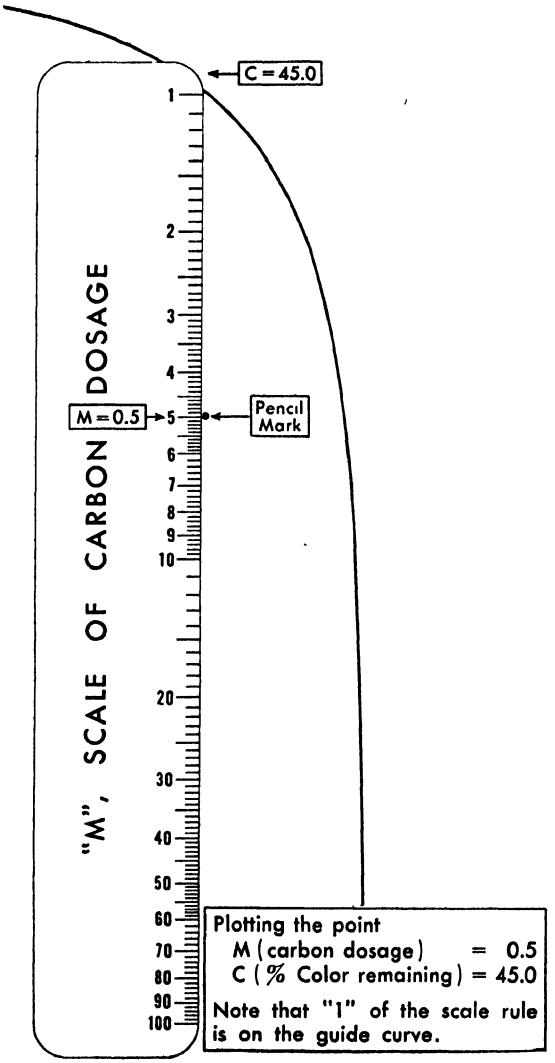

FIGURE 3

The slope $1/n$ of the Freundlich equation is an index of the ease or difficulty with which a color or odor is adsorbed. In view of the wide possible range of proportionality between these and actual concentrations of adsorbate, such isotherms have

a range of slopes varying from 0.1 or less to high values of 2.0 and even 3.0; $1/n$ is always greater than zero.

Deviations from the Freundlich Equation. There are two types of cases in which continuous straight line plots are not obtained. In one of these, frequently encountered in vegetable-oil decolorization and occasionally with other liquids, there is an abrupt discontinuity of adsorption. This is indicated by a sharp break known as the "apparent end point" at the low-concentration end of the isotherm; dosages of carbon greater than that which is just sufficient to reach the color at the end point effect no significant further decrease in color. The logarithmic plot of X/M vs. C for such dosages therefore is a line extending steeply downward from the end-point; C and X remain substantially unchanged, and the quotient X/M becomes rapidly smaller as the M values increase.

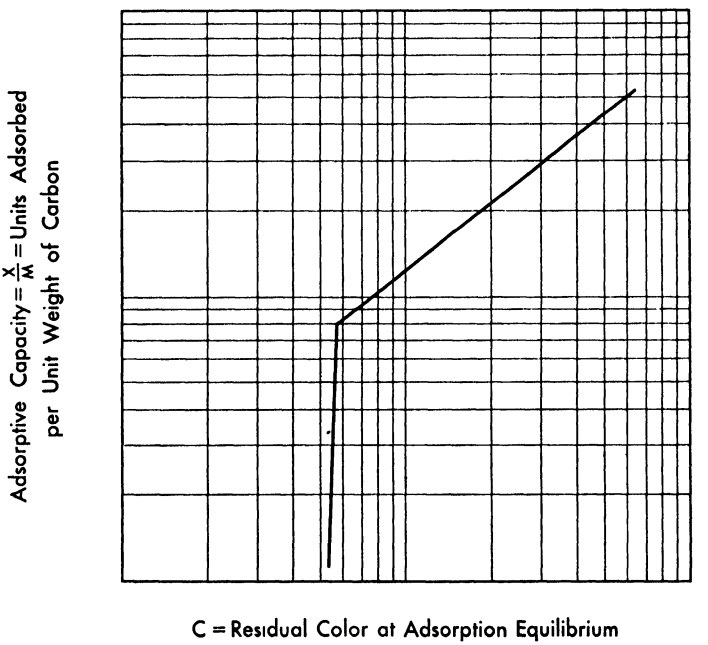

FIGURE 4. Isotherm with apparent end point.

The most reasonable explanation of this phenomenon is that the residual color below the end point is associated with a material that is not appreciably adsorbed by the carbon in question. The end point for a particular liquid having this characteristic is not necessarily at the same color for all carbons; furthermore, an end point will not necessarily be found to exist for all carbons tested on that liquid.

The second type of case in which adsorption data do not give a continuous straight line plot for color isotherms occurs in instances where the carbon contains extractable matter which imparts a color to the liquid. The most common offenders are extractable iron, alkalies, and sulfides. Iron is capable of causing appreciable darkening when carbon containing it is used on many organic acids, or on liquids containing tannates and related substances. Alkalies will cause darkening of many of the color bodies in sugar liquors and solutions of other crude organic compounds, and sulfides may cause darkening by reacting with traces of metal compounds present in the solution treated.

The residual colors measured on filtrates from carbon treatment in such cases will be resultants of the actual color adsorbed and the color developed in the solution by the extracted soluble matter. The effect of the latter is most pronounced at higher carbon dosages; the colors read corresponding to these dosages will be erroneously high, and the color reduction per unit weight of carbon erroneously low, so that the isotherm bends downward with increasing rate of curvature at the low C (high M) points.

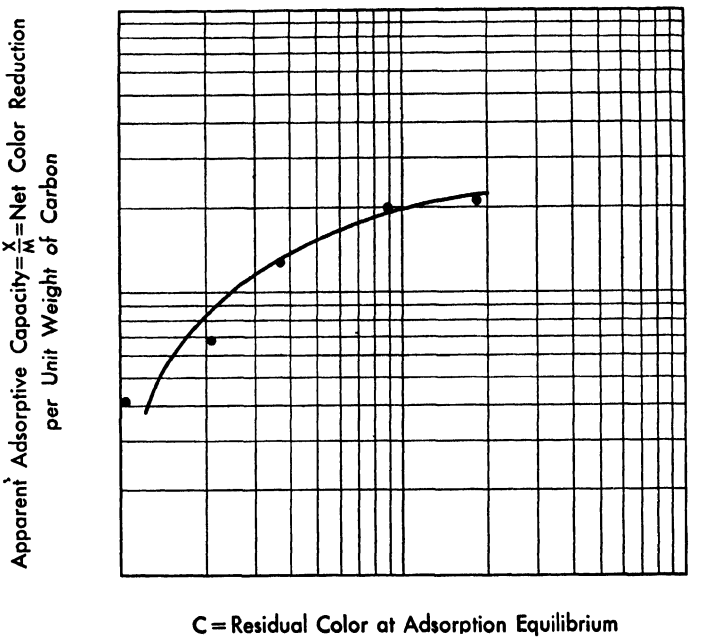

FIGURE 5. Isotherm curvature caused by soluble iron in carbon (tartaric acid decolorization).

To these two types of deviation from a straight line plot should be added a third, which arises from an error in color measurement that is not uncommon. The quotient X/M which is plotted against C is calculated as follows: for each dosage M used, the corresponding residual color C is subtracted from C_o, the color of the liquid without carbon treatment (measured on a blank sample that has been handled in exactly the same way as the carbon-treated samples, except that no carbon was added to it). Original color minus final color gives X, color removed, which is then divided by M to give X/M.

Now, C_o in many cases is a rather dark color, the measurement of which in many colorimeters is susceptible to considerable error. If an erroneously high value is obtained, all the X/M values for the test series will be erroneously high, and the effect of this error will be proportionately greater at low X (high C) values. The isotherm will therefore curve upward in this region; conversely, it will curve downward if the C_o value measurement is erroneously low. Where such curvatures are found, error in C_o measurement should be suspected, and this value carefully rechecked.

The discontinuity involved in the apparent end point phenomenon, and the curvature of the isotherm resulting from solubles in the carbon or from error in C_o measurement are sometimes cited as invalidating the usefulness of the Freundlich

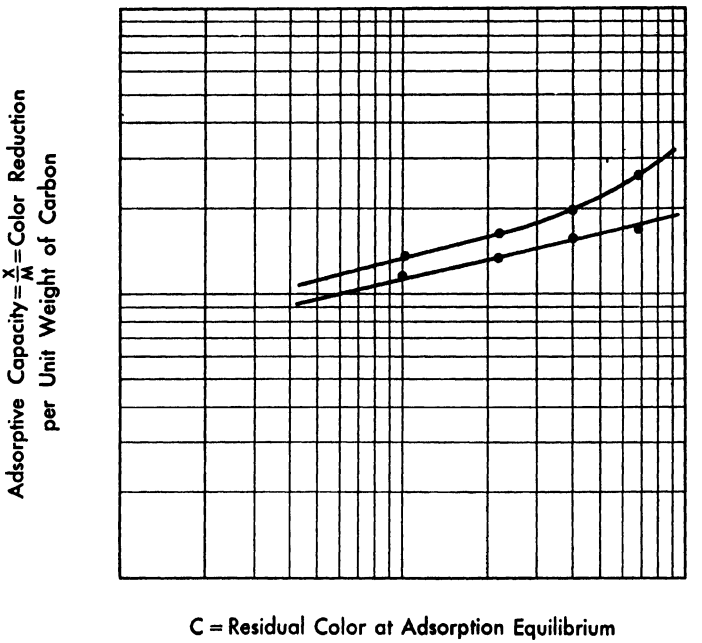

FIGURE 6. Isotherm curvature from erroneously high C_o value (straight isotherm plotted with correct C_o value).

isotherm. This is unfortunate and misleading, because in the great majority of cases adsorption data plots very satisfactorily as a straight line over the entire range of color or adsorbate concentration involved in industrial applications. In fact, failure to obtain a linear plot is so exceptional that it may be considered an indication of abnormality. For example, the important fact that an apparent end point exists can be established unmistakably only by the Freundlich isotherm plot; that a curvature of the isotherm is due to solubles in a carbon may be established by the linearity of isotherms obtained with carbons of low solubles content on the same liquid, and the characteristic curvature due to C_o error serves as a warning to recheck this value.

Calculations and Operating Charts Based on the Freundlich Isotherm:

The real usefulness of the Freundlich equation and isotherm lies in the computations and charts which may be derived from it.

Relative Efficiency of Carbons. For example, the adsorptive capacities of a series of carbons in a particular application may be compared directly from their isotherm lines. The equation indicates that adsorptive capacity, *i.e.*, X/M, is a function of equlibrium concentration of adsorbate; comparison of adsorptive capacity for a series of carbons can therefore be made only at a common C value. (Unless the isotherms in question are parallel, the X/M ratios at one C value will be different from those at another C value). As a practical matter, the C value at which comparisons are usually made is the C_t, or permissible residual concentration of impurity.

The X/M ratios at a common C value are really the reciprocal ratios of the carbon dosages required to reach the C value in question, since if C is common, X is also common:

$$\frac{X/M_A}{X/M_B} = \frac{M_B}{M_A}$$

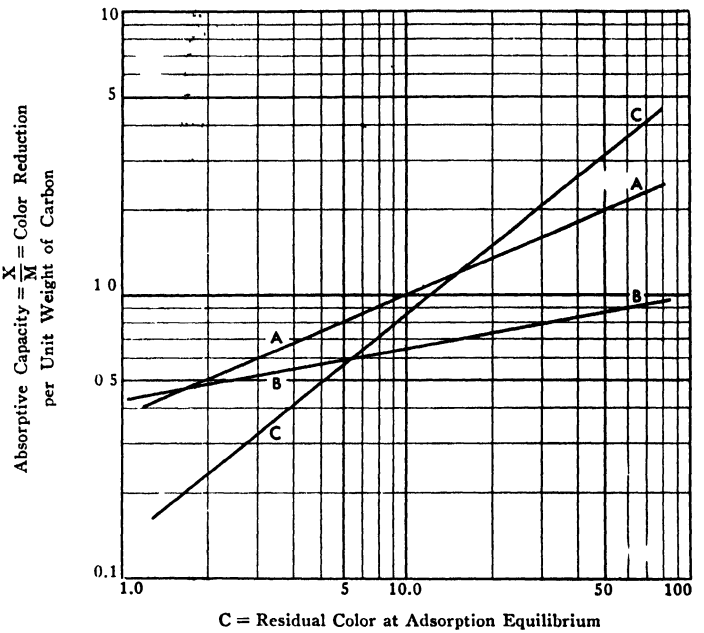

FIGURE 7. Use of isotherm to compare relative efficiencies of carbons.

The extent to which these ratios may differ at different C values is indicated in Fig. 7 and Table 2 which represent a common type of occurrence. Carbon A is used as the reference sample.

Table 2.

Concentration	$\frac{M_A}{M_B}$	$\frac{M_A}{M_C}$
5	1.35	1.55
10	1.58	1.19
20	1.87	0.91

Carbon B is seen to be consistently less efficient than Carbon A over this range of concentration; but as concentration decreases, Carbon B approaches Carbon A in efficiency, and as the isotherms show, becomes equal to it at a concentration of 1.6. On the other hand, Carbon C is poorer than Carbon A at concentrations 5 and 10 but better at 20, where Carbon A has only 91 per cent the efficiency of Carbon C. The X/M ratios thus give the *relative efficiencies* of the carbons, or R.E. values, as they are commonly called by manufacturers and industrial users of carbon.

Carbon Dosage Charts. In the day-to-day control of the use of activated carbon in a plant, especially in decolorizing applications, it frequently happens that the color of successive batches of solution to be treated will vary somewhat. If uniformity of carbon treatment is to be assured, the carbon dosage M needed to secure with each batch the same permissible residual of impurity (C_f) must be varied in proportion to the color of the batch to be treated (C_o). One way to ascertain this dosage

is of course to run a laboratory test on each batch, plot the isotherm, and determine M from this for the desired C_f.

The time and effort which this entails can be avoided, however, by taking advantage of a characteristic of the Freundlich equation. If for X, we use its equivalent $C_o - C_f$, the equation becomes:

$$\frac{C_o - C_f}{M} = KC_f^{1/n}$$

In the problem under consideration we are dealing with a constant, C_f, and a variable C_o and M; the rearranged equation $C_o = KMC_f^{1/n} + C_f$, being of the form $y = ab^{1/n}z + b$, is seen to be linear in form, when M is plotted against C_o on ordinary coordinate paper.[8]

To obtain this plot a series of adsorption isotherms is determined, each isotherm being the outcome of a test with solution of different original color (C_o). From these isotherms the dosages required in each case to reach the same C_f are obtained, and are plotted against the corresponding C_o values, as shown in Fig. 8.

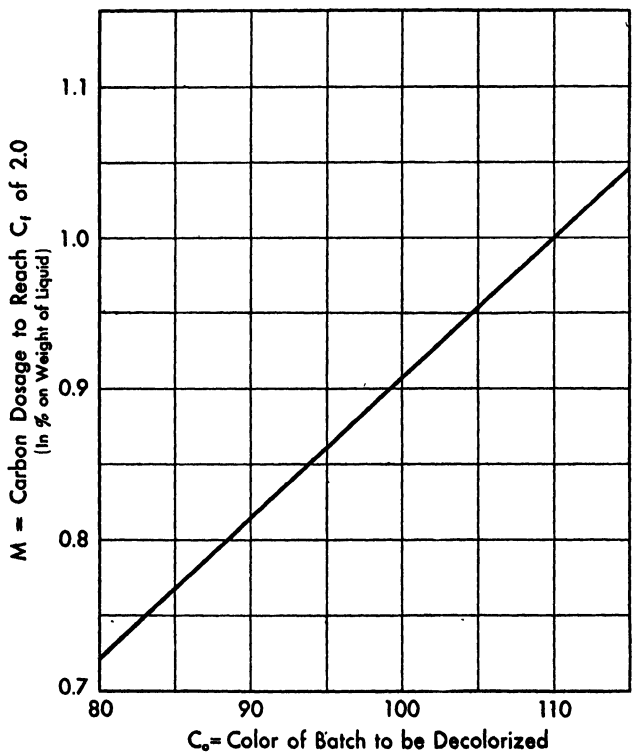

FIGURE 8. Typical carbon dosage chart for decolorization control in plant scale operation.

Such a plot constitutes a carbon dosage chart; to use it in plant control, it is necessary only to determine the C_o of a particular batch and read off the corresponding dosage from the chart. It must of course be borne in mind that the chart fails if the batches vary not only in amount of color, but also in nature of color, for such variation usually involves a change in K and $1/n$ of the adsorption equation, under which the simple linear variation of M with C_o no longer holds.

Countercurrent Treatment. The situation frequently arises, in industrial use of activated carbon, that the dosage required to reach the permissible residual of impurity exceeds the limit imposed by cost considerations, or by the capacity of filtration equipment. This may be the case when a very low residual (C_f) must be reached, or when the slope of the isotherm is steep, *i.e.*, carbon dosage increases rapidly with decreasing values of C.

When carbon is applied countercurrently, a given C_f can be reached with an appreciably smaller dosage than in single-step treatment. For example, if the C_f to be reached is 1 per cent of C_o, and the slope of the isotherm $1/n$ is 0.42, the countercurrent dosage is only one-fourth the single-step dosage; in an extreme case, such as $C_f = 0.1$ per cent of C_o and $1/n = 0.75$, the ratio is as low as 1:20.

Two-stage countercurrent treatment is conducted as follows. The liquid being purified is given a first treatment with carbon that has already been used once. After agitation and filtration in the usual manner, the now twice-used carbon is discarded, and the liquid is given a second treatment with a weight of new carbon equal to that of the once-used carbon in the first step. The second treatment brings the liquid to the desired C_f, and the carbon filtered off from it is the once-used carbon employed for the first treatment of the next batch of liquid.

It will be apparent that to achieve the desired result as batch after batch of liquid is treated, the process must be kept in balance. It is therefore necessary to know quite accurately what carbon dosage, applied in the manner described, will give the desired C_f without the addition of supplementary carbon in either decolorization step. Such supplementary addition would of course throw the process out of balance for the next batch of liquid treated, requiring further dosage adjustment, etc.

The equations for determining countercurrent dosage have been derived by Sanders [9] from the Freundlich equation. The two-stage equations are

$$\frac{M_{cc}}{M_s} = \frac{C_i - C_f}{C_o - C_f} \tag{1}$$

and

$$\frac{M_{cc}}{M_s} = \left(\frac{C_f}{C_i}\right)^{1/n} \tag{2}$$

In these, M_{cc} is countercurrent dosage, and M_s, single treatment dosage required to reach C_f, final concentration desired; C_i is the intermediate concentration obtained in the first step of countercurrent treatment; C_o is original concentration, and $1/n$ is the slope of the isotherm obtained with new carbon in single-step treatment.

These equations are seen to be independent of the constant K of the Freundlich equation, and to involve six variables, of which M_s and $1/n$ are known from the isotherm, and C_o and C_f are known because they are given. The unknown variables are C_i and M_{cc}, and of these C_i must be found to determine M_{cc} from either (1) or (2).

The relationship between C_o, C_i, C_f, and $1/n$ is found by equating the right-hand members of (1) and (2) and rearranging:

$$C_i^{1/n+1} - (C_f)[C_i^{1/n}] = (C_o - C_f)C_f^{1/n} \tag{3}$$

Equation (3) cannot be solved algebraically for C_i. Sanders [9] has given a nomograph for determining C_i and M_{cc} over a range of $1/n$ from 0.0 — 1.6, and a C_f range of 7 — 91 per cent expressed as a percentage of C_o.

Because of the widespread use of countercurrent treatment, a chart [10] has been constructed (Fig. 9) from which $\frac{M_{cc}}{M_s}$ can be read directly, for $1/n$ values from 0.1 to 1.6, and C_f values from 0.1 to 25 per cent. The ratio $\frac{M_{cc}}{M_s}$ is given in terms of per

cent of single-use dosage required for countercurrent treatment. Reference to this chart indicates at once the saving in carbon dosage possible by two-stage countercurrent treatment, for a particular isotherm.

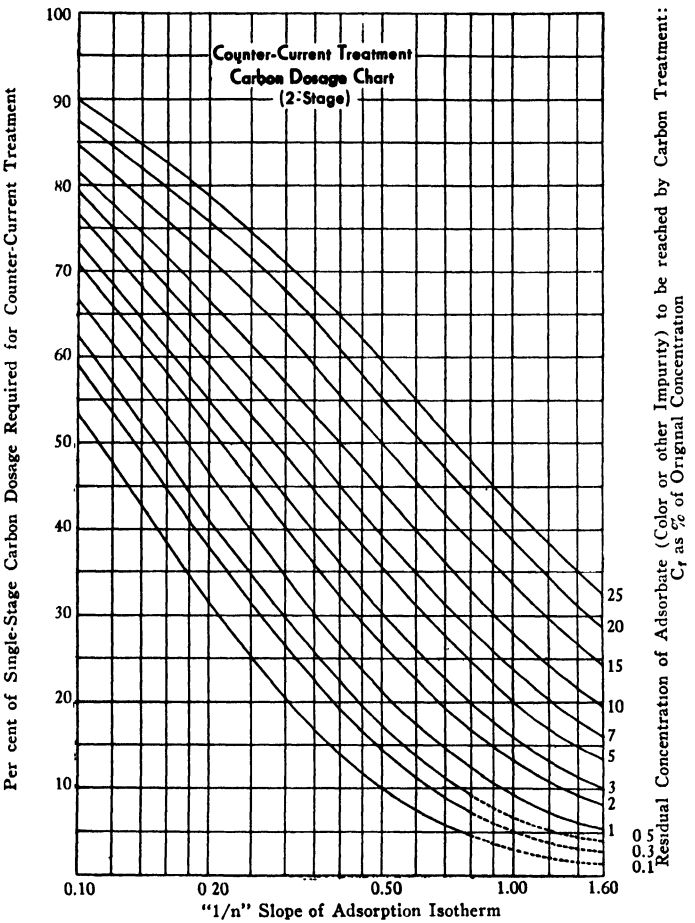

FIGURE 9

Fig. 10 is a similar chart, hitherto unpublished, giving $\frac{M_{cc}}{M_s}$ for three-stage countercurrent application.

By comparison of Figs. 9 and 10 it will be seen that the saving in carbon dosage under comparable conditions is greater between single-stage and two-stage use, than between two-stage and three-stage use. The decrement between three-stage and four-stage treatment is still less. Since countercurrent treatment involves extra handling and filtration steps, the net cost saving is given by subtracting the cost of these from the cost of the carbon saved. As the number of countercurrent steps is increased, the net saving falls off rapidly. For this reason three-stage treatment is used much less than two-stage, and four-stage treatment is almost never used. Three-stage treatment is justified only when the slope of the isotherm is very steep, and a very low C_f must be reached.

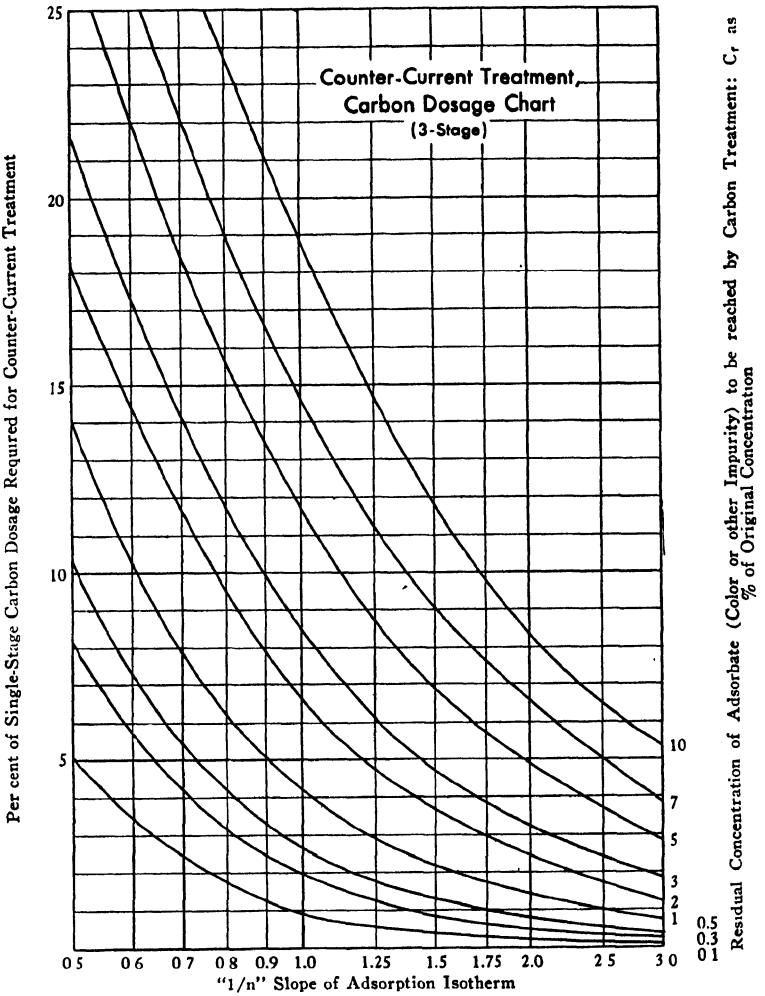

FIGURE 10

Split Feed Treatment

In many chemical plants it is the practice to make certain products at more or less irregular intervals, as orders are received or as warehouse stocks need to be replenished. Countercurrent use of activated carbon on such products is often not feasible, because of the necessity for storing partially spent carbon between production runs. Such storage may give rise to complications, through fermentation, oxidation, or other undesirable changes in the material adsorbed on the carbon.

Where the necessity exists, however, appreciable savings can be effected by using split feed treatment. This consists of two successive treatments, each with new carbon, and discarding of the carbon without reuse.

Walker, Lewis, and McAdams [11] describe the particular solution for the two successive carbon dosages which will give the same total adsorption as a given single dosage, from a particular adsorption isotherm. The general solution of this problem is given below:

Calling the first dosage M_1, the second dosage M_2, the single addition dosage M_s, the intermediate adsorption equilibrium concentration C_1, and the final concentration C_f, we have, from the Freundlich equation:

$$M_s = \frac{C_o - C_f}{KC_f^{1/n}}$$

$$M_1 = \frac{C_o - C_1}{KC_1^{1/n}}$$

$$M_2 = \frac{C_1 - C_f}{KC_f^{1/n}}$$

$$M_1 + M_2 = \frac{C_o - C_1}{KC_1^{1/n}} + \frac{C_1 - C_f}{KC_f^{1/n}}$$

Since $C_1^{1/n}$ is greater than $C_f^{1/n}$, it will be seen that $(M_1 + M_2)$ is less than M_s. Also, $(M_1 + M_2)$ must have a minimum value, since it can vary from $0 + M_2 = M_s$ to $M_1 + 0 = M_s$. The minimum is found by calculating $\frac{d(M_1 + M_2)}{dC_1} = 0$, which simplifies to $1 - 1/n = \left(\frac{C_1}{C_f}\right)^{1/n} - \frac{1/nC_o}{C_1}$

C_1 for a particular isotherm is calculated by trial and error or by graphical means, and M_1 and M_2 from C_1 by the equations given above, or more conveniently, by the graph and scale rule illustrated in Fig. 3.

As in two-step countercurrent treatment, two filtrations are necessary in two-step split feed treatment, and the saving in carbon is partially offset by the cost of the extra filtration. Theoretically, it should be possible, in the case of irreversible adsorptions, to conduct split feed treatment without an intermediate filtration: *i.e.*, to bring M_1 to adsorption equilibrium, and then, without filtration, to add M_2, using a single filtration to separate all the carbon after the second equilibrium has been reached. However, tests on a number of process liquids indicate that truly irreversible adsorptions are rare. In all cases tested, split feed treatment without intermediate filtration did not give the expected C_f value, but a value substantially equal to that which would have been reached had $(M_1 + M_2)$ been applied as a single dosage. This would indicate that upon addition of M_2, the equilibrium previously reached with M_1 readjusted itself through partial desorption, such that the final equilibrium approached that reached by $(M_1 + M_2)$ as a single addition.

It is recommended, however, that whenever split feed application is being considered, a test be run to ascertain whether intermediate filtration can be dispensed with, as this possibility involves an attractive saving in operating cost. This saving may be sufficient to put split feed treatment on a par with two-step countercurrent treatment, even though the latter permits a greater reduction in carbon dosage than the former.

As in countercurrent treatment, the carbon saving in split feed use, represented as the ratio $\frac{M_1 + M_2}{M_s}$, is greatest for low values of C_f, and high values of $1/n$, the isotherm slope. No simple method is possible for comparing $\frac{M_{cc}}{M_s}$, the countercurrent ratio, with $\frac{M_1 + M_2}{M_s}$, but in general the ratio $\frac{M_1 + M_2}{M_{cc}}$ ranges from about 1.3 to 2.0. Thus, for a given slope and C_f, the countercurrent dosage is roughly 50 to 75 per cent of the split feed dosage.

It has been pointed out in the section on time as an adsorption factor, that the contact time required to reach equilibrium is inversely proportional to carbon dosage. In split feed treatment this should be taken into account; since M_1 and M_2 are both

smaller than M_s, longer contact times are required for them than for M_s. Contact-time curves should be plotted to establish these respective times, for laboratory test work; and in plant operation, the contact times employed should be those which give the C_1 and C_f values called for by the calculations.

As for three-step and n-step split feed treatments, practical considerations render their usefulness doubtful. The calculations required to establish the successive dosages whose sum shall be a minimum are exceedingly complex. The savings to be accomplished fall off rapidly as the number of steps increases, and are quickly nullified by the cost of the additional filtrations. The sum of the required contact times quickly becomes impractical. Finally, in cases where two-step split treatment does not involve sufficient net saving, the more efficient two- or three-step countercurrent treatment can be resorted to, with such precautions as may be necessary in storage of partially spent carbon between production runs.

Stirring and Filtration in Plant Operation

As has been pointed out in the discussion on contact time, powdered activated carbon must be thoroughly stirred with the liquid being treated in order that each particle may completely "sweep" adsorbable matter from its "sphere of adsorption." The technique of stirring must therefore be such that turbulent motion of the liquid is produced, so that motion of carbon particles relative to the liquid results. Stirring which causes only stream-line motion of the liquid or "swirling" is ineffective; in such stirring the carbon particles merely ride with the liquid.

Turbulent stirring does not necessarily mean rapid stirring; swirling can best be avoided by judicious selection and placing of the agitating mechanism, and by the use of baffles suitably placed in the treating tank.

Excessively rapid stirring, and also excessive turbulence, may be quite harmful because of the air beaten into the liquid under such conditions—not because the air interferes with adsorption, but because it may oxidize the impurity and thus change its response to adsorption, or oxidize the solute being purified. In cases where sensitivity to oxidation is a serious factor, it may be necessary to conduct carbon treatment under vacuum, or under an inert atmosphere such as nitrogen.

In a few instances, even the air held in the carbon (between particles in the dry mass of carbon, and also that held within the pore structure of the particles) may have an adverse effect on the liquid. This air can be satisfactorily displaced by boiling the carbon with water for 20 to 30 minutes before using it; if the carbon is to be used on a non-aqueous liquid, incompatible with water, some other suitable liquid can be employed for the boiling operation. Displacement of adsorbed air by water or other solvent is probably not complete, as oxygen is tenaciously retained by carbon, but sufficient displacement occurs to permit use of the carbon in all cases hitherto encountered.

The stirring time necessary to reach adsorption equilibrium in plant-scale operation is not in general the same as the time required in laboratory tests, because in general the stirring conditions are usually quite different. The laboratory contact time may be used as a first approximation for plant use, and revised as may be indicated by samples taken from the treatment tank at suitably spaced time intervals.

Filtration is begun when adsorption equilibrium has been reached. Stirring should not be discontinued, however, because filtration usually requires an appreciable time, and the carbon remaining in the treatment tank should be kept uniformly suspended throughout this period. The reason for this is that the carbons furnished for industrial use are ground and screened to a distribution of particle sizes that will impart maximum filterability; if a portion of the carbon is allowed to settle in the treatment tank during filtration, the distribution of particle size in the carbon remaining suspended is quite different from that of a uniform suspension of all the carbon.

In filtration, carbon may be classed with the incompressible solids, as the filter cake undergoes substantially no change of bulk density within the pressure ranges ordinarily encountered in industrial filtrations. The filter cake densities of commercial carbons range from about 15 to 25 pounds of dry weight carbon per cubic foot of cake; for all ordinary purposes, they are equal to the maximum bulk densities of the dry carbons as determined by tamping these until no further diminution in volume occurs. A rapid method of determining this value consists in placing a weighed amount of dry carbon into a glass-stoppered graduated cylinder; the cylinder is tapped on a slightly resilient surface until a constant volume reading is obtained.

There is a direct relationship between maximum bulk density of a carbon and the amount of liquid that will just saturate it: the lower the bulk density (*i.e.*, the greater the bulk volume) the greater is the amount of liquid held at saturation. Fig. 11

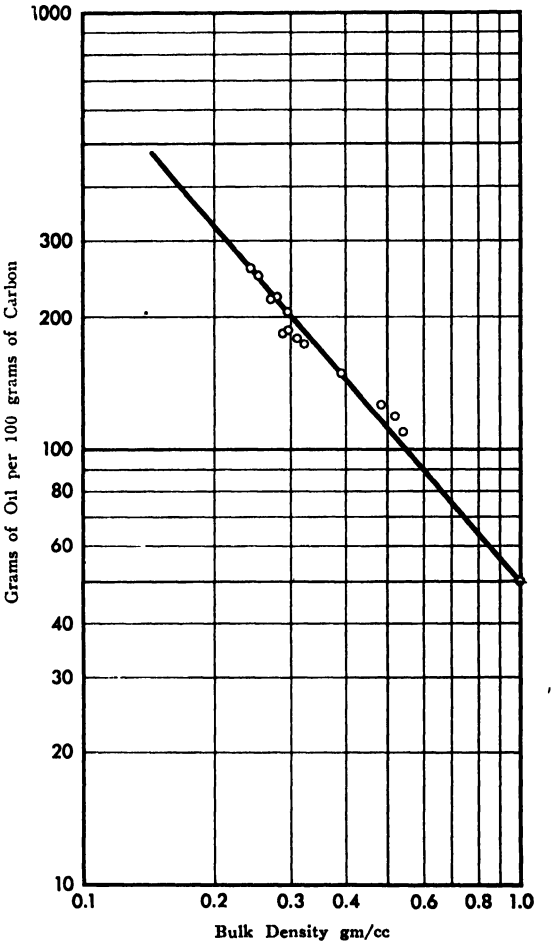

FIGURE 11. Effect of bulk density on oil retention.

shows this relationship for cottonseed oil, experimentally determined for fourteen different samples of carbon. The saturation values were obtained by adding oil drop by drop from a burette, to a sample of dry carbon in a porcelain casserole; the carbon was stirred gently after each addition, care being taken that all traces of oil had

disappeared before adding more oil. The end point is indicated by the first trace of streakiness on the porcelain surface.

Saturation values are an index of the amount of liquid retained by the carbon filter cake upon completion of filtration, which may be a significant factor in carbon treatment cost with expensive liquids, or in cases where large carbon dosages must be used.

The filtration characteristics of activated carbons are determined by their particle size distribution, as has already been mentioned, and also by the shapes of the particles. Irregular, "coal-shaped" particles offer less resistance to flow of liquid through them than do flat particles. Absolute particle size is of secondary importance; for example, a carbon with 90 per cent of its particles passing a 300-mesh screen (approx. 50 microns) may filter better than one with only 70 per cent of its particles finer than 300 mesh. Filterability of carbon may be determined by the method developed by Sanders and described by Harris,[11] and expressed in terms of seconds per ml of water filtered (at 20°) per cm thickness of carbon cake, per sq cm of filter area. In these units, commercially available carbons range from about 0.2 to 1.5. Filtration rates obtained with water under constant filtration pressure, such as these, cannot of course be translated directly into rates on other liquids, but the values do give information on relative performance under plant filtration conditions.

Even though activated carbon itself behaves as an incompressible solid in a filter cake, it very frequently happens that the liquid from which carbon is being filtered contains compressible solids as well, such as flocculent materials. To minimize resistance to flow, therefore, careful regulation of pressure should be maintained at the pump delivering liquid to the filter. At the beginning of filtration, pump pressure should be regulated at as low a value as will give a reasonable flow of liquid from the filter, and pressure should be increased only gradually, as the solids cake builds up, to maintain this rate of flow. Excessive pressure early in the filtration will so compress non-rigid solids already present in the cake as to cause abnormally high resistance to flow; and once such compression has occurred, it cannot be remedied by reduction of pressure. The flow rate for the rest of the filtration will be slow, and further increase of pressure in an attempt to increase the rate will only aggravate the condition.

In the purification of products which are themselves colloidal, such as pectin or gelatin, rather difficult filtration problems may arise. An extreme case occurs in the filtration of carbon from aqueous soap solutions: the colloidal particles, or more probably aggregates of these, carry the finest of the carbon particles through even very retentive filters. (Alcoholic soap solutions, on the other hand, do not present this difficulty). Gelatin and pectin solutions show, to a much lesser extent, the same phenomenon as aqueous soap solutions; they can be handled, however, by precoating the filter with 1/16 to 1/8 inch of a retentive filter aid of the diatomaceous earth type, and adding up to several per cent by weight of more free-flowing filter aid to the carbon treatment tank just before filtration is begun. The filter aid added to the treatment tank insures porosity of the filter cake as it is built up.

Flow rates in plant scale filtration are commonly expressed in gallons per hour per square foot of filter area. The rates obtained in filtering carbon will vary from 3-4 gal/sq ft/hr on 60 Brix sugar solution, to 30-40 gals/sq ft/hr or more on low-viscosity liquids such as electroplating solutions. These rates refer of course to the average over the filtration run, *i.e.*, total gallons filtered divided by total filtration time in hours, divided by total filter area in square feet.

Percolation Methods of Using Carbon

Powdered Carbon. There are certain conditions under which the best method of applying powdered carbon is to deposit it as a cake in a filter, and then to pass the liquid to be purified through this cake.

In general, this is an excellent procedure when a liquid in continuous use must be kept at a low level of impurity content, as in the case of dry-cleaning solvents or electroplating solutions. In both these cases, the liquid is continuously circulated through a filter holding a carbon cake, thence to its cycle of use, and back again through the filter. The impurities gained by the liquid during its use—color, odor, and fatty acids from the clothes in the case of dry-cleaning solvents; grease, oil, colloids, anode slimes, etc. in the case of plating solutions—are thus never allowed to accumulate to a concentration at which the usefulness of the liquid is impaired.

The carbon in the filter must of course be renewed periodically at intervals governed by experience under the operating conditions involved. Deposition of the carbon cake is effected by making a slurry of carbon with a suitable liquid, in a proportion of about one pound of carbon to one gallon of such liquid; the slurry is picked up by the suction of the filter pump, sent through the filter where the carbon is retained, and the effluent liquid is returned to the slurry container. This process is continued until only clear liquid remains in the slurry container. The amount of carbon used for precoating should be calculated to give a cake thickness of ½″ to 1″ over the total filter area. The weight of carbon which will occupy such a volume can be calculated from the bulk density of the carbon.

It must be emphasized that this method of using powdered carbon is limited to cases in which only low impurity concentrations are to be handled. The method permits only a very short contact time, which is ineffective for satisfactory purification when the liquid to be treated contains an appreciable concentration of impurity and a low C_f must be reached. In such cases the necessary contact time must be provided in a carbon treatment tank, by proper agitation of carbon in the liquid for a sufficiently long interval.

Granular Carbon. Granular carbons of vegetable origin differ from granular bone char in that their carbon content is much higher, ranging 75 to 90 per cent. The grades made for adsorption from solution are softer than bone char, and of lower bulk density (15-20 lbs per cu ft, as against 50-60 lbs per cu ft for bone char). They cannot be used in adsorption heat regeneration cycles as bone char is used in sugar refining, because they break up too easily in mechanical handling.

Such carbons do, however, find application where large volumes of liquid with very low impurity content are to be handled. Their most widespread use is in the purification of water, for removing substances causing taste and odor. Although the concentrations of odor and taste substance ordinarily handled cannot be measured accurately, the order of magnitude appears to be parts per million. Because such very low loads are imposed, granular carbon water filters frequently give effective service for periods of one to three years, before the charge of carbon is exhausted.

In general, granular carbon filter beds for water treatment are 20 to 30 inches deep, and are supported on sand which in turn rests on layers of graded gravel. Flow may be either upward or downward through the bed; one advantage of upward flow is that it virtually eliminates formation of channels in the bed. Rate of water flow is usually regulated at about 0.67-1.0 gallon per minute per cubic foot of carbon and at this rate, the cross-section area of the bed is determined by the depth selected for the bed and by the rate in gallons per minute at which treated water is desired.

A vital precaution to be observed in the operation of granular carbon filters, is that the liquid entering the filter must be completely free of suspended matter. This would coat the carbon granules and thus prevent access of the liquid to their internal adsorptive surface; the writer has seen a filter which should have had an effective life of at least twelve months become ineffective within eighteen hours, only because the water passed through it contained a very moderate amount of suspended matter. Water passed through granular carbon filters should always be carefully prefiltered through sand, with preliminary coagulation by filter alum if necessary.

Another precaution which must be observed arises from the fact that activated carbon is electropositive toward metals, and will therefore give rise to corrosion when in contact with metal in the presence of an electrically conductive liquid. The magnitude of the difference in electrical potential is proportional to the degree of activation of the carbon, and with the highly active vegetable carbons, is great enough to cause destructive corrosion of an unprotected filter shell housing the carbon, because of the prolonged contact conditions. (When powdered carbon is in contact with the metal of a filter press, the time factor is so short that corrosion is not measurable).

It is therefore necessary to coat any metal surface in contact with granular carbon, with an inert insulating material.[12] For water filters bituminous preparations are satisfactory, provided a temperature of 100° F is not exceeded; for other liquids and conditions, a resinous coating compatible with the liquid to be treated and with the treatment temperature should be selected.

Granular vegetable carbons are also used industrially in the purification of ethyl alcohol, to remove small traces of impurity remaining after distillation in rectifying columns to 190 proof. Carbon treatment of such alcohol is not effective at high proof, however; dilution with water to not over 120 proof, and preferably to less than 100 proof, is necessary. The reason appears to be that the impurities involved are increasingly soluble with increase of alcohol concentration, with corresponding decrease of adsorbability. This applies particularly to the higher alcohols, commonly grouped under the name of "fusel oil"; really effective adsorption of these requires dilution of the alcohol to 70 proof or lower. If adsorption of taste and odor causing substances other than fusel oil is the only objective sought, treatment may be conducted at a proof as high as 120.

The operating conditions and precautions mentioned in the previous discussion on water filtration with granular carbon apply in general to alcohol filtration as well, except that beds as deep as 36″-48″ are frequently used. Also, the life of a carbon bed used on alcohol is very much shorter, and is measured in hours rather than months or years. The adsorption load on the carbon is greater, and the response to adsorption poorer, than in water filtration.

Offsetting the shorter life of alcohol filters is the possibility of their simple regeneration by means of steam. Since the alcohol entering the filter has previously been subjected to at least two distillations, any impurities remaining in it must be volatile in nature, to have come through the stills along with the alcohol (assuming of course that the stills have been properly operated and that no entrainment of nonvolatile impurities in the vapor has occurred.)

Experience has indicated that it is best not to allow the carbon to become completely spent before regenerating it, as under these conditions satisfactory regeneration has been found difficult. General practice is to determine by laboratory experiment the full life of the bed in terms of the volume of alcohol that can be filtered before an objectionable concentration of impurity appears in the effluent. For this laboratory test, depth of carbon bed and rate of flow must be the same as in plant operation, as only in such case is the ratio of alcohol to carbon at full spending, the same in both laboratory and plant. From the laboratory results, the volume of alcohol that will fully spend the plant filter is calculated by simple proportion, and for operation of the plant filter, one-half to two-thirds of this volume is arbitrarily taken to fix the length of the carbon use before steam regeneration.

Regeneration is accomplished by draining the bed of alcohol, and then allowing clean steam to drift upward through the bed, at a pressure just sufficient to carry it through. The steam is vented at the top of the bed, and the progress of regeneration can be followed by noting periodically the odor of the issuing vapor. Some three to six hours may be required to reach freedom from odor, and experience has shown that steaming should be continued for a further length of time, equal to that con-

sumed in reaching absence of odor at the vent. In difficult cases, it may be desirable a number of times to close the vent and build up steam pressure within the filter to improve the desorption process.

When the steaming process has been completed the filter is allowd to cool, any condensate is drained off, and filtration of alcohol is resumed. In continuous operation, it is desirable to maintain triplicate units—one filter in operation, one undergoing steam regeneration, and the third cooling, draining and standing by for service until the first filter becomes spent.

Steam regeneration is effective only if the impurities adsorbed by the carbon can thereby be completely volatilized; if the liquid filtered through the carbon contains adsorbable non-volatile impurities, these will of course accumulate on the carbon in successive cycles of operation, and will usually spend the carbon fairly quickly. With volatile adsorbates only, a carbon bed may remain in continuous useful service for 20 to 40 days, depending upon the adsorption conditions imposed on it. Steam regeneration cannot keep the carbon in much longer use, both because steaming eventually breaks down the granules, and because a portion of the adsorbate is usually difficulty volatilizable, so that under the compromise of reasonable steaming periods, it tends to accumulate on the carbon.

Application of Carbon by Dispersion and Settling

In the application of carbon by dispersion and settling, powdered carbon is added to the liquid to be treated, often with little or no mixing, and separation of the carbon is effected by settling with a coagulant. Efficiency of contact depends upon the use of very finely powdered carbon, to provide thorough dispersion throughout the liquid and a slow settling rate of the carbon particles.

This method has been used to a limited extent in the carbon treatment of wines, with a very pure carbon and settling by means of a suitable grade of bentonite. By far the largest scale use of the procedure, however, is in the treatment of water at municipal purification plants.

It had been known for many years that activated carbon will remove taste- and odor-causing substances from water, but its use for that purpose was not general until Spalding[13] demonstrated at the New Milford (New Jersey) plant of the Hackensack Water Co. that very small dosages of powdered carbon dispersed in the water will effectively correct such conditions.

The volumes of water handled daily at a municipal water purification plant are so large that the ordinary methods of treating liquids with carbon thus far discussed, with the exception of percolation through granular carbon filters, are not practical: even a relatively small city will treat hundreds of thousands of gallons per day, and in Detroit, the largest city at present using carbon treatment of its water, the average daily pumpage is close to three hundred million gallons.

The sequence of principal purification steps in such plants is usually addition of a coagulant such as aluminum sulfate (filter alum) sedimentation in large basins, of the basic aluminum hydroxide floc formed, and filtration of the settled water under gravity through sand filters. Carbon may be added at any suitable point in this sequence prior to the sand filtration.

The most common point of addition is just in advance of the sedimentation basins, at substantially the same time as the filter alum. The detention time in these basins is usually two to four hours, within which time the dispersed carbon must effect adsorption of odor- and taste-producing substances while settling slowly through the water. At the same time the filter alum undergoing hydrolysis is forming floc of gradually increasing size, and this also settles as the water carrying it moves from the influent to the effluent end of the basin. The function of the floc is to entrap suspended matter and microörganisms; and when carbon is present, it entraps this as well. Thus the greater part of the carbon will have been settled out of the water

before it reaches the effluent end of the basin; any carbon and floc which remain in suspension are caught on the sand filters which follow.

Efficiency of carbon contact in this process is about 50-60 per cent, expressed as the ratio of odor adsorbed to that which could have been adsorbed had the carbon been stirred actively with the water to permit adsorption equilibrium to be reached.[6, 7] Carbon contact efficiency is greatly improved if the plant is equipped with flocculators —basins preceding the settling basins in which large paddles agitate the water gently to assist and accelerate formation of the alum floc. Also, some plants with long sedimentation basins add carbon to the basin at a point where most of the alum floc has settled, but considerable time (one to two hours) remains before the water reaches the filters. This has a double advantage: the carbon is not carried down prematurely by the floc, and the amount of odor to be adsorbed is less, since the floc alone is a fairly effective odor remover. Contact efficiency under these conditions has been found to be as high as 90 per cent.

The carbon dosages employed in water treatment are on the order of parts per million, an average dosage being about 2 ppm, or 16-17 lbs per million gallons. The carbons employed are very finely ground; the particle count is on the order of one to two hundred billion per gram, and the fineness 95-98 per cent passing 300 mesh (50 microns). At a dosage of 2 ppm, the number of particles held in a drop of water (0.05 ml) will thus be ten to twenty thousand.

The substances ordinarily causing taste and odor in water are products of the decay of vegetation, compounds (believed to be of the nature of essential oils) associated with algae and other microscopic organisms living in water, and waste products discharged into streams by industrial plants. These have usually reached a high degree of dilution by the time they arrive at the water purification plant.

Although the composition and concentration of these odor- and taste-causing substances is in most cases not determinable, an indication is given by *p*-chlorophenol. Phenol and related compounds are frequent causes of odor and taste in water, being introduced through the waste effluents of coke plants, and these are converted to chloro-compounds at the waterworks plant when chlorine is added there as a bactericide. The concentration of *p*-chlorophenol at the threshold of odor perceptibility in water at 60° has been reported by various observers as lying between 0.01 and 0.04 ppm. A number of other odor-causing substances (not, however, ordinarily identifiable as present in water supplies) show comparable values,[14] ranging from 0.01 to 1.0 ppm.

These indications of the order of magnitude of adsorbate concentration help to explain why such extraordinarily small dosages of carbon are effective in the removal of tastes and odors from water supplies; the dosages, though small, are still many times greater than the amount of adsorbate they remove.

In passing, it is interesting to note that the Freundlich adsorption equation holds at these low concentrations; for example, excellent straight-line isotherms are obtained with phenol adsorption data at concentrations of 0.01 to 0.10 ppm of phenol, colorimetrically determined with 2, 6-dibromo quinone chloro-imide, according to the procedure described by Baylis.[15] Straight-line isotherms can also be obtained with data in odor units, using the dilution method of determining odor intensity described by Spaulding,[16] but this requires very careful attention to technique in making the odor measurement.

Miscellaneous Uses of Activated Carbon

Activated carbon will react chemically with chlorine; this fact is of industrial interest in connection with the filtration of water through granular carbon. With water of high bacteria count, or water badly contaminated with industrial wastes, for example, chlorine dosages considerably above normal are used. Also, well waters high in hydrogen sulfide are treated with chlorine to oxidize the H_2S. In general,

the chlorine dosage in such cases is well in excess of the minimum, so that appreciable residual concentrations remain after the chlorine has performed its function.

This excess chlorine is readily removed by activated carbon, but removal is effected, not by physical adsorption, but by chemical reaction. The carbon is oxidized to carbon dioxide, and the chlorine is reduced to chloride ion, appearing in the effluent as HCl. This can readily be established by passing strong chlorine solution through a column of granular carbon; both CO_2 and HCl can be found in the effluent, and titration with suitable indicators will show a close concentration balance against chlorine concentration of the influent solution according to the equation

$$2Cl_2 + C + 2H_2O \rightarrow 4HCl + CO_2$$

The acidity of the effluent in granular carbon water filters is not great; it must be borne in mind that ordinary chlorine residuals at water-treatment plants are on the order of a few tenths of a part per million, and the heavier residuals involved in the cases mentioned above are never much greater than a few ppm. The effluent acidity is therefore of the same order, and negligible for all ordinary purposes.

The capacity of a carbon filter used for dechlorination only is very large; instances have been encountered in which a carbon charge had an effective life of nearly five years.

Conclusion *

It has been the object in this discussion to limit its scope to the industrial application of activated carbon for adsorption from solution, and to present the subject in terms of the quantitative relationships involved wherever possible. Such a presentation, it is believed, will be of greater usefulness to technologists considering activated carbon treatment in an industrial operation than would the citation of a series of specific uses.

For similar reasons, the discussion does not include extensive reference to the many theories which have been formulated to explain adsorption, nor does it draw upon the voluminous literature reporting experimental data of a non-industrial nature. It is an unfortunate fact that adsorption is not yet sufficiently well understood to permit any summation of such experimental data into broad generalizations. While this material is of great value to the student, its specificity renders it of questionable dependency for the industrial technologist, who rarely finds himself able to apply uncorrelated material of this nature to his particular problems.

No mention is made of the catalytic use of activated carbon, partly because such use is largely confined to gas- and vapor-phase operations, and partly because the few industrial uses of carbon for this purpose in liquid and solution work are held as trade secrets.

It is hoped that the material presented will extend the use of activated carbon in the many new industrial processes where purification problems arise. Much of this material has previously been given in separate publications as indicated in the bibliography, and some has hitherto not been published.

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Editor's Note

Although some of the details as to the production of penicillin from mass cultures of the mould *Penicillium notatum* are still shrouded in wartime secrecy, enough has already been published to indicate extensive use of colloid chemical principles, not only in the production of this potent medicine but also in its practical utilization.

For example, C. L. Gabriel [*The Chemist*, 22, 86 (1945)] states that following deep-culture fermentation to produce great quantities of the mould, "the broth is run through filters to remove the mycelium, treated with activated carbon to adsorb the penicillin, and run through a filterpress to collect the carbon adsorbate. The latter, after being washed, is eluted with an 80 per cent solution of acetone in water. This solution is then subjected to repeated extractions with a water-immiscible solvent. The concentrated eluate is chilled to 0° and acidified. Under these conditions, penicillin is readily soluble in amyl acetate. The penicillin is then extracted continuously from this solvent solution with dilute sodium bicarbonate. These various solvent treatments are for the purpose of separating penicillin in as pure a form as possible from other products which are adsorbed with it on the activated charcoal and to end up with a sodium penicillin solution."

Parkins, Wiley, Chandy and Zintel [*Science*, 101, 204-6 (1945)] report that "blood concentrations of penicillin were maintained at measurable levels for as long as seven or eight hours following single intramuscular injections of penicillin in the dog and in patients, by means of vehicles containing 6 per cent to 20 per cent ossein gelatin and a long-acting vasoconstrictor drug. Intramuscular administration of penicillin can thus be carried on with three instead of eight injections per day with less variation in the extremes of penicillin blood levels. . . . We believe that the colloid gelatin delays absorption and extends the effect of the vasoconstrictor as well as the penicillin, and that the vasoconstrictor, in turn, delays the absorption of the gelatin used as a vehicle for the penicillin."

Chow and McKee [*Science*, 101, 67 (1945)] found, by dialysis experiments, that penicillin combines with human serum albumin and that, unlike the sulfonamide-albumin complex, the penicillin-albumin exhibits antibiotic activity; in mice it was excreted more slowly than the sodium salt of penicillin.

Vapor Adsorbent Carbons

E. L. Luaces

President, Chemical Developments Corporation.

The adsorption of water vapor by silica gel has been discussed by E. B. Miller in Volume III of this series.

Silica gel adsorbs water vapor preferentially from a mixture of water vapor and organic vapors, such as those of volatile solvents. Active carbon, on the other hand, adsorbs organic vapors preferentially. For this reason, silica gel and active carbon are frequently used conjointly, the one to remove water vapor and the other to remove organic vapors from a given body of gas. One such typical application is in the treatment of fermentation carbon dioxide to be used in the production of "Dry Ice" (solid carbon dioxide), and this typical application will be discussed hereinafter.

Although Miller [1] has discussed at some length the use of silica gel for the recovery of organic solvent vapors, the method has no industrial significance.

Mechanism of Adsorption

Active carbon adsorbs organic vapors in the same fundamental manner in which silica gel adsorbs water vapor, and within the limits of commercial use, the formula of Freundlich

$$\frac{x}{m} = ap\ 1/n$$

wherein x represents the weight of vapor adsorbed,
m the unit weight of adsorbent,
p the partial pressure of the vapor after equilibrium has been reached, and
a and n are constants

is perhaps the simplest and that which most adequately applies. Its validity or application in any given case may be determined by plotting the logarithm of x/m against the logarithm or p so that the formula then reads

$$\log x/m = \log a + 1/n \log p$$

If the data are accurate, they will give a straight line when plotted on logarithmic paper. Results obtained by the application of these formulas agree closely with experimental and industrial data.

Nature of Active Carbon

Active carbon is commercially available in the form of hard granules or pellets. The granular material is obtained from coconut shell and fruit pit charcoal, while practically any type of charcoal may be utilized in the manufacture of the pellets. The active carbon may be obtained varying in density from less than 25 to more than 35 pounds per cubic foot and possessing particular physical characteristics adapted to the use for which it is intended. Active carbon in finely divided form is

also obtainable commercially, but this type of material finds little if any use for vapor-phase adsorption.

Broadly speaking, active carbon is produced by selective oxidation of carbonaceous material or by chemical attack at an elevated temperature. The purpose of the activating process is to increase the porosity and thus the total surface area of the carbonaceous raw material without materially reducing the hardness of the granules or pellets.

Recovery of Volatile Solvents

The principal application of active carbon for the recovery of organic vapors in industry lies in the field of solvent recovery. In its present state of development, the active carbon process as applied to the recovery of volatile solvents, is extremely simple and safe in operation. The initial cost of the installation is decidedly lower than that of the older mechanical and liquid adsorption systems. The operating costs are substantially lower and the efficiency extremely high. The solvent recovered is of the highest quality and does not have to undergo any purification (except rectification in the case of water-miscible solvents) before re-use, but perhaps the most attractive feature of the process is its ability successfully to operate with solvent vapor concentrations far beyond the effective range of the older processes.

Practical experience has shown that it is possible to operate with a high overall recovery yield when the concentration of solvent vapor in the vapor-laden air is from 5 grains per cubic foot down to 0.5 grain, and in extreme cases even as low as 0.09 grain per cubic foot. This makes it possible to aspirate large volumes of air, thereby increasing the captation efficiency of the installation and permitting the operation of the recovery plant itself with solvent vapor concentrations in the solvent-laden air far below the lowest explosion limit. The factor of safety introduced thereby has resulted in many cases in a reduction of from 10 to 15 per cent in the insurance premiums paid. In at least one case the reported saving in insurance rates was 22 per cent.[2]

Since the per cent overall recovery efficiency is determined by dividing the total amount of solvent recovered for re-use into the amount evaporated, the most important factor in obtaining the highest overall recovery yield is the captation or collection of the solvent vapors. It is necessary to provide the equipment from which the solvent evaporates with suitably designed and fitted hoods or covers which will not make any part of the machine or apparatus inaccessible, or in any other way interfere with its operation. Once this has been done the rest is comparatively simple. Fig. 1 illustrates a typical installation on horizontal spreading machines.

The recovery installation consists of suitable filtering apparatus having a specially designed compartment to arrest the propagation of any accidental spark or flame originating in the workrooms; the adsorbers containing the active carbon; a condenser to condense the solvent vapors removed from the adsorbent; and a decanter to separate the solvent from the condensed steam when the solvent is immiscible with water. If the solvent being recovered is partly or wholly miscible with water, an automatic continuous rectifying column is provided with the installation.

The solvent-laden air, after being filtered to remove any dust or finely divided matter which it might carry in suspension, is propelled by the captation fan at a pressure of about 4 or 5 inches of water, through a bed of active carbon held in the adsorber, as shown in Figure 2. The adsorption will go on for a period of from not less than 30 minutes up to several hours—or even a whole day or week for the smaller installations and those larger ones which are only operated during short intervals of time. When the practical saturation point has been reached, the flow

of solvent-laden air is diverted to the second adsorber and the first enters the second stage of the recovery process—regeneration or distillation.

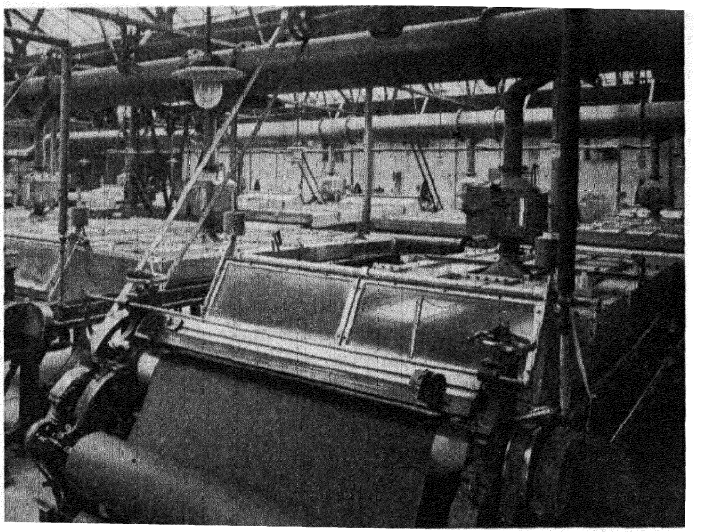

FIGURE 1. Collection of vapors from horizontal spreading machines in English artificial leather plant.

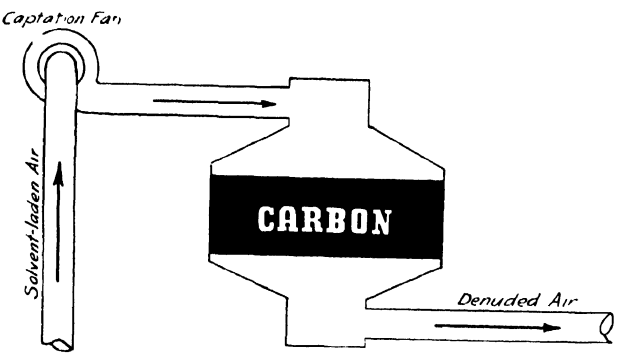

FIGURE 2. The solvent-laden air is put through the activated carbon bed by the captation fan and the denuded air is evacuated outside the building or returned to the workrooms. A pressure of from 4 to 5 inches of water proves sufficient.

The purpose of regeneration is to remove from the active carbon the vapors which it has adsorbed and is retaining in its pores. To this end the temperature of the active carbon is increased sufficiently to distill out the adsorbed solvent. Regeneration, as shown in Fig. 3, is carried out simply by injecting low pressure steam directly into the adsorber and continuing the application until all of the adsorbed solvent has been vaporized and driven out. When this operation has been completed the active carbon is quite moist due to steam condensation in bringing up the temperature of so poor a conductor of heat as active carbon. Moisture is highly detrimental to solvent vapor adsorption in many cases, and if left in the active carbon the efficiency of the latter would suffer very definitely. For this reason the active carbon is dried with warm air until all the moisture has been

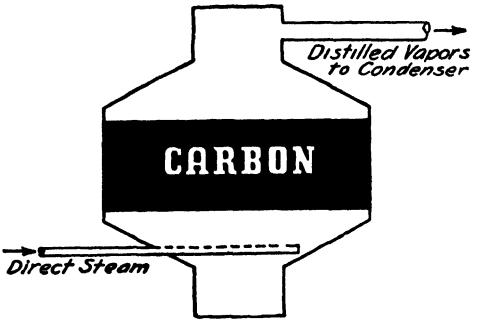

FIGURE 3. Steam is injected at the base of the adsorber to drive out or distill the adsorbed solvent. The vapors are taken off and condensed.

driven out, and is then cooled down to room temperature with cooled air, as in Fig. 4.

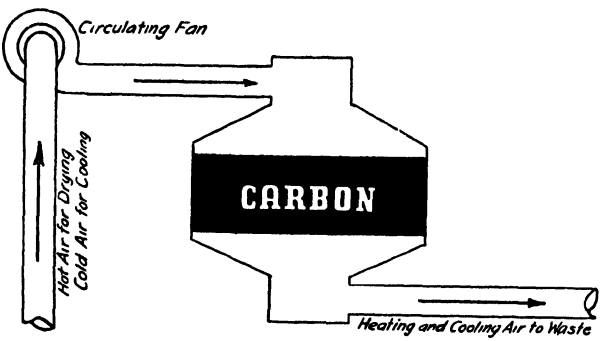

FIGURE 4. After steaming, the activated carbon is dried by passing warmed air through the adsorber. It is then cooled with air.

The distilled vapors are put through a suitable condenser forming part of the recovery installation. If the solvent is immiscible with water, as is the case with benzine, naphtha, benzene, trichloroethylene, etc., the decanter separates the water, which is discharged into the sewer, from the solvent, which is ready for re-use. If the solvent should happen to be miscible with water—as is the case in plants using ethyl acetate, alcohols, acetone, and similar solvents—the condensate is delivered to an automatic continuous rectifying column, where the solvent is separated from the water. In some cases a miscible and an immiscible solvent form part of the solvent mixture used. In such cases, the decanter separates the immiscible solvent, and the water containing the miscible solvent is delivered to the rectifying column where the solvent is separated from the water.

While solvent recovery installations have been made with capacities as low as 10 gallons per day, there is no upper limit to the capacity for which an installation might be designed, and some in operation recover millions of gallons annually. Either single- or multiple-adsorber installations can be made. Where the amount of solvent to be recovered is very small the plant is designed to operate six, twelve or more hours without regeneration. In such cases the regeneration might be carried out during the lunch hour and at the close of day, or once only after working hours, depending upon local conditions. Recovery plants have been designed to operate fully automatically on a predetermined cycle without any attention whatever, and have been successfully doing so over substantial periods of time.

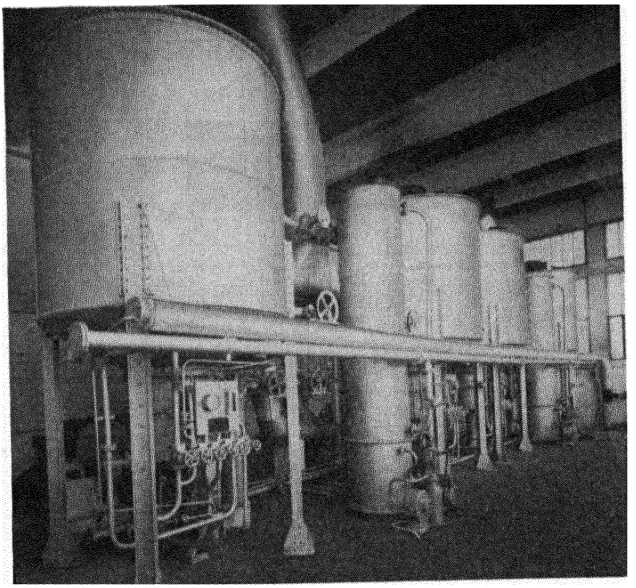

FIGURE 5. Typical duplex four-adsorber installation in a dry-cleaning plant.

In most installations two adsorbers are used and perforce one is adsorbing while the second is being regenerated and cooled. When three adsorbers are used, one is adsorbing while the second is being regenerated and the third is being cooled. When four adsorbers are used, the operation is staggered so as to have two adsorbing—but reaching saturation at different times—one being regenerated and the fourth being cooled. The operating cycle of such an installation is illustrated diagrammatically in Fig. 6. Except in the extraction of gasoline from natural gas, more than four adsorbers are rarely used.

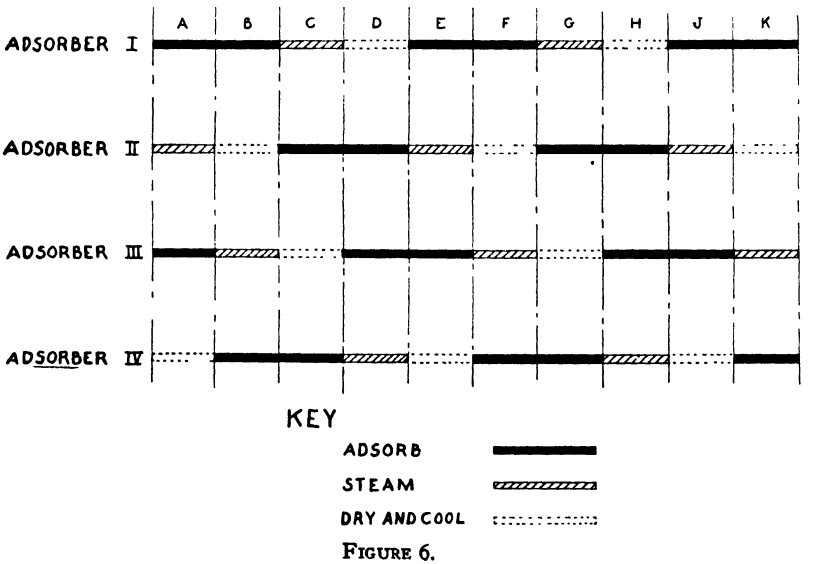

FIGURE 6.

Examination of operating data accumulated over nearly a quarter century of practical use definitely shows that an active carbon recovery system, when properly designed and operated, can effect such large savings that it will be amortized within a period of from six months to two years. The amount of labor required is negligible and except in those exceptional cases where it is necessary to place the recovery plant down in the cellar, up on the roof or in a building away from the workrooms where the solvent is evaporated, it is possible properly to attend to it without additional help. The operation is so simple and foolproof that unskilled labor can be trained to run the installation properly, or full automatic control may be used for greater economy and efficiency.

These practical data also show that it is possible to recover for re-use from 97 to 99 per cent of the solvent vapor in the solvent-laden air and to attain overall yields up to 94 per cent of the solvent evaporated.

Recovery of Gasoline from Natural Gas

Early experiments in the extraction of gasoline from natural or "casinghead" gas were carried out in the United States as early as 1918. The work of Burrell [8] and his collaborators deserves particular credit as a pioneer endeavor in the development of a new industry. It is true that those early extraction plants, designed and installed without any background of experience and very little experimental data of practical use, were far from efficient on the basis of present day standards; but they provided the impetus which led to the commercial development of active carbon systems for industrial adsorption of gases and vapors.

Not only were the early plants installed in the United States, but the first foreign installation was of American design. In recent years the active carbon process has almost disappeared from the American scene insofar as the extraction of gasoline from natural gas is concerned,* while at the same time it has flourished in foreign lands and reached an extremely high standard of efficiency.

Modern practice makes use of from four to eight adsorbers. Usually the initial installation consists of four adsorbers, and more are added in groups of two. There is one plant where the number has reached a total of twelve. The operating scheme provides for two adsorbers in the adsorption cycle, one steaming, and one drying and cooling. The cycles of adsorption are so arranged that the end-points of the two adsorbers come a half hour apart. If a new plant is started and the cycle of adsorption is to be 90 minutes, then two adsorbers are placed in parallel service but the first one is cut out at the end of 45 minutes (when only half full). A third adsorber is then cut in, and at the end of the first 90 minutes of operation this third adsorber will be half full while the second will be full. Then the second is cut out and the fourth cut in. In this way the greatest of flexibility is attained. Fig. 6 diagrammatically illustrates the overall cycle. The gas comes into contact with the carbon at a maximum temperature of 90° F. Multiple-bed adsorbers are used, the gas flow being in parallel through the several beds. This calls for elaborate internal construction. The adsorbers are provided with built-in heat regenerators. Gas flow is upward and steaming downward. The temperature of the steam is seldom higher than 270° F throughout the entire cycle. The steam passing downward through the carbon vaporizes the gasoline, and the mixture of steam and gasoline vapors passes through the heat regenerator on the way out of the adsorber. The regenerator picks up part of the heat load. When the steaming has been completed, either air, or more safely and conveniently, denuded gas, is passed upward through the adsorber for drying and cooling the carbon. In passing through the regenerator, the drying and cooling fluid will pick up heat from it, and in passing through the carbon beds will give up this heat to evaporate the moisture in the carbon. The regenerating mass (generally a bed of small stones) and adsorbent mass are so

* Liquid absorption methods were mainly reverted to.

proportioned that by the time the heat has been removed from the regenerator the carbon will be dry. Then it is only necessary to continue the flow of drying and cooling fluid through the adsorber to cool it down to substantially room temperature.

During recent years the matter of selective adsorption has come up again for attention, and the work done so far indicates that success is to be realized. In substance, the scheme provides for double adsorption of the gas: first with an adsorbent of comparatively large pores and low activity, and secondly with the usual type of adsorbent and in the usual manner hereinbefore described. In practice, the first set of adsorbers is utilized for the recovery of products which are liquid at ordinary temperature and pressure, and the second set for the recovery of products which are not liquefiable at ordinary temperature and pressure. The only products that will pass through are methane and ethane, which are then used as sources of heat or are transformed catalytically or otherwise into synthetic gasoline or other products. The second set of adsorbers removes products such as butane and pentane, which are polymerized.

It was formerly believed that one of the few disadvantages of the active carbon process was that it had to have much attention for the setting of the valves. This disadvantage does not exist, because the entire process may be carried out completely automatically on a predetermined cycle by proper application of suitable instruments such as program cycle-repeat controllers. In the double adsorption system, the first set of adsorbers generally handles gas at from 7 to 12 atmospheres, while the second set of adsorbers handles gas at from 6 to 8 atmospheres pressure.

Recovery of Alcohol from Fermentation Gases

In the fermentation of sugars form alcohol, approximately one-half of the sugars are transformed into alcohol and the balance into carbon dioxide. The gas is given off at a non-uniform rate and the temperature of fermentation varies. Depending upon the stage of fermentation and the temperature, from 0.75 to 1 per cent of alcohol vapors is carried off with the gas. The Backhaus process[4] for the recovery of this alcohol provides for the removal of the alcohol vapors by scrubbing the gas with water, which is then used for diluting the molasses to be fermented, the scrubbed gas being then deodorized by passing it through active carbon.

In the Acticarbone process the removal of the alcohol vapors is accomplished by adsorbing them on carbon. The system generally consists of four adsorbers, two of which are alternately used for alcohol recovery and two for deodorizing. The gas from the fermenters is put through a separator to remove entrained water and is then admitted to the alcohol recovery unit. When the adsorber is saturated with alcohol vapors, the flow of gas is diverted to a second adsorber and the first is steamed to remove the adsorbed alcohol. The distillate is condensed, giving a solution of from 10 to 12 per cent alcohol which is subsequently rectified. After steaming, the adsorber is dried with warm air and cooled to at least 90° F for re-use.

The deodorizing unit takes the de-alcoholized gas and removes odors from it. Since the major proportion of odorous impurities has been taken out in the recovery unit, the cycles of adsorption are much longer in the deodorizing unit, which is generally much smaller in size. Great care must be exercised in designing the deodorizing unit, in view of the fact that the removal of the last trace of impurities is a delicate and necessary procedure in order to produce a gas suitable for the manufacture of Dry Ice (solid carbon dioxide).

The value of the alcohol recovered is generally sufficient to cover the cost of the recovery, the entire system being operated automatically.

Recovery of Carbon Disulfide in Viscose Rayon Production

In the manufacture of viscose products raw cellulose material is treated with caustic soda to produce "alkali cellulose." After ageing, the alkali cellulose is

treated with carbon disulfide to form "cellulose xanthate." During this reaction, heat is generated and carbon disulfide is driven off. When the reaction has been completed, the xanthate is dissolved in weak caustic solution and the resulting viscous mass or "viscose" is stored at low temperature to mature. When the proper degree of ripeness has been attained, the viscose solution is forced or extruded through fine orifices into an acid coagulating bath and filaments in the form of rayon fibers are formed. The viscose solution also may be cast in suitable molds to form articles of various shapes, or extruded through thin slits to form sheets. Coagulation of the viscose solution decomposes it with the formation of regenerated cellulose, while hydrogen sulfide, carbon disulfide and other compounds are liberated.*

Methods hitherto used for the recovery of carbon disulfide vapors driven off in the production of viscose products, have not been fully successful. Recent developments in the United States have emphasized the desirability of recovering this material on account of its toxic nature. The concentration of these vapors in the air collected around the points of evaporation is extremely low, and recovery methods based upon direct condensation or on refrigeration cannot successfully be applied. Liquid absorption methods likewise suffer because of the low concentration of vapors in the laden air. Adsorption on solid adsorbents is also difficult because the hydrogen sulfide present in the vapors collected materially reduces the effectiveness of the adsorbent, which quickly becomes spent and must be replaced. The Sorbit process [5] provides for the removal of hydrogen sulfide and other impurities from the laden air by washing with a suitable liquid and by subsequent recovery of the carbon disulfide vapors with a solid adsorbent.

In practice, the vapors given off from the various parts of the viscose process are collected mixed with large volumes of air. The laden air is passed through a scrubbing tower through which is circulated the liquid absorbent which dissolves hydrogen sulfide and other impurities from the air but permits the carbon disulfide vapors to pass. The washed air is then passed through adsorbers provided with a bed or beds of a suitable adsorbent carbon, and the denuded or stripped air is permitted to pass out from the upper portion of the adsorber. Three adsorbers are used, but only one is in the adsorption cycle at any given time.

When the adsorbent carbon bed or beds in the adsorber have reached practical saturation, the flow of laden air is diverted to a second adsorber and the first is regenerated by passing steam through it in a downward direction. The steam drives out the adsorbed carbon disulfide, which is then condensed and separated by decantation.

The adsorbers are equipped with heat regenerators in their lower sections. These regenerators adsorb part of the heat load of the steam-CS_2 mixture passed through them during steaming, and are warm at the completion of this operation. The beds must be dried and cooled to condition them for further use. Room air is passed upward through the adsorber, first passing through the heat regenerator in the lower section of the adsorber and then through the carbon bed or beds in the upper section of the adsorber. In so doing, the air picks up heat from the heat regenerator and gives it up to the carbon, thereby driving out moisture held by the carbon from the steaming operation. This is continued until the regenerator has given up all the heat retained by it, when the carbon will have been dried out. The cooling cycle follows by continuing the passage of room air through the adsorber.

When three adsorbers are used, one is in adsorption, one being steamed, and one dried and cooled. This makes it possible to have a continuous stream of warm water flowing from the condenser in which the steam-CS_2 mixture is condensed, and this water is used for washing freshly coagulated viscose products. The tem-

* See paper in this volume, by S. A. Moss, Jr., pp. 945-950. J. A.

perature is controlled so that it will be above the boiling point of carbon disulfide, preferably between 65-70°. Any excess water is circulated through a cooling tower and returned to the process together with makeup water.

It appears possible to recover carbon disulfide in viscose plants when the concentration is as low as 5 grains per cubic foot.

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Removal and Recovery of Proteins by Water-Soluble Lignin

JAMES S. WALLERSTEIN AND RALPH T. ALBA

Overly Biochemical Research Foundation, Inc.

Lignin, which can be considered as a complex polyphenol derivative,[1] is present in wood and in a variety of plant materials.

In the production of cellulose pulp, the lignin portion of the wood is solubilized, and may be recovered from the digestion liquor. Where the digestion is carried out with sulfite under acid conditions, lignin sulfonic acid is formed, the crude concentrate being known as "sulfite waste liquor." Alkali-cook lignin[2] is formed in the so-called black liquor resulting from the alkaline cooking of wood. It may be precipitated by acidification of the black liquor by mineral acids or the introduction of carbon dioxide gas, and purified by washing and reprecipitation.

These water-soluble forms of lignin have a marked affinity for proteins and may be employed to precipitate them from solution.[3] A study of the depressive effect of lignin upon the decomposition of proteins by bacteria showed that a complex is formed when lignin and gliadin[4, 5] or casein, were allowed to interact. This lignin-protein complex possessed the various chemical, physico-chemical, and biological properties characteristic of the major portion of the organic matter (humus) of the soil. It has been shown that lignin sulfonic acid effects a chemical combination with hide protein.[6]

Complexes of protein and lignin are soluble in alkali and become increasingly insoluble as the solution is acidified. The reversible solubility and insolubility of the protein lignin under alkaline and acid conditions lends itself to a variety of industrial applications.

Purification of Fermentation Mashes

The shortage of molasses under wartime conditions has led to the extensive employment of cereal grains as a source of carbohydrates for industrial fermentations. These cereal mashes contain large amounts of proteinaceous matter, the removal of which may improve the purity and the recovery of the fermentation end-products.[7]

In the production of glycerol by fermentation, for example, the fermented glycerol mash is concentrated to a thick syrup from which the glycerol is recovered by distillation with superheated steam under reduced pressure. Presence of any substantial amount of protein in the concentrate creates persistent foaming and greatly reduces the efficiency of glycerol recovery. Some 85 to 90 per cent of the nitrogeneous matter in a wheat or corn mash may be removed, however, by the addition of sulfite waste liquor to the acidified mash (pH 2.0 to 3.5). The insoluble protein-lignin complex flocculates on heating the solution. The efficiency of the recovery depends on the degree of aggregation of the protein and thus had best be carried out with the unhydrolyzed protein.

Recovery of Protein from Alcohol Stillage

Cereal mashes of wheat or corn have also been employed extensively for industrial alcohol fermentation. At the close of the fermentation after removal of the alcohol

by distillation, the stillage is strained for removal of the larger insoluble grain particles, which are dried and converted into cattle feed. The screened stillage, however, still contains smaller insoluble particles and soluble proteins from the grains and yeast, and is rich in feed value in respect to both proteins and vitamins from the fermentation yeast.

Recovery of these nutrient materials is sometimes accomplished by evaporation of the stillage when evaporating equipment is available. Recovery of at least 80 per cent of the proteins in the stillage may also be accomplished by the addition of sulfite waste liquor.[8] Settling of the protein-lignin occurs on heating the stillage to approximately 80°. Since the stillage is already appreciably acid (about pH 4.0), no adjustment in the acidity is required. The protein-lignin sludge may be collected in a settling tank. The dried protein-lignin is suitable for feeding purposes. It is palatable and of a nutritive value comparable to its protein content.

The supernatant liquid, after sludge removal, still contains appreciable nitrogenous matter and unfermentable carbohydrates. It may be suitably employed as a medium for the growth of *Torula utilis,* a yeast valuable for feed purposes.

Clarification of Juices and Beverages

To complete precipitation of protein by lignin sulfonic acid heat is required. Alkali-cook lignin, however, forms insoluble complexes with protein even at ordinary temperatures. This form of water-soluble lignin accordingly may be employed where heating is undesirable. Insoluble complexes of protein and alkali-cook lignin, moreover, are formed at milder acidities than with lignin sulfonic acid (pH 4.0 to 5.0). This type of lignin compound may be employed for the clarification of cereal beverages and fruit and vegetable juices.[9] It has a purifying and adsorptive action.

In the clarification of apple juice, for example, a small amount of lignin alkaline solution is added to the juice. A solution of gelatin and lactic acid sufficient to neutralize the alkalinity of the lignin solution is then added over a period of hours, leaving behind a clear, light-colored supernatant.

Compounds of protein and lignin show marked adsorptive properties and have been employed for the purification of water.[10]

Precipitation of Enzymes

The reversible solubility and insolubility of the complex of protein and alkali-cook lignin in relation to the hydrogen ion concentration may also be applied to the precipitation and recovery of enzymes. These biological catalysts are derived from a variety of plant and animal sources and from the growth of appropriate microorganisms on a suitable medium. These are utilized for numerous industrial applications as, for example, the unhairing of hides, the desizing of starch, the conversion of sucrose, or the tenderizing of meat.

Aqueous extracts of enzymes derived from microorganisms are prepared at their stage of maximum enzyme formation and the enzymes recovered by precipitation with salts, as, for example, by saturating the solution with sodium or ammonium sulfate. Precipitation of enzymes may also be accomplished by organic solvents added in a proportion several times that of the aqueous extracts.

The use of alkali-cook lignin for the precipitation and recovery of enzymes[11] offers advantages in respect to economy.

An alkaline solution of the lignin is added to the agitating enzyme extract, and the pH adjusted gradually to the range of 4.0 to 4.5. A complex of enzyme-lignin is formed which is readily removed by centrifugation or filtration. The material may be conveniently dried at room temperature after admixture of a mild alkaline salt, sodium bicarbonate, etc. to neutralize the acidity in the precipitate. The dried preparation is stable for an indefinite period and may be employed for enzymatic digestions.

By this procedure, virtually complete recovery (90 to 100 per cent) was achieved

for a variety of enzymes, including mold protease, malt diastase, mold amylase, pancreatic protease, and papain. The method, however, is applicable only to enzymes having their optimum range of activity at pH 5.0 or higher, since exposure to a pH range substantially below 5.0 will cause the enzyme-lignin complex to reprecipitate.

The nature of the lignin complex and of its reversible solubility and insolubility remains to be determined. Formation of the complex may be dependent upon the hydrogen ion concentration, so that the complex is dissociated in alkali and reassociated under acid conditions.*

Summary

Complexes of protein and water-soluble forms of lignin may be formed which are soluble in alkali and reversibly insoluble in acid.

The precipitation of protein by lignin lends itself to a variety of technical applications, including the purification of fermentation mashes, recovery of protein from alcohol stillage, the clarification of beverages, and the precipitation and recovery of certain enzymes.

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* See paper in Vol. II of this series by Richard Willstätter on "The Adsorption of Enzymes"; see also reference to the work of T. Svedberg on molecular assemblage in proteins, in Vol. V of this series, p. 562-8. J.A.

Part II

Synthetic Polymers and Plastics

Some Principles Underlying the Behavior of Plastics

JEROME ALEXANDER

Nature solves with ease the varied and often complicated problems we pose by experiment—whereupon we rack our brains to understand the mechanism by which the final results were reached, so that we may plan new procedures in the hope of obtaining useful products. Technologists of ancient and medieval times often knew *how* to accomplish results, and it is amazing to see how much practical knowledge is to be found in the Bible (e.g., in Leviticus) and in the one-man encyclopedia * of the elder Pliny, who perished at the age of 56 in an eruption of Vesuvius in 79 A.D. But it was not until men began to understand the *why* of practical procedures that science and technology began to make rapid, orderly and coordinated progress.

On the evening of Feb. 5th, 1909, in the meeting room of The Chemists' Club, then in Mendelsohn Hall in 55th Street just west of Sixth Avenue, New York City, Dr. Leo H. Baekeland described his new synthetic resin, Bakelite, and exhibited specimens of it before the American Chemical Society. A report of this address is to be found in the first volume of the *Journal of Industrial and Engineering Chemistry,* pages 149-161 (1909). The writer, who had recently begun work with the ultramicroscope, realized that the product had colloidal as well as chemical aspects, but refrained from asking Dr. Baekeland for samples for scientific investigation, because foreign interests immediately began their futile attempt to appropriate this important invention. However, the colloidal properties of Bakelite and analogous products gradually gained recognition, and a paper on Synthetic Resins appeared in Vol. IV of this series. Among natural waterproof "plastics" may be mentioned asphalt, shellac, and rubber, in particular "hard rubber."

The attempt is here made to take an over-all or bird's-eye view of the principles involved in the dispersion, aggregation and polymerization of plastics and their

* Caius Plinius Secundus was the author of *Historia Naturalis* in 37 books, which filled about 2,000 Roman "volumes" and quoted nearly 500 authors. The importance of this work may be gauged from the fact that about 63 A.D., when 160 "volumes" had been filled, Larcius Licinus, Praetorian Legate in Spain, offered the equivalent of approximately $16,000 for it. A few interesting statements may be mentioned: Verdigris is often adulterated with shoemakers' black (ferrous sulfate), which may be detected by heating the suspected material on an iron shovel, whereupon it turns red if adulterated. "Another way to detect the adulteration is by papyrus previously steeped in extract of gall-nuts. [I know of no earlier form of test paper. J. A.] This blackens immediately if it is smeared with verdigris containing shoemakers' black." Alum is recommended for "offensive odors of the axilla." A non-rusting variety of iron was preferred for nails in military boots. Technological information is interspersed with remarks like these: "It occurs to one to marvel at the persistent experimenting of humanity, which has exempted neither dregs nor foulest residues from the most varied examination." "Connoisseurs (of art) pretend to a very special knowledge which they do not possess." "I am loath to dilate further . . . , by Hercules, on the use of earths in wrestlers' ointments, which assist our young men to develop their physical strength at the expense of their mental vigor." "With iron we plough the earth, plant trees, prune orchards, compel the vines to put forth young shoots by pruning away each year the withered growth, build houses, quarry rocks, and accomplish every other useful purpose. But iron is also the minister of war, murder, and robbery, not merely as a weapon at close quarters, but forged for swift flight, now hurled by an engine, by the most infamous cunning devised by the human mind, for, to bring death more speedily to our fellowman, we have given wings to iron and taught it to fly. Let the blame for such death be brought home to man, and not to Nature."

mixtures and admixtures (*e.g.*, with plasticizers, fillers, etc.), in order to understand the mechanisms whereby there emerge such desirable properties as insolubility, flexibility, elasticity, and temporary or permanent ability to flow under heat and pressure. Since there are innumerable possible combinations of materials and conditions, only those principles are considered which seem to have general application. In advancing theoretical explanations, we must always bear in mind the actual physical happenings, so that we may avoid that ever-present hazard referred to by the cynical Talleyrand when he said that language is used to conceal thought.

Co-dispersion

Where two or more kinds of particulate units are thoroughly mixed so that their relative distribution follows the laws of chance, we have what may be termed a *co-dispersion*. This expression makes no assumption as to the size or structure of the particulate units, and would, therefore, include true solutions, colloidal solutions, and mechanical mixtures. During or following dispersion, some of the units may undergo changes of many kinds: ionization, chemical reaction, polymerization, adsorption, adhesion, flocculation, deflocculation, or mechanical fragmentation. Thus there may emerge new structures whose properties, as particulate units in the co-dispersion, will greatly influence the qualities of the product resulting from the original mixture and its subsequent treatment. Even in the ideal case, where only one molecular species remains, the molecules may form crystalline or non-crystalline groups of varying structures and dimensions, thus establishing an iso-dispersion, which in some instances may be an iso-colloid. The plastic may be used in the form of a fine or colloidal dispersion. Thus Freeland and Yopst [4] describe such a dispersion of a polyamide stabilized by sodium lauryl sulfate as a protective colloid, which is applied to a wire by dipping. After drying, this is heated to the melting point of the polyamide to fuse the residual film to a homogeneous coating.

In the case of organic and inorganic polymers built up by the linkage of "residues" into "chains" or "three-dimensional structures," there may be a variety of effective particulate units of the same ultimate chemical analysis but of widely differing structures and practical properties. This is seen, for example, in silica (tridymite, cristobalite, quartz crystal), in starch (amylose, amylopectin), in glycogens, in celluloses, in polystyrenes, in polythenes and other plastics. A striking example of the importance of structure, as apart from ultimate chemical analysis, is shown by sulfur, which, when heated to 400° C and suddenly chilled, yields a transparent, elastic mass. This, on standing, is transformed by molecular readjustment into brittle, crystalline sulfur.

Commercial plastics are, for the most part, deliberate mixtures containing fillers, plasticizers, catalysts, etc., in addition to such impurities as may occur in these or in the main "plastic" or mixture of plastics. Commercial plastics may thus be considered as co-dispersions containing particulate units of many orders of size and complexity.* We cannot attain a true understanding of plastic behavior by considering only what happens at the purely chemical or molecular level; we must try to follow the behavior of all the particulate units, added or emergent, be they molecules, polymers, particles of wood or mineral, strips of veneer, or textile fabric.

Forces Operative in Plastic Mixtures or Co-dispersions

Stripped of the concealments interposed by theories, by definitions, and by failure to consider the many levels of structure involved, the final "plastic" formed by the treatment of a plastic co-dispersion is mainly the resultant of three sets of factors at the lower structural levels.

* Many commercial plastics thus have analogies to the vertical or CIO unions (Congress of Industrial Organizations), rather than to the superficially diverse trade or A. F. of L. unions (Am. Federation of Labor).

(1) *Aggregative forces,* tending to assemble the particulate units into larger aggregates, or into units having new properties.

(2) *Dispersive forces,* tending to separate these units, *e.g.*, attraction of solvent molecules, thermal and mechanical agitation.

(3) *Protective action* of particles so held or fixed that they militate against the junction of units which are separate or become separated, and the closely allied *deflocculative action* of particles which, becoming fixed (*e.g.*, by adsorption) at interparticulate surfaces, so weaken the attraction of these surfaces for each other that their particles separate, or tend to separate.

Whether the forces involved are "chemical" or "physical" will depend upon our definitions of these terms and upon the levels of structure of the units under consideration. As a rule, the larger the units the feebler are the forces controlling them, and the closer the approach of units the stronger is their mutual reaction. Nuclear forces are enormous; chemical forces are less powerful; and the forces of adhesion are still weaker. In diamond the carbon atoms approach to within 1.54 Å or less, while in graphite the carbon layers that slide past each other so easily are 3.40 Å apart. In benzene, the singly bonded carbons are 1.39 Å apart; in the ethylene double bond they are 1.33 Å apart; and in acetylene the triple-bonded carbon atoms are 1.20 Å apart.

The forces influencing aggregation and/or dispersion may, in some cases, result in the formation of frank and readily demonstrable chemical compounds. Thus when magnesia or magnesium carbonate is stirred with alginic acid and water, the two insoluble substances react to form soluble magnesium alginate. In the case of the deflocculation of clay by glue, the forces involved are weaker and less definite, though they are sufficiently potent to effect dispersion. In our attempts to understand and to classify infra-chemical forces, we have evolved such terms as secondary or residual valences, coulomb forces, van der Waals forces, and hydrogen bonds.

The notion of hydrogen bonds, originally advanced in 1912 by Moore and Winmill,[1] applies basically to units at the molecular level. The bond involves the linking of two atoms by hydrogen and assumes (1) a suitably connected H atom (usually bound to N, O, F or S), and (2) a suitable electron donor system. In a sufficiently large molecule the hydrogen bond may result in a chelate or crab-claw effect, one portion of the molecule binding another, somewhat as though an angry crab could fasten one of its claws onto its carapace. When exerted between different molecules, the H bond is a common cause of molecular association,* an outstanding case being that of water. Thus from a study of Raman spectra, I. R. Rae[2] reported the following:

	H_2O	Dihydrol $(H_2O)_2$	Trihydrol $(H_2O)_3$
Ice	0	41	59
Water at 0°	19	58	23
at 38°	29	50	21
at 98°	36	51	13

And T. C. Barnes[3] reported that *Spirogyra* showed markedly more growth in water from melted ice than in water from condensed steam, while water that had stood at room temperature showed intermediate growth.

While the union of a simple molecule, such as water, into double or triple molecules is not so hard to visualize, when we have, as with the proteins, long chains of amino-acid residues with hydrogen bond possibilities sprouting like ribs from the molecular backbones, we may not be quite so certain as to how the chains are spot-welded together.[6] In plastic co-dispersions, where the main binder forms a ramifying, distorted, and interlocked three-dimensional system, the temporarily persisting structure may be consequent on the laws of chance, weighted, of course, by the innumer-

* See papers in Vol. I of this series on "Molecular Association" by W. E. S. Turner, and on "Attraction Intensity and Attraction Pressure" by J. Traube.

able and diverse specific molecular and other attractive and dispersive forces, which establish themselves as far as local conditions, impurities and adjuvents will permit. According to Vieweg and Schneider,[5] residual internal stresses in polystyrene and other organic glasses frequently, on storage, develop a haze growing to complete loss of transparency. Light reflection tests and microscopic measurements showed formation of small cracks perpendicular to the surface.

In discussing the X-ray examination of plastics (the pure substances themselves) W. T. Astbury (Chemistry and Industry, April 14, 1945) points out the complexity of the problem of trying to align their properties with their state of aggregation and orientation. "The problem is not simple, and certainly not as simple as might appear from the current light-hearted use of the phrase 'crystalline-amorphous ratio' to express the state of aggregation, almost as though there were a straightforward mixture of two discrete phases instead of, as is actually the case, a continuous gradation in size, perfection, and interlinking of chain-bundles, not to mention a range of chain lengths and possible variation in chemical constitution besides." Astbury points out that unstretched thermoplastics may be either disoriented amorphous or disoriented crystalline (and one might add, mixed). When stretched, the latter may become oriented, while the former may remain amorphous and disoriented, or may become oriented amorphous or oriented crystalline. "The mechanical properties of plastics are always the outcome of this sort of battle between the tendency of the chains towards disorientation and irregular aggregation and the forces leading to regular crystallization—between factors favoring mobility and those favoring permanence." Twelve X-ray diffraction patterns of plastics are shown.

As we go to progressively larger units, the binding forces become more uncertain, irregular and weaker, while the effects of impurities, fillers, and plasticizers may become more marked. Thus the fat worked into piecrust dough is called "shortening" because it makes the crust flaky and "short," that is, tender and readily broken. On the other hand, small amounts of water-insoluble soaps precipitated on broken stone make asphalt adhere better to the stone and strengthen the stone/asphalt aggregate. The strength of many crystals seems to depend on hydrogen bonds, for when the water of crystallization dries out, the crystal falls to powder.

When gelatin is soaked in cold water, the absorbed water loosens the strong bonds binding its units at the colloidal level. The gelatin swells and thermal or mechanical agitation will liquefy it. As the water dries out, the powerful idio-attraction of the gelatin units again asserts itself; drying gelatin often tears the surface from glass or porcelain. But if sufficient glycerin is added to the gelatin solution prior to drying, there remains a rubber-like composition, commonly called "flexible glue," used industrially for printers' rollers and for binding books and pads (paper "blocks") where lasting flexibility is desired. It would appear that the glycerin units are permanently held by and between the gelatin units in such a manner that the attraction of the gelatin units is sufficiently weakened to permit considerable relative motion without fracture. The glycerin is a "plasticizer" for the gelatin.

If we disperse some wood flour, whiting, or other "filler" in the hot and fluid gelatin-glycerin-water mixture, the resulting dried mass will be stronger but less flexible, but will be more suitable for making picture mouldings and the like. The gelatin units tend to bind the "filler" units together in a fashion recalling the hydrogen bond, though at a much higher level of structure or organization. The size, shape, and specific surfaces of the filler units, coupled with their degree of dispersion in the mixture, will materially influence the properties of the final product. At higher structural levels than we first considered, there emerge readily comprehensible mechanical factors, the larger units interlocking in various ways, *e.g.*, interlacing, dovetailing, tangling, etc. The structures of the mechanically functioning units are, of course, dependent on forces at the lower structural levels, where changes

may vitally affect the outcome. But the functioning of a clinch-nail or of a rivet, though it involves cohesion, is not to be understood in terms of cohesion alone.

Fibrous plastics, containing fibers as fillers, are said by W. E. Parsons to constitute over half of the rigid plastics output of 1943, estimated at 275 million pounds. In a paper read before the Chemurgic Council meeting at St. Louis, Mo., March, 1944, he described plastic products, *e.g.*, cafeteria trays, made of paper pulp and thermoplastic resins, the exterior layer being mixed with more resin than the core. On curing, the resin melts and spreads but remains most concentrated toward the surface, where it gives a fine, impervious finish. Here, the moulded unit will vary continuously in cross-section. Parsons said: "It can almost be said that the fibrous plastic article which has been produced in this manner is as much a product of the pulp moulding technique as it is a product of the plastics industry." This does not gainsay the basic and creative importance of chemistry in the plastics industry, but it does indicate that to understand plastics we must see and think at structural levels which are above the purely chemical.

Fiberglas *

Although Edward D. Libbey had made crude glass fibers which were exhibited at the Columbian Exposition in Chicago in 1893, it was not until 1936 that the Owens-Corning Fiberglas Corporation began to produce the fine, strong and flexible glass fibers now used in making textiles and for many other purposes. Their average diameters run from 22 to 38 one-hundred-thousandths of an inch, but their tensile strength is of the order of 300,000 pounds per square inch. (See Vol. III, p. 12 *et seq.*, in this series, paper on "Cohesion and Adhesion" by J. W. McBain and J. Alexander.) Staple fibers are formed by jets of high pressure steam which impinge upon thin streams of molten glass as they emerge from "spinnerets" in the melting chamber. This recalls the process long used in making "rock wool," which is utilized as an insulator, etc. Continuous filaments are made by what corresponds to the "stretch-spinning" of rayon, 100 or more filaments of fluid glass emerging from the melt being wound up on a rapidly revolving winder and greatly reduced in diameter.

Used alone or in conjunction with various plastics or varnishes, the cloths, tapes, braids, and other structures made or woven from glass fibers are widely used as electrical insulators in motors, generators, transformers, etc., as well as for many structural units such as luggage, radio cabinets, airplane parts. Glass curtains are not combustible, though of high decorative value; and they are not susceptible to attacks of mildew, nor will they shrink or stretch.

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Nitrocellulose

J. Barsha

Hercules Experiment Station, Hercules Powder Company, Wilmington, Delaware

Nitrocellulose, the oldest of the cellulose derivatives, was first prepared by Schonbein in 1845. Its early history was associated largely with the attempts to develop it for use as a military explosive; this was followed by the development of celluloid, the first of the synthetic plastics. The years following World War I saw the rapid expansion of the nitrocellulose lacquer industry. The properties of nitrocellulose were dealt with in the chapter on "Cellulose Esters" in Volume IV in this series and it is proposed in this article to review some of the investigations on nitrocellulose that have been reported in the literature since then.

Preparation

Sources of Cellulose

Cotton linters have served as the chief raw material for the manufacture of nitrocellulose, but efforts have not been lacking to substitute wood pulp for cotton linters,[1-6] particularly in war time when the demand for nitrocellulose for smokeless powder is very great.[7] These efforts have been stimulated by improvements in recent years in the technique of manufacturing and purifying wood pulp, especially for use in viscose rayon. Schur and Hoos [8] report that suitably purified pulps made from coniferous woods can be satisfactorily nitrated by the same methods that are used with cotton linters. A marked advance in the preparation of wood pulp for nitration was made with the development of a shredding machine which yields shredded pulp which can be nitrated satisfactorily in the usual equipment and by essentially the same procedure as is used for cotton linters.[9]

The possibility of preparing cellulose for nitration from a wide variety of agricultural products has also been investigated.[10, 11] Some regenerated cellulose film (scrap cellophane) is used in the manufacture of low viscosity nitrocellulose for lacquers.[12]

Nitration Reagents

Although many different types of nitration mixtures have been investigated, the commercial preparation [13, 14] of nitrocellulose still consists essentially of the treatment of cellulose with a mixture containing nitric acid, sulfuric acid, and water; in this reaction, the original form of the cellulosic raw material is retained. The type of nitrocellulose (N content and viscosity) produced is determined by the duration and temperature of the nitration and the composition of the nitrating mix. Following nitration, the spent acid is removed by centrifuging and washing with water; the nitrocellulose is then subjected to stabilization treatments and in some cases is treated to reduce its viscosity to some predetermined level.

A number of experimental studies [15-20] have been reported which deal with the effect of variations in the HNO_3—H_2SO_4—H_2O ratio on the properties (N content, viscosity, etc.) of the nitrocellulose produced. Of practical interest is the report [21] that the presence of insoluble matter in nitrocellulose has been traced, in one case, to

partial denitration of the nitrocellulose during centrifugal separation of the spent acid, which is caused by dilution of the acid with moisture sucked in with the air. Miles and Milbourne [22] observed the physical changes in ramie cellulose fibers when nitrating to various N contents (2-12 per cent) with various HNO_3—H_2SO_4—H_2O mixtures. The physical changes occurring in the fibers at about 7.5 per cent N seem dependent on the N content rather than on the acid composition. The extreme rapidity of cellulose nitration has been demonstrated by Spalding.[23]

Many other nitrating mixtures have also been studied. Among these are mixtures in which H_2SO_4 has been replaced by H_3PO_4. This method has been of interest because it yields products of high stability. Krauz and Blechta [24] found that the N content of the nitrocellulose produced falls very rapidly as the water content of the bath is increased. Lenze and Rubens [25] studied nitration with HNO_3—P_2O_5 mixtures and found that the maximum N content of 14 per cent was obtained in one hour. The optimum proportion of P_2O_5 seemed to be 25 per cent. Experiments to obtain nitrocellulose completely soluble in ether-alcohol showed that solubility is dependent on the extent of viscosity decrease. Berl and Rueff [26, see also 27] nitrated cellulose with H_3PO_4—HNO_3 mixtures (anhydrous or containing a little P_2O_5) and obtained products of much higher viscosity and with greater N content than by nitration with HNO_3—H_2SO_4 mixtures. Marked swelling facilitated the diffusion of the HNO_3, thus leading to uniform nitration. The products had high stability. The disadvantages of this process include the need for using anhydrous mixed acid and the high cost of H_3PO_4. Under certain conditions,[28] nitration with HNO_3—H_3PO_4—P_2O_5 was very rapid and a practically completely nitrated nitrocellulose (13.5 per cent N) was obtained in 1½ minutes. Bouchonnet and coworkers [29] found that a mixture of HNO_3 (92 parts) and HPO_3 (8 parts), or mixtures containing slightly more H_2O, gave products of about 13.5 per cent N which, after stabilization by boiling with water, were satisfactory for guncotton. A comprehensive study was carried out at Poudrerie Nationale d'Angoulême [30] and it was concluded that this method is not suitable for the production of nitrocellulose with about 12 per cent N (CP_2 guncotton) because small divergences from the optimum nitrating composition have an adverse effect on the product. It can be used satisfactorily for preparing nitrocellulose with 13.7 per cent N (CP_1 guncotton).

Attempts have been made to simplify the preparation of nitrocellulose by treating cellulose with HNO_3 vapor. Rogovin and Tichonov [31] found that treatment of cellulose with HNO_3 vapor for 96 hours at 20° C yielded a product with 13.4 per cent N which was completely soluble in acetone and highly stable. In a more comprehensive study, Bouchonnet, Trombe and Petitpas [32, 33] obtained homogeneous nitrocelluloses with high stability by treating cellulose with HNO_3 vapors at low pressures and taking care to avoid condensation. Nitration times were relatively short; *e.g.*, 12.65 per cent N in one hour. Indications were obtained that the heat of reaction could be readily dissipated even in large-scale operations. Additional information on experimental nitration conditions and on the properties of the nitrocelluloses has been obtained by Trombe, Champetier and Foex.[34-36] X-ray examination [37] of nitrocelluloses prepared by this method indicate that the reaction proceeds from the outside of the fiber to the inside. X-ray diagrams of products with 7.6-12.2 per cent N have the appearance of mixtures of unreacted cellulose and cellulose trinitrate. The higher substituted products (13 per cent N and higher) appear to be uniform. From a study of the nitration of ramie with HNO_3 vapor, Wilson and Miles [38] concluded that two HNO_3 molecules are involved in the reaction with each hydroxyl group, one to nitrate it and the other to take up the water liberated.

Nitrogen oxides have been used experimentally to nitrate cellulose. Pinck [39] found that nitrocellulose of any desired N content could be prepared with a nitrating bath in which HNO_3 had been replaced by N_2O_4. An increase in the amount of N_2O_4 in the usual nitration mixture (HNO_3—H_2SO_4—H_2O) was found to decrease

the yield and N content of the nitrocellulose.[40] Treatment of cellulose directly with N_2O_4 [41] and with N_2O_4 in the presence of H_3PO_4, $HClO_4$, HCl and HCOOH [42] results only in oxidation without nitration. The degree of nitration with N_2O_4—HNO_3 mixtures reaches a maximum at 30 per cent N_2O_4.[42] Addition of nitrogen oxides to HNO_3 (in absence of H_2SO_4) causes a higher degree of nitration (a maximum with N_2O_5). N_2O_3 and N_2O_4 cause greater depolymerization of cellulose than N_2O_5. Addition of 5 per cent N_2O_5 to 95 per cent HNO_3 yields nitrocellulose with 13.7 per cent N compared to 13.0 per cent N with 96 per cent HNO_3 alone. The more vigorous action of N_2O_5 in comparison with P_2O_5 can be explained by the more rapid diffusion into the interior of the fiber and the greater esterification in the interior by the HNO_3 resulting from the combination of N_2O_5 with water.[43] Dalmon and coworkers [44] treated cellulose with N_2O_5 dissolved in carbon tetrachloride at 130° C for six hours in the dark and obtained a high yield of nitrocellulose with about 14 per cent N. Treatment of dry cotton with pure N_2O_5 in a current of dry air or oxygen yielded pure cellulose trinitrate with 14.12 per cent N.[45, 46]

Nitration with mixed acids containing organic diluents has been studied.[47] Nitration with a mixed acid emulsion containing carbon tetrachloride or pentane and stabilized with a few drops of naphthalenesulfonic acid, yielded products with about 11 per cent N and fairly good solubility; the acid mixture contained much less HNO_3 and H_2SO_4 than usual.[48] To avoid the gelation of fibers which occurs on the nitrating of cellulose with concentrated HNO_3 alone, Trogus [49] used a mixture of HNO_3 and glacial acetic acid. To obtain nitrocelluloses with over 12.5 per cent N, it was advantageous to have present a small amount of water binding agent such as acetic anhydride or P_2O_5. Darzens [50] nitrated cellulose with a homogeneous mixture of nitric acid, acetic anhydride and chloroform, and obtained a product with 13.7 per cent N. Further study of this process by Brissaud [51] showed that nitration is effected very slowly and that the products are insoluble in ether-alcohol. Cellulose trinitrate was obtained by treating cotton linters with a mixture containing 50 per cent HNO_3, 25 per cent acetic acid, and 25 per cent acetic anhydride for 5 hours at 15° C and then boiling the product in water; stability was satisfactory.[52]

The effect of adding inorganic salts to the nitration mixture has also been investigated. The degree of cellulose nitration with 89-95 per cent HNO_3 is increased by about 0.6 per cent N on addition of 15 per cent $NaNO_3$. Similar additions of KNO_3 or NH_4NO_3 reduce the degree of nitration; the latter behavior is ascribed to complex formation ($R_{cell}.NO_3 \cdot HNO_3$) which decreases the concentration of HNO_3 available for nitration.[53] The addition of NH_4NO_3 or KNO_3 to pure nitric acid prevents the hardening and contraction of cotton fibers which occurs when HNO_3 is used alone. A maximum of 13.87 per cent N was obtained when 15-20 per cent NH_4NO_3 or 30 per cent KNO_3 was added to pure nitric acid as compared with 13.3 per cent N when HNO_3 was used alone.[54, 55] K_2SO_4, KH_2PO_4 and $NH_4H_2PO_4$ showed a similar action. The use of 97 per cent HNO_3 was less satisfactory than pure HNO_3.[54]

Mechanism of Cellulose Nitration

According to evidence obtained by Berl and coworkers [56, 57] and other investigators,[58, 59] an equilibrium exists between the nitrating medium and the nitrocellulose over a large range of substitution. The nitrogen content of nitrocellulose is determined by the final composition of the nitrating bath. The opinion that an equilibrium exists is supported by the observation that it can also be approached from the other direction, *i.e.*, long contact of nitrocellulose with relatively dilute mixed acid causes denitration to the same nitrogen content as would be obtained by direct action of this mixed acid on cellulose.

Farmer [60] has tried to explain the failure to obtain cellulose trinitrate (with the theoretical N content of 14.14 per cent) with HNO_3—H_2SO_4—H_2O mixtures on

the basis that nitration proceeds most readily through the "pseudo" form of nitric acid, *i.e.*, ($O_2N \cdot OH$). In his opinion, the nitrating action of the concentrated mixed acids needed for maximum nitration of cellulose is suppressed by the formation of nitronium sulfate—$(HO)_3N(SO_4H)_2$; the resulting removal of part of the pseudo-nitric acid prevents the formation of cellulose trinitrate. Atsuki and Ishiwara [61] suggest that the failure to obtain cellulose trinitrate is due to dilution of the mixed acid in the fibers by water formed in nitration and by selective absorption of water from the nitrating bath. The failure to obtain complete nitration can be explained best by the ability of H_2SO_4 to participate in the esterification reaction and the resultant formation of sulfuric-nitric mixed esters of cellulose.[62]

In an investigation of the formation of intermediate compounds during the nitration of cellulose Katz and Hess [63] found that the $(C_6H_{10}O_5 \cdot HNO_3)_x$ addition compound reported by Knecht [64] has a constant composition and a characteristic x-ray diagram; on washing with water, this addition compound yields a regenerated cellulose with the x-ray diagram of mercerized cellulose. Andress [65] also found a definite structure for the Knecht compound but ascribed to it the composition $[2C_6H_{10}O_5 \cdot HNO_3]_x$. Trogus and Hess [66, 67] consider the latter formula to be erroneous and confirm the earlier findings of Katz and Hess.[63] Tomonari [68] has also pointed to the formation of an intermediate compound (possibly a mononitrate) in the nitration with mixed acids rich in H_2O and HNO_3, which, in his opinion, plays an important part in the nitration mechanism. Carrière [69] found a higher $HNO_3 \cdot H_2SO_4$ ratio in the water in which nitrocellulose is drowned after nitration than in the wringer acid and suggested that a "pernitrocellulose," having more than the theoretical N content for cellulose trinitrate, is formed during nitration and decomposed on contact with water. Demougin and Bonnet [70] studied this phenomenon and obtained results which indicate that an adsorption product is obtained but not a chemical compound. Berl and Rueff [71] treated nitrocellulose with pure HNO_3 or mixed acids and obtained an adsorption product (14.8 per cent N) similar to that of Knecht; water decomposed it to nitrocellulose and HNO_3. X-ray diagrams, after treatment of cellulose with dry HNO_3, show spots due to cellulose, nitrocellulose and Knecht's compound.

Sendo [72] attributes the nitrating capacity of mixed acids to the free energy of the nitrating mixture and offers an equation for calculating the free energy. Kagawa [73] considers this view as theoretically unfounded and offers data to support the theory that for mixed acids in equilibrium with a nitrocellulose of given composition, the ratio of the partial vapor pressures of HNO_3 and water should be the same. A linear relation was found to exist between the ratio of the partial vapor pressures of HNO_3 and water in the mixed acid and the molar ratio of nitrate to hydroxyl groups in the nitrocellulose; the latter can, therefore, be considered thermodynamically as an ideal solution of $-ONO_2$, $-OH$, and cellulose groups.[74] Data were also presented on the heat of nitration of cellulose.[75] The properties of various nitration mixtures, and their relation to the nitration of cellulose have been studied by Danilov and coworkers.[76]

Two general concepts have been advanced to explain the manner in which the nitration reaction proceeds in cellulose fibers.[77] According to the first of these concepts, the nitration reagent penetrates between the cellulose micelles and nitration proceeds progressively from the outside to the interior of the micelle (micellar heterogeneous reaction). The second concept suggests that the nitration reagent penetrates uniformly into all parts of the cellulose fiber and all the molecules are nitrated at approximately the same time (homogeneous or permutoid reaction).

On the basis of x-ray studies of the structure of nitrocellulose, Herzog, Náray-Szabó, and Susich [78, 79] gave early support to the heterogeneous reaction theory for nitration and claimed that all nitrocelluloses (below the trinitrate) are made up of mixtures of cellulose trinitrate and unchanged cellulose.[67, 80, 81] Sakurada and co-

workers [82, 83] proposed the following equation to cover all micellar heterogeneous reactions including cellulose nitration: $x = kz^m$ (x = amount of cellulose reacted, z = reaction time, k and m are constants). Chemical and x-ray analysis confirm, in their opinion, the view that the kinetics of cellulose nitration are determined by the velocity of diffusion rather than the velocity of nitration. Tomonari [84] also favors the theory of heterogeneous reaction for nitrations to high N content with HNO_3—H_2SO_4—H_2O mixes low in water because the rate of nitration is greater than the rate of diffusion. In the extreme case of acid mixes high in water, the reaction approaches the permutoid type because of the greater speed of diffusion. The same mechanism is believed to hold for nitration with HNO_3—H_3PO_4—H_2O mixtures.[85]

The permutoid theory of cellulose nitration is supported by the considerable body of evidence showing than an equilibrium exists between the nitrating medium and the nitrocellulose.[56-59]

Opposition to the micellar heterogeneous theory of cellulose nitration has also resulted from the failure to find any appreciable amount of unchanged cellulose in the examination of hundreds of nitrocellulose samples.[86]

Miles and Craik [87, 88] determined the x-ray diagrams of a wide variety of nitrocelluloses prepared with various HNO_3—H_2SO_4—H_2O mixtures. They divided the products into three groups depending on their position on the chart (Figure 1) of

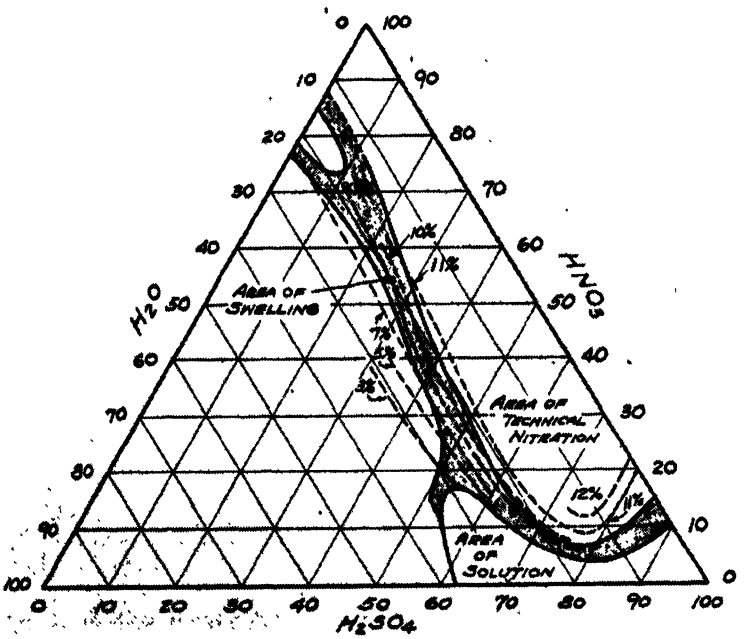

FIGURE 1. Effect of mixed acid composition on the nitrogen content of Nitrocellulose. *After Miles and Craik.*[87]

the composition of the mixed acid with which they were prepared: (1) N content less than 7.5 per cent, fiber structure unimpaired, insoluble in all solvents, (2) N content 7.5-10.5 per cent, fiber structure more or less impaired, swell or dissolve in acetone, (3) N content over 10.5 per cent, fibrous, completely soluble in acetone, comprises all technical nitrocelluloses. On the basis of x-ray results, the view is held that in preparing nitrocelluloses in group (1) the reaction is heterogeneous,

whereas in groups (2) and (3) all the chain molecules are nitrated to about the same extent in such a way that there is little chance of any one molecule being completely nitrated to trinitrate before the rest, *i.e.*, the reaction is permutoid. Evidence based on the behavior of nitrocellulose in solution and on fractionation experiments is also cited against the heterogeneous reaction theory for cellulose nitration.[87]

A study of the effect of fiber structure (ramie, cotton and wood pulp) on the kinetics of nitration showed that increasing the rate of diffusion of the mixed acid into the fibers by decreasing orientation or by swelling accelerates the rate of nitration.[89]

Viscosity Control

In the manufacture of nitrocellulose, it is necessary to control not only the N content of the product, but also its viscosity, because of the different viscosity requirements for various uses. For some purposes (*e.g.*, lacquers) it is desirable to produce very low-viscosity nitrocellulose.[90] The viscosity of the cellulose [8, 90a, 91, 92] and the temperature [91-94] and duration [94, 95] of the nitration all exert an effect on the final viscosity. Viscosity reduction may also be effected by treating the nitrocellulose with hot dilute solutions of acids [90a, 94, 96] or alkalies [90a, 91, 92, 94, 96, 97] or by digesting the nitrocellulose in water under pressure.[90a, 91, 94, 96-98] A marked advance in the commercial production of low-viscosity nitrocellulose was achieved by Milliken [99] in the development of a continuous digester which avoids the hazards associated with the older method of batch digestion in autoclaves.

Stability

The industrial or military usefulness of a given lot of nitrocellulose is dependent to a great extent upon its stability, *i.e.*, its ability to withstand long storage at or above room temperature without undergoing excessive decomposition which causes deterioration in mechanical properties. When nitrocellulose is removed from the nitrating bath it contains free acids which must be removed by washing. Wiggam [100] has shown that the stability of nitrocellulose is lowered to a degree depending on the amount of acid absorbed. The role of the porosity of nitrocellulose fibers in stabilization treatments has been studied by Kullgren [101] and Centola.[102] The formation of sulfuric acid esters of nitrocellulose, which have an adverse effect on stability, varies with the composition of the mixed nitrating acid. An increase in the nitrosylsulfuric acid content of the mixed acid increases the combined sulfate content.[28] An increase in the proportion of water in the mixed nitrating acid will result in nitrocellulose of improved stability.[103] When the formation of sulfuric acid esters of nitrocellulose is avoided, as in nitration with HNO_3 vapors, highly stable nitrocellulose is obtained by simply washing the product with cold water.[88]

The combined sulfate groups in nitrocellulose can be removed by treating the nitrocellulose with boiling dilute mineral acid. At equal concentrations, the stabilizing action of the following acids in the wash water decreases in this order: HNO_3, HCl and H_2SO_4.[104] If nitrocellulose which has been stabilized by an acid boil is washed with water containing $CaCO_3$, a further improvement in stability is obtained.[105] This improvement is reversible since it is removed by treatment with acid and reappears on treatment with $CaCO_3$. Landon [106] has suggested that salt formation with an organic acid in the nitrocellulose is responsible for this behavior. The excess carbonate present after the treatment can be removed without harming stability by suitable washing with 0.1 *N* HCl solution.

The stability of nitrocellulose can be improved by subjecting it to an extraction treatment with various alcohols.[107]

Numerous compounds have been evaluated as stabilizers for nitrocellulose.[108] A satisfactory stabilizer should absorb the products of nitrocellulose decomposition, be completely compatible with the nitrocellulose and not react with it. Calcium

carbonate, one of the first compounds used as a stabilizer, reacts with nitrocellulose under some conditions and actually lowers its stability.[109, 110] The best stabilizers are weak organic bases, such as amines and urea derivatives. Diphenylamine, which has been used as a stabilizer for many years, has been found to react with nitrocellulose especially in the presence of copper salts such as are frequently found in nitrocellulose.[111] p-Nitrodiphenylamine behaves in the same way. Nitrosodiphenylamine was found to be a better stabilizer than diphenylamine. Diethyldiphenylurea (Centralite I), which is an efficient gelatinizing agent for nitrocellulose, is an excellent stabilizer. Unlike diphenylamine, Centralite I has no active H atoms and it therefore does not react with nitrocellulose.[111] Urbanski and coworkers have found that some aromatic nitro compounds increase the stability of nitrocellulose.[113]

Studies of the mechanism of decomposition of nitrocellulose indicate that the decomposition takes place in two stages. In the first stage, the decomposition is slow; in the second stage the initial decomposition products react with the nitrocellulose so that the reaction becomes autocatalytic and speeds up rapidly. A good stabilizer will remove the decomposition products formed in the first stage and thus prevent the reaction of the second stage from occurring; as a result, the decomposition is held down to a relatively slow rate.[112]

Muraour disagrees with the view that nitrocellulose is fundamentally unstable even at room temperature and that heat stability tests merely accelerate a phenomenon occurring at room temperature. He found that suitably washed nitrocellulose lasts indefinitely at room temperature. The decomposition of nitrocellulose may be due to two general causes: (1) thermolysis, and (2) hydrolysis. Hydrolysis is believed to be the real cause of deterioration of nitrocellulose at room temperature. The trace of acid necessary to start hydrolysis may result from incomplete washing of nitrocellulose or from the presence of a small amount of an ester unstable at room temperature.[114]

According to Desmaroux, the decomposition of nitrocellulose in absence of secondary reactions caused by N oxides is probably due to internal combustion (by oxygen from nitrate groups) of one of the glucose rings in the chain; this results in scission of the chain while the neighboring glucose units are only slightly modified. If the N oxides are not vigorously removed, they form with the water present an aqueous solution of nitric and nitrous acids which constitutes the medium for secondary reactions which may be classed as follows: (a) oxidation of glucose units, (b) hydrolysis of nitrate groups, and (c) scission of the chain.[115, 116]

Muraour[117] has shown that water also plays an important part in the decomposition of nitrocellulose by hydrolysis. At 15-20° C water exerts no action on suitably prepared nitrocellulose even after 20 to 30 years. At 50-75° C in a humid atmosphere, the deterioration of nitrocellulose is rapid; the initial hydrolysis of the ester causes formation of dilute nitric acid which by further hydrolysis causes rapid decomposition of nitrocellulose. The action of HNO_3 on nitrocellulose is strongly dependent on its concentration. A decrease in the moisture content (but not to complete dryness) of smokeless powder containing even a trace of free acid may cause an increase in the rate of decomposition. A large amount of water dilutes the HNO_3 and thereby retards or completely stops the decomposition. A minimum concentration of HNO_3 is necessary to produce hydrolysis.

From a study of the loss in weight, denitration, viscosity change, and Taliani tests on reworked smokeless powder which had contained diphenylamine and from the known fact that diphenylamine not only stabilizes nitrocellulose by absorbing N oxides but also saponifies and degrades nitrocellulose, Demougin and Landon[118] conclude that the amount of stabilizer to be added should be determined by whether the powder is to be (1) used at once, (2) stored for a definite period at room temperature, or (3) stored at an elevated temperature.

Numerous investigations have been carried out on methods for determining quantitatively the stability of nitrocellulose.[119-125]

Denitration

Although cellulose nitrate is an ester, removal of the nitrate groups is not effected suitably by the usual saponification agents (aqueous alkalies), because such denitration is accompanied by extensive oxidation and decomposition of the cellulose molecules.[126] A quantitative study[127] of the alkaline decomposition of nitrocellulose has shown that a relatively small amount of CO_2 is produced and a relatively large proportion of the nitrate groups is reduced to nitrite. The production of CO_2 and reducing substances appears to be related to concentration of alkali, ratio of alkali to nitrocellulose and to time and temperature.

Regeneration of cellulose from nitrocellulose by denitration is practiced commercially in the manufacture of rayon by the "nitrocellulose process" and is effected by reducing hydrolytic agents such as the alkaline hydrosulfides. Denitration of nitrocellulose also occurs on treatment with a more dilute mixed acid than was used in preparing the nitrocellulose. According to Tomonari,[128] denitration of nitrocellulose with alcoholic $(NH_4)S_2$ solution or with dilute mixed acid is a micellar heterogeneous reaction. The effectiveness of denitration with dilute acid solutions decreases with increase in size of the acid anion.[129] Nitrocellulose is also denitrated by irradiation with ultraviolet light, the rate of decomposition increasing with increase in temperature.[130]

Constitution and Structure

The elucidation of the constitution and structure of cellulose has been exhaustively investigated during the past forty years. The concept that the cellulose molecule is made up of a large number of β-glucose anhydride units joined together by ether linkages through the 1 and 4 positions has now won practically universal acceptance because it accounts satisfactorily for the properties and reactions of cellulose. These same considerations apply in the main to nitrocellulose except, of course, that most of the hydroxyl groups have been esterified with nitrate groups.

Evidence in support of the macromolecular theory of cellulose structure was claimed by Sheppard and coworkers[131] from work with thin nitrocellulose films. The limiting film thickness of nitrocelluloses of different viscosities was found to be 2.5-5.0 A. These results indicate that nitrocellulose separates from solution with one dimension at least of the solute units much less than any dimension of the elementary cell of the structure deduced from x-ray examination of the solid. The decrease in limit film thickness with increase in viscosity is believed to be due to the greater tendency to vertical piling and overlapping by the shorter chain molecules. DeVore and Davey[132] measured the thickness of thin films of nitrocellulose with a Langmuir tensiometer and concluded from their results that the ultimate particles in a nitrocellulose dispersion are not greatly different in size from the unit cell of cellulose or of nitrocellulose.

Various methods have been used to measure the molecular weight of nitrocellulose and other cellulose derivatives. Dobry[133, see also 134-137] determined the osmotic pressure of nitrocellulose and other macromolecular compounds in a variety of solvents at low concentrations and extrapolated the curves to zero concentration. At concentrations less than 0.1 per cent the apparent molecular weight was found to be independent of the solvent and of the concentration at which it was measured.

Scheiber and Baier[138] found that the relative molecular weights of different nitrocelluloses are the same regardless of the solvent used in the viscosity measurements. Staudinger and coworkers[139, 140] have done a great deal of work on the development of the viscosity method for determining the molecular weight of macro-

molecular compounds. They have proposed the general equation $\eta_{sp}/C_{gm} = K_m M$ in which η_{sp} = specific viscosity, C_{gm} = per cent concentration in basic building units, K_m = a constant, and M = molecular weight. Much of this work has been directed towards the determination of K_m whose values depend on the product and solvent used. Starting with a series of nitrocelluloses whose molecular weights had been determined by the osmotic pressure method, they obtained a value for K_m of 11×10^{-4} for nitrocellulose (12-13 per cent N) in acetone and 14×10^{-4} for nitrocellulose in butyl acetate.

Wehr [141] has drawn a series of curves showing the relation between the molecular weight of various nitrocelluloses and the relative viscosity of their 1, 5, and 10 per cent solutions in butyl acetate. On the basis of osmotic pressure and viscosity measurements with nitrocellulose, Meyer and Wolff [142] conclude that the value of K_m is affected markedly by the uniformity of the product. From the variation in relative viscosity with change in temperature or with change in solvent or treatment of nitrocellulose and from increase in viscosity brought about by simple physical means, McBain and Scott [143] conclude that cellulose derivatives are association colloids like soaps. They consider Staudinger's viscosity method for molecular-weight measurement to be "oversimplified" and that it does not give a true measure of molecular weight.

Kraemer [144] determined the molecular weight of cellulose derivatives using the ultracentrifuge and obtained the following values for nitrocelluloses:

Dynamite nitrocellulose	725,000-875,000
Plastics nitrocellulose	125,000-150,000
½-sec. nitrocellulose	45,000

He found a simple relation to exist between molecular weight and intrinsic viscosity and considered this fact to support Staudinger's viscosity method for determining molecular weight.

Mosimann [145] has also investigated the conditions for determining the molecular weight of nitrocellulose using the ultracentrifuge. Gralén [146] and Campbell and Johnson [147] compared viscosity, ultracentrifugal and diffusion methods for determining the molecular weight of nitrocellulose. Gralén reported that a comparison of the molecular weights of the nitrocelluloses with those of the celluloses from which they had been prepared showed that the nitration with HNO_3—H_3PO_4—P_2O_5 causes some depolymerization.

The molecular weights of nitrocelluloses, as ordinarily prepared, are only average values because the nitrocelluloses contain molecules of various sizes. This point has been established by fractional solution [148-150] and fractional precipitation [151-156] experiments which have shown that while there is little variation in N content between the different fractions, the lower the solubility, the greater is the viscosity and the molecular weight of any given fraction. In the most exhaustive fractionation study of nitrocellulose, sixty-six separate fractions were obtained as the result of repeated refractionation.[157] However, the last fractionation showed that even after this rigorous treatment, the individual fractions were not homogeneous because considerable separation was still occurring.

The degree of polymerization (*i.e.*, the number of anhydroglucose units in the molecule), determined viscometrically, of a number of nitrocelluloses was found by Staudinger and Sohn [158] to be appreciably higher than that of the original celluloses calculated from viscosity measurements in cuprammonium hydroxide solution. When the celluloses were dissolved in cuprammonium hydroxide solution, recovered by precipitation and then nitrated, the degree of polymerization of the nitrocelluloses was the same as that of the original celluloses. This behavior may be explained by the assumption that (a) ester linkages are formed in the cellulose chain by oxidation

(particularly with acidic agents) which are stable in the nitrating acid but are readily hydrolyzed by alkali, or (b) end groups of a broken chain molecule in the cellulose fiber are condensed and linked together by the dehydrating action of the nitrating acid.

Davidson [159] has obtained evidence supporting the view that the viscosity behavior discussed above is due to the presence of alkali-sensitive linkages in the cellulose. In a study of the oxidation of cellulose, he found that oxycellulose produced by neutral or acid oxidation suffers a loss in nitrocellulose viscosity (*i.e.*, the viscosity of a solution of nitrocellulose prepared from a given cellulose) on treatment with alkali.

An attempt has been made to determine the distribution of nitrate groups in partially nitrated cellulose based on the knowledge that sodium iodide replaces primary nitrate groups with iodine in simple sugar nitrates. The method was unsuitable for highly nitrated nitrocellulose (13.2 per cent N) because of oxidative side reactions. On treatment of other nitrocelluloses (2.5-9.0 per cent N) with sodium iodide, about one-half of the nitrate groups were replaced by iodine, about one-third remained unchanged and the rest were removed. The results are taken to indicate that at least one-half of the nitrate groups in the low-substitution nitrocelluloses are in the primary position.[160]

X-ray analysis of structural changes in nitrocellulose with change in N content show that, regardless of N content, the chain molecules remain separated by a distance of 13.86 A which agrees closely with the calculated dimensions of the nitrate group.[161, 162] The nitrate groups seem to be distributed at random along the chains and regularity of structure tends to reappear only when nitration approaches completeness. Trinitrocellulose with about 13.5 per cent nitrogen has a monoclinic unit cell whose dimensions indicate that the molecular chains are folded at intervals of five glucose units along the chain.[163, 164] Denitration results in approximate return of the original cellulose lattice.[163]

A linear relation has been found between the double refraction and N content of nitrocellulose.[165]

Action of Solvents

The solubility of nitrocellulose in solvents is affected by many factors including the properties of the nitrocellulose (N content, viscosity, etc.), the chemical nature of the solvent and such conditions as temperature, time, and concentration. According to Wadano,[166] the solubility of nitrocellulose is independent of viscosity or degree of polymerization when the latter is greater than 100-150; below this value, the solubility increases with decreasing viscosity. The N content has the greatest influence on solubility.[167] Variation in the solubility of fibrous nitrocellulose with change in physical form was shown by the observation that extraction of highly nitrated nitrocellulose with ether-alcohol results in solution of only part of the nitrocellulose. When the fibrous residue was dissolved in acetone and recovered as a finely divided precipitate, additional material could be extracted from it with ether-alcohol.[168] The effect of uniformity of nitration and denitration upon the solubility of nitrocellulose was studied by Tomomari.[169] The presence of inert substances on the exterior of the micelle tends to prevent solution of the material in the interior. The solubility behavior of nitrocellulose which has been subjected to further nitration or to denitration is explained in part by Tomomari on the basis of the micellar heterogeneous theory of cellulose reactions. The solubility of nitrocellulose (*e.g.*, in alcohol) is determined in part by the amount of solid phase present.[170]

Kraus [171] has determined the solubility in 84 solvents and plasticizers of seven laboratory samples of high viscosity nitrocellulose with 10.36-12.71 per cent N. More recently, the same investigator [172] reported extensive solubility data for 14 commercial samples of nitrocellulose of 10.20-12.29 per cent N and covering the entire viscosity

range used in lacquers. Kraus has also determined the solubility of nitrocellulose in: (1) solvents containing water,[178] (2) mixtures of CS_2 and other solvents,[174] (3) mixtures of nitro compounds and other solvents,[174] (4) mixtures of ethyl alcohol and various organic acids,[174] (5) a wide variety of alcohols,[175] (6) ethers and mixtures of ethers and alcohols,[176] (7) mixtures of alcohol and benzene,[177] and (8) mixtures of alcohols and halogenated hydrocarbons.[178]

The solvent power of mixtures of various alcohols with ether appears to be at a maximum when the amounts of the components are equimolecular.[179] The effect of temperature (−20° to 30° C) on the solubility of nitrocellulose (10.97-13.23 per cent N) in ether-alcohol was determined by Uchida.[180] The solvent power of hydroxy compounds was found to decrease in the following order regardless of the type of nitrocellulose: methyl, ethyl, allyl, benzyl, cyclohexanyl, propyl, phenylethyl, butyl, isopropyl, isoamyl, heptyl, isobutyl, hexyl, isohexyl, octyl, tert-butyl alcohols, "amylene hydrate," sec-octyl alcohol, and phenol.[179] Eimont and Suirkin[181] have tabulated the solubilities of various nitrocelluloses in binary and tertiary mixtures of alcohols, acetone, and ether. The effect of N content and temperature on the solubility of nitrocellulose in acetone-benzene mixtures has been investigated by Inoue and coworkers.[182]

Various methods have been developed, especially for use in lacquer formulation, for determining the power of solvents and solvent mixtures to dissolve nitrocellulose. A system for the complete evaluation of the solvent power of nitrocellulose solvents has been proposed by Doolittle,[183] in which data obtained by both dilution ratio and viscosity methods are combined in a single phase diagram. Ware and Teeters[184] have developed the so-called "constant viscosity procedure" for nitrocellulose solvent evaluation by means of which a single value may be assigned to the combined viscosity characteristics and diluent acceptance of the solvent. The method was applied to determine the effect of toluene dilution on the solvent power of a number of esters.[185] Evaluation of three types of diluents by the constant viscosity procedure[186] showed that the solvent power for nitrocellulose decreases in the following order: toluene (aromatic), high-solvency naphtha (mixed aromatic-aliphatic), and gasoline (aliphatic). A study of the increase in solvent action of eight nitrocellulose solvents (alkyl acetates and propionates) caused by the admixture of one or other of eight alcohols showed that solvent action increases and the point of maximum solvent strength tends to move in the direction of higher alcohol content as the volatility of the ester decreases relative to that of the alcohol.[187]

Properities of Solvents Which Determine Solvent Power

Attempts have not been lacking to find some property of solvents which determines their solvent power for nitrocellulose.[188, 189] Calvert[190] noted that nitrocellulose contains 58 per cent oxygen and that practically all nitrocellulose solvents contain oxygen. He found that an increase in the percentage of oxygen in a homologous series of solvents, and within limits, increases the solvent power for nitrocellulose; however, no general relation could be derived.

Sakurada and Taniguchi[191, 192] have pointed out that swelling and solubility of nitrocellulose increases with increase in the dipole moment of the liquid. In developing a theory for the solution mechanism of macromolecular compounds, Ostwald and Ortloff[193, 194, also 195, 196] brought out the importance of the function μ^2/ϵ (μ = dipole moment, ϵ = dielectric constant) and showed that with one exception, all the liquids dissolving cellulose acetate had μ^2/ϵ values of 0.25-0.53. Liquids having lower values had a swelling action, while the inert liquids fell into a still lower group. Papkov[197] subsequently found that surface tension of a liquid also affected its solvent power for cellulose esters. Further work by Moll[198] in Ostwald's laboratory showed that if surface tension values of solvents are plotted against their μ^2/ϵ values, liquids having a solvent action for nitrocellulose fall within a small, definitely circumscribed zone.

Sorption of Solvent Vapors

The interaction of solvents and nitrocellulose has also been studied by observing the sorption of solvent vapors by nitrocellulose. The extent of sorption of acetone vapors by nitrocellulose increases as the temperature difference between the nitrocellulose and liquid acetone decreases.[199] Sorption of acetone, methyl ethyl ketone, Methyl Acetone * and ethyl acetate increases to a maximum with rising N content of the nitrocellulose and then falls off with further increase in N content. Sorption of methanol (liquid temperature 20° C) by nitrocellulose (at 40° C) decreases continuously with increasing N content. Variations in viscosity do not affect the extent of sorption. The amount of acetone sorbed by nitrocellulose depends only slightly on the side from which equilibrium is approached; with the other solvents the amount sorbed depends to some extent on the direction from which equilibrium is reached. The higher the boiling point of the solvent, the longer the time required to reach equilibrium. In most cases, nitrocellulose exposed to solvent vapor at a certain temperature does not revert to its original state when the temperature is lowered, *i.e.*, sorption and desorption are not completely reversible.[200]

Good solvents and poor solvents can differ a hundredfold in the amounts retained by nitrocellulose in equilibrium with their vapors. At low relative pressures sorption laws are followed, but as the relative pressure is raised, increased sorption causes pore formation and capillary condensation ensues. Gels were found to have more pore space than ungelatinized fibers. The predominating factor in these experiments is believed to be true adsorption.[201]

Thin sheets of nitrocellulose (12.1 per cent N) exposed above various mixtures of ether and alcohol in castor oil showed no preferential absorption for the vapors of ether or alcohol. On desorption small amounts of ether were retained more tenaciously than small amounts of alcohol.[202] On the basis of thermodynamic equilibrium studies and x-ray examination Desmaroux and Mathieu [203-206] conclude, contrary to Trogus, Tomomari, and Hess [207], that sorption of acetone vapors (from castor oil) does not result in compound formation and that there is a regular solution of acetone in nitrocellulose. Acetone causes enlargement of the nitrocellulose space lattice which reaches a maximum when one mole of acetone is fixed for each C_6 group. The fixation is reversible as long as the fiber structure is retained. Gelatinization takes place when the number of acetone molecules fixed is equal to the number of $-ONO_2$ groups; at this point a sharp break occurs in the crystalline structure. Starting from this basis, Alberto [208] calculated that nitrocellulose of 13.1 per cent N would require 54 per cent of its weight of acetone for complete gelatinization; this value is very close to the empirically established ratio of 1:0.56.

Kanamaru and Chao [209] studied the adsorption of many solvent vapors by fibrous nitrocellulose (13.5 and 9.9 per cent N), nitrocellulose film (13.5 per cent N), and other cellulose derivatives. At low relative vapor pressures, the films showed lower adsorptive power than the fibrous products, but at higher relative vapor pressures, the films showed higher adsorption. An empirical equation was derived for calculating the zeta-potential from the dielectric properties of the liquid and solid phases. Comparison of the zeta-potential values so obtained with those of adsorption for a variety of solvents showed that the two series stand in the same order. The authors believe that this supports their theory that zeta-potential is the best measure of "lyophility" of cellulose and its derivatives.

Schulz [210] measured the amount of acetone vapors absorbed at various vapor pressures by four nitrocelluloses of different molecular weight. The relation between swelling pressure and amount of solvent absorbed was found to be independent of the molecular weight and structure of the nitrocellulose. Schulz concluded from this that the swelling is intramicellar (molecular) and is due almost entirely to the

* A mixture of methanol, methyl acetate and acetone.

forces between the molecules of nitrocellulose and the solvent. The swelling follows the Freundlich equation $Pq = ks^{-v}$ (Pq = swelling pressure, s = specific swelling volume, *i.e.*, the volume to which 1 g of nitrocellulose has swelled, k and v are constants). Above $Pq = 20$ atmospheres, the equation is not followed; at that point about four molecules of acetone are present for each C_6 unit.

Gelatinization

Studies have been made of the gelatinization of nitrocellulose, primarily because this is of interest in the manufacture of smokeless powder.[211] Desmaroux[212] developed a method for determining the gelatinizing power of nitroglycerin for nitrocelluloses of different N content. The action of various gelatinizing agents on nitrocellulose shows that it is gelatinized only by polar molecules but that the dipole moment of the solvent is not the only factor affecting gelatinization.[213] Variation in the gelatinizing power with change in the composition of various binary mixtures of ethyl alcohol with dioxane, cineole, methylfuran, and methylal was measured by viscosity, swelling, and solubility tests. Approximately the same values for optimum composition for gelatinization were obtained from minimum viscosity and maximum swelling and solubility values.[214] The oxalic esters from methyl to amyl were found to be excellent gelatinizing agents for nitrocellulose; however, they are too susceptible to hydrolysis to be used in smokeless powder.[215] Petitpas[216] examined the gelatinization of nitrocellulose (13.8 per cent and 11.8 per cent N) by acetone, cyclopentanone, and methyl nitrate vapors (from castor oil solution) or by immersion in solutions of acetone and cylcopentanone in inert solvents (hexane, cyclohexane, benzene). X-ray examination showed a maximum change in the lattice dimensions and greatest clarity of the diagrams when one mole of solvent was taken up for each C_6 unit. Mangenot and Raison[217] have described the various changes observed under the microscope during the gelatinization of nitrocellulose fibers (from cotton and ramie) by nitroglycerin, methyl nitrate, diethylene glycol nitrate, and cyclopentanone. Soler and Vian[218] made a study of the gelatinization of nitrocellulose by three stabilizers: urethan, diphenylurethan and diethyldiphenylurea.

Solvation

Wilson and Miles[219] calculated the amount of acetone attached to nitrocellulose dissolved in acetone-water mixtures from the lowering produced in the total vapor pressure of the solvent mixture. There is always a positive absorption or solvation of acetone which does not vary much with different nitrocelluloses. With a nitrocellulose concentration of 12 per cent, the solvation is greatest with that mixture of acetone-water which just effects solution and falls off to zero with 100 per cent acetone. With lower concentrations of nitrocellulose, however, the solvation is higher in some mixtures richer in acetone. To explain their results, Wilson and Miles suggest that in mixtures rich enough in acetone to cause solution, water is solvated along with acetone and this causes solvation of acetone to seem to fall off as the acetone-water ratio increases. In dilute nitrocellulose solutions, however, it is considered that water is not absorbed in this way and that although actually no more acetone is solvated, the apparent value is much higher.

Nitrocellulose has a positive heat of solution. Treatment of nitrocellulose with benzene-acetone mixtures results in the liberation of a relatively large amount of heat at low acetone concentrations where little solution occurs; it is believed that this heat is mainly heat of solvation.[220] Calvet and coworkers have investigated the thermal effects during absorption of acetone,[221, 222] methyl nitrate, ethyl nitrate,[223] methyl acetate and ethyl acetate[224] by nitrocellulose. Kargin and Papkov[225, 226] have carried out similar studies with acetone-pyridine and ether-alcohol mixtures. Experiments by Okatov and Emmanuilova[227] on the interaction of nitrocellulose and ether-alcohol mixtures indicate that the following stages are passed through: wetting,

solvate formation, swelling, and solution. If solvate formation is limited then swelling is limited. The heat of wetting of nitrocellulose with ether-alcohol mixtures was greatest with a 1:1 mixture and smallest with ether alone. As expected from thermodynamic considerations, swelling and solution formation were accelerated by lowering temperature and increasing pressure.[227] Berl and Koerber[228] observed that nonsolvents for nitrocellulose at room temperature may become solvents at low temperatures (−50° C) and explained this behavior by the formation of soluble molecular compounds which are not stable at ordinary temperature and by the exothermic nature of the swelling reaction.

The x-ray structure of nitrocellulose fibers is changed when the latter are swelled by organic liquids; as the solute evaporates, the original structure returns.[229] Similarly, freshly prepared nitrocellulose films were found by x-ray examination to have a crystalline structure different from that of the original nitrocellulose; on evaporation of the solvent (acetone, ethyl acetate) the original crystalline structure of nitrocellulose returns. It is concluded from these results that the change in structure is due to compound formation between nitrocellulose and the solvent.[230] Similar studies of the action on nitrocellulose of binary mixtures of acetone and a nonsolvent indicate that acetone forms two loose addition compounds with nitrocellulose. The results suggest that for mixed solvents one component may form the addition compound which then dissolves in the second component.[207] Kanamaru[231] immersed nitrocellulose fibers (ramie) for long periods in polar liquids and observed that orientation of the crystallites decreased with increase in time of contact; similar treatment of nitrocellulose with nonpolar liquids caused little or no change. Solvation of the nitrocellulose by the polar liquids or solution of some of the intermicellar substances by the polar liquids is offered as a possible explanation of the behavior observed.

Scheiber and Baier[188] report that the time required for attaining solvation equilibrium in nitrocellulose solutions increases with increase in nitrocellulose chain length. This is shown by the time required for viscosity to reach a constant value.

Starting from the assumption that the swelling or dissolving of polar cellulose derivatives in organic liquids is brought about primarily by solvation (*i.e.*, by the orientation of electrostatically attracted polar molecules on the micellar surface of the derivative), Kanamaru and coworkers[232-235] undertook a study of the electrical phenomena occurring at the interface between nitrocellulose and organic liquids. They found that the degree of swelling or solvation of nitrocellulose in organic liquids is proportional to the zeta-potential (determined by the streaming potential method). The zeta-potential varies with time going through a minimum and then a maximum before approaching its limiting value. The greater the swelling capacity of the liquid for nitrocellulose, the higher is the zeta-potential (ζ_0) immediately after immersion and the lower is the limiting value (ζ_∞) of zeta-potential. Nitrocellulose has zero potential when it is so strongly solvated that it is about to dissolve. With decrease in the viscosity of nitrocellulose, the initial zeta-potential (ζ_0) and also the relative lowering of zeta-potential with time increases, *i.e.*, the degree of solvation of nitrocellulose increases with decreasing viscosity.

Kanamaru and Kohno[236] also determined the potential on the surface of nitrocellulose particles in acetone solution from the displacement which occurred when the solution was run in a fine stream between two charged electrodes immersed in acetone. With increasing concentration of nitrocellulose, the positive charge decreased and after passing through the neutral point became increasingly negative. The higher the viscosity of nitrocellulose the lower was the concentration at which the neutral point was reached. Calculation from viscosity data of the volumes of liquid immobilized in the solutions showed that nearly all of the solvent in the solution is immobilized at the concentration corresponding to the neutral point. Variation in the composition of the solvent used to disperse the nitrocellulose or of the solvent surrounding the electrodes alters the concentration of nitrocellulose at which

the neutral point is reached. The process of solvation was also found to affect the boundary surface conductivity of nitrocellulose in water, methanol, and ethanol; Kanamaru and Takada [237] concluded from their results that the surface conductivity originates not only in the ionic double layer but also in the dipole double layer (solvate layer).

Lee and Sakurada [238] calculated the apparent specific polarization of nitrocelluloses from the dielectric constant of their solutions. The apparent specific polarization of nitrocellulose was only slightly dependent on viscosity or N content; it was practically independent of nitrocellulose concentration in acetone and ethyl acetate solutions but varied with nitrocellulose concentration in acetone-hexane solutions. The authors concluded that nitrocellulose is so strongly solvated in strongly polar solvents (acetone, ethyl acetate) that dipole association and change in solvation do not take place within a large range of nitrocellulose concentration.

Nitrocellulose Solutions

Taniguchi, Sakurada, and Shojino [239, 240] determined the diffusion coefficients of nitrocellulose dispersed in different organic solvents and calculated the particle radius from the diffusion coefficient and the specific volume from viscosity data. Both the particle radius and specific volume decrease with increase in solvent power of the solvent showing that nitrocellulose is more strongly dispersed in the better solvents.

From a study of the dependence of the streaming double refraction of various polymer homologous nitrocelluloses in solution on the velocity gradient and the concentration, Signer and Gross [241] concluded that dilute and concentrated solutions represent states of different molecular mobility, in agreement with Staudinger's definition of sol and gel solutions.[242] It is apparent, from the comparison of the streaming double refraction of nitrocellulose solutions with the anisotropy of the nitrocellulose fiber that the streaming double refraction results from the orientation of stretched out anisotropic threadlike molecules and not from the elongation of isotropic particles.

According to Glikman,[243] the phenomena observed by him in a study of the viscosity, zeta-potential, and coagulation of nitrocellulose solutions can be explained by assuming the existence in nitrocellulose solutions of reversible aggregates which dissociate almost entirely in dilute solutions and form a structure like that of a gel in concentrated solutions.

Viscosity *

Nitrocellulose solutions generally do not obey Poiseuille's law that the shearing stress of a liquid is directly proportional to the rate of shear. Wiggam [244] studied the flow properties under various shearing stresses and found that the following equation developed by Williamson and modified to take account of the viscometer tube radius, expresses satisfactorily the flow relationship of all the solutions examined:

$$\frac{V}{F^1T} = a + bF$$

where, V = volume of flow in time t.

a = a constant corresponding to the fluidity at zero shearing stress.

b = a constant which is a measure of the structural character of the solution.

$F^1 = \frac{R^3F}{4}$; F = shearing stress

R = average radius of viscometer tube.

* A more detailed and theoretical discussion of the viscosity of colloidal systems is given in another chapter in Vol. V of this series.

On the basis of viscosity measurements of nitrocellulose solutions in many solvents, McBain and coworkers [245] claim that structural viscosity is the chief factor in the effective viscosity of nitrocellulose solutions. Rogovin and Ivanova [246] found no structural viscosity in dilute nitrocellulose solutions but observed that it increased very rapidly with increase in concentration. The higher the specific viscosity of nitrocellulose the greater the increase in structural viscosity with rise in concentration. The concentration at which structural viscosity begins to appear is highest in butyl acetate, lower for acetone and lowest for ethyl acetate; Scheiber and Baier [138] conclude from this that butyl acetate is a better solvent for nitrocellulose than acetone or ethyl acetate even though the absolute viscosity of butyl acetate solutions of nitrocellulose is the highest throughout. No direct relation was found between structural viscosity, specific viscosity and the lowering of viscosity caused by mechanical stirring (thixotropy). Nisizawa [247] found increasing structural viscosity of nitrocellulose solutions in ether-alcohol with increasing proportion of ether in the solvent. According to Mark,[248] the permanent decrease in the viscosity of nitrocellulose solutions caused by subjecting them to ultrasonic waves is due to degradation of the nitrocellulose molecules.

The variation of the viscosity of dilute nitrocellulose solutions, with change in temperature, does not seem to follow any general rule.[249] Lipatova and Lipatov [250] found that high viscosity nitrocellulose fractions in nitrobenzene solution have a high temperature coefficient of viscosity whereas the solution viscosity of lower fractions is less affected by temperature. Since the temperature coefficient of solvation should be constant for all the fractions, these investigators concluded that viscosity is not connected with solvation but presumably depends on the aggregation or disaggregation of micelles.

Several equations have been proposed [142, 251-255] to express the relation between the viscosity and concentration of solutions of nitrocellulose (and other macromolecular compounds) which is shown graphically [256] in Figure 2. Dobry and Duclaux [257, 258] examined dilute solutions of nitrocellulose in a variety of solvents and found by graphic extrapolation that for a given nitrocellulose, $\eta sp/C$ is a constant for all solvents at infinite dilution. Neale and Waite [259] have been unable to confirm this observation.

Brownsett and Davidson [260] studied the viscosity behavior of acetone solutions (0 to 0.25 per cent concentration) of nitrocelluloses prepared from hydrocelluloses, dichromate oxycelluloses and periodic acid oxycelluloses. They observed a different viscosity-concentration relationship for each of the three types of nitrocellulose and explained this behavior as being due to variations in the degree of association of nitrocellulose molecules which are caused by the chemical treatments of the original celluloses. They found that the viscosity-concentration relation of all their nitrocelluloses is represented satisfactorily by the equation $\log \frac{\eta sp}{C} = \log [\eta] + mC$, where ηsp is the specific viscosity, C is the concentration, $[\eta]$ is the intrinsic viscosity, and m is a constant.

Wannow [261] studied the viscosity behavior of nitrocelluloses of known molecular weight (determined osmometrically) and found that at constant molecular weight the viscosity increases with increase in N content.

Nisizawa [262] has investigated the effect on the viscosity of nitrocellulose solutions of the addition of water and of a wide variety of organic compounds. The addition of alcohol [263] or water [264, 265] to solutions of nitrocellulose in various solvents decreases the viscosity to a minimum beyond which further additions cause the viscosity to rise again. Addition of benzene [263] or xylene [266] causes the viscosity of nitrocellulose solutions to increase unless the solvent contains an alcohol as one of its components; in the latter case the viscosity goes through a minimum before rising again.

According to Pam,[267] the viscosity of a nitrocellulose solution is the same for a definite proportion of solvents and nonsolvents, irrespective of the order of their addition to nitrocellulose, provided sufficient time and agitation are allowed. The per cent reduction of viscosity on the addition of thinners to a solution of nitrocellulose is not proportional to the percentage of thinner added but rather to the logarithm of that value.

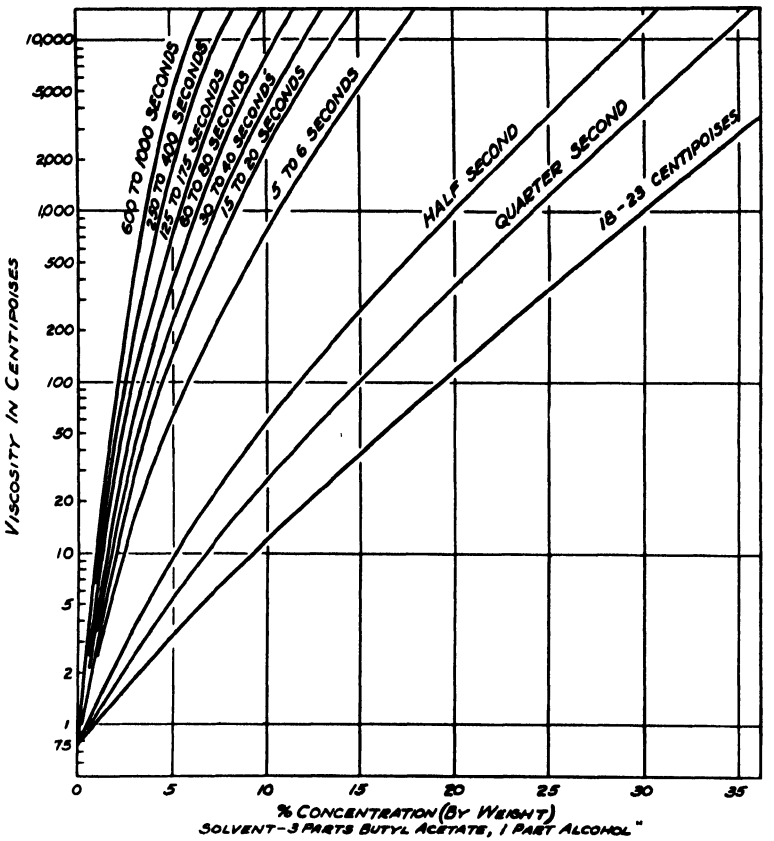

FIGURE 2. Viscosity-concentration curves[256] for Hercules Nitrocellulose (11.8-12.2 per cent nitrogen).

Solvents of like molecular weight and containing the same number of hydroxyl groups have been found to form nitrocellulose solutions of equal viscosity. The relation between the viscosity of nitrocellulose solutions and the molecular weight of the solvent was independent of the chemical nature of the solvent, within groups having similar constitution, *e.g.*, ketones and aliphatic esters.[268]

Electrolytes exert important effects on the viscosity of nitrocellulose solutions.[262, 269] As the content of alkaline earth hydroxides (especially $Ca(OH)_2$) in concentrated nitrocellulose solutions increases there is also a large increase in viscosity;[270, 271] the viscosity of dilute solutions remains unchanged. Electrodialysis,[272] boiling in distilled water or treatment with a solution of sodium hexametaphosphate,[273] all lower the viscosity of nitrocellulose in concentrated solution. Addition of HCl to lime-containing nitrocellulose solutions causes an immediate viscosity reduction;

Rogovin and Shylakhover [274] suggest that a nitrocellulose-$Ca(OH)_2$ complex is formed which increases the aggregation of particles in solution. Since HCl has no effect in lime-free solutions, they believe that the HCl destroys the nitrocellulose-lime complex. According to Gourlay,[275] the presence of small amounts of sodium chloride or calcium chloride causes a decrease in the initial viscosity of acetone solutions of nitrocellulose and an increased rate of viscosity drop on aging. Grévy [276] observed that the presence of ammonia in a freshly prepared ether-alcohol solution of nitrocellulose causes a large increase in viscosity whereas the addition of ammonia to an old solution of nitrocellulose has little effect on viscosity.

The viscosity of nitrocellulose solutions usually decreases on aging;[277] this viscosity decrease is accelerated by exposure to light.[278] Drinberg [279] attributes this effect to the influence of electrolytes while Grévy [280] has obtained evidence showing that the viscosity decrease of nitrocellulose solutions stored in glass is due, at least in part, to alkali from the glass. Nitrocellulose solutions that exhibit structural viscosity (*i.e.*, they do not obey Poiseuille's law) undergo lowering of total viscosity (true viscosity plus structural viscosity) with age, while solutions that obey Poiseuille's law do not. It was concluded from these results that the lowering of viscosity on aging is due, not to depolymerization of nitrocellulose, but to the destruction of the internal structure of the solution.[281]

Goldman [282] found that the rate of viscosity drop on aging gradually decreases. In acetone-alcohol mixtures, the viscosity drop increases with the proportion of acetone in the solvent. In the nitrocellulose concentration range of 2 – 16%, the most dilute solutions showed the greatest viscosity drop. However, Wehr [141, see also 283] observed that the viscosity decrease on aging is independent of the concentration and of the solvent, provided that the latter is pure. The degradation as measured by change in degree of polymerization, is independent of the original degree of polymerization. Viscosity drop is accelerated by acids and oxygen and is slowed down by antioxidants.

Coagulation

Nitrocellulose solutions may be coagulated by the addition of nonsolvents or of suitable electrolytes. Glikman [284] suggests that coagulation by a nonsolvent results from a decrease caused by the coagulant in the attractive forces between solvent and solute particles. Apard [285] observed that the addition of finely ground PbO, CaO, or $Ca(OH)_2$ to a 1% solution of nitrocellulose in acetone, alcohol-ether, or amyl acetate causes first an increase in viscosity and then gelation. Morozov [286] found that nitrocellulose solutions can be coagulated in the presence of small amounts of alkali by boric acid and the oxides of Pb, Al, Mn, Fe, Ni, Cu, and Zn. With the oxides of Mn, Fe, Ni, Cu, and Zn, the resultant gel passes into a solution on standing; with Pb or Al oxides syneresis of the gel occurs. Experiments on the coagulation of acetone solutions of nitrocellulose by the addition of water and aqueous solutions of $ZnSO_4$, $MgCl_2$, and $AlCl_3$ indicate that the particles in nitrocellulose organosols carry little or no electrical charge.[287] Addition of small amounts of bronzing powders and copper salts to nitrocellulose solutions produce clear green, solid gels; Gloor and Spurlin [288] suggest that a combination between Cu and the NO_3 groups is formed as the result of secondary valence forces. The higher the molecular weight of the nitrocellulose, the smaller the amount of gelling agent required to produce a strong gel. In studying the effect of metals and their salts on the viscosity of nitrocellulose solutions, Pamfilov and coworkers [289, 290] found that stabilization increases the time required for gelation to occur. Nitric acid and N oxides accelerate the gelation. These investigators believe that the above-mentioned gelation of nitrocellulose solutions is due to a physical change and not to a chemical one. The gelation of a sol containing nitrocellulose, antimony oxide or titanium oxide, and diglycol laurate in butyl acetate-alcohol is attributed by de Waele [291] to reaction between the pigment

and carboxyl groups formed in the nitrocellulose by oxidation; the reaction causes tridimensional linkage between emulsoid nitrocellulose particles. According to Vodyakov [292] the amount of metal in nitrocellulose gels, obtained by absorption of metallic oxides or hydroxides or by electrolysis of an acetone solution of nitrocellulose, is approximately proportional to the N content of the nitrocellulose.

Action of Plasticizers on Nitrocellulose

Camphor is absorbed by nitrocellulose from solution in a saturated hydrocarbon solvent only above a certain critical concentration.[293] X-ray examination of the solid product shows that a camphor-nitrocellulose compound is formed containing at least one mol of camphor for each C_6 group.[294] The reaction of nitrocellulose and camphor to form celluloid was found to occur more readily in alcohols than in ligroin; in addition to the earlier known compound, camphor-nitrocellulose I, two new compounds II and III were found by Hess and coworkers [295] and identified by x-ray and chemical analysis of the solid phase. The formation of camphor-nitrocellulose I in ligroin was catalyzed by small amounts of alcohols and ketones.[296] In the case of acetone, which was studied most thoroughly, a nitrocellulose-acetone compound is first formed and the acetone is subsequently replaced by camphor.[296] The compounds of *d-*, *l-*, and *dl*-camphor with nitrocellulose are indistinguishable from one another by x-ray analysis.[297]

X-ray examination by Trillat [298] of nitrocellulose fibers containing 0 to 300 per cent camphor (based on the weight of nitrocellulose) also shows that nitrocellulose has a particular affinity for camphor and forms a solvate with it when the proportion of camphor is sufficient. The camphor-nitrocellulose complex dissolves in excess camphor to form a solid solution. Trillat suggests that the action of plasticizers may be due to saturation of the lateral forces of attraction between the primary valence chains resulting in easier slipping of the nitrocellulose chains.

X-ray and double refraction measurements on stretched films indicate that in addition to camphor,[299, 300] compound formation also occurs between nitrocellulose and the following plasticizers: fenchone, menthone, carvone, cyclopentanone, cyclohexanone, cyclohexanol, diethyldiphenylurea, ethylacetanilide, dimethyl phthalate and triisoamyl phosphate.[301] Since ketones, amides, and esters all have the carbonyl group in common, it has been suggested that compound formation takes place through the latent valences of this group.[301]

McNally and Sheppard [302] studied the effect of camphor content upon the rate of elongation of celluloid films under static stress and offered the following explanation of the discontinuity observed at 35 per cent camphor content. At this concentration, there is present in celluloid one camphor molecule for each C_6 group which suggests stoichiometric combination of the two components; the ease with which camphor can be removed from celluloid shows that this combination must be unstable. Below 35 per cent camphor, celluloid consists of a mixture of nitrocellulose and nitrocellulose-camphor complex; above 35 per cent camphor the components are camphor and nitrocellulose-camphor complex.

Treatment of nitrocellulose with cyclohexanone, p-methylcyclohexanone, and fenchone in presence of ligroin results in formation of compounds whose composition is dependent on the nature of the ketone. Compound formation between nitrocellulose and m-xylene occurs only in presence of a ketone which, however, does not enter into the compound formed.[303]

Four stages were observed by Desmaroux and coworkers,[304, 305] in the absorption by nitrocellulose (13.8 per cent and 11.8 per cent N) of cyclopentanone in the liquid phase from hexane, cyclohexane and benzene and in the vapor phase from castor oil: (1) fibers intact and unchanged with small absorption of cyclopentanone, (2) fibers swollen and partly agglomerated, (3) formation of a rigid gel, and (4) formation of a solution. Benzene was not inert and caused gelatinization even when no cyclo-

pentanone had been absorbed. A sharp x-ray diagram was obtained when one molecule of cyclopentanone per C_6 unit had been fixed; total disappearance of regular structure occurred when one molecule per ONO_2 group had been taken up.[306]

Wadano [307] studied the mechanical properties of celluloid and found that celluloid from high-viscosity nitrocellulose has greater strength, modulus of elasticity, and total elongation, but less plastic elongation than celluloid from low-viscosity nitrocellulose. The effect of camphor on the mechanical properties of celluloid is greater with nitrocellulose of over 11 per cent N than with nitrocellulose of lower N content. According to Wadano,[308] nitrocellulose plastics made with camphor, dibutyl phthalate, and castor oil yield two types of celluloid: (a) nitrocellulose and the plasticizer (castor oil) form a solid solution having limited solubility, and (b) nitrocellulose and the plasticizer (camphor or dibutyl phthalate) form a molecular complex which produces solid solutions of definite solubility with nitrocellulose and the plasticizer. The properties of the celluloid are strongly influenced by the properties of the molecular complex.

Properties of Nitrocellulose Films

The mechanical properties of nitrocellulose films are affected to some extent by N content but are determined largely by the viscosity (or molecular weight) of the nitrocellulose.[96, 309-311] There is a limiting viscosity below which nitrocellulose loses its ability to form coherent films.[312] As the viscosity increases above this lower limit, the strength properties increase rapidly at first and then more gradually; a zone is finally reached beyond which further increase in viscosity results in only slight increase in strength properties.[141, 310] Staudinger and Jurisch [313] have observed a similar relation between the tensile strength and degree of polymerization of nitrocellulose fibers. In a detailed study of the stress-strain curves of nitrocellulose films, Blom [314] found no close proportionality between breaking load and viscosity; the elongation did increase with increase in viscosity. Spurlin [157] systematically fractionated a sample of nitrocellulose and prepared films from the 17 fractions obtained and from unfractionated nitrocelluloses and blends of high- and low-viscosity nitrocelluloses selected to have the same range of viscosity as the fractions. A definite viscosity limit was found below which the films did not withstand folding. The fractions gave higher fold values than unfractionated materials of the same viscosity and these were better, in turn, than blends of high- and low-viscosity nitrocelluloses. The solvent used in casting nitrocellulose film also affects its properties markedly;[309, 310] Sakurada and Watanabe [315] found that tensile strength decreases and elongation increases as the solvent power of the film-casting solvent increases.

Variations in the double refraction of nitrocellulose (and cellulose acetate) films were found by McNally and Sheppard [316] to be dependent on the forces acting on the film during drying. When no differential tension was applied during drying, isotropic films were obtained because of random arrangement of anisotropic particles. Equal tension on all edges of the film during drying resulted in uniaxial films, *i.e.*, the particles were parallel to the axis of the film. Greater tension in one direction than the other produced biaxial films in which the particles were lined up in the direction of pull and parallel to the axis of the film. Kargin and coworkers [317] investigated the structural changes that take place when nitrocellulose films are subjected to rapid deformation. Raison and Marcal [318] determined the plasticity of nitrocellulose films containing varying amounts of softening agents from the shape of the load-extension curves.

In a study of the effect of heat and light on plasticized films, Gloor [319] found that heat causes softening and a gradual decrease in viscosity and water resistance (permeability). Ultraviolet irradiation causes brittleness, a rapid decrease in viscosity and water resistance, and accelerates development of acidity; its action is principally on the nitrocellulose in the film. Lawson and Nason [320, see also 321] found

that the degradation of nitrocellulose by ultraviolet went faster in an atmosphere of air or oxygen than in nitrogen; in all atmospheres the viscosity dropped more rapidly during the initial period of exposure and then leveled off. Mindlin and coworkers [822] report that the light stability of nitrocellulose films is dependent on impurities introduced during preparation, the most harmful being ferrous salts and copper. Kozlov and Druyan [823] obtained nitrocellulose films of improved stability to heat and light by washing commercial nitrocellulose with alcohol. Sollner and coworkers [824-830] have carried out a series of investigations on the electrochemical behavior, base exchange capacity and related properties of nitrocellulose (collodion) membranes.

Uses *

Nitrocellulose finds its chief commercial uses in the manufacture of lacquers, plastics, photographic film, and coated fabrics (*e.g.*, artificial leather). At the time of writing, a tremendous amount of nitrocellulose is being manufactured for smokeless powder. The types of nitrocellulose used for commercial [256, 831] and military purposes vary widely in viscosity and N content, and, hence, in solubility and other properties. The solubility is determined largely by the N content. Viscosity is primarily a function of molecular size; commercial nitrocelluloses are available in viscosities ranging from 15 to 377,000 centipoises (in 12.2 per cent solution). A broad classification of the types of nitrocellulose now being manufactured is given in Table 1.

Table 1

General Types of Manufactured Nitrocellulose

Nitrogen Content (%)	Field of Application	Common Active Solvents
10.7-11.2	pyroxylin plastics, lacquers	ethyl alcohol
11.2-11.7	film, lacquers	ether-alcohol; methanol; ethyl, butyl and amyl acetates; acetone; methyl ethyl ketone
11.8-12.2	film, lacquers, rayon coated fabrics, cements	ether-alcohol; methanol; ethyl, butyl and amyl acetates; acetone; methyl ethyl ketone
12.5-13.5	smokeless powder	acetone

Lacquers [832-837]

It is seen in Table 1 that nitrocelluloses with various N contents are available for use in lacquers. Nitrocellulose with 11.8-12.2 per cent N is the type most widely used in lacquers and its solutions in active solvents may be diluted with hydrocarbons such as toluene, and petroleum naphtha. Nitrocellulose with 11.2-11.7 per cent N is soluble in the same active solvents as the previous type, but alcohol is more suitable as the diluent. Nitrocellulose with 10.7-11.2 per cent N, is soluble in ethyl alcohol or, better still, in ethyl alcohol-toluene, and is used in odorless lacquers, lacquer sealers, and in conjunction with alcohol-soluble resins.

One of the major trends in the nitrocellulose lacquer industry has been the effort to increase the amount of film former in the lacquer without raising its viscosity so as to deposit a thicker coating in a single application.[838] This effort, combined with improvements in formulation, has resulted in the production of increasingly lower viscosity types,[839, 840] so that there is now available nitrocellulose with a viscosity as low as 10-15 centipoises. Films obtained from 10-15 centipoises nitrocellulose are less flexible, but just as hard as films from higher viscosity nitrocellulose. This low-viscosity nitrocellulose is being used to increase the hardness of lacquers films containing high proportions of certain soft resins.[841] In another method of in-

* The discussion of the uses of nitrocellulose presented here is only a bare summary since a detailed report on this subject falls outside the main purpose of this article.

creasing the solids content of lacquers, the viscosity of the higher-solids lacquer is reduced to normal spraying viscosity by heating the lacquer as it is fed to the spray gun.[342-346] It has also been proposed to achieve this same result by the use of stronger solvents.[346]

Another interesting development is the use of nitrocellulose lacquer emulsions, which are prepared by making a very concentrated lacquer solution in a water-immiscible solvent, and then emulsifying this heavy base solution as the disperse phase in water.[347-351] Among the advantages claimed for this type of lacquer are (a) reduction in solvent cost, (b) increased solids content, (c) reduction in fire hazards, (d) low penetration into porous surfaces such as paper and leather.[349]

A successful method of producing fine pigment dispersions for use in lacquers consists in mixing up a heavy paste containing nitrocellulose, plasticizer, pigment, and solvent and then working the paste on a heated two-roll mill. The sheeted plastic is broken up into chips which disperse readily in lacquers and yield enamels with very high gloss and intense color.[352]

Nitrocellulose lacquers (clear or pigmented) are used to provide protective coatings on automobiles, metal hardware, furniture, leather goods,[353-355] and many other articles too numerous to mention.

Plastics [356]

Celluloid (nitrocellulose + camphor) is the oldest of the synthetic plastic materials. The chief drawback to celluloid is its inflammability, but its great toughness, water resistance, and brilliant clarity have combined to keep this plastic in active use.[357] While some newer plastics have recently surpassed celluloid in volume of production, it is interesting to note that production of celluloid plastics has increased from 1932 to 1937 and was about 41 per cent higher in 1939 than in 1938.[358] Special plasticizers containing chlorine or phosphate groups have been used to reduce the flammability of nitrocellulose plastics.[359, 360]

While nitrocellulose has been replaced by less flammable cellulose esters in some types of photographic film, it has retained its place in commercial motion-picture film because of its superior mechanical strength and dimensional stability.

Coated Fabrics *

The basic process for the production of artificial leather has not changed very much. Dyed cloth is coated with a "dope" containing nitrocellulose, pigment, castor oil, and solvents (a mixture of ethyl acetate, alcohol, and naphtha). The coated cloth is dried in a drier connected to a solvent recovery system and is then embossed to simulate one or other variety of natural leather.[361] Cloth is also coated with nitrocellulose compositions for the production of window-shade cloth and other miscellaneous fabrics.[362]

Miscellaneous Uses

In addition to the broad uses mentioned above, nitrocellulose is used in a large number of miscellaneous products. Nitrocellulose compositions are used in textile printing,[363, 364] and in applying moistureproof coatings to cellophane and paper;[365] they are employed widely in the shoe industry as adhesives and cements and in the stiffening of box toes and other fabrics used in shoe manufacture. Nitrocellulose is also used in the manufacture of rapid-drying printing inks, household cements, adhesives, mimeograph stencils, "canned heat," airplane dopes, and many other products.

* Dresses stiffened with nitrocellulose to produce a bouffant effect are easily ignited and burn explosively; several serious accidents have occurred. Such uses should be legally banned, under severe penalties. J. A.

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Chemistry of Cellulose Acetate

G. W. SEYMOUR

Celanese Corporation of America

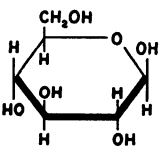
Fundamental Concepts

Cellulose acetate is the simple ester of cellulose and acetic acid. In order to appreciate fully the preparation and properties of cellulose acetate, it is necessary to have some conception of the structure of the cellulose itself. As is well known, cellulose is probably the most abundant and widely occurring organic substance in nature. As such, it forms the skeletal framework of all the higher forms of plant life and comprises 40-60 per cent of all plant growth.

Since cellulose is so widely occurring, it has been the subject of study and speculation for over 100 years. About the first recorded chemical investigation of the structure of cellulose was in 1819,[8] when it was demonstrated that glucose formed part of the structure of cellulose and could be isolated as a decomposition product. In 1883, Flechsig [7] produced accurate data showing that cellulose could be almost quantitatively hydrolyzed by acids to glucose. With this fact established, it was obviously necessary to determine accurately the structure of glucose and its relationship to the structure of cellulose.

Many years of speculation followed, but the ideas brought forth were based upon insufficient data. The constitutional formulas which were under observation in the early 1920's have been summarized by Hibbert.[15] It was not until 1934 that Haworth [12] proposed a structure for cellulose which could be accepted by the organic and cellulose chemists without qualification.

In brief, Haworth's conception of cellulose is that of an organized, well-ordered structure. This is substantiated by the crystalline behavior of native cellulose when subjected to x-ray and microscopic observation. When cellulose is hydrolyzed by mineral acids, it is decomposed quantitatively into only one form of glucose which is recognized as *d*-glucose and which Haworth chooses to call β-glucose. It was necessary for Haworth to establish the structure of glucose before proceeding with the structure of cellulose itself. He proposes a 6-membered ring consisting of five carbons and one oxygen—that is, a pyran ring. Since glucose contains a primary alcohol group, this must be affixed to the pyran ring, and Haworth suggests the following structure:



β-ord-Glucose

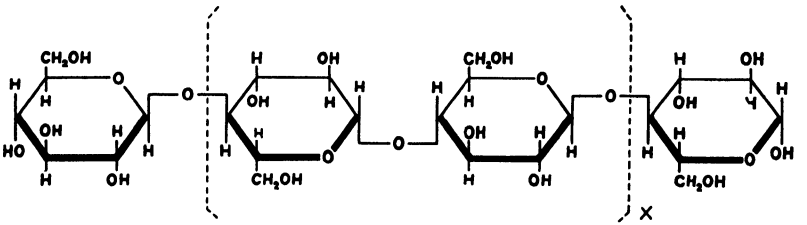
FIGURE 1.

By Haworth's nomenclature, therefore, glucose may be called gluco-pyranose.

The differences between α-, β- and γ-glucoses lie in the relative positions of the

hydroxyl groups to one another. In β-glucose, the most symmetrical arrangement exists, with alternate hydroxyls on the opposite side of the plane of the pyran ring.

If one molecule of water is split from the 1- and 4- positions of the β-glucose, the unit would be anhydro-glucose. This is the fundamental unit of the cellulose molecule. In order for the cellulose molecule to be constructed from the gluco-pyranose units without strain, it is necessary to rotate alternate glucose units through 180°.[13] Thus Haworth's proposed structure for cellulose is as follows:



Cellulose (12)

FIGURE 2.

For the proof of this structure, the following simple outline is given:

As noted, mineral acid hydrolysis of cellulose yields *d*-glucose entirely. When a similar decomposition is carried out, using sulfuric acid in the presence of acetic acid, however, cellobiose octaacetate is the lowest molecular weight material isolable. (The decomposition of cellulose in the presence of both sulfuric and acetic acids is known as acetolysis.) The yield of cellobiose octaacetate is by no means quantitative.

The cellobiose octaacetate thus formed may be saponified to β-cellobiose, which can be shown to be a dimer of glucose. Cellobiose may be oxidized to cellobionic acid.

Glucose, cellobiose, and cellobionic acid may be completely methylated to produce pentamethyl glucose (tetramethyl-methyl glucoside), octamethyl-cellobiose (heptamethyl-methyl bioside), and octamethyl-methyl-cellobionic acid ester, respectively.

Pentamethyl glucose is non-reducing. It may be acid-hydrolyzed, however, to yield tetramethyl glucose, which has a reducing group. Thus, by acid hydrolysis the glucosidic groups alone are hydrolyzed, while the ether groups are stable.

When octamethyl cellobiose (heptamethyl-methyl bioside) is subjected to hydrochloric acid hydrolysis, 2:3:6-trimethyl glucose and 2:3:4:6-tetramethyl glucose are formed.

If octamethyl-methyl-cellobionate is hydrolyzed in a similar manner, the final products are 2:3:4:6-tetramethyl glucose and 2:3:5:6-tetramethylgluconic acid. Since 2:3:4:6-tetramethyl glucose is formed as a result of each hydrolysis, it follows that the reducing unit of the glucose molecule is involved in the formation of the chain structure.

Since 2:3:6-trimethyl glucose is formed as a result of hydrolysis of the octamethyl cellobiose, the 1- and 4- positions must be involved in the chain structure.

Since, also, 2:3:5:6-tetramethylgluconic acid is formed from the hydrolysis of the methylated cellobionic acid and the 1- and 4-positions are involved in chain structure, the 1- and 5-positions must be involved in the ring closure. This may be shown by summarizing the above reactions graphically:

Thus, from Haworth's proof of structure, cellulose consists of a long chain of gluco-pyranose units connected in the 1- and 4-positions and terminated on one end with a potential aldehyde or reducing group. The molecular weight of cellulose is thus some multiple of the molecular weight of anhydro-glucose—that is, $(C_6H_{10}O_5)_x = (162)_x$.

While the structure of cellulose as described by Haworth is generally accepted by organic and cellulose chemists, the absolute evaluation of the subscript x is far from certain. Haworth and Machemer [14] have attempted to evaluate it by hydrochloric acid hydrolysis of fully methylated "cellulose." In doing so, however, it was found convenient to acetylate the cellulose first and then hydrolyze it to the acetone-soluble form. In solution the methylation could be carried out easily.

The completely methylated cellulose was then subjected to hydrochloric acid hydrolysis in the same manner as the cellobiose, etc., and it was found that trimethyl

glucose was formed almost quantitatively, but that 0.6 per cent of tetramethyl glucose could be isolated also. The tetramethyl glucose can be formed only by the terminal gluco-pyranose unit on the opposite end of the chain from the reducing group.

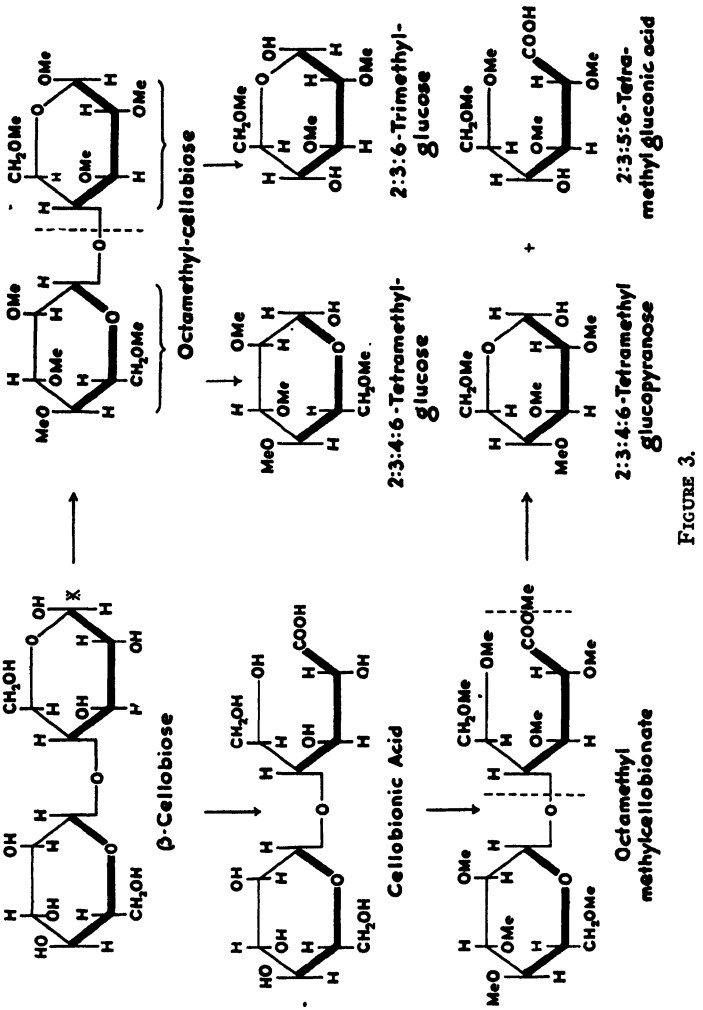


FIGURE 3.

Thus, by calculating the ratio of tri- to tetramethyl glucose, Haworth found that he could evaluate the subscript x as "not fewer than 100 and not more than 200 β-glucose units." [14]

The exception that has been raised to the work of Haworth and Machemer is based on Haworth's work showing that acetolysis or molecular fission can be carried out in the presence of sulfuric and acetic acids. It is apparent that Haworth was dealing with dextrinized cellulose, or a lower molecular weight material than the original cellulose with which he started. Haworth has apparently determined the molecular weight of cellulose acetate rather than that of cellulose.

The method of determining molecular weights by the end-group method was carried further by Bergmann and Machemer.[2] They attempted to take advantage

of the reducing characteristics of the potential aldehyde on the other end of the cellulose chain.

Normally, the reducing value of cellulose would be determined by measuring the copper numbers. Realizing that such determinations may be affected by the concentration of the alkali, traces of oxygen, and other conditions of the determination, they sought other means. The hypoiodite method was adopted. By such procedure they further substantiated the evaluation for the subscript x, as had been determined by Haworth. From the iodine numbers listed by Bergmann and Machemer,[2] the molecular weights may be calculated from their formula:

$$\text{Mol. Wt.} = 20{,}000/\text{iodine number}.^{1}$$

An exception may be taken to these results, however, since they presuppose that the reducing end-groups have not been subjected to oxidation prior to the reducing value determination.

Numerous investigators have attempted to evaluate the subscript x, by other means. Of the methods employed, however, only the determination of osmotic pressure, measuring the sedimentation velocity and diffusion, and the viscosity measurements of Staudinger are of general interest.

Büchner and Samwel,[4] employing the osmotic pressure method, have substantiated Haworth's molecular weight approximately. They also were working with cellulose acetates and cellulose nitrates of differing viscosities, however, and propose molecular weights of 35,700 to 46,400, depending upon the viscosity of the solubilized form of cellulose employed.

Their work, of course, is open to the same criticism as the determination of the end-group by Haworth in that they were probably working with a dextrinized form of cellulose.

Stamm,[31] employing the Svedberg ultracentrifuge, has measured sedimentation velocity and diffusion rates. From these measurements he proposes a molecular weight of 40,000 ± 5000, or from 200 to 260 anhydro-glucose units.

The reproducibility of these methods is open to some question, since Kraemer and Lansing,[17] employing the same method as Stamm, arrive at higher values. They find molecular weights of 220,000, equivalent to 1360 anhydro-glucose units.

According to the majority of these observers, therefore, cellulose has a relatively low molecular weight. That is not in keeping with the fibrous form of the cellulose nor with its behavior in solution. In order to reconcile the low molecular weight for cellulose with its appearance and behavior, recourse must necessarily be had to the work of Sponsler and Dore,[30] Meyer and Mark,[21, 22] etc. In these investigations, x-ray evidence is interpreted to show that cellulose exists in its fibrous form in unit cells. The unit cells consist of five molecular chains embodied in a cell and held together by van der Waal's forces,[21] molecular attraction, hydrogen bonding,[8] intermolecular forces, etc.

Since it is possible that the cellulose molecules formed through the primary valence chains may exist in more than one cell,[18] the possibility for large aggregates or micelles [23] is explained. This conception also suggests that cellulose may vary widely in micellar size, and therefore the viscosities of different celluloses in the same concentration might not be identical.

It is well known that different celluloses, or cellulose from different sources, do give widely varying viscosities. It is also known that cellulose solutions in basic solvents will alter in viscosity on aging. Nevertheless, it is a characteristic of cellulose, as well as of other high molecular compounds, to exhibit high viscosities in relatively dilute solutions.

Staudinger has made extensive investigation of this phenomenon employing rubber, synthetic polymers, and cellulose. Most high molecular substances exhibit viscosities in relation to concentration that may be predicted by Einstein's formula.[6]

These materials must exist in solution in spherical or ellipsoidal particles; otherwise, the formula does not hold. Since, however, viscosities of cellulose are not predictable by this means, it follows that they exist in solution in some form other than spheres or ellipsoids.

Staudinger [32] proposes that cellulose exists in solution in molecular form. The molecules are connected by primary valence linkages only, and in dilute solution are in long straight chains. The volume occupied in the solution may be calculated from x-ray data. When the volume of the dissolved cellulose is the same as the volume of the solution, the molecules are free to rotate without mutual interference. This concentration is termed the "limiting concentration." At greater concentrations the molecules in solution interfere with each other and the viscosities cannot be predicted mathematically. This condition is termed by Staudinger as a "gel solution."

At lower than the limiting concentration a "sol solution" exists and the viscosities are proportional to the concentrations.[32] Since cellulose exists in molecular dispersion, it follows, therefore, that below the limiting concentration the viscosity of cellulose solution is proportional to the molecular weight. Based on empirical data, Staudinger has set up the following mathematical relationship:

$$\eta_{sp}/c = M.K_m$$

η_{sp} = specific concentration, or increase in viscosity of a solvent due to the presence of the dissolved substance.
c = concentration as a primary molar solution—that is, the concentration in terms of the unit-building cell ($C_6H_{10}O_5$).
K_m = constant for any particular *polymer-homologous* series.
M = molecular weight.

It is immediately obvious that in order to use this equation and determine molecular weights by viscosities alone, some other means must be employed to evaluate K_m. Staudinger [33] has employed osmotic pressure experiments for evaluating this constant for relatively low molecular weight substances. The proper value for K_m to be used in determining molecular weights of various substances is still open to some discussion.[17]

Another difficulty which exists in the use of the Staudinger equation is in finding a proper range of concentrations in which the viscosity is proportional to the concentration. Usually at low concentrations a curve rather than a straight-line relationship is found. To evaluate viscosities, therefore, rather than using η_{sp}, the empirical η_{sp}/c is used, in which c is extrapolated to zero concentration. This value is known as the intrinsic viscosity and is designated by the symbol $[\eta]$.

Assuming the value of K_m to be approximately 10×10^{-4}, Staudinger has proposed a molecular weight for cellulose of approximately 120,000, or an evaluation of x in the formula for cellulose $(C_6H_{10}O_5)_x$ as 750. The term generally employed for the evaluation is "d.p." or "degree of polymerization."

To summarize, it is generally agreed that the Haworth structure of cellulose is accurate and enables cellulose chemists to explain and predict the behavior of cellulose and its derivatives from an organic chemical point of view. His evaluation for x (or the determination of the d.p.), however, is conceded to be that of a dextrinized cellulose, while Staudinger's d.p. is more probably correct.

The reconciliation of the various estimations of the actual chain length of cellulose due to primary valences or glucosidic linkages is yet to be achieved. The essential difference appears to rest in the proposal of Haworth that the maximum d.p. is 150, with 5 chains held together in unit cells by forces which are as yet unexplained, while Staudinger and others are of the opinion that cellulose may have d.ps. as high as 750 for cotton cellulose and 1000 for wood cellulose, and that it exists as a long straight chain.

It is appreciated and has been demonstrated [28, 17, 19] that cellulose is a heterogeneous material; furthermore, there is no reason to suppose that all forms of cellulose

have the same molecular weight. It is increasingly evident that cellulose is an extremely reactive material and will undergo numerous chemical alterations that cannot be controlled completely.

Having arrived at the fundamental conception of the structure of the cellulose as it exists in pure form, it is not difficult to account for the numerous reactions undergone by cellulose.

The terminal reducing groups are potential aldehyde groups and as such are reactive when subjected to even mild oxidation. Numerous literature references could be quoted to show that even mild extractions with alcohols, ethers, etc., cause some degree of oxidation. Different celluloses may be characterized by their base-combining power, and this capacity to neutralize basic salts can be demonstrated to be due to the presence of carboxyl groups.

The carboxyl groups could also be formed in a cellulose molecule by oxidation of the primary and secondary alcohol in the molecule. These primary and secondary alcohol groups, as well as the terminal groups, are capable of being sulfated and esterified, and of forming ethers; in short, the cellulose molecule itself is capable of any reaction which is known to occur to an aliphatic alcohol, aldehyde, or acid. In addition, hydrolysis readily occurs; in the presence of acetic anhydride, this may be known as acetolysis, or in the presence of aqueous mineral acids as molecular hydrolysis.

In the industrial utilization of cellulose, it is essential to have a thorough knowledge of the physical as well as the chemical behavior of cellulose in order that the final products may be satisfactory both from the standpoint of uniformity and stability. From the contributions of Haworth and Staudinger and numerous other investigators, it is now possible to control, measure, and understand the reactions of cellulose and its derivatives.

Raw Materials

The raw materials from which cellulose acetate is fabricated in commercial production are: cellulose, acetic acid, acetic anhydride, and catalysts. If preparation of cellulose acetate yarns for textiles is considered also, acetone must be included.

Cellulose

There are two chief sources of cellulose: wood and cotton. The cellulose isolated from these sources is designated as "chemical cellulose," and may be defined as cellulose purified for the chemical industry by chemical means.

Cellulose from Wood. If wood is used as a source, the *Coniferae* are usually employed. Originally, this was due to the long fiber necessary for paper-making; however, a wider latitude may be allowed for chemical cotton, particularly if the fiber identity is to be destroyed in processing, as in the cellulose acetate industry.

Spruce and pine in particular occur naturally with approximately 50 per cent cellulose content (disregarding water). The remainder is composed principally of lignin, hemicelluloses, resins, tannins, terpenes, and a number of other minor components. It would be difficult to discuss chemically these materials composing wood since very little is known of the structure of any of them except cellulose and lignin; for instance, the term "hemicelluloses" is used to include sugars, poly-uronides, and a great amount of ignorance.

When cellulose is desired as the end-product, it is produced at the expense of the remaining 50 per cent of the composition of the wood by the processes employed in paper-making, that is, sulfate, sulfite or soda cooking. In order that the cellulose be suitable for cellulose acetate manufacture, excessive purification is necessary; hence chlorination of the remaining lignins and further alkali extractions are em-

ployed. In any case, however, chlorine bleaching is necessary to remove colored ingredients.

It is apparent that the recovery of cellulose from wood is a tedious and expensive process and is the main deterrent in tapping this almost limitless supply. The use of wood cellulose, therefore, is contingent upon the availability of the more desirable cotton linters.

Cellulose from Cotton Linters. Cotton is the only source in which cellulose exists in a relatively pure condition. The cotton fiber contains approximately 91 per cent cellulose and 9 per cent impurities, consisting of pectins, waxes, albumens, and salts.

There are a number of species of *Gossypium*, and authorities differ as to the classifications. Botanically, it has been classified in from 3 to 42 distinct species. The differentiation, however, is mainly academic and need not be considered here. It is of importance, however, to classify the cottons commercially as to the climatic and soil conditions under which they are grown. It is necessary, further, to observe the cotton in relation to the crop conditions in which it developed.

The cotton used for chemical cellulose is only what is left on the cottonseed after the longer textile fibers have been removed. These short fibers, known as linters, are removed by a re-ginning with closely set knives. The geographical and the crop climatic conditions are of importance, since immature fibers may be included in the close ginning. These are not removable by alkali and are particularly resistant to the action of acid. If they swell at all, the process is difficult; therefore, a large percentage of these "dead" fibers is deleterious to the grade of the cellulose acetate produced from linters.

Since cotton contains only 8-10 per cent impurities, the purification of cellulose is relatively simple. Alkalies will remove most of the non-cellulosic materials. A subsequent bleaching completes the process. The purified material contains 99+ per cent α-cellulose and has a degree of polymerization, ranging between 700 and 800 (molecular weight ca. 125,000).

Acetic Acid

Before the industrialization of organic chemical research, the main sources of acetic acid were the wood distillation industry and the oxidation of ethanol by the vinegar process. As the growing cellulose acetate industry increased its demands for acetic acid in an anhydrous (glacial) condition, the known processes were soon out-moded.

An attempt was made to modernize the production of acetic acid by the development of the Suida process, which consists in extracting the acetic acid from the dilute aqueous solutions and final dehydration by azeotropic distillation. By the time these processes had been worked out, however, they could not compete with the new and more modern methods.

At present, the main source of acetic acid is the oxidation of acetaldehyde. The processes differ principally in the preparation of the acetaldehyde. The most promising means of producing acetaldehyde in the future under normal economic conditions appear to be hydration of acetylene made with cheap power or controlled oxidation of waste aliphatic hydrocarbons.

Acetic Anhydride

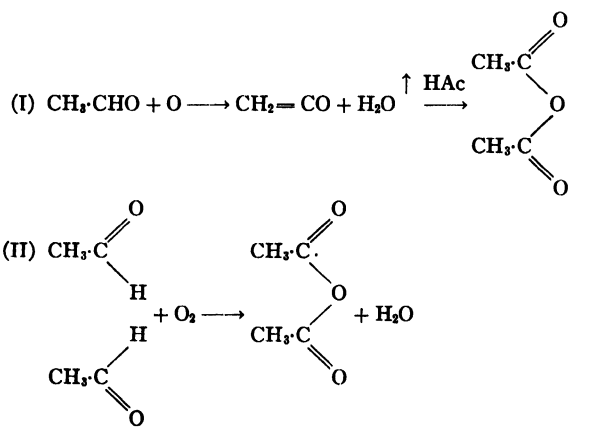
The recent history of acetic anhydride is interesting in that it exemplifies the trend of modern commercial chemical industries to profit quickly from the fruits of research. For years, acetic anhydride was produced by large-scale amplification of laboratory methods. In this process, acetic acid was the essential raw material and acetic anhydride was prepared from acetyl chloride and sodium acetate.

This method was later modified by treating anhydrous sodium acetate with sulfur and chlorine or with sulfur-chlorine compounds, to form the acetylchloride *in situ*. This innovation made an otherwise very laborious process somewhat less rigorous, but was not sufficiently inexpensive to warrant continued use.

In the preparation of cellulose acetate, it is necessary to use acetic anhydride in the acetylation. For each mol of acetic anhydride used, one mol of free acetic acid is formed. Consequently, the cellulose acetate industry must either prepare acetic anhydride or sell its acetic acid. The laborious sodium acetate method of making acetic anhydride has finally given way to the simpler vapor-phase pyrolysis. This consists essentially in passing acetic acid vapors over a suitable catalyst at a high temperature. The most recent discovery, however, that acetic anhydride may be prepared directly from the oxidation of acetaldehyde,[88] is of more far-reaching importance.

Textbooks of organic chemistry state that normal oxidation of an aldehyde forms the corresponding acid. This method of producing acetic acid from acetaldehyde was used for years without the knowledge of the producers that acetic anhydride is an intermediate in the reaction.

There are two probable means of explaining the reaction: one is that the oxidation of the aldehyde removes two hydrogens from the adjacent carbons to form ketene, which is a true mono-molecular anhydride of acetic acid. This then may react with the acetic acid to form acetic anhydride. Another possible explanation pre-supposes that two molecules of acetaldehyde are involved in the oxidation and that acetic anhydride and water are formed. These two suppositions may be expressed graphically, as follows:



It is highly probable that both reactions occur. It is necessary in this oxidation only to remove the water as it is formed in order that acetic anhydride and not acetic acid be isolated.

Another explanation of this reaction has been offered in which it is postulated that ethylidene diacetate may be involved as an intermediate product. It is more probable, however, that the ethylidene diacetate is formed by either ketene or acetic anhydride reacting with the acetaldehyde present.

The discovery that acetic anhydride is the intermediate between the aldehyde and the acid has made it possible to produce acetic anhydride at a price competitive with acetic acid and assures the discarding of the sodium acetate-acetyl-chloride process as economically unsound.

Catalysts

The principal catalyst for the acetylation of cellulose is sulfuric acid. Numerous other catalysts, such as phosphoric acid, perchloric acid, zinc chloride, etc., are known and are sometimes used in some smaller quantities. In any case, the quantities of these materials used in the cellulose acetate industry are insufficient to affect their general supply and are not, therefore, of sufficient interest for further comment.

Acetone

Prior to 1915, acetone was made principally from the destructive distillation of wood. It was marketed as an azeotropic mixture with methanol and was known as methyl acetone. In order to isolate the pure acetone from this mixture, it was necessary to proceed through the bisulfite complex in order to free it from the alcohol. The acetone could then be recovered by distillation from a sodium carbonate solution.

An alternative method for preparation of acetone was by heating calcium acetate. This method, however, was discarded when it was found that acetone could be made directly from acetic acid by vapor-phase pyrolysis, a method devised by Squibb.

With the advent of the World War, the demand for acetone rose considerably so that the known methods for the industrial manufacture of this commodity were inadequate. Acetone was much in demand for the preparation of Cordite, and later for cellulose acetate doping of airplane wings. New methods of manufacture had to be devised. The principal source of acetone during this period became the fermentation of certain polysaccharides using the appropriate bacteria. When the demand for acetone dropped after 1918, the production of this material far exceeded the need and it became difficult for the producers to recover their costs. In spite of this, however, the years between 1920 and 1940 saw the perfection of two new and important methods for acetone synthesis. These consist in the oxidation of isopropyl alcohol and the direct oxidation of naturally occurring hydrocarbons. These processes made it possible to produce ample acetone for the war and post-war periods.

Manufacture of Cellulose Acetate

The manufacture of cellulose acetate requires five essential steps. These are:

(1) Pretreatment
(2) Acetylation
(3) Ripening, or deacetylation
(4) Precipitation
(5) Washing

Briefly, the process consists in swelling the cellulose fiber so that all the hydroxyl groups are available for acetylation. Acetylation is carried out using acetic anhydride and acetic acid, with sulfuric acid or some other suitable catalyst. The cellulose is acetylated to the triacetate and an excess of acetic acid is used as a solvent.

The cellulose acetate thus formed is then deacetylated to the proper acetyl content. It is then precipitated from the acetic acid solution, stabilized (if necessary), washed free of acids, and dried.

In order to understand the process completely and to tie it in with the chemical structure of the cellulose itself, it is necessary to consider each of the above five processes separately.

Pretreatment

In the early stages of the development of the cellulose acetate industry, it was found particularly difficult to control acetylation. The initial temperature at which the acetylation would start was found to vary widely and the maximum temperature reached during acetylation was not constant. This resulted in a non-uniform prod-

uct. The procedure of pretreatment was introduced to level out the differences in operating conditions in the manufacture of the acetate.

The primary purpose of pretreatment is to activate the cellulose so that the differences in grades of cotton may be minimized. Pretreatment is largely mechanical in that the fibers are swollen and the hard cuticle on the outside of the cotton is rendered pervious to liquids.

In the patent literature it has been claimed that practically every substance having any swelling or softening action on cellulose may be used for a pretreating material. These patents are probably justified by the fact that each pretreating material is employed for a specific purpose.

On an economic basis, however, it is apparent that the cheapest pretreating materials are the most desirable; therefore, if the pretreatment can be carried out with the substances in which the acetylation is to proceed, the most efficient combination has been obtained.

Since the main purpose of the pretreatment is to swell the fibers to make them sorptive to reactants, mixtures of acetic acid and water have been found to be the most satisfactory.

It is known that cellulose, when subjected to purification, absorbs large quantities of water which swell the fibers. It would obviously be best not to dry the fibers and reduce the swollen condition, but unfortunately, cotton purification plants are usually situated at a great distance from the cellulose acetate plants and it is expensive to ship water. For this reason, it is removed from the fiber.

Pretreatment, therefore, would consist essentially in hydrating the cellulose to return it to its swollen condition. The use of large quantities of water, however, would be uneconomic since it would react with the most expensive ingredient in the acetylation, acetic anhydride.

Commercial pretreatments consist in the introduction of the minimum amount of water into the pretreating mixture. The water is usually introduced in solution in acetic acid.

Since, as has been pointed out, cellulose is an extremely reactive substance, the process of pretreatment is sufficient to cause molecular degradation, or in this case, hydrolysis. Pretreatment may be controlled by observing the decrease in viscosity in cuprammonium solution, or better still, by measuring the decrease in the degree of polymerization.

Chemical cotton as purchased has a d.p. of approximately 750 (molecular weight 125,000). Cellulose processed by the normal type of pretreatment has a d.p. of approximately 400 (molecular weight 64,000).

It is apparent that pretreatment does degrade the cellulose appreciably but it is not found to be harmful as long as it is properly controlled. It is essential to start with the high initial d.p. before acetylation, since excessive degradation of the cellulose may occur in the acetylation reaction.

Acetylation

Superficially, the reaction of acetylation is a simple esterification of a polyhydric alcohol with acetic anhydride and a catalyst, the ratio of reactants being determined by the reactions involved and the apparatus in which the process is being carried out.

In reality, however, there are at least five reactions involved in acetylation:

(1) The sulfuric acid employed as catalyst reacts with the acetic anhydride instantaneously, to give acetyl-sulfuric acid ($CH_3 \cdot CO \cdot O \cdot SO_2 \cdot OH$).

(2) The acetyl-sulfuric acid then reacts with the cellulose, but the extent of this reaction is not known. It may be presumed, however, that the terminal reducing groups of the cellulose are involved since these are the most reactive hydroxyl groups present. Of the remaining hydroxyl groups available for reaction, it is known that the primary alcohol group is more reactive than the secondary alcohol groups. (The

secondary alcohol groups are those hydroxyls which are attached to the carbons in the pyran ring structure.) There is perhaps some sulfation of the most reactive of these hydroxyls.

(3) The cellulose chain is split by the acetyl-sulfuric acid and the liberated reducing groups probably combine with the free acetyl-sulfuric acid. This phenomenon may be known as "acetolysis."

While each chemical reaction in the preparation of cellulose acetate subjects the cellulose to some degradation, the greatest amount of molecular fission occurs in the acetylation process.

(4) The acetic anhydride reacts with the water present in the cellulose and with any water formed in the reactions.

(5) The hydroxyl groups in the cellulose are esterified by the acetic anhydride or the acetic acid. It is not clear from the meager data available on acetylation whether the acetyl-sulfuric acid, the acetic acid, or the acetic anhydride is the actual acetylating agent.

The chief problem in the commercial acetylation of cellulose is the control of the reactions involved in order that a suitable end product may be prepared. In considering the ratio of the reactants to the cellulose, it is obvious that the most economical quantities to be used are those which will give the greatest yield of the product per batch and the largest number of batches per unit of time. It is well, therefore, to consider the minimum quantity of the reactants which can be employed.

In calculating the quantity of acetic anhydride necessary to carry out the reaction, it is apparent that sufficient material will have to be used not only to react with the hydroxyl groups in the cellulose but also to react with the incidental water added and formed, and with the sulfuric acid introduced as catalyst. This ratio is, therefore, fairly well fixed and constant.

The amount of catalyst and the diluent cannot be calculated, however, and must be arrived at empirically to suit the apparatus. Some of the factors affecting the choice of the quantities of sulfuric and acetic acids to be used are not without interest. They will be listed here briefly.

(1) Within limits, the reaction time is inversely proportional to the amount of catalyst employed; hence, the maximum amount of sulfuric acid is desirable.

These limits are set by the equilibrium relationship between the mixture of sulfuric acid and acetic anhydride and its reaction product, acetyl-sulfuric acid plus acetic acid. Under the proper conditions, also, the acetyl-sulfuric acid rearranges to give sulfoacetic acid. As far as is known, this reaction is not an equilibrium reaction since it is apparently not reversible.

Under normal conditions of acetylation, the sulfuric acid probably exists in the reaction mixture mainly as acetyl-sulfuric acid, and sulfoacetic acid is not formed except under unusual conditions, principally elevated temperature. Acetyl-sulfuric acid is a strong acetylation catalyst, while the sulfoacetic acid does not promote esterification. It is apparent, therefore, that the temperature of acetylation must be maintained below that point at which the rearrangement to sulfoacetic acid occurs.

Since in a normal acetylation the amount of acetic anhydride is large in relation to the amount of sulfuric acid employed as catalyst, it is very probable that no free sulfuric acid exists in solution and the catalyst is mainly, if not entirely, the mixed anhydride or acetyl-sulfuric acid.

(2) The imbibition of the acetic acid solvent by the fully acetylated cellulose is also a function of the catalyst. The more sulfuric acid employed, the less is the tendency for the reaction mixture to set to a non-reversible gel with a given quantity of acetic acid. Hence, more diluent must be used with smaller quantities of catalyst, etc.

(3) Since acetolysis, or molecular degradation, is also directly proportional to the amount of catalyst, this serves to limit the quantity.

(4) It is obviously desirable to keep the quantity of diluent to a minimum since it must be recovered. Aside from the limit fixed by (2) above, there must be sufficient diluent so that a mobile solution results, and it is therefore possible to stir the mixture to obtain homogeneity.

(5) Since most, if not all, of the reactions involved are exothermic, means of dissipating the heat are necessary. In addition to external cooling, it is possible to take advantage of the latent heat of fusion of the crystallized acetic acid diluent by cooling it below its freezing temperature.

Considering the above five points, a reasonable formula for acetylation of cellulose would be as follows:

1		mol cellulose
3.5	– 5.0	mols acetic anhydride
<0.01	– 0.25	mol sulfuric acid
15	– 40	mols acetic acid

The formulation must be carefully chosen in order that a cellulose acetate of proper viscosity will result. For a given set of conditions, the time-temperature relationship is of the utmost importance in determining the viscosity of the finished acetate.

The viscosity of a relatively uniform cellulose acetate is a function of the d.p., and this d.p. is determined primarily by the amount of acetolysis which occurs during acetylation. The reaction of acetolysis is increased rapidly with small rises in temperature. This may be exemplified by Figure 4.

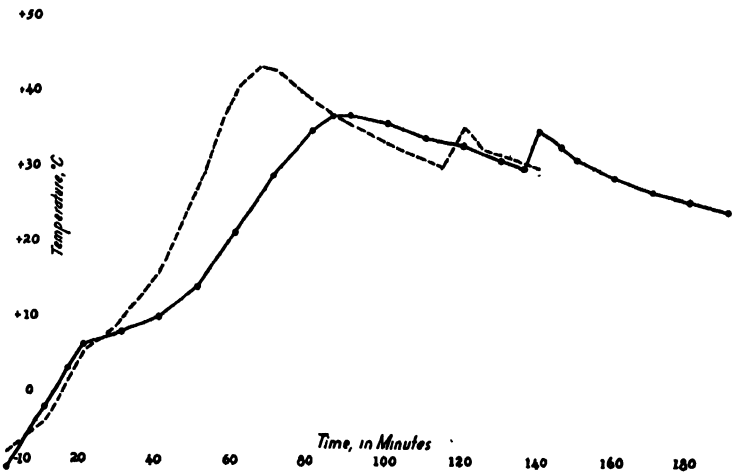


FIGURE 4. Acetylation. Time vs. temperature.

These two acetylations differ in the amount of catalyst (0.25 mol vs. 0.15 mol sulfuric acid) and the amount of diluent (10 mols vs. 16 mols acetic acid per mol of cellulose). The viscosities of the finished acetates at a given concentration in acetone will be identical. It is apparent that the explanation of the similarity of the two reactions which are seemingly so different rests in the rate of dissipation of the heat generated. The quantity of heat generated in the two reactions is identical, since the same amount of cellulose is involved. The difference lies mainly in the mass of material to be heated.

In carrying out the more rapid reaction at the higher temperature, however, it is necessary to avoid localized overheating. If localized overheating should occur

throughout the charge, the product will suffer from lack of uniformity—that is, it will be comprised of a mixture of acetates of widely varying d.p.

It is probable that the two charges as shown do differ somewhat in uniformity, but within certain limits the physical properties of plastics, etc., prepared from such acetates are a function of the average d.p. and are not affected by reasonable heterogeneity.

It is obvious that the conditions for the reaction of acetylation must be nicely balanced in order that a desirable produce be isolated.

Ripening, or Deacetylation

The evidence of complete acetylation is the disappearance of all fibers from the solution. Since the cellulose has been esterified completely, it is necessary to deacetylate to the proper acetyl value so that the desired solubility is obtained.

As has been pointed out previously, the solubility of the cellulose acetate depends on the presence of the free hydroxyl groups. Since these groups are the most reactive, they acetylate first, and fortunately, deacetylate before the secondary alcohol groups. Consequently, it is necessary to acetylate to the triacetate and then deacetylate.

Cellulose acetates may differ in solubility because of the ratio of the primary to secondary alcohols unacetylated. The conditions of ripening (acid hydrolysis) determine the solubility of the product.

There are a number of side reactions which are being carried out during the ripening process in addition to the simple deacetylation of the acetate:

(1) The acetyl-sulfuric acid is hydrolyzed to acetic acid and sulfuric acid.
(2) Combined sulfates are removed from the cellulose molecule.
(3) Some combined acetic acid is hydrolyzed from the cellulose molecule.
(4) The cellulose molecule is further decomposed.
(5) Excess acetic anhydride is hydrolyzed to acetic acid.

Acetyl-sulfuric acid is readily decomposed by water, but in the reaction mixture at the completion of acetylation it may be demonstrated easily that the sulfuric acid is not liberated immediately but that a certain time element is necessary to complete hydrolysis. This hydrolysis is, of course, markedly affected by temperature and the time involved may vary widely.

This may be taken as evidence that some of the sulfuric acid is combined directly with the cellulose.

It is of interest to note that it has been found necessary to hydrolyze until most of the sulfates exist as free sulfuric acid before a suitable precipitation can be carried out by adding an excess of water to the cellulose acetate solution.

It is significant that during the period in which the sulfuric acid is being hydrolyzed, very little if any deacetylation of the cellulose acetate occurs. Up until the time that the sulfuric acid is completely hydrolyzed, therefore, a completely acetylated cellulose acetate may be precipitated by employing the proper means.

Reaction (4), or molecular hydrolysis of the cellulose molecule, can be controlled during the ripening procedure. By altering the conditions for ripening, molecular hydrolysis may proceed very rapidly, or the cellulose may be deacetylated without any measurable decrease in d.p. The known variables for controlling the degradation of cellulose acetate are: temperature, per cent sulfuric acid present, and the quantity of water employed.

In the rapid reaction in Figure 4 in which 15 per cent sulfuric acid is used on the weight of the cellulose, if only sufficient water is added to convert the acetic anhydride to acid and to hydrolyze the acetate to a combined acetyl value of 54 per cent as acetic acid, the temperature must be kept low or excessive molecular disintegration will be encountered.

The amount of sulfuric acid in the hydrolysis bath may be reduced by adding a

soluble magnesium salt to react with the sulfuric acid. Magnesium salts are employed, since the magnesium sulfate formed is highly insoluble in the concentrated acetic acid solution, but is reasonably soluble in dilute acetic acid and may therefore be removed in the final precipitation and washing. Substances forming water-insoluble sulfates could not be employed for neutralizing the sulfuric without contaminating the final product.

If large quantities of water are added to the ripening mixture, the rate of deacetylation of the cellulose acetate is decreased. The d.p. of the cellulose, however, remains constant, indicating that molecular hydrolysis is not occurring. It is noteworthy, however, that if the temperature of ripening be increased, the rate of deacetylation of the cellulose acetate is increased, but if sufficient water has been added, molecular hydrolysis does not occur. This is true up to approximately 100°.

Thus, by controlling the quantity of sulfuric acid in the ripening, the proper amount of water and temperature may be established so that a minimum time is employed for the hydrolysis of the combined sulfates and deacetylation, and the amount of depolymerization of the cellulose molecule can be controlled as desired.

The primary purpose in ripening, or deacetylation, of cellulose acetate is to free the proper number of alcoholic hydroxyl groups in order that the cellulose will be soluble in organic solvents. For this reason, the process of ripening is followed carefully by alterations in solubility. The relationship of solubilty of cellulose acetates of varying acetyl values is of sufficient interest to be considered separately.

When the proper acetyl value and consequent solubility point has been reached, the cellulose acetate is ready to be precipitated.

Precipitation

It is difficult to determine whether the process of precipitation is properly a chemical process or merely mechanical; it is conceivable that chemical reactions may occur.

It is preferable to neutralize all the sulfuric acid before precipitation. This is necessary to prevent hydrolysis during the precipitation when water is beaten into the reaction mixture. For this neutralization some form of soda may be employed.

The physical form of the precipitate is of importance and is determined by the subsequent processing to which the cellulose acetate is to be put. It is possible to precipitate the acetate in any form desired by mechanically controlling the conditions. The acetate may be isolated in the form of rods, films, pellets, or as coarse, intermediate, or fine fibers. Precipitation in the form of a gel is usually avoided since it is difficult to remove the acetic and sulfuric acids which are occluded.

A fibrous form of precipitate is sought since it facilitates washing.

Washing

Washing is carried out until the cellulose acetate is free from all forms of soluble acidity. It is preferable to wash with hot water to facilitate the removal of the sulfuric and acetic acids present. It is preferable, also, but not necessary, to control the hardness of the water so that the carboxyl groups which have been formed in the cellulose molecule will be present as salts and not as free acids. The neutralized carboxyl groups are somewhat more stable to caramelization.

After proper washing, the cellulose acetate is in suitable form for solvation for further processing.

Spinning

Spinning Solutions

The phenomenon of the solubility of cellulose acetate in organic solvents is of interest, and in order to understand the variation in behavior it is well to review briefly the nature of solubility.

In general, the solubility of cellulose acetate is determined by five conditions:
(1) Degree of polymerization (d.p.)
(2) Amount of combined acetic acid (acetyl value)
(3) The position of the combined acetates in the cellulose molecule
(4) The presence of impurities and
(5) Nature of the solvent

It has been thought that cellulose triacetate is insoluble in acetic acid. This idea is difficult to prove; but it is related to the phenomenon of formation of solid gels in acetylation if insufficient acetic acid is used as a diluent. Gelation, which is the imbibition of the solvent to form a thixotropic solid gel, is probably connected with the presence of acetyl-sulfuric acid either in the solution or combined in the cellulose acetate molecule.

If the acetyl-sulfuric acid is decomposed and possibly hydrolyzed from the cellulose acetate molecule by proper means, it is possible to precipitate a cellulose acetate with an acetyl value of 62.5 as acetic acid, which may be dissolved in glacial acetic acid. The degree of solubility of this acetate in glacial acetic, however, will vary with the molecular weight or degree of dextrinization.

There are very few solvents for fully acetylated dextrinized-cellulose acetates. The most familiar of these are chloroform, ethylene formal, and dioxane. Here again, the degree of solubility and the viscosity of the solutions are affected by the d.p. of the cellulose acetate. Lipscomb [20] has described the behavior of cellulose acetate in chloroform as the acetyl value is altered by hydrolysis.

As the acetyl value is reduced, the behavior of the acetate in chloroform changes from complete solution at 62.5 through typical gels at lower acetyl values. It is interesting to observe that whereas for the upper acetyl values the chloroform is the solvent and the cellulose acetate is the solute, at the lower acetyl values the acetate is the solvent and the chloroform the dissolved material.

An acetate of high acetyl value and high molecular weight is soluble in relatively non-polar solvents, whereas as the acetyl value decreases the solubility is increased in more highly polar solvents. It is usually possible, therefore, to obtain solution of the lower acetyl value acetates in the non-polar solvents by adding small amounts of highly polar materials. The polar materials may be water for the water-miscible solvents and alcohols for the water-immiscible materials.

The phenomenon of variation in solubility of the cellulose acetate in various solvents has been the source of much speculation. Information on the subject, however, has been particularly meager, but it is probable that the presence of highly polar groups in the cellulose acetate molecule are necessary.

Cramer and Purves [5] have offered a partial explanation of the solubility. It is shown that the most reactive hydroxyl group in the gluco-pyranose unit is the primary alcohol on the No. 6 carbon atom. It is apparently necessary to have some primary alcohol hydroxyl group free in the cellulose molecule in order to obtain solubility in acetone. Since the primary alcohol is the most reactive group, it is acetylated first, and this necessitates complete acetylation and then partial deacetylation to re-form this polar radical.

In the utilization of cellulose acetate for industrial fibers in particular, however, it is necessary to reduce the acetyl value so that the acetate becomes soluble in acetone. For cellulose acetates of the d.p. normally utilized for this purpose, the solubility of the cellulose acetate in acetone is not appreciable until 58-59 acetyl value as acetic acid is reached. Lower degrees of acetylation usually require the presence of relatively small quantities of water to control the fluidity of the solutions.

Thus, at the acetyl value usually employed for cellulose acetate fibers, the fluidity of the solution may be altered to suit commercial purposes by adjusting the quantity of water in the acetone. The relationship of viscosity to per cent water in the acetone is given in Figure 5. The cellulose acetate shown has an acetyl value of approxi-

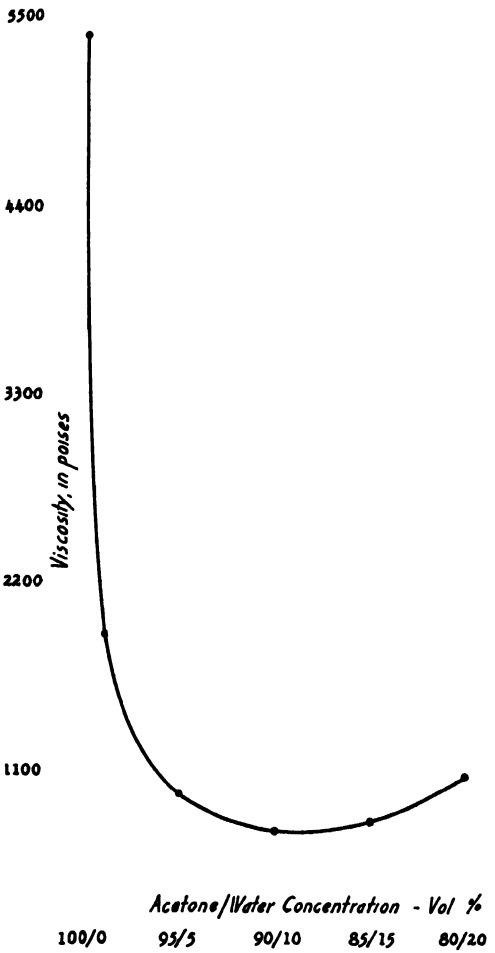


FIGURE 5. Viscosity of cellulose acetate in aqueous acetone.

mately 54.5 per cent as acetic acid, and a degree of polymerization of 165 anhydroglucose units.

As has been shown previously, it is only below the critical concentration that the viscosity of the solution is directly proportional to its concentration. Approaching the concentrations employed for commercial uses of cellulose acetate, the viscosity increases very rapidly with small alterations in concentration.

Choosing a point at random from Figure 5 of 5 per cent water in acetone, the variation in viscosity with concentration is found to be as shown in Figure 6.

The general shape of these curves is typical of acetates of the various types. Thus a cellulose acetate of lower acetyl value than depicted in Figure 5 would have a similar parabolic curve, but it would be broader and displaced toward the more water-rich solvents. The converse is true for higher acetyl value acetates. It is obvious, also, that as the d.p. increases above that for the acetate shown, the viscosity of the solution would be increased and there would be a greater rate of build-up of viscosity as the concentration is increased.

For cellulose acetate solutions which must be subsequently filtered and spun into

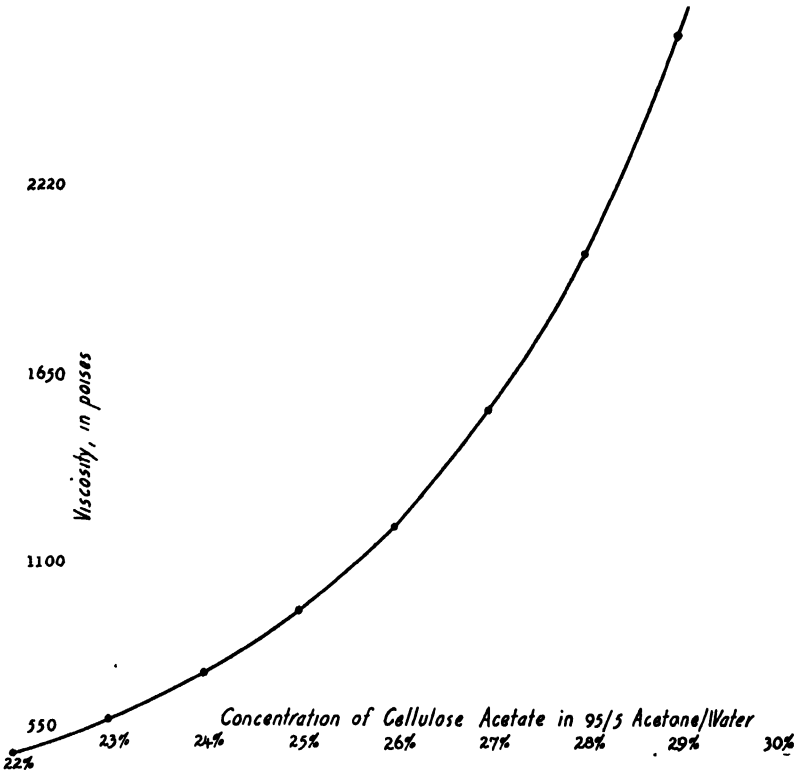


FIGURE 6. Concentration—viscosity relationship.

fibers, it is necessary to select the proper acetate and the proper solvent mixture. The acetate and solvent adopted will be determined by the facilities for filtration and spinning.

Heterogeneity. In the above, cellulose acetate has been considered as a single compound. In actual practice, however, commercial acetates are relatively non-uniform. Since the solubilities of acetates alter with the four variables noted above, it is a comparatively simple matter to characterize uniformity by both solvent extraction and fractional precipitation.

An indication of the uniformity, or rather heterogeneity, of commercial acetates may be obtained from the d.p. of their fractions:

Commercial Acetate	Fraction No.	Composition (% by Weight)	Degree of Polymerization
A	1	57.7	236
	2	24.9	174
	3	12.5	95
B	1	53.7	226
	2	26.7	172
	3	16.0	87
C	1	28.7	210
	2	56.1	172
	3	12.7	79

It has been shown, however, that the properties of a blend of acetates are, for all practical purposes, identical with the properties of a pure acetate of corresponding analyses.[11]

Spinning

The operation of spinning consists in forcing the cellulose acetate in acetone solution ("dope") through a plate in which the proper number of orifices have been drilled. In order that the spinning jets may be subjected to the minimum blockage, it is necessary to filter the solutions extremely carefully to obtain maximum freedom from small gels and solid foreign substances. The amount of filtration will depend upon the inherent clarity of the cellulose acetate as produced and will also be affected by the law of diminishing returns—that is, whether it is more economical to give multiple filtrations or to change the spinning jets more often. In all commercial spinning units, therefore, the problem of filtration is a troublesome one, but has been solved by employing multiple filtrations through filter-presses using dressings of varying porosity.

The actual operation of spinning is simple in conception, but it has required the efforts of brilliant engineers to accomplish the end commercially. The multiplicity of the problems involved may be suggested by calling attention to a few facts:

To obtain yarns of the proper commercial dimensions, it is necessary to spin individual filaments which have cross-sections varying in diameter between 10 and 30 microns. This necessitates drilling orifices of the proper diameter to produce such filaments.

After the dope emerges from the jet, the solvent and diluent must be removed before the yarn can be properly handled. If we assume a 25 per cent solution of cellulose acetate in acetone, it is necessary to reduce this acetone content to approximately 25 per cent on the weight of the yarn before it can be handled without damage. This necessitates the absorption of 345 gram calories/gram of yarn produced to vaporize the acetone. A spinning jet will extrude between 0.75 and 1.5 grams/second of yarn as bone-dry cellulose acetate. While this does not seem an enormous quantity of heat to be absorbed, the conditions of heat transfer are very poor.

Since, also, there is a large discrepancy between the volatility of the acetone and the water used as diluent, the problem of removing acetone and water simultaneously must be considered. This is necessary since if water is present in too high a concentration, it will cause precipitation of the cellulose acetate as particles rather than in the form of a continuous filament. It is apparent, therefore, that the humidity in the spinning room is an important factor.

As is known, the cellulose acetate cannot be precipitated from an acetone solution and exhibit the optical properties associated with crystalline structures. Since the strength of the yarn is affected greatly by the degree of crystallization of the acetate, it is necessary to stretch the acetate somewhat during the spinning operation. The final size and strength of the cellulose acetate fiber are determined, therefore, by the size of the orifice in the spinneret, the rate at which the dope is forced through the orifice, the rate at which the spun fiber is taken up on the package, and the rate and temperature of evaporation of the solvent. In order to have uniform cross-sections of the yarn, it is necessary to feed the dope through the orifices at an absolutely constant rate and to control accurately the temperature at jet level.

Rideal [27] states: "Present methods of preparing or spinning artificial threads entail the ejection of a viscous suspension of the macromolecules through a nozzle, followed by some process of fixing or coagulation. A brief consideration indicates that this is really a very undesirable method of forming fibres. . . . Clearly the result of such a flow (through an orifice) is to ensure a reasonably good orientation of the macromolecules effected by the high rate of shear at the walls but an imperfect orientation towards the axis."

It is pointed out further that such orientation is quite the opposite of conditions existing in natural fibers and the ideal fiber should have a highly oriented core with random aggregation at the periphery.

In the modern spinning of cellulose acetate, however, the condition of a "case-

hardened" tube need not exist if the fiber is spun into an atmosphere of high acetone concentration until the core has gelled. In the highly concentrated acetone vapors, the surface is shrunk and random orientation is thus obtained. X-ray investigation shows the fibers to be almost completely unoriented.

The problem of spinning, therefore, involves principally two steps: the first is to spin into a chamber of stagnant acetone in which the case-hardening is rectified. After that, it is necessary to remove the acetone from the fiber as rapidly as possible to complete the drying operation.

To add to this complexity, the difficulty of drying consists in adding heat to a fine filament in semi-plastic condition by circulating warm air. It is apparent that a real problem of heat transfer is involved.

It is necessary to keep in mind, also, that acetone in air forms explosive mixtures at concentrations between 3.0 and 11.15 per cent.[86] These concentrations must be avoided within the cabinet.

In commercial operation, acetone solutions are forced through multiple-orifice jets at the top of a spinning cabinet and the filaments dropped vertically through a rising column of air. This removes the major portion of the acetone and water. It is necessary to apply a spinning lubricant to control the pliability and lubricity of the yarn. This is usually done by applying the proper oil directly or in the form of an emulsion onto the yarn before it is passed over a take-up roll which controls the rate of delivery of the yarn and the degree of drawdown. The yarn is then packaged on a suitable spool and the remainder of the acetone permitted to evaporate spontaneously.

The necessity for the application of a lubricant is obvious when the processes to which the yarn must be subjected are considered. Textile operations require insertion of the proper amount of twist and packaging for further textile operations. As this processing requires running the yarn over a multiplicity of guides, bars, etc., the coefficient of friction must be accurately controlled to prevent damage to the yarn and yet provide enough friction to permit proper control.

Since in the spinning operation large dilution with acetone is employed, it is necessary to recover the volatilized solvent. Commercially, the solvent may be recovered from the air directly by adsorption on carbon and isolation by steaming the carbon and subsequent fractionation from water. An alternative method is the absorption of acetone from the air into water and suitably fractionating the acetone in a relatively anhydrous condition.

Dyeing *

When cellulose acetate fabrics were first introduced commercially, it was found that there were no suitable dyestuffs available for dyeing them. The range of cotton, wool, and silk dyestuffs did not have sufficient dyeing affinity for a commercial range of shades. There was some questionable suitability of the basic dyestuffs, but even with these, heavy shades could not be dyed nor was the range of colors sufficient to satisfy the discriminating public.

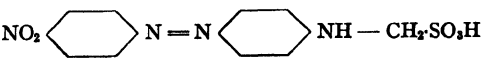
It was mainly due to the efforts of Drs. Camille and Henry Dreyfus, Dr. Rene Clavel, and the chemists of British Celanese, Ltd., under the direction of G. H. Ellis, that dyestuffs for cellulose acetate were developed. While the history of the development of dyestuffs for cellulose acetate is of interest, it probably would not justify exposition. The types of dyestuffs will be discussed briefly from a partially theoretical standpoint. An attempt will be made to classify the dyestuffs according to their desirable characteristics and their weaknesses.

It was noted originally that cellulose acetate dyed differently from any of the known textile fibers. Silk and wool hold the majority of their dyestuffs in chemical

* Vol. IV of this series contains papers on various theories of dyeing by G. Georgievics, Wm. Harrison, and Wilder D. Bancroft. J. A.

union, while cotton and probable viscose hold the dyestuffs within the fibers, due principally to absorption within the capillaries. With cellulose acetate, however, it appears that the dyestuff is dissolved within the fiber in solid solution. It was found that dyestuffs which had been solubilized in water were particularly unsuitable for dyeing cellulose acetate since they were more soluble in the dyeing medium than in the fibers. Consequently, very little if any exhaustion of dye solutions, or so-called affinity for the fibers, could be obtained. It was realized that the dyes would have to be applied from aqueous dispersions rather than from solution.

There was a notable exception to this which was made by Green.[9] Dyestuffs were prepared which were essentially neutral sulfonic acid esters of an aliphatic hydroxyl on aromatic nuclei. When dissolved in water, the dyestuffs hydrolyzed and the free amine was absorbed by the fiber.



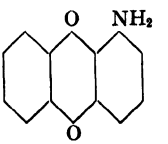
At the present time, this type of dyestuff is not widely available. The dyestuffs enjoying the widest popularity may be classified into five groups:

(1) Amino-anthraquinones
(2) Direct-dyeing azos
(3) Developed azos (which include some of the "insoluble" azos used on cellulosic fibers)
(4) Diphenylamines
(5) Vatted dyestuffs

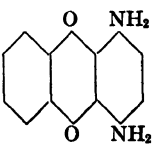
Amino-Anthraquinones

Anthraquinone in itself has no affinity for cellulose acetate fibers, that is, it is not absorbed from aqueous dispersion. The alizarin dyestuffs (the hydroxylated anthraquinones) do not dye on cellulose acetate to any usable extent. It is apparently necessary to introduce basic constituents in the form of amino groups or substituted amino groups, in order that these dyestuffs will be absorbed by cellulose acetate fibers.

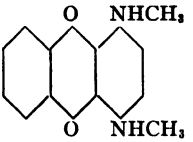
In general, the cellulose acetate dyestuffs from anthraquinone vary only in the number and position of the amine or substituted amine in the anthraquinone nucleus. The variation in color of the anthraquinones may be expressed graphically, as follows:



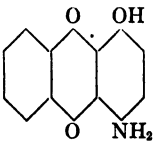
1-amino-anthraquinone (orange)



1:4-diamino-anthraquinone (blue-red—heliotrope)

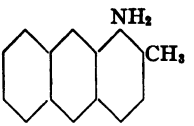


1:4-monomethylamino-anthraquinone (bright blue)



1-hydroxy-4-amino-anthraquinone (bright red)

It is immediately apparent that a wide range of shades may be prepared by substituting variously in the 1, 4, 5, and 8 positions of the parent substance. The β position is not usually occupied since the dyestuffs formed therefrom are usually not fast to light. Thus:



1-amino-2-methyl-anthraquinone

This dye is a reddish-orange but will not stand up on exposure to sunlight. There are one or two other cases of anthraquinones supposedly 1 : 4 : 5 : 8-substituted, which are not fast to light, but it is believed that the structures of these particular dyestuffs are not well defined. It is possible, also, to substitute in the β position in the anthraquinone nucleus without sacrificing light-fastness, but these are special cases and will be considered briefly later.

It is of particular significance that the type of group introduced in the 1, 4, 5, and 8 positions determines the fastness property of the dyestuff to other conditions. Thus, hydroxyl groups render the dyestuff subject to acid/base color change. That is, the dyestuff reacts as an indicator and moderately strong soap solutions are sufficiently alkaline to cause the alteration in shade.

It should be emphasized that dyestuffs exist in cellulose acetate in solid solution. Being in solution, they are particularly susceptible to chemical reaction, and the cellulose acetate seems to be an excellent reaction medium. It follows, therefore, that dyestuffs to be used successfully on acetate must be exceptionally stable chemically.

The gravest objection to the simple anthraquinone dyestuffs is the fact that they are not completely chemically stable and are subject to acid fading. This phenomenon may be attributed to the absorption of oxides of nitrogen from the air and the reaction of these oxides with the amino groups in the anthraquinone dyestuff.

It can be shown readily that open flames produce small amounts of oxides of nitrogen. When these oxides are generated in a confined space they are readily absorbed by the cellulose acetate.

It was known as early as 1880 [87] that nitrogen tetroxide reacts at a low temperature with amines to give diazonium salts. Treat B. Johnson and B. Houston [16] have investigated the reaction of nitrogen tetroxide as a diazotization reagent and substantiate Witt's observations. Rowe and Chamberlain [29] have investigated the effects of oxides of nitrogen on amino-anthraquinone and have isolated the reaction products. Greenspan and Spoerri [10] investigated the effects of the various nitrogen ox-

ides as diazotizing reagents and demonstrate, furthermore, that the presence of cellulose acetate is an effective catalyst for the reaction.

There seems no doubt, therefore, that the phenomenon of acid fading is clearly understood, but it must not be confused with simple salt formation or acid/base color alteration.

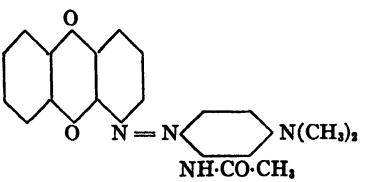
When an anthraquinone dyestuff contains a primary amino group, this group then is susceptible to diazotization and subsequent decomposition of the diazonium compound. The bathochromic effect of the amino group is thus lost, with a resulting alteration in color.

When the anthraquinone nucleus contains a secondary amine, as in the case of the bright blue above, a nitrogen-nitroso group is formed, and this may exist as a strongly colored compound, or rearrange to a nuclear nitroso compound which is weakly tinctorial. In any case, the dyestuff suffers a change in shade. In general, the alteration in shade is to a redder or yellower tone.

Thus, while the anthraquinone dyestuffs offer a valuable range of colors, they must be used only when the finished fabric will not be subjected to acid-fading atmospheres. Fortunately, the anthraquinones may be substituted widely, and in so doing the life of the dyestuff to acid-fading conditions may be improved so that it equals the useful life of the fabric upon which it is dyed.

It should be possible to replace the anthraquinone with tertiary amines so that no replacable hydrogens would be available. In most cases, however, it is very difficult if not impossible to di-substitute a nitrogen on an anthraquinone nucleus. In cases where this has been done successfully, the resulting dyestuff lacks tinctorial value and has remarkably poor affinity for cellulose acetate.

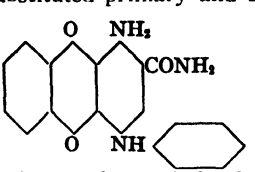
Considerable ingenuity has been exercised in devising means to render the dyestuffs resistant to acid-fading, but only a few cases will be noted. Monoaminoanthraquinones have been diazotized and united with coupling agents which do not destroy the bathochromic effect of the amino group, nor decrease appreciably the affinity of the prepared dyestuff for cellulose acetate.



1-azo-(4'-dimethylamino-2'-acetylamino-benzene)-anthraquinone (red)

This dyestuff has good affinity for cellulose acetate, is reasonably resistant to acid-fading, and sensitive to acid/base color change with only strong alkalies. It may be noted that it is difficult to prepare this dyestuff in substance; but when the 1-amino-anthraquinone is dyed on cellulose acetate fibers it may be readily diazotized and coupled. This is a striking example of the suitability of cellulose acetate as an excellent chemical reaction medium.

Certain stable substituents in the β position have been found to inhibit the action of nitrogen oxides on the α-substituted primary and secondary amines:



1-amino-2-carboxylamino-4-phenylamino-anthraquinone (medium blue)

This dyestuff has a moderate affinity for cellulose acetate and is resistant to acid-fading and is satisfactory to light. Condensation of formaldehyde with hydroxyl-amino-anthraquinones has been found particularly effective in increasing the resistance of this class of dyestuffs to a remarkable degree.

Direct-Dyeing Azos

These dyestuffs comprise a large and valuable class of dyestuffs for cellulose acetate. They are particularly valuable since they are readily made. A wide range of colors may be prepared—from brilliant yellows through oranges, reds and violets, to deep blues—and the simpler forms of the mono-azo dyestuffs, at least, are readily applied from mild soap dispersions.

Like the anthraquinone dyestuffs, the affinity, color value, and stability of the shade are controlled by the type of groups substituted in the aromatic nuclei and in the relative position of the groups to the azo linkage.

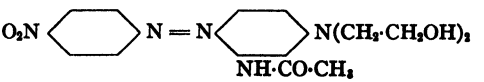
The direct azos are similar to the anthraquinones, also, in that moderately basic groups are necessary in the dyestuff molecule to give a reasonable affinity of the dyestuff for cellulose acetate. The simple amino substitutions to the aromatic nuclei render the dyestuff subject to acid-fading and phenolic azos are also altered in shade by salt formation.

It is of interest to note, however, that originally acid-fading was not observed on unsubstituted amino dyestuffs. This was principally because the unsubstituted amines were undesirable for other weaknesses and because di-substitution on the amino group can be carried out readily by processes which are suitable for commercial purposes.

The direct-dyeing azos differ from the anthraquinones, however, in that color values and stability of shade are more affected by the presence of polar groups within the molecule.

When aniline is diazotized and coupled with the better known developing agents, the dyestuffs formed are not fast to light. This resulted in the conclusion that all azo dyestuffs were not sufficiently resistant to light to warrant their large-scale consumption. It has been found, however, that the azo linkage *per se* is not readily decomposed by the action of light, particularly if it is stabilized by the presence of a polar group in the proper position. Thus, a wide range of stable dyestuffs may be prepared from the parent diazotizable base, para-nitroaniline.

In preparing light-fast azo dyestuffs, however, it is necessary to apply a coupling agent which is in itself not affected by light. By way of example, the dyestuff formed from para-nitroaniline and meta-dihydroxyethylamino-acetanilide is stable to light even in weak shades:



(yellowish red)

If the nitro group in this dyestuff is ortho or meta to the azo linkage, the resulting dyestuff has poor light resistance. Also, if another nitro group is introduced into the molecule either ortho or meta to the azo linkage, light-fastness is again sacrificed to increase in the depth of shade.

Weakly polar groups such as methoxyl groups or chlorine may be introduced into either or both of the positions ortho to the azo linkage with slight bathochromic effect but with no loss in light-fastness. In fact, the dyestuffs from 2:6-dichlor-4-nitroaniline are superior to the corresponding dyestuffs from 4-nitroaniline and compare favorably with the best of the anthraquinone dyestuffs in this regard.

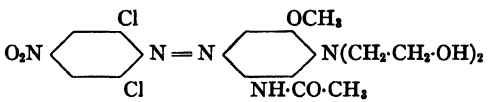
Methyl-sulfone groups are also strongly polar and may be substituted for the

nitro group in the above formula. The bathochromic effect of the methyl-sulfone group is not quite as great as that of the nitro group. Hence the dyestuffs are correspondingly lighter in shade; that is, if the blues are green-blues the sulfone blues will be red-blues, and if the dyestuff prepared from nitroaniline is a bluish-red, the dyestuff prepared from the methyl-sulfone substituted aniline is a yellowish-red.

As far as is known, however, substitution of the methyl-sulfone group for the nitro group does not alter the resistance to light of the completed azo dyestuff, and similar ortho-substitution may be made with chlorine or methoxyl groups and the light resistance increased even more.

As has been indicated, the depth of shade increases with the multiplicity of the substitution in the dyestuff and the bathochromic effect of the molecule introduced.

In the simple azo dyestuffs depicted above, it was noted that the coupling agent, or right-hand component, may contribute also to the stability of the dyestuff when subjected to sunlight. This may be demonstrated by substituting a methoxyl group ortho to the β-hydroxyethylamino and para to the acetylated amino groups. While the resulting dyestuff is darker in shade, it is particularly poor in resistance to light. Thus, the dyestuff 2:6-dichlor-4-nitroaniline plus ortho-dihydroxyethyl-para-acetyl-amino-anisole:



is a blue-violet fast to acid, but poor in light resistance. It is apparent that a methoxyl group meta to an azo linkage is as poor to light as a methoxyl group meta to a nitro group in a diazotizable base. It is obvious, therefore, that the proper choice of intermediates must be made in order that light-fast azo dyestuffs may be prepared.

During the growth of the cellulose acetate dyestuff industry, another shortcoming was attributed to the acetate which was properly a characteristic of the dyestuffs. This phenomenon was known as "dry-bleeding."

Dry-bleeding occurs when an attempt is made to dye too much dyestuff into the fiber. It thus occurs on dark shades and is particularly in evidence with dark reds and maroons. The excess dyestuff within the fiber is loosely held and if not washed off it tends to rub off ("crock") and sublime at ordinary room temperature. Thus, if certain maroon shades of cellulose acetate are left in contact with white acetate or viscose fabrics, the red dyestuff is transferred from the dyed acetate to the undyed material.

When the phenomenon of dry-bleeding was investigated scientifically, it was found that the relative positions of certain groups in the molecule could be used to control the solubility of the dyestuff in water and also to alter its vapor pressure or tendency to sublime.

The most satisfactory arrangement was found to be the configuration shown above, in which the coupling agent consists of two amino groups meta to each other; one is acetylated while the other is dihydroxyethylated with ethylene oxide, glycerol, epichlorhydrin, etc.

Developed Azos

By the term "developed azos" is meant those dyestuffs which are applied to cellulose acetate fabric, subsequently diazotized, and then coupled with suitable developers to give the final shade desired. The diazotizable bases as applied may in themselves be dyestuffs for cellulose acetate but are unsatisfactory due to the presence of the free amino group.

The developed azos may be subdivided into three main classes depending on the type of compound with which the diazotized base is developed. The three classes may be listed as follows:

(1) derivatives of aniline or meta-diamino-benzene,
(2) the naphthols and naphthoic acids, and
(3) the anilides or the naphthoic acids.

In choosing the proper type of dyestuff to be used as a developed azo, it is necessary to keep in mind the principles described above, that is, the relative positions of the various groups must be properly chosen in order to obtain the proper fastness characteristics.

While this statement must be qualified somewhat, the relationship of the groups with regard to acid-fading and light fastness must be observed. Dry-bleeding, however, is rarely a property of a developed azo dyestuff, probably because of the large size of the final molecule. Numerous cases of dry-bleeding have been recorded, but this has been found to be due entirely to the lack of purity of the dyestuff, *i.e.*, the presence of some incompletely removed intermediate.

Satisfactory developed azo dyestuffs include some of the popular developed azos for cellulose. They differ in the mode of application to the fiber, however, in a way which distinctly exemplifies the difference between cotton fibers and cellulose acetate fibers. This refers particularly to the Naphthol AS type dyestuff.

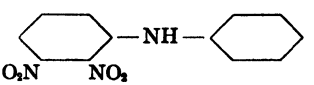
When these are applied to cotton fiber, usually the proper developing agent is padded onto the cotton. This is necessary since they are water-insoluble and would not be absorbed by the cotton from aqueous dispersions. The diazotized base is then prepared in solution and the fabric is passed through. Sufficient of the base is picked up to couple properly with the pre-padded coupling agent in the capillaries of the fiber. When cellulose acetate is processed, however, both the coupling agent and the diazotizable base possess substantivity for the fiber. In fact, the diazotizable base, being a free amine, is readily absorbed by the acetate from its aqueous dispersion.

The base thus applied is diazotized with nitrous acid while the base is in solution within the fiber. A subsequent bath is made up containing the developing agent, and this is absorbed within the fiber, where it reacts with the diazonium compound. It is not necessary to cite examples of coupling agents in the three classes listed above since, in class (1) they are entirely similar to the direct azos described previously, while the materials in classes (2) and (3) are well known to one conversant with the dye industry.

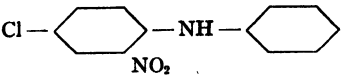
Diphenylamines

The diphenylamines are principally oranges and yellows and owe their popularity to their ease of manufacture. They were among the earliest of the dyestuffs introduced for cellulose acetate. Briefly, the characteristics of the dyestuffs from the diphenylamines depend, as do all the other dyestuffs, upon the substituents and their positions. Since they do not constitute as important a range of dyestuffs as the anthraquinones or the azos, they will be considered only briefly.

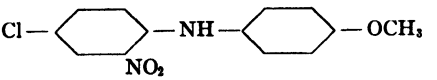
Here, as with the azos, there is a relationship between the position of the polar groups in the molecule and the light fastness of the resulting dyestuff. The following group will serve to exemplify this principle:



2·3-dinitro-diphenylamine
(pure yellow; poor light fastness)



2-nitro-4-chlor-diphenylamine
(reddish-yellow; good light fastness)



2-nitro-4-chlor-4'-methoxy-diphenylamine
(yellowish-orange; excellent light fastness)

An unusual characteristic of certain of the diphenylamine-dyestuffs is that they can be used for dischargeable shades. It is general practice that a dischargeable color be prepared from azo dyestuffs since these can be readily severed by reduction and removed from the fiber. The exception of certain of the diphenylamines lies in the fact that they reduce to colorless materials which have poor affinity for cellulose acetate fibers.

Vatted Dyestuffs

This class of dyestuffs may be considered extremely briefly. In themselves, they have no substantivity for cellulose acetate fibers and do not receive consideration at all in normal processing.

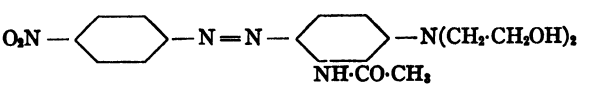
The procedure of reducing a dyestuff to its leuco form is to solubilize it in water as the sodium salt. As sodium salts they have still no affinity for cellulose acetate fibers. The fact that vatted dyes in caustic soda solution show any tinctorial value on acetate at all is due undoubtedly to the fact that the acetate is partially saponified and the cellulose partially regenerated. Vat dyes must be considered, however, since they are used in illuminating cellulose acetate fabrics which have been dyed and discharge printed.

Dischargeable Dyestuffs

Dischargeable dyestuffs have not been listed in the classification above since they are included in other types of dyestuffs, that is, not only the direct-dyeing azos and the developed azos, but also in the diphenylamines. However, discharge printing is of sufficient scientific interest to warrant brief amplification.

In discharge printing, as differentiated from direct printing, the fabric is predyed with dyestuffs which give colorless compounds when reacted with strong reducing agents. Many of the direct azos and developed azos used on Celanese fabrics are thus reduced with the salts of formaldehyde-stabilized sulfoxylic acid.

The principal reason appears to be that the reduction products are dyestuffs for the cellulose acetate and are therefore incapable of being completely removed after reduction. Thus, white discharges are not permanent unless the proper dischargeable dyestuffs have been used. This may be exemplified by considering the dyestuff discussed previously:



Reduction of this dyestuff with sodium sulfoxylate formaldehyde would result in formation of para-phenylene diamine and a triamino-benzene. Both these compounds have strong affinity for cellulose acetate and it is difficult to remove them. The subsequent action of light and air on these compounds would form highly colored oxidation products.

Fortunately, however, it has been found that the compounds formed are not the free amines but the salts of the amino compounds. As such, they are capable of being removed by certain chemical processes.

Again the relationship of the groups on the benzene nuclei is of importance. It has been found, for instance, that if the dyestuff is formed from 2:4-dinitroaniline, reduction must be carried out with an acid discharge paste. This is accomplished by employing the zinc salt of the sulfoxylic acid. If a basic discharge agent is used, such as the sodium sulfoxylate formaldehyde compound, the reduction does not result in the fission of the azo nucleus and highly colored triazoles are formed. There are certain objections to employing the acid reducing agents and so it becomes necessary to alter the dyestuffs to round out a usable range of shades. A complete line of dyestuffs is now obtainable for cellulose acetate fabrics so that successful discharging and illumination can be carried out commercially.

The illumination of the discharged areas consists of employing a dyestuff such as a vat which is reduced to a colorless leuco but is not destroyed. The leuco is impregnated in the fiber simultaneously with the destruction of the ground shade. Subsequent oxidation returns the vatted dyestuff to its original shade, and it is thus incorporated in the cellulose acetate fabric as a colored and extremely stable compound.

It is thus apparent from the brief consideration given to dyestuffs above that the development of cellulose acetate decorated fabrics has required considerable research. The industry at the moment is in the fortunate position of having dyestuffs available for every conceivable commercial purpose to which the unique fabric can be put.

Plastics

While the most important use for cellulose acetate is for the production of synthetic yarns and fibers, a considerable amount of it is consumed by the plastics industry. In 1941, 163,745,000 lbs of cellulose acetate rayon yarn [26] were produced, while 36,934,768 lbs of plastics [35] were produced. Despite the discrepancy in consumption, cellulose acetate as a plastic plays a prominent role in the modern world and has found many uses in the defense industries.

A plastic may be defined as an amorphous (resinous) material that is capable of changing its shape under pressure. Industrial plastics require elevated temperatures to facilitate this change. In general, plastics are divided into two classes: (1) the thermo-setting, and (2) the thermo-plastic.

The first class comprise the phenol-formaldehyde, the urea-formaldehyde, the melamine-formaldehyde, and others. After final heat-treating, they are usually rigid and incapable of further change. The second class is permanently thermo-plastic and as such is capable of being remolded an indefinite number of times. Cellulose acetate plastics are in the thermo-plastic class. In addition to being heat plastics, however, these compositions are capable of being cold- or deep-drawn.

Compositions

Cellulose acetate is in its own right a thermal plastic—that is, without the incorporation of other ingredients, it is capable of being melted and formed into a desired shape. The temperature at which the cellulose acetate is sufficiently plastic for molding, however, is so close to the scorching, or incipient decomposition, temperature that the acetate must be very carefully processed by heat and pressure to avoid discoloration or thermal decomposition. In the uncompounded form, therefore, very little industrial use is made of cellulose acetate.

In order to lower the melting point of the cellulose acetate, synthetic chemical plasticizers have been developed. These materials may be either active solvents for the cellulose acetate, or swelling agents—that is, a plasticizer must either be a solvent for the acetate or be dissolved in it. In numerous cases, however, the plasticiz-

ing agent is in a poorly defined category in which it appears neither a solvent nor a solute, and in this condition is known as having limited compatibility.

In addition to lowering the melting point of the cellulose acetate so that it can be readily formed under heat and pressure, the plasticizer is used to control the hardness of the molded object. For permanence, therefore, the plasticizer must have a low vapor pressure at the temperature of use so that it is not volatilized from the article. In general, the chemical structures of the plasticizers are similar to those of the volatile solvents, that is, they are forms of esters, ester-alcohols, alcohol-ethers, cyclic ethers, phenolics, etc.

In considering any particular molding problem, the plasticizer is chosen which is compatible with the acetate employed, will give the proper fusion temperature under the conditions of molding, and will produce the object of proper hardness and rigidity. In addition to the plasticizers used in compounded thermal plastics, compatible resinous materials may be employed to control the final hardness, toughness, etc. Pigments and dyestuffs may also be added to give the desired color effects and degree of transparency.

Molding

Compounded cellulose acetate may be purchased by the molder in a variety of forms. It can be obtained as a fine powder, in pellets of definite weight, in extruded rods and tubes, or in sheets.

The molding of the raw stock into the final object utilizes the thermo-plastic property of the composition. The type of molding to be used is usually dictated by the final shape desired. Four methods of molding are commonly used.

(1) *Stuffing.* The operation of stuffing is carried out in a machine which consists of an advancing screw rotating in a confined, jacketed cylinder. The dry powder is fed into a hopper at the back; the advancing screw carries the powder through a heated chamber, while a change of pitch of the screw compacts the mass as it melts, and extrudes the plastic through a die.

It is obvious that such a mechanism lends itself to the continuous formation of rods and tubes of circular, square, or irregular cross-section.

(2) *Compression Molding.* This type of molding is used when the object cannot be made by other means. It is usually employed when molding thermo-setting resins, but cellulose acetate can be used equally well.

A pre-formed die consisting of male and female members is preheated, the powdered acetate added, the die closed, and pressure exerted mechanically. The die must be cooled before the molded object can be removed.

(3) *Injection Molding.* This method combines the principles of the two previous methods and consists essentially in stuffing the molten plastic into a fixed mold. It possesses the advantage that the mold itself need not be heated; hence considerable energy as well as time may be saved in processing.

(4) *Machining.* Cellulose acetate plastics in particular possess excellent machining qualities and may be altered to the final desired shape by any of the common types of machining. As a rule, however, machining is used only when small quantities of finished objects are desired and the expense of a mold is not warranted. In exceedingly rare cases when a mold is not possible, machining may be used, also. While it is not desirable, machining operations are employed as a final finishing procedure for pre-molded articles.

(5) *Drawing.* Cellulose acetate plastics have the novel characteristic of being capable of deep-drawing. This is not necessarily a form of molding but represents one of the convenient methods of processing. The raw stock in this case is a plasticized cellulose acetate sheet. Any desired thickness may be employed.

The warm sheet is drawn over a mandrel or die. Since the deep-drawing process

accentuates any imperfections in the original film, it is usually necessary to buff or polish the finished object to the desired degree of smoothness and gloss.

Properties of Cellulose Acetate Plastics

The outstanding characteristics which are responsible for the wide use of cellulose acetate plastics may be tabulated as follows:

(1) Ease of molding,
(2) Wide range of colors producible,
(3) High clarity,
(4) Low flammability,
(5) Wide variety of ductility and hardness,
(6) Low specific gravity,
(7) High impact strength,
(8) Electrical insulation properties, and
(9) Low thermal conductivity.

Concerning item (8), the characteristics of interest to the electrical industry may be found in numerous textbooks on plastics.[24, 25]

In addition to the properties as listed above, it may be noted that fractured plastics may be mended by the use of heat or solvent, and objects which have been injured in the molding or thereafter may be easily re-molded.

Uses

Perhaps the widest use of cellulose acetate plastics is due directly to their decorative qualities, and ease and cheapness of molding. This popularity may be attributed to their eye appeal and pleasant touch when handled. Innumerable objects in the novelty field have been designed using this material.

Another use of cellulose acetate plastics which is probably equally widely known is for automobile hardware and trim, that is, steering wheels, knobs, dashboard, etc.

It finds another essential use in automobile construction, however, and that is in the manufacture of safety glass. When used as an inter-layer between the glass surfaces, cellulose acetate plastic has excellent adhesion, will not crack, and will not discolor on prolonged exposure to sunlight. It was largely due to these properties of cellulose acetate that safety glass become so widely used in the construction of automobiles.

Another interesting use which was found for cellulose acetate plastics was in the extrusion of conduits for electrical insulation in airplane construction. Its excellent insulation properties, the low specific gravity, and ease of formation by extrusion were the particular properties responsible for its use in this field. The ease of fabrication in particular prompted its use in the speed-up of airplane building.

Another use which has been found for cellulose acetate plastics in which it enjoys wide popularity is in handles for electricians' tools. Here again the proper electrical characteristics, the cheapness and ease of formation, its thermo-plastic properties after molding, and the low thermal conductivity are responsible largely for its use.

Continuously extruded cellulose acetate moldings are being widely employed in wallboard construction. While the use of acetate plastics has been found necessary because of metal shortages, there is no doubt but that it will continue to be used even though metals again become available.

The deep-drawing characteristics of cellulose acetate sheets suggests numerous uses. Among these are the well-known transparent boxes, and its use for wing tips on small Army training planes.

A wide use for cellulose acetate is in the foils for wrapping. It is particularly adaptable for this purpose since it has high transparency and is capable of being printed upon directly if desired. The printing ink becomes part of the cellulose acetate plastic and does not remove by washing or rubbing.

In the foregoing discussion of a few of the uses of cellulose acetate plastics, no attempt has been made to cover the field comprehensively. An attempt has been made merely to give examples of a few of the uses to illustrate the manner in which the plastic has been properly employed where the inherent characteristics of the plastic itself have been utilized.

In addition, however, to the large civilian uses to which these plastics are put, advantage has been taken of it in the National Defense Program. It may be noted that injection molding is the cheapest and easiest form of molding, and when possible, objects are usually formed by this method. Cellulose acetate represents the greatest volume of material fabricated by this process. Among the products which are formed by injection molding and used directly in the National Defense Program may be cited handles for mechanical and electrical equipment, non-fogging lenses, mouth-pieces and valves for gas masks, instrument boards for airplanes, automobiles, etc.

The multitudinous uses for cellulose acetate plastics in both civilian life and National Defense are examples of the versatility of this novel plastic. It may be predicted with certainty that the uses of cellulose acetate and the fields in which it will be employed will increase as the demand on the industry makes it necessary to increase the availability of cellulose acetate.

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Cellulose Acetate Butyrates

C. J. MALM AND C. R. FORDYCE

Eastman Kodak Co., Rochester, N. Y.

Cellulose acetate butyrates have recently attracted a considerable amount of attention. Certain types of these esters are now commercially available and have found uses in fields where solubility in cheap solvents, good compatibility with resins and high boiling plasticizers, high moisture resistance, and good flexibility are of importance.

Manufacture

Production of cellulose acetate butyrates involves the same general processes used for cellulose acetate manufacture, although direct application of these processes is not possible. This is especially the case with cellulose acetate butyrates containing large amounts of butyryl.

In the manufacture of cellulose acetate butyrates, sulfuric acid is the most practical catalyst; however, with increase in the butyryl content of the esterification mixture, the catalytic efficiency of sulfuric acid decreases because its adsorption by the cellulose from the esterification mixture decreases.[4] Fig. 1 shows

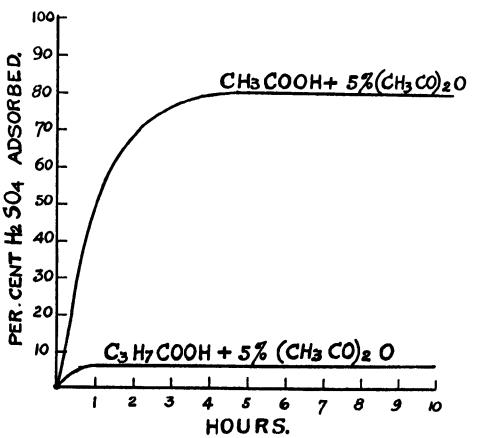

FIGURE 1

the difference in sulfuric acid adsorption when cotton linters are kept in a mixture of acetic acid containing 5 per cent acetic anhydride and 0.5 per cent sulfuric acid and in a mixture of butyric acid containing 5 per cent acetic anhydride and 0.5 per cent sulfuric acid. The treatment was carried out at 25°, employing 20 parts of liquid for 1 part of cellulose. The amount of sulfuric acid adsorbed is plotted against the time of treatment. Butyric anhydride is decidedly less reactive than acetic anhydride;

both these factors tend to slow the rate of esterification and cause breakdown of the cellulose before it is protected by acyl groups.

To overcome these handicaps it has been found advisable to decrease the liquid-to-cellulose ratio in the esterification mixture, thereby increasing the anhydride and catalyst concentration but still keeping their ratio to the cellulose the same. This speeds up the reaction. The cellulose is esterified and protected by acyl groups before it becomes too much degraded, resulting in products of higher viscosity and improved physical properties.[1]

A cellulose acetate butyrate of a definite composition can be made by controlling the ratio of acetyl to butyryl groups in the esterification mixture. It does not make any difference, as far as the composition of the final product goes, whether the various acyl groups are added to the esterification mixture as the anhydrides or the corresponding acids. In the presence of the esterification catalyst an equilibrium takes place almost instantaneously. When equal moles of acetyl and butyryl groups are taken in a mixture of acids and anhydrides, the ratio of butyric to acetic anhydride in the equilibrium is 1.35:1[8].

It has been found that the relationship shown in Fig. 2 exists between the per

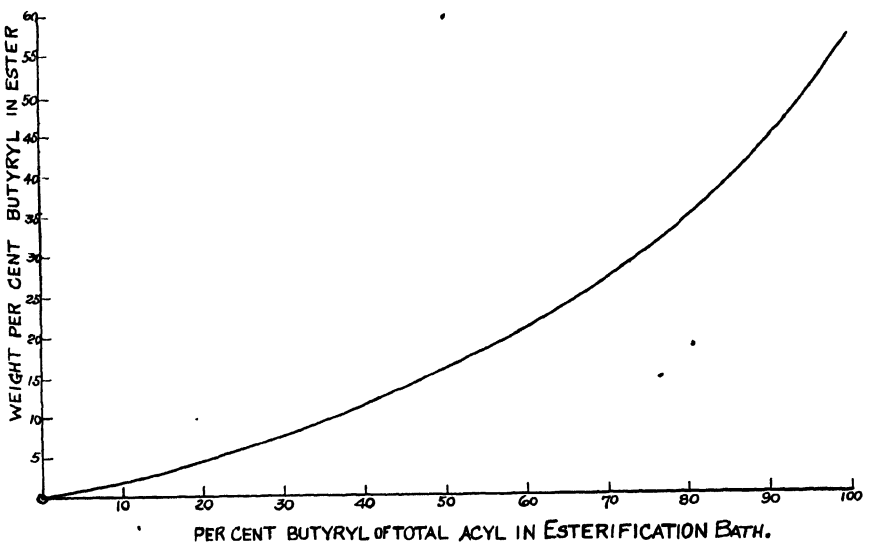

FIGURE 2. Relationship between composition of esterification bath and per cent butyryl introduced into product.

cent butyryl of total acyl in the esterification mixture and the per cent butyryl in the resulting fully esterified cellulose acetate butyrate. This relationship varies slightly with extreme variations in ratios of esterification mixture to cellulose. For economic reasons it is, of course, better to use as much acetic anhydride and as little butyric anhydride as possible; however, for the activation of the cellulose prior to esterification, as much acetic and as little butyric acid as possible should be employed to obtain optimum results. The proper proportions of these chemicals must be selected in every case, and depend upon the composition and viscosity of the ester to be prepared and the reactivity of the cellulose used.

Because of the better solubility of the fully esterified cellulose acetate butyrates compared to fully esterified cellulose acetate, there is much less danger of gel formation toward the end of the esterification. This property has been used to advantage for making cellulose acetate butyrates which in general have the same properties as

cellulose acetate, but have improved clarity due to the presence of small amounts of butyryl.[5]

When water is added to the esterification mixture to hydrolyze the excess anhydride and to start hydrolysis of the cellulose ester, it is desirable to add it slowly and at the same time bring the temperature of the reaction mixture to 100° F or above, in order to remove simultaneously as much as possible of the combined sulfuric acid from the cellulose.[6] Hydrolysis is then carried out in the same manner as for cellulose acetate.

In the precipitation of cellulose acetate butyrates great care must be taken to obtain an open, even precipitate. It is rather difficult to wash the products thoroughly because of their hydrophobic nature, and more care must be taken in their washing than in the case of cellulose acetate.

Analysis

In analyzing cellulose acetate butyrates the same methods are employed as in the analysis of cellulose acetates, but it is, of course, of great importance to have a reliable method for analyzing the esters for acetyl and butyryl. Such a method has recently been described.[7] It involves the following steps:

(a) Determination of total combined acids.
(b) Saponification and distillation of these combined acids in water solution.
(c) Determination of the partition coefficients between butyl acetate and the acid distillate and also separate measurement of the partition coefficients of each of the two acids.
(d) Calculation of the molar ratios of the acids using simultaneous equations and calculation of the weight per cent of the acids, or combined acyl, from the molar ratios and the total acid content of the ester.

Physical Properties

The physical properties of the cellulose acetate butyrates can be widely changed by changing the composition of the ester. In general, it can be stated that with increasing butyryl content the melting point, specific gravity and sorption of moisture decrease, and the solubility in solvents and plasticizers and compatibility with plasticizers and resins increase. With increasing hydroxyl content the melting point goes through a minimum and the specific gravity and moisture sorption increase. The influence of increase in hydroxyl content upon the solubility in solvents and plasticizers and compatibility with plasticizers and resins depends upon the nature of the solvents, plasticizers and resins. The solubility and compatibility increase with more polar, and decrease with less polar materials.

The most convenient way of showing the changes in physical properties is by representing the cellulose acetate butyrates graphically on trilinear charts, the three variables of which are acetyl, butyryl and cellulosic residue. In the graphs of the accompanying figures, point *C* represents cellulose; 44.8 per cent along the line *CA*, represents cellulose triacetate, and 57.3 per cent along the line *CB*, cellulose tributyrate; hydrolyzed cellulose acetates and butyrates fall above these points along the lines *CA* and *CB*, respectively. A line connecting the cellulose triacetate and tributyrate points identifies all fully esterified mixed esters of these acids. Hydrolyzed mixed esters fall within the area above that line. Data on these charts have been limited to compositions between the di- and tri- esters, inasmuch as these compounds cover the range of products in standard use.

Melting Point. The melting points of cellulose acetate butyrates are influenced not only by the composition of the ester, but also to a certain extent by other factors. Large fluctuations in viscosity influence the melting point to a certain degree, giving lower values with decreasing viscosity. The amount and nature of the ash content of the ester also affect the melting point. An increase in ash causes an increase in

melting point, especially if the ash consists mainly of alkaline-earth metal salts. The general tendencies of the effect of composition upon the melting points of cellulose acetate butyrates of medium viscosity washed with water having a total hardness of 100-150 parts per million are given in Fig. 3.[5]

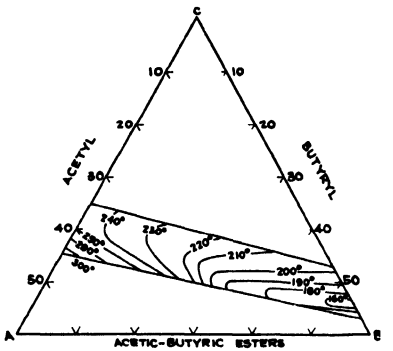

FIGURE 3. Melting points in °C of cellulose esters of acetic and butyric acids.

Variations of melting point with composition are shown by means of lines connecting points of equal melting point value. These variations are somewhat irregular; cellulose acetate gives a lowered melting point with hydrolysis, while esters containing appreciable amounts of butyryl have a range of minimum melting points with moderate hydrolysis. Cellulose triacetate has the highest melting point of any of these esters; very high butyryl content esters give quite low values.

Specific Gravity. Fig. 4 [5] shows the changes in specific gravity with changes in

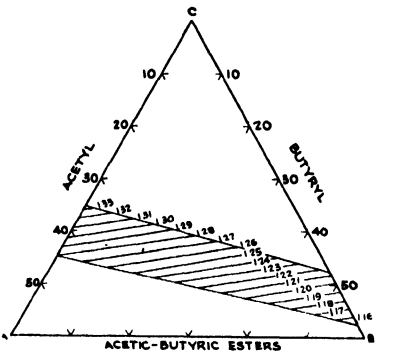

FIGURE 4. Specific gravity of cellulose esters of acetic and butyric acids.

composition. This property is of importance in some uses, and is of general interest in that it influences the cost of an article made from the ester. Slight variations in observed values for specific gravities are obtained, depending upon the method of measurement employed. The measurements made in this work were based upon weight determinations in air and in heptane.

Sorption of Moisture. Fig. 5 [5] shows the influence of ester composition upon moisture sorption at 25, 50, 75, and 90 per cent relative humidity. Cellulose triacetate is the most moisture-resistant of acetates. It will be noted that the butyric esters are quite superior to acetate in this property when fully esterified, and mixed esters containing moderate amounts of butyryl may be hydrolyzed to a considerable extent before becoming as moisture-susceptible as the acetates. Advantages in toughness of molded articles are to be gained by some degree of hydrolysis. Mixed esters, therefore, may be chosen which have at the same time superior moisture resistance

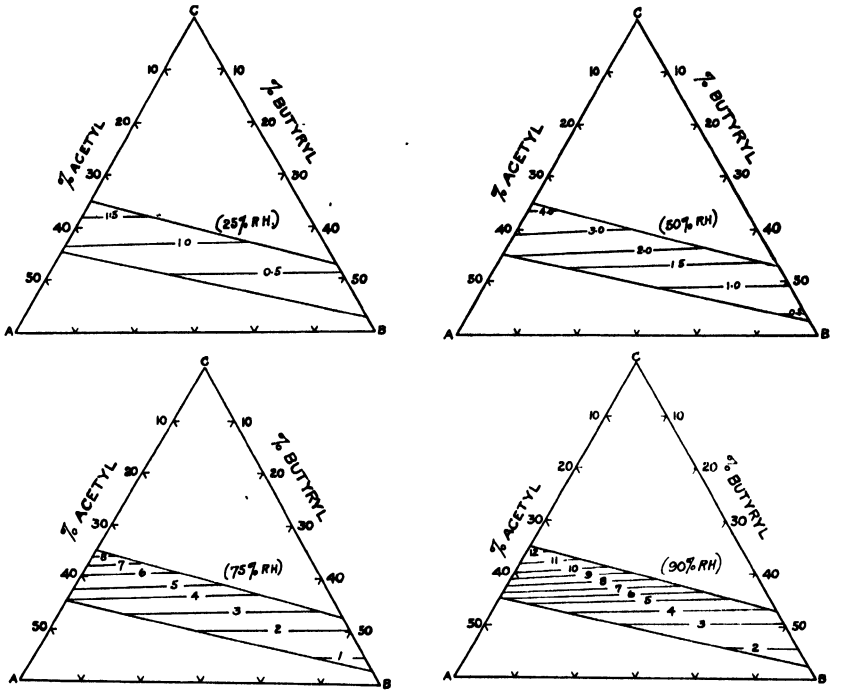

FIGURE 5. Per cent sorption of moisture at different relative humidities by cellulose esters of acetic and butyric acids.

to acetate and sufficient hydrolysis for toughness in the resulting product. On the other hand, as the weathering resistance of an ester is dependent not only upon the moisture resistance, but also upon ease of oxidation when exposed to ultraviolet light, it should be pointed out that of two esters which have the same moisture sorption that with less free hydroxyl content has the better weather resistance.

Solubility. The graphs in Fig. 6 [5] show the effect of composition of cellulose acetate butyrates upon their solubilities in a series of solvents. The line between solubility and insolubility is not a sharp, but a gradual one, and a variation in the viscosity of the cellulose ester changes somewhat the location of this line, the solubility increasing with decreasing viscosity. These solubilities were determined in 10 per cent concentrations at 25°.

Chlorinated solvents are in general more effective with fully esterified than with hydrolyzed cellulose esters. Methylene chloride is an active solvent over a very wide range of composition, and by addition of alcohols forms good solvent mixtures for cellulose triacetate. Ethylene and propylene chlorides will dissolve only esters containing some butyryl, which have not been greatly hydrolyzed. Addition of lower alcohols to these solvents widens their solubility ranges to include cellulose acetate; ethylene chloride gives very active solvent mixtures, whereas propylene chloride-alcohol mixtures give cellulose acetate solutions which often tend to "blush" upon evaporation. Mixed esters of 10 per cent or more of butyryl show good behavior with this solvent mixture. Acetone is a good solvent for hydrolyzed cellulose acetates, dissolving products within the range of about 36 to 42 per cent acetyl. Higher ketones are more restricted in their solvent power, but may be used as diluents, particularly with cellulose esters near the area in which they are soluble. Methyl acetate exhibits solubility behavior very similar to that of acetone. Ethyl and butyl acetates

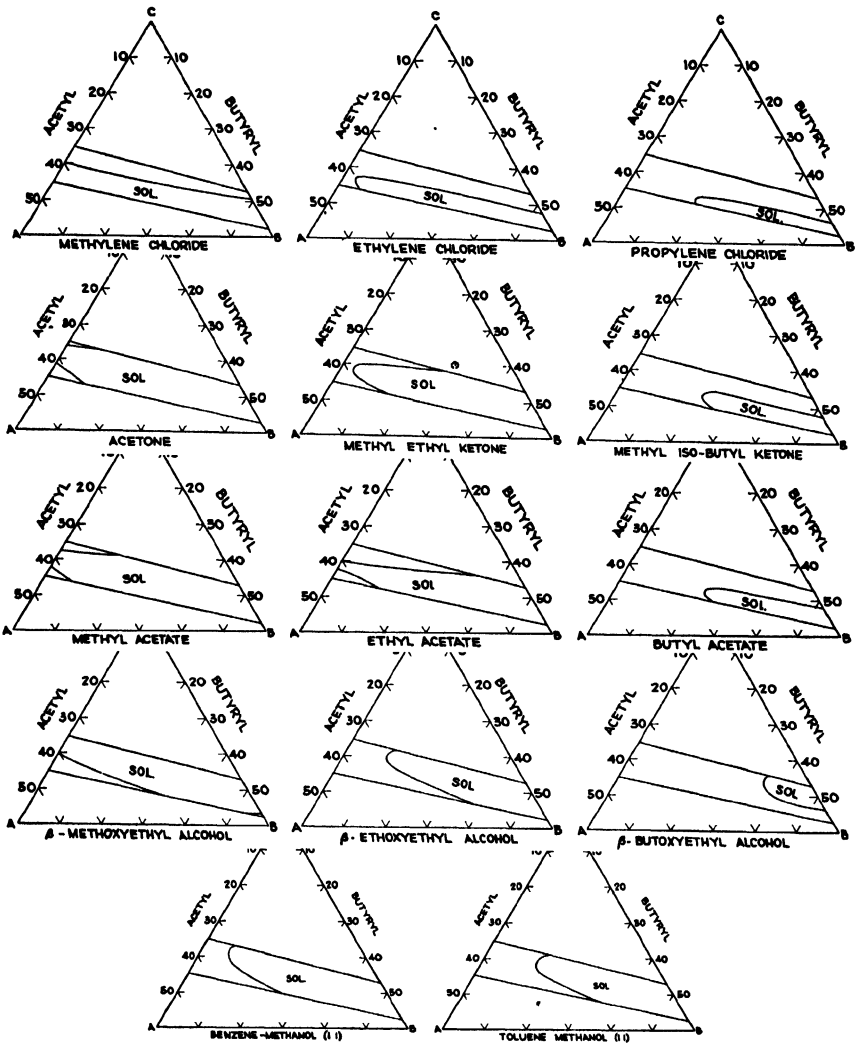

FIGURE 6. Solubilities of cellulose esters of acetic and butyric acids in organic solvents.

are less effective, butyl acetate being confined to products of high butyryl content and of comparatively limited hydrolysis. Glycol monoethers exhibit interesting solubility behavior, in that they are considerably more effective with hydrolyzed esters than with those which are fully esterified. Ethylene glycol monomethyl ether is a particularly good solvent for hydrolyzed products. Benzene and toluene in mixtures with alcohols offer very cheap solvent mixtures and diluents, and may be used with a wide range of cellulose esters, particularly those of at least 10 per cent butyryl content which have been moderately hydrolyzed.

Plasticizer Compatibility and Solubility. Change in composition of cellulose acetate butyrates has a great influence upon their compatibility with and solubility in plasticizers. The graphs of Fig. 7 [5] show regions of solubility of the cellulose

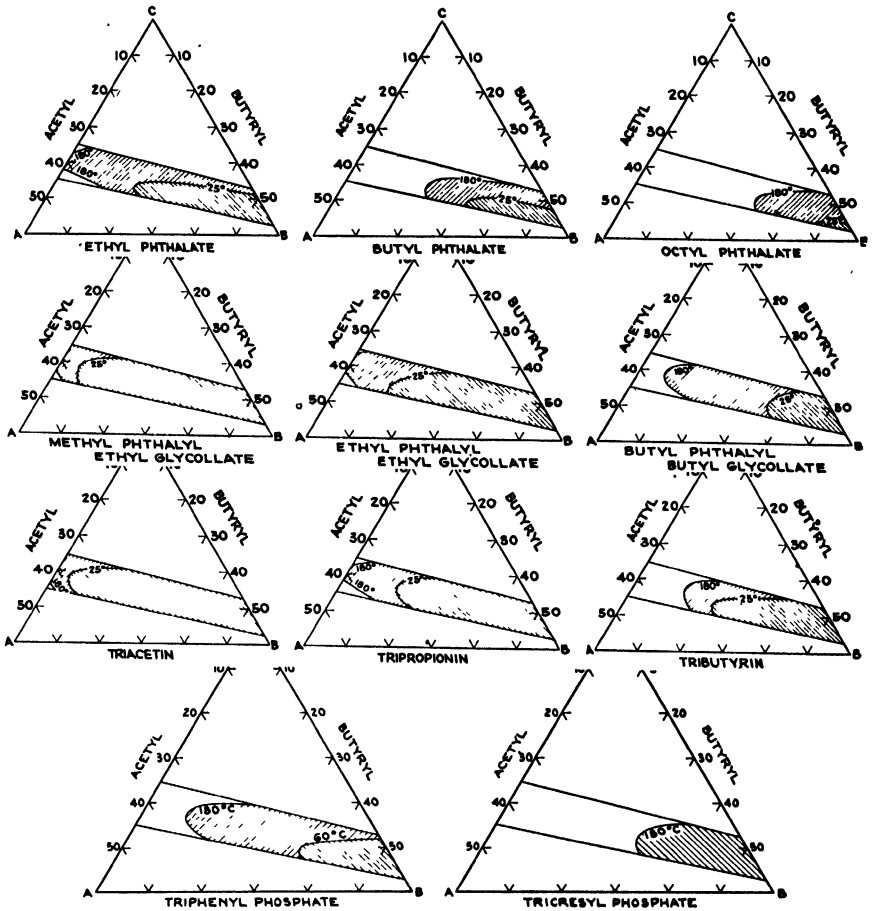

FIGURE 7. Solubilities of cellulose esters of acetic and buryric acids in plasticizers.

esters in several related groups of plasticizers at 25° and 180° C. This property is of direct application only to the workability of plasticized compositions and tells nothing as to their durability or aging properties. In general, plasticizer retention is better with higher molecular weight members of a group of plasticizers, as compared with the more volatile lower compounds. Advantage is often thus to be gained by using cellulose esters which permit desirable solubility characteristics with these more permanently retained materials, in many cases at the same time taking advantage of the lower melting points of the butyric esters to permit use of lower concentrations of plasticizer for suitable flow.

Compatibility with Resins. The influence of cellulose acetate butyrate composition upon compatibility with some resins is shown in the charts of Fig. 8.[2] It may be seen that cellulose esters containing appreciable amounts of butyryl are compatible with sufficiently high proportions of resins to the extent that useful qualities of adhesion and surface hardness of lacquer coatings may be obtained, while cellulose acetate or esters containing small amounts of butyryl are very limited in this property.

All the above data are given for cellulose acetate normal butyrates. The use of

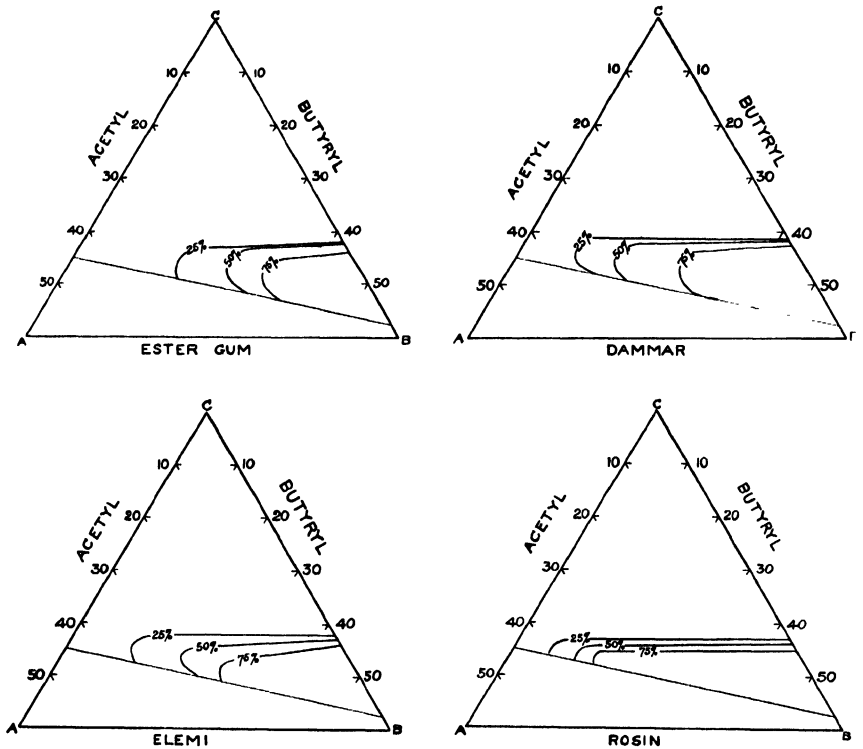

FIGURE 8. Compatibility of cellulose esters of acetic and butyric acids with resins.

isobutyric acid in the manufacture of cellulose acetate butyrates has not been found to be of practical interest. Since isobutyric acid is less reactive than normal butyric acid, proportionally more of it must be used to introduce a certain amount of butyryl. Due to the comparatively restricted solubility of isobutyric acid in water, the precipitation and washing of cellulose acetate isobutyrates is greatly complicated.

Uses

Cellulose acetate butyrates have so far found use in the manufacture of plastics, photographic film, thin sheeting and lacquers. In plastics they have advantages over cellulose acetates in their greater moisture resistance, their compatibility with plasticizers of low vapor pressure and high moisture resistance and their lower melting points, which make it possible to produce plastics of good flow with comparatively small amounts of plasticizer. The resulting plastics have therefore good dimensional stability and show very little change with temperature and relative humidity.

In photographic films their high moisture resistance and good solubility make it possible to economically produce film base which shows very little distortion in the film developing processes.

When used in the manufacture of thin sheeting cellulose acetate butyrates yield a product of excellent physical properties and good water resistance.

The good light stability, moisture resistance and solubility in cheap solvents is rapidly creating a place for cellulose acetate butyrates in the lacquer field.

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Methylcellulose

A. E. YOUNG AND M. KIN

Dow Chemical Company, Midland, Michigan

Methylcellulose is an ether of cellulose formed by interaction of the methyl ester of an inorganic acid with cellulose which has been swollen by treatment with a strong base. The methylation of cellulose has been the subject of many investigations since it was observed in 1905 [1] that the treatment of alkali-swollen cellulose with dimethyl sulfate brought about a reaction. The earlier investigations had one of two objects. One of these was to produce a modified, soluble cellulose capable of being dissolved and therefore suitable for making artificial filaments, films, and other structures. Prominent as the author of this type of investigation is L. Lilienfeld who, beginning in 1912,[2] published in the form of patent specifications the results of a long series of researches on the etherification of cellulose. These and similar investigations are recorded by Worden.[3]

The methylation of cellulose also served to provide a tool for the elucidation of the structure of cellulose itself. This was undertaken by Irvine and led to the preparation of trimethyl cellulose which was quantitatively hydrolyzed to 2,3,6-trimethyl glucose,[4, 5, 6, 7] thus proving that cellulose is composed of identical glucose units.

Preparation of Methylcellulose

The most intensively studied method for the methylation of cellulose involves the treatment of alkali cellulose with methyl chloride or dimethyl sulfate.[4] This is the chief method used industrially. Modifications of this method have been used wherein bases other than caustic soda are employed for preparing a swollen complex that will react with the methyl ester. Some of these bases swell the cellulose structure more effectively than does aqueous caustic soda and thus facilitate contact of the methylating agent with the internal surfaces of the cellulose. Noteworthy among these are aqueous caustic soda in conjunction with copper hydroxide [NaOH·—$Cu(OH)_2$] [8, 9, 10, 11, 12, 13] and the quaternary ammonium hydroxides.[11, 14, 15, 16]

The ability of diazomethane to react with alcohols to form methyl ethers has been applied to cellulose by Nierenstein [17] and by Reeves and Thompson.[18] Methylcellulose has also been prepared by simultaneous saponification and methylation of cellulose acetate. This is accomplished by dissolving the ester in acetone and treating it with aqueous caustic soda and dimethyl sulfate.[19]

Types of Methylcellulose

Introduction of methyl groups into the structure of cellulose brings about a gradual modification of the properties of the cellulose. The degree of modification is dependent on the amount and, to a large extent upon the uniformity, of methylation. The modification of cellulose by varying degrees of methylation is best seen in the change in its solubility properties. The effect of uniform methylation can readily be pictured if each methyl group which enters during methylation to form part of the cellulosic structure is considered as a wedge tending to pry the long, comparatively rigid, chain-like cellulose molecules apart. It is apparent that uniform

spacing of these 'wedges' will greatly facilitate the entry of solvent molecules and increases the ease of dispersion of the chain molecules.[20]

With increased degree of substitution, methylcellulose goes through several different solubility stages. By uniform methylation of alkali cellulose, products containing as little as 0.1 methoxy group per anhydro-glucose unit ($dS = 0.1$) are obtained which are soluble in 4-8 per cent caustic soda solution on freezing.[21] Products of $dS = 0.38$ are similarly soluble.[22] When the degree of substitution is increased to between $dS = 0.4$ and $dS = 0.6$, the product is soluble in 4-8 per cent caustic soda at room temperature.[4, 23] Solubility in cold water is observed when the degree of substitution lies between 1.3 and 2.6.[24] In the higher portion of this range, solubility in alcohol is encountered, and compatibility with organic solvents increases as the degree of substitution is increased above 2.6.

The subject of the greatest amount of commercial methylcellulose development is the water-soluble type. It is produced and sold under the name "Methocel" in the United States, "Tylose" in Germany, and "Rhomellose" in France. As these are commercial products of widespread availability, much information, both technological and scientific, is available concerning water-soluble methylcelluloses, and all succeeding remarks and discussions refer to these types.

Properties of Water-Soluble Dimethylcellulose

Dimethylcellulose, which is the product of the methylation of alkali cellulose, dissolves in water to yield neutral solutions which are odorless, colorless, and nontoxic.[25] It is insoluble in hot water and the common organic solvents and is unaffected by oils or greases. Temperatures up to 225° or long exposure to light do not discolor this methylcellulose. It is stable to alkalies and dilute acids.

Aqueous solutions of methylcellulose are stable on long standing and are resistant to mold growth. They are not affected by changes in acidity or alkalinity over a pH range of 2 to 12. They will tolerate dilute acids including boric, phosphoric, acetic, citric and tartaric, but are coagulated by tannic and phosphotungstic acids. Alkalies, including caustic soda, caustic potash and lime water, act to increase the viscosity of methylcellulose solutions, but have no other effect on them. Concentrated peroxides decompose methylcellulose in solution. It has been found that methylcellulose in solution has no electrical charge.[26]

The solubility of methylcellulose in cold water and its insolubility in hot water are at first sight peculiar phenomena. When methylcellulose dissolves in cold water its long thread-like molecules attract enormous numbers of water molecules, forming completely hydrated chains which are spaced at sufficient distance to allow the penetration of water between them and cause complete dispersion. Heat tends to destroy this hydrate structure, thus bringing the chains back into closer relationship with one another, so that attractive forces between them are increased; if a sufficient concentration of methylcellulose is present in the solution, gel structure results. If the concentration is insufficiently high, separation of small, discrete particles occurs. Addition of certain electrolytes[27] to a methylcellulose solution also breaks down the hydration layer around the methylcellulose macromolecules, leading to precipitation at lower temperatures.

The temperature at which gelation of an aqueous methylcellulose solution occurs is governed by the concentration and the viscosity type, as shown in Table 1. This table indicates the temperatures at which solutions of methylcellulose of various viscosity types form gel structure. The viscosity type of a methylcellulose is defined by the viscosity of a 2 per cent (by weight) aqueous solution as measured at 20° using an Ubbelohde viscosimeter.

It should be emphasized that the data included in Table 1 refer only to methylcellulose that has been manufactured by the methylation of alkali cellulose. Methylation of other swollen cellulose complexes may give water-soluble products that gel

Table 1. Gelation Temperature of "Methocel" Solutions

Concentration in (% by weight)	"Methocel" Viscosity Type					
	15	25	100	400	1500	4000
0.5	No gel	No gel	No gel	No gel	58-60	58-60
1.0	No gel	No gel	64-66	56-58	56-58	56-58
2.0	No gel	64-68	54-56	54-56	54-56	54-56
3.0	64-68	58-64	52-54	52-54	52-54	52-54
4.0	60-64	55-58	50-52	50-52	50-52	50-52
5.0	56-60	53-55	48-50	48-50	48-50	48-50
6.0	53-56	50-53	46-48	46-48	45-48	45-48
7.0	50-53	48-50	44-46	43-46	*	*
8.0	48-50	46-48	43-44	42-43	*	*
9.0	47-49	44-46	42-44	*	*	*
10.0	46-48	42-44	40-42	*	*	*
11.0	44-46	40-42	36-40	*	*	*
12.0	42-44	38-40	*	*	*	*
13.0	41-42	*	*	*	*	*
14.0	40-41	*	*	*	*	*
15.0	38-40	*	*	*	*	*

* Non-flowable at 25° C.

at considerably higher temperatures than those shown in Table 1, or which do not gel at all at temperatures below the boiling point of water. Thus it is reported that a sample of methylcellulose containing 19.0 per cent methoxyl, prepared by methylation of sodium cupricellulose, failed to show gelation on heating even an 8 per cent aqueous solution.[28] A 5 per cent solution of the same methylcellulose in a 0.025 per cent aqueous solution of sodium sulfate gelled at 78°. These differences in behavior between the products of methylation of alkali cellulose on the one hand and of sodium cupricellulose on the other can be correlated with differences in the uniformity of substitution of the products resulting from different methods of manufacture. It is apparent that a comparatively small number of water molecules surrounding the hydroxyl groups of a uniformly substituted chain molecule will effect complete separation of it from a parallel chain molecule, whereas a comparatively large number will be required to separate non-uniformly substituted molecules.

When spread on a flat surface methylcellulose solutions dry to form colorless, transparent, tough films. The physical properties of these films are indicative of many of the uses to which methylcellulose may be put.

The load-elongation curve of methylcellulose is compared with those of regenerated cellulose and ethylcellulose respectively in Figure 1. The data were determined on films 1½ mils thick that were conditioned at 50 per cent relative humidity and 70° F before testing. The curves indicate that methylcellulose is inherently a tough, strong material. It is somewhat stiff under atmospheric conditions of 50 per cent RH at 70° F. At higher humidities, however, methylcellulose films are softer and more flexible. Hygroscopic materials are, therefore, indicated as plasticizing agents for increasing the elongation and flexibility of methylcellulose coatings. The amount of moisture absorbed by methylcellulose films plasticized with various hygroscopic materials is given in Table 2. The data show that the plasticizer has little effect on the moisture content at 50 per cent relative humidity, but greatly increases it at 90 per cent relative humidity. This is particularly true of glycerin, sorbitol and invert sugar.

Insolubilization of Methylcellulose

The presence of free hydroxyls in the dimethyl cellulose permit controlling its water solubility by several methods. A convenient method of insolubilization is the condensation of the methylcellulose with urea or melamine formaldehyde water-soluble resins. The degree of water resistance of the product is greatest when an acidic catalyst is used and a high temperature and long curing time are employed.[29, 30]

The incorporation of polybasic acids,[31] such as citric and tricarballylic, in methyl-

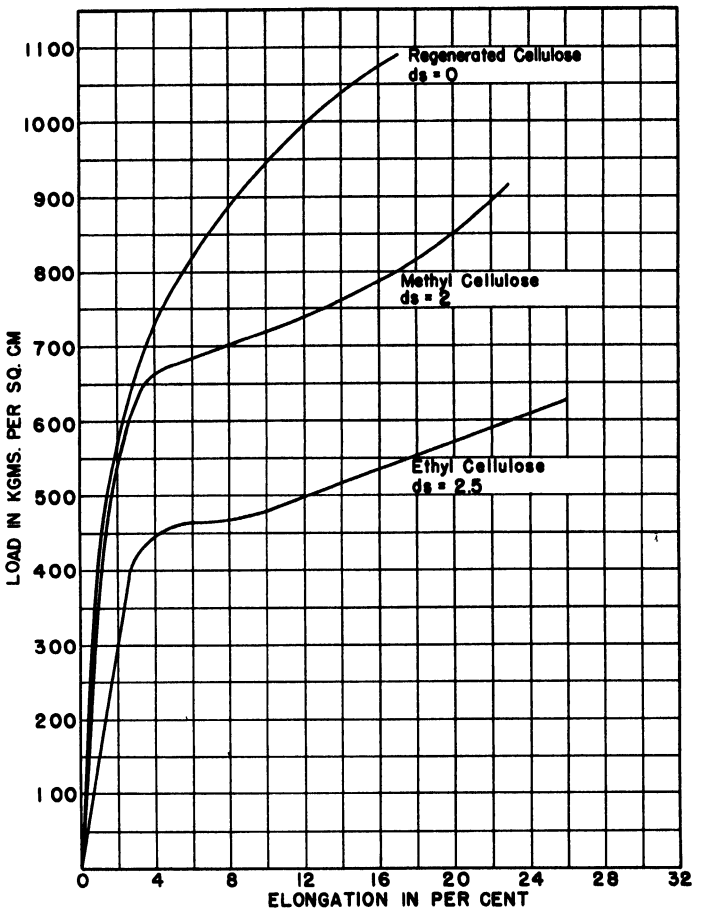

FIGURE 1.

cellulose solutions will also result in condensation products of appreciable water resistance. Other substances which are known to insolubilize this cellulose derivative are chloral derivatives,[32] water-soluble aldehydes,[33] drying oils[34] and tanning agents.[35]

Uses and Applications of Methylcellulose

Being a good film-forming material, methylcellulose is useful in sizing and coating and in making adhesives. Because it produces solutions of high viscosity, methylcellulose also finds application as a thickener and emulsifier. The variety of application of methylcellulose in all these uses is increased by reason of its compatibility with a variety of water-soluble substances, including soaps, water-soluble resins derived from polyhydric alcohols, most wetting agents, starch, glue, casein, dextrin, and natural gums.

The value of methylcellulose as a thickening agent, as compared with various natural gums, is illustrated in Figure 2. Methylcellulose has been used as thickening agent in the preparation of hair dressings,[36] depilatory creams,[36, 37] gumless lotions,[38] hand and face creams,[36, 39] ointments,[40] toothpastes,[36, 41, 42] liquid denti-

Table 2. Effect of Plasticizers on Properties of "Methocel" Films

Name	15% Plasticizer: Yield Point (kg/cm²)	Tensile Strength (kg/cm²)	Elongation (%)	Moisture Absorption 50% RH	Moisture Absorption 90% RH	Flexibility Rating
Polyhydric Alcohols						
No plasticizer	680	900	20	2.5	21.0	B
Invert sugar	475	741	33	4.0	27.5	A
Sorbitol	520	835	35	5.0	46.5	A
Glycerin	380	800	50	5.5	45.5	A
Mannitol	505	610	20	5.0	22.0	B
Triethylene glycol	360	400	16	1.0	24.5	C
Tetraethylene glycol	360	545	28	2.0	27.5	A
Miscellaneous						
Triethylphosphate	550	780	28	4.5	15.5	A
Triethanolamine	400	666	37	3.0	30.0	A
Sorbitan monolaurate	585	770	25	2.0	20.0	B
Mannitan monolaurate	585	670	20	2.0	20.5	B
Mannitan monooleate	490	600	19	2.0	18.5	B
Calcium chloride	320	450	21	19.0	23.0	B

Flexibility rating; comparison of the elongation of the plasticized film with that of unplasticized film.
A = Increased elongation
B = Equal elongation
C = Decreased elongation

Name	30 % Plasticizer: Yield Point (kg/cm²)	Tensile Strength (kg/cm²)	Elongation (%)	Moisture Absorption 50% RH	Moisture Absorption 90% RH	Volatility Rating 15%	Volatility Rating 30%
Polyhydric alcohols							
No plasticizer	—	—	—	—	—	—	—
Invert sugar	325	590	45	5.5	36.5	A	A
Sorbitol	365	675	45	6.0	59.5	A	A
Glycerin	205	405	50	6.0	65.5	C	D
Mannitol	400	510	25	5.5	18.5	A	A
Triethylene glycol	125	275	44	0.5	27.5	C	D
Tetraethylene glycol	125	355	56	2.0	33.0	B	D
Miscellaneous							
Triethylphosphate	461	800	42	4.5	14.5	A	C
Triethanolamine	165	430	60	3.0	34.5	A	C
Sorbitan monolaurate	440	685	35	2.0	20.0	A	A
Mannitan monolaurate	400	515	22	2.0	18.0	A	A
Mannitan monooleate	380	545	19	2.0	16.5	C	C
Calcium chloride	60	225	95	24.0	31.0	A	A

Volatility rating; loss of plasticizer from Methocel films after heating 2 weeks at 70°, calculated as per cent of plasticizer taken.
A = 0 to 10%
B = 10 to 25%
C = 25 to 50%
D = More than 50%

frices,[36, 43] wave-set lotions [36] and other pharmaceutical and cosmetic products.[36, 37, 38, 44, 45, 46]

Methylcellulose has been found to improve the stability of resin emulsions,[47] as well as the brushing qualities of water-dispersible paints. In paint removers [48] methylcellulose has been incorporated to retard the evaporation of solvents as well as to thicken the organic solvents to allow application on perpendicular surfaces.

Powers and Glarum,[49] as well as Hoyle,[50] have found methylcellulose very useful in thickening textile printing pastes. It has been found especially effective as a thickener for fast-color salts and diazotized bases for printing on naphthol-prepared grounds.[51] Methylcellulose is not recommended for use with vat colors or direct dyestuffs.

Champion [52] has dissolved methylcellulose in hot propylene glycol, which upon cooling gave a firm gel that could be used as a hectograph blanket.

When used as an adhesive, methylcellulose forms a firm bond by virtue of its tough, strong character. It is being used in the leather industry as a pasting adhesive for controlled drying of chrome leather on glass or metal panels.[29] In the manufac-

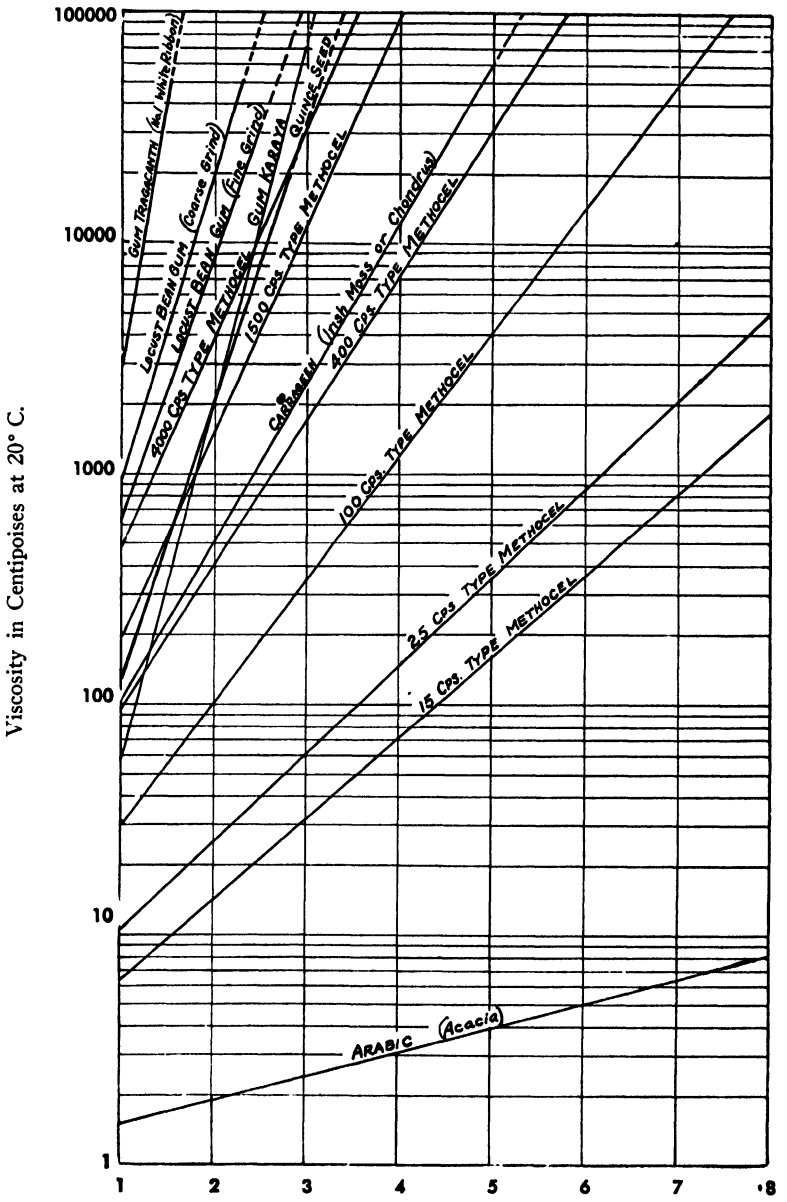

FIGURE 2. Viscosity comparison of methocel with natural gums

ture of pencil leads and colored crayons, methylcellulose acts as the binder [53] for the filler and pigments.

The binding and dispersing power of methylcellulose has been used with success to obtain shoe polishes and cleaners.[45, 54] By selecting the correct viscosity type of methylcellulose, cleaning products are obtained ranging in consistency from a liquid to a paste. Calcium carbonate, lithopone, titanium oxides, kaolin, and zinc oxide mix readily with methylcellulose solutions.

Methylcellulose may be used as the binder and adhesive in cementing the tobacco leaf in the manufacture of cigars.[55] It is also a useful binder in the manufacture of pharmaceutical tablets,[29, 38] pigment-coated papers,[56, 57] soaps,[45, 58, 59] and water paints and bodied colors.[60, 61]

The imperviousness of methylcellulose films to oily or greasy materials of animal, vegetable or mineral origin makes this material ideal as a surface sizing and grease-proofing agent. A light prime coat of methylcellulose applied on waxing stock,[25, 30] greatly reduces the penetration of paraffin during waxing. A similar prime coat [25, 30] on paper or paperboard prevents the penetration of inks or varnishes improving the gloss and brightness of the printed paper product.

When continuous coatings of methylcellulose are deposited, a surface is obtained which is entirely grease-proof.[25, 62] Such coatings are usually applied by doctoring, roll coating or brush coating.

The toughness, flexibility, transparency and adhesive characteristics of methylcellulose films, as well as its compatibility with the usual textile sizing and modifying agents, have resulted in many investigations and subsequent adoption of methylcellulose as a warp sizing and a textile-finishing material.[45, 63, 64, 65, 66, 67, 68, 69]

Methylcellulose lowers the surface tension of water. This quality, as well as the high viscosities of its solutions [30, 70] and other inherent properties, has suggested its use in the preparation of emulsions of fatty,[38, 71, 72] mineral [38, 70, 73] and essential oils,[45] waxes,[45] resins,[74] and lacquers.[75] Erspamer [76] has found that methylcellulose is a powerful dispersing agent for paper fibers because of the formation of a hydration film on the separate fibers.

An application utilizing the film properties of methylcellulose was developed by Pickrell.[77, 78, 79] He conceived the idea of a preformed transparent sulfadiazine film which could be used in the treatment of burns and other wounds. In this application methylcellulose has a number of functions. It gives a transparent eschar from which serum exudation is at a minimum. The protective film releases the sulfa drug to the blood over an appreciable period of time so that blood levels are maintained. The methylcellulose is completely innocuous to the tissues, so that there is no scarring. Klose [80] formulated a methylcellulose paste which, when applied to any object, would give a tough, flexible protective film impervious to dirt, grease, oils, paint, and other foreign materials. This film can be stripped intact without recourse to washing or scraping.

Hueper, Martin and Thompson [81] have reported their work on the use of methylcellulose solutions as a plasma substitute for the treatment of shock.

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Ethylcellulose

A. E. YOUNG

Cellulose Products Division, Dow Chemical Company, Midland, Michigan

Ethylcellulose is one of the more recently introduced plastic and film-forming cellulosic substances.[1] The article of commerce is an ether of cellulose and ethyl alcohol. It is manufactured through the reaction of cellulose, aqueous alkali and ethyl chloride to a stage where approximately 2.1-2.6 out of every three hydroxyl groups contained in the original cellulose has been replaced by ethoxyl groups. Ethylcellulose of this degree of substitution is soluble in a wide variety of organic solvents and is thermoplastic.

Although ethylcellulose is of recent introduction commercially, methods for its manufacture have been the subject of research practically continuously since 1905, when Suida [2] was the first to observe that cellulose can be etherified. This author treated cotton fibers with caustic soda solution and dimethyl sulfate and found that the dyeing characteristics of the fibers were thereby modified.

In 1912 Lilienfeld, Leuchs and Dreyfus [3, 4, 5] independently showed that the etherification of cellulose can be carried beyond a mere surface reaction and that cellulose can be sufficiently, completely, and uniformly etherified to render it soluble in organic solvents. Following these initial preparations of organo-soluble ethylcellulose, there came a period devoted to process improvements which has been recorded in detail by Worden.[6]

MANUFACTURE OF ETHYLCELLULOSE

The manufacture of ethylcellulose involves the steps of preparing alkali cellulose and the reaction of the latter, at elevated temperatures and under pressure, with ethyl chloride. The degree of substitution of the ethylcellulose obtained by this process is a function of the alkali cellulose composition, although the course of the reaction is influenced also by other factors, such as the temperature schedule, presence of diluents, and kind and amount of agitation.

Alkali Cellulose

Alkali cellulose for the preparation of organo-soluble ethylcellulose may contain from 0.3 to 3.0 parts of water and, correspondingly, 1.0 to 4.0 parts of caustic soda per part of cellulose.[7] These ratios have been established as the result of a great deal of empirical research. They hold only for the ethylation of cellulose to the organo-soluble stage: to prepare alkali-soluble or water-soluble ethylcellulose, or other alkyl or aralkyl ethers, different alkali celluloses are required. Thus the composition of the alkali cellulose is important. The ratio of sodium hydroxide to water affects the speed of reaction and the extent of etherification. In general, the higher the concentration of caustic soda maintained in the reaction mixture, the greater is the speed of reaction and the higher is the degree of substitution of the product.[8] This may be explained by postulating compound formation between cellulose and caustic soda.[9, 10]

Thus, according to the law of mass action, if some such equilibrium as is pictured in equation (1) exists, the reaction shown in equation (2) is favored by high sodium hydroxide concentration.

$$\text{Cell.}(OH)_3 + NaOH \rightleftharpoons \text{Cell.}(OH)_3NaOH \rightleftharpoons \text{Cell.}(ONa) + 1H_2O(OH_2) \quad (1)$$
$$\text{Cell.}(OH)_2(ONa) + C_2H_5Cl \rightarrow \text{Cell.}(OH)_2OC_2H_5 + NaCl \quad (2)$$

Little is known about such compound formation in alkali cellulose, although it has been shown that sodium cellulosate is formed by the reaction of sodium [11] or sodamide [12] with cellulose immersed in liquid ammonia, and it has been further shown that such sodium cellulosates will react with alkyl halides to form cellulose ethers if they are suitably swollen with anhydrous ammonia or with water.[13]

The function of the water content of alkali cellulose is two-fold. It acts as a solvent and carrier of the caustic, distributing it between the reaction centers (hydroxyls), and it behaves as a swelling agent, loosening the structure of the cellulose fibers so as to facilitate penetration of the etherifying agent.[9] It is significant that the alkali cellulose found most suitable for reaction with benzyl chloride,[14] a compound of comparatively large molecular volume, contains a larger proportion of water than does that found most suitable for the production of organo-soluble ethylcellulose (see above). The small ethyl chloride molecule penetrates the cellulose structure comparatively easily, so that a high degree of swelling by water is not necessary.

It is to be observed that the quantities of caustic soda solutions necessary to prepare alkali celluloses within the aforementioned range of composition are insufficient to wet the cellulose thoroughly and distribute the alkali uniformly through it. Furthermore, some of the necessary alkali solutions are liquid only at elevated temperatures. To meet these difficulties in the preparation of alkali cellulose suitable for making organo-soluble ethylcellulose, a number of methods of operation are available:

(1) Cellulose is treated with excess aqueous caustic soda of 18-40 per cent concentration to form a uniformly impregnated mass. Excess water is removed from the alkali cellulose by evaporation or by dehydrating agents.[15, 16, 17, 18]

(2) Cellulose, in divided form, is mechanically incorporated with the required amount of water and caustic soda, preferably in a ball mill.[19, 20, 21]

(3) Cellulose is immersed in caustic solution. The excess solution is pressed off, leaving a deficiency of alkali which is made up by incorporating with the press cake either solid alkali or concentrated alkali solution.[22, 23, 24, 25, 26]

(4) Cellulose is dipped in a hot, concentrated solution of caustic soda containing the required relative proportions of alkali and water.[27, 28, 29]

(5) Cellulose is ground with solid caustic soda in an inert liquid such as benzene, following which water and etherifying agent are added.[30]

(6) Powdered cellulose is stirred into a slurry of solid alkali in an inert liquid. To this mixture, water is added.[31]

(7) Concentrated alkali solution is emulsified in an inert liquid such as benzene. Granulated cellulose is mixed with the emulsion.[32]

For the preparation of alkali cellulose to be used in the manufacture of high quality ethylcellulose, absorptive cellulose of high alpha content is employed. This may be obtained by purifying cotton linters or wood pulp. However, direct conversion of most commercially purified high alpha pulps to alkali cellulose followed immediately by ethylation usually yields ethylcelluloses of high intrinsic viscosity. The production of lower viscosity types may follow one of three procedures:

(a) pretreatment of the cellulose with acid under carefully controlled conditions before converting it to alkali cellulose; [33, 34, 35]

(b) ageing the alkali cellulose after it is formed; [36]

(c) acid treatment of the finished cellulose ether.[37]

Reaction of Alkali Cellulose with Ethyl Chloride

Temperature and Pressure of Reaction. Although ethylations using ethyl chloride are said to have been carried out at room temperature,[38] temperatures usually employed lie between 90 and 140°. Since the ethylating agent and certain by-products of reaction are volatile, the etherification is performed in a closed vessel, preferably nickel-lined,[39] to avoid discoloration of the product. The pressures used are the vapor pressures of the contents of the reactor at the temperatures employed.

Use of Diluents. Ethylcellulose may be prepared by heating fragmented alkali cellulose suspended in a large excess of ethyl chloride in a closed reactor.[40] At the end of the reaction, excess ethyl chloride is separated from by-product ethyl ether and ethyl alcohol and re-used. An inert organic liquid may replace most of the ethyl chloride as a suspending agent for the alkali cellulose. Besides acting in this role, it is claimed that loss of ethyl chloride through saponification is reduced and that better penetration of the ethyl chloride into the alkali structure is attained, thus giving a more uniform etherification. Among the inert liquids that have been proposed for use are benzene, toluene, xylene,[41] dioxane, polyethers derived from the commoner polyhydric alcohols such as the dimethyl ether of ethylene glycol and the trimethyl ether of glycerol, monochlor benzene, mineral spirits and other aliphatic hydrocarbon fractions,[42] as well as tertiary alcohols [43] and acetals.[44]

Multiple Stage Reactions. It appears that maximum efficiency in the production of organo-soluble ethylcellulose, as measured by the consumption of ethyl chloride, is attained only by the use of multiple-stage reaction conditions, *i.e.*, by starting the ethylation with only a portion of the requisite alkali present and perhaps only a part of the necessary ethylating agent, and adding the remainder in one or more increments at later stages of the reaction. The advantages of this type of procedure are apparent from the data of Nowakowski,[45] who carried out comparative butylations of cellulose in single and multiple stages.

The chief side reactions that occur during the ethylation of alkali cellulose are represented by equations (3) and (4).

$$C_2H_5Cl + NaOH \rightarrow C_2H_5OH + NaCl \quad (3)$$

$$C_2H_5OH + C_2H_5Cl + NaOH \rightarrow (C_2H_5)_2O + NaCl + H_2O \quad (4)$$

The reaction of equation (3) is favored by moderately low concentrations of caustic soda (about 20 per cent) and its velocity is comparatively low at high concentrations of alkali.[46] Conversely, the formation of ether, according to equation (4), is rapid at high alkali concentrations.[9] It is apparent that multiple-stage addition of caustic soda will avoid the necessity of very high alkali concentrations in the reaction mixture at the beginning of the reaction, and thus avoid undue ether formation. Similarly, additions of caustic soda during the reaction will prevent its concentration in the reaction mixture—which falls off both on account of the conversion of caustic soda to sodium chloride and by the dilution effect of the water formed in the reaction—from reaching such a level that rate of ethyl alcohol formation is unduly high.

Conditions for the multiple-stage ethylation of cellulose have been described [47] in which the initial stage consists in the ethylation of cellulose by excess ethyl chloride to an ethoxy content of 34-40 per cent. Additional alkali is then added and the reaction is continued to produce organo-soluble ethylcellulose.

Mechanism of the Ethylation Reaction. The ethylation of cellulose, involving as it does mutually insoluble reactants, is a heterogeneous reaction. For reaction to take place, it is necessary for the ethyl chloride to dissolve in the caustic solution and penetrate the cellulose structure to reach the hydroxyl groups of the internal, molecular surfaces. The structure of cellulose can be expected therefore, largely to determine the mechanism of the ethylation.

Effect of Morphology of the Cellulose Fiber. Lorand and Georgi [14] have demonstrated that the gross structure of cellulose has a profound effect on the course of

the benzylation reaction. They swelled cellulose fibers with aqueous caustic soda and reacted them with benzyl chloride.

Microscopic observation showed that the reaction began at locations on the surface, then spread completely over the outside of the fiber, and finally proceeded inward from one growth layer to the next. Reaction similarly took place on the internal surfaces, which were reached near small cracks and capillaries that exist in fibrous cellulose, to produce a low substitution layer which swelled but did not dissolve in the benzyl chloride. Reaction in the subsequent layers was dependent upon the diffusion through the jellified swollen surface layer. This diffusion was slow until reaction in the surface layers had reached a point where the reaction product was highly swollen or soluble in the etherifying agent.

A similar mechanism obtains in the ethylation reaction.[9] The conditions are modified by the fact that the ethyl chloride molecule is smaller than that of benzyl chloride, which leads to more favorable diffusion conditions during ethylation.

Effect of Molecular Structure. Cellulose consists of long chains of anhydroglucose units joined together by ether linkages.[49] The disposition of these chains in fibrous cellulose is such that degrees of organization are exhibited by different areas of a given sample, varying from arrangement in a geometric pattern whereby crystal properties are shown, to a completely haphazard arrangement.[49] Thus cellulose contains at least two phases, *viz.*, closely packed crystalline portions of crystallites and more loosely packed amorphous portions. There is evidence [50, 51] that the amorphous part is more readily etherified than the part that is crystalline. In order to open up the crystalline portions for reaction, they must be completely swollen, for example, with aqueous alkali, which means that the preparation of alkali cellulose must be carefully performed to ensure complete swelling. During etherification, apparently the amorphous portions of the cellulose are permeated with the etherifying agent first, and later the reaction centers of the crystallites are reached.[52]

Properties of Ethylcellulose

The excellent physical properties of ethylcellulose derive mainly from the fact that it is an ether of cellulose. Being composed of long, unbranched chains,[53, 54] cellulose possesses good tensile strength and toughness, and these properties are inherited by its derivatives. In common with other cellulose derivatives, properly prepared ethylcellulose shows great uniformity of molecular weight distribution,[55] which is in contrast with synthetically prepared polymers, and gives it favorable properties as a plastic material.

Dependence of Properties on Degree of Substitution

Certain of the physical properties of ethylcellulose vary considerably with its ethoxy content. It has been reported that an ether of degree of substitution of from 0.5 to 0.7 ethoxy groups per anhydro-glucose unit is soluble in 4-8 per cent caustic soda solution at room temperature.[56, 57] Similarly, ethers of degree of substitution between 0.8 and 1.3 are soluble in cold water; as the substitution is increased above 1.4, the resulting ethers are less and less affected by water and increasingly soluble in alcohol, until at a degree of substitution of 2.1 a product is obtained which is not swollen by water and is completely soluble in alcohol.[58]

Commercial ethylcellulose contains from 2.1 to 2.6 ethoxy groups per anhydroglucose unit.[59, 60] In this range of substitution, mixtures of polar and non-polar solvents provide the best solutions of ethylcellulose, products of the higher degrees of substitution requiring higher proportions of non-polar solvent.

Technical Ethylcellulose

The properties of commercial ethylcellulose have naturally been much more completely recorded [7, 8] than have those of ethylcelluloses of other degrees of substitution.

The properties of organo-soluble ethylcellulose are a function of three main factors, namely, degree of substitution, uniformity of substitution, and intrinsic viscosity.

Degree of substitution of ethylcellulose has a marked effect on softening temperature, hardness, moisture absorption and compatibility with solvents, plasticizers and resins. The relation between softening temperature and ethoxy content is shown in Figure 1.

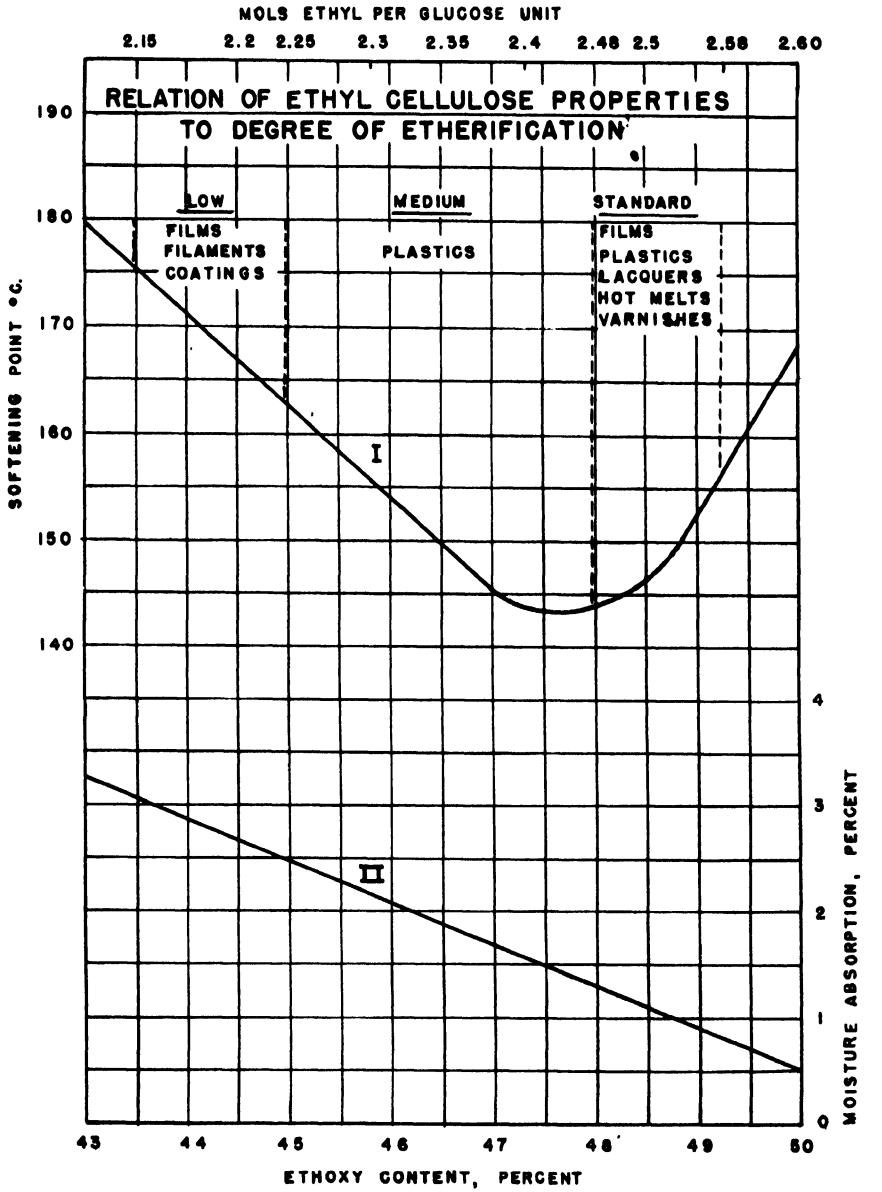

FIGURE 1.

Ethylcellulose of minimum softening point is found to be completely soluble in a wider range of solvents and to be more compatible with plasticizers and resins than are ethylcelluloses of higher and lower degrees of ethylation. This variation of physical properties with degree of substitution may be explained by taking into consideration the attractive forces between the molecules. Increasing substitution on the cellulose chains of ethoxyl groups, up to a degree of substitution of about 2.5 ethoxyl groups per anhydro-glucose unit, tends to increase the overall distances between the chains and thus reduce the degree of attraction between them. As the substitution approaches completion, however, the macromolecules become more uniform in structure and the area of contact between them increases with consequent increased forces of attraction.[55]

Figure 1 also shows the moisture absorption of films of ethylcellulose 0.0015 in thick at 21° and 90 per cent relative humidity after exposure for 6 days.[61]

The effect of the degree of uniformity of substitution of ethylcellulose is chiefly apparent in the solubility and compatibility characteristics of the material. A material which has been non-uniformly substituted may give solutions containing gels or undissolved particles, whereas ethylcellulose of good uniformity of substitution will give smooth clear solutions in the same solvent.

Because uniformity improves as substitution of the cellulose macromolecules approaches completion, effects of poor uniformity will tend to be more apparent in preparations of ethylcellulose of low ethoxy content.

Intrinsic viscosity of ethylcellulose is an expression of the chain length of the macromolecules and the chain length distribution. Like cellulose [62] and cellulose esters [63, 64] the tensile strength of films of ethylcellulose increases with the intrinsic viscosity. This relationship is shown in Figure 2, which represents approximately the elongations and ultimate tensile strengths of films from the various viscosity types of a commercial ethylcellulose containing 48.5 per cent ethoxyl.[61] The viscosity types are designated 10 cps, 20 cps, etc. These figures represent the measured viscosity in centipoises of 5 per cent by weight solutions of the ethylcellulose in a

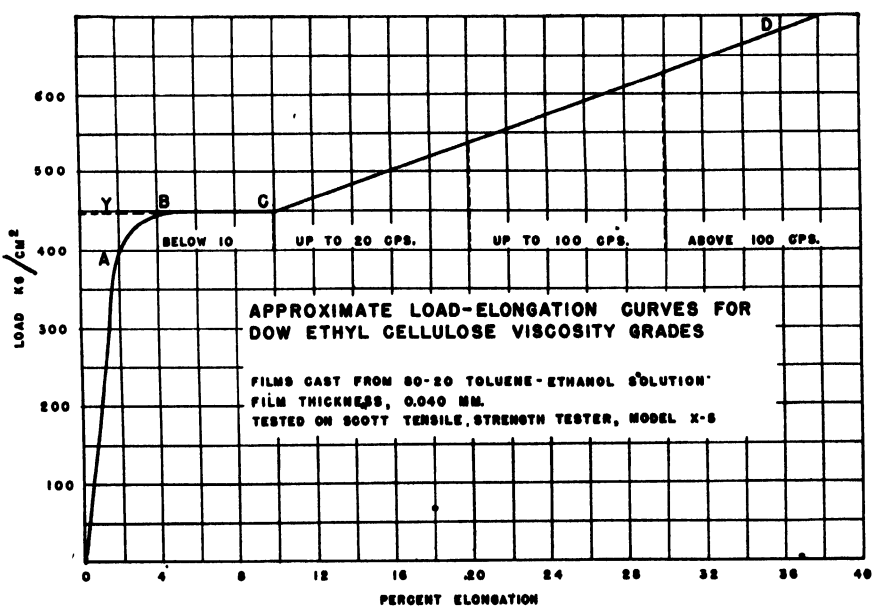

FIGURE 2.

solvent consisting of 80 parts by volume of toluene and 20 parts by volume of ethanol.

As is the case with other cellulose derivatives,[55] there is a low limit of chain length or intrinsic viscosity of ethylcellulose below which it possesses poor physical properties and loses the ability to form films. Conversely, a point is reached on increasing the molecular weight beyond which further increases results only in slight improvement in physical properties. For these reasons, technical ethylcellulose is available in viscosity types ranging only from 6-7 cps to a few hundred centipoises.

Technology of Ethylcellulose

Ethylcellulose has found three main classes of uses in the industrial arts. In the form of sheeting it has been utilized for wrapping purposes and in electrical applications. As an ingredient of thermoplastic molding compounds, ethylcellulose is finding increasing utility. Finally, in the field of protective coatings it is used in many special lacquers, hot melts and varnishes.

Ethylcellulose Sheeting

Ethylcellulose sheeting is manufactured by casting a solution of ethylcellulose on a polished surface, then stripping the film from the surface after evaporating the solvent. Ethylcellulose sheeting is made in thicknesses between 0.001 and 0.020 inch and is available both in the plasticized and unplasticized form. Some properties of unplasticized ethylcellulose sheeting are presented in Table 1.

Ethylcellulose sheeting has found particular application in the construction of semi-rigid containers.[65, 66] As a result of the intrinsic properties of the material from which they are constructed, these containers are noteworthy for their toughness and flexibility, which is retained on ageing or on exposure to sunlight. Ethylcellulose sheeting is readily cemented with solvent-type adhesives and is easily heat-formed or drawn. It may also be stapled, riveted, crimped or sewn to other materials. A variety of methods for making containers from ethylcellulose sheeting are therefore available. Dimensional changes due to variations in temperature or humidity are small. As a consequence, ethylcellulose sheeting is suited to mass production methods of making packages.

Table 1. Properties of Ethylcellulose Sheeting
(All data on 0.001" films at 70° F and 50 per cent relative humidity)

General	
Square inches per pound	24,000
Density	1.14
Moisture content (%)	1.5
Moisture permeability (gms/sq m/24 hours)	1590
Thermal	
Softening Temperature (°F)	270
Melting Temperature (°F)	330
Mechanical	
Tensile strength (lbs/sq in)	10,000
Elongation (%)	30
Folding endurance (number folds)	2,500
Optical	
Refractive Index	1.47
Transmission of White Light (%)	94
Ultraviolet cut-off (Å)	2250
Electrical	
Dielectric Constant 60— .cycle	3.2
Dielectric Constant 1000 "	3.0
Dielectric Constant 1,000,000 cycle	2.7
Power Factor 60— cycle	0.135
Power Factor 1,000 "	0.004
Power Factor 1,000,000 "	0.02
Resistivity (ohm centimeters)	$0.3 - 1.0 \times 10^{14}$

In the electrical industry, the dimensional stability of ethylcellulose films and their good retention of insulating qualities on exposure to water, light, and heat indicate their utility as a primary insulation for electric motors, and other low-voltage insulation. In addition, the toughness and flexibility of ethylcellulose films make them useful as a wrapping tape for fine wires and bars in transformer insulation. The thermoplasticity and insolubility of ethylcellulose in mineral oils makes possible the fusion of such wrapped insulation to a homogeneous single continuous covering by immersing the piece in a heated oil bath under pressure.[61]

Ethylcellulose Plastics

Plastics of ethylcellulose are compositions which have been colloided by addition of a plasticizer with the help of heat or a solvent. These colloids are hard solids at ordinary temperatures, but become soft and flowable under pressure at higher temperatures. The plasticizer lowers the temperature at which the ethylcellulose is softened by heat and decreases its resistance to flow under pressure. When the heat-softened plastic is forced into a mold, this property of flowability permits it to fill every part of the mold cavity. Upon cooling somewhat, the molded plastic becomes hard enough to be ejected as a formed object. The fact that this process is reversible characterizes ethylcellulose as a thermoplastic.

In manufacturing ethylcellulose plastics it is necessary only to add sufficient plasticizer to bring the temperature at which adequate flow is obtained under molding conditions to a point which is safely below that at which thermal decomposition may occur. For injection-molding plastics, a quantity of plasticizer equivalent to 10-20 per cent by weight of the total mix is generally enough. A greater quantity of plasticizer may be used for extrusion-molding purposes.

There exist a very large number of substantially non-volatile organic liquids which are compatible with ethylcellulose and may be used to plasticize the material in making plastic compositions.[67] Of these, however, only a limited number are commercially available and, of the latter, the majority detract from one or more of the useful properties of ethylcellulose. In general, compounds which possess some solvent power for ethylcellulose, have very low volatility and are not readily oxidized or affected by heat, light or weathering, are suitable plasticizing ingredients for ethylcellulose plastics.

In selecting an ethylcellulose plastic with particular end use for the molded article in mind, the type of ethylcellulose used must be considered. A wide range of properties of finished molded articles is possible through variation of ethoxy and viscosity types. The higher viscosity types of materials give moldings of high impact strength, but they flow with some difficulty under molding conditions. The very low-viscosity type materials give moldings that are so brittle that they are virtually useless. The ethoxy content of ethylcellulose in a plastic composition affects the amount of plastic flow that will occur under any set of temperature-pressure conditions. This is a direct result of the changes that are observed in the melting point of ethylcellulose with changes in ethoxy content (see Figure 1). Thus ethylcellulose of 47.5-48.5 per cent ethoxy content may be molded at lower temperatures than can ethylcellulose of any other ethoxy range. Despite the advantage of using a plastic that can be molded at a temperature as far as possible below its thermal decomposition temperature it is found preferable to utilize a lower ethoxy type of ethylcellulose for most plastic uses, even though higher molding temperatures are required. This preference arises from the fact that ethylcellulose of the minimum melting point is somewhat soft and easily abraded at room temperatures. Furthermore, injection moldings of such material, which have been made under the best possible molding conditions, show some tendency to laminate or foliate when abraded. To avoid this defect, it is recognized that ethylcellulose of 44-46 per cent ethoxy content should be used and the viscosity type should also be controlled.[46, 68]

The most outstanding properties of commercial ethylcellulose plastics are their toughness and strength, low-temperature shock resistance and retention of original properties on ageing or on exposure to a wide range of temperature-humidity conditions. The moldings also possess good dimensional stability and high resistance to water and to distortion by heat.[69, 70] The feature which distinguishes ethylcellulose plastics most strongly from other cellulose derivative plastics and from most other thermoplastics is their toughness at sub-zero temperatures. This is illustrated in Figure 3, which shows the impact strengths of L. T. Ethocel [70] in comparison with other injection-molding compositions over a range of temperature.

Ethylcellulose in Protective Coatings

Ethylcellulose is used in extremely varied types of protective coatings.[71] It derives its utility in this field from its good film-forming properties, its toughness and abrasion resistance, its inertness to alkalies, its resistance to heat, light and water, and its compatibility with a wide selection of plasticizers, resins, and solvents.

It is convenient to consider two general types of ethylcellulose finishes (a) those in which ethylcellulose has been incorporated in minor quantity to introduce extra toughness and solution viscosity or better film-forming qualities; (b) those in which ethylcellulose is one of the major constituents and which in consequence possess much of the abrasion, weather, heat, and chemical resistance of unmodified ethylcellulose. In the first group are certain wax-type "hot melts," varnishes, and lacquers.

The compatibility of ethylcellulose with a variety of waxes [72] has been used to advantage in making paper coatings which combine the moisture proofness of paraffin wax coatings with the gloss and good appearance of lacquer coatings. These coatings are applied to paper or other sheet material in the molten state, and are called

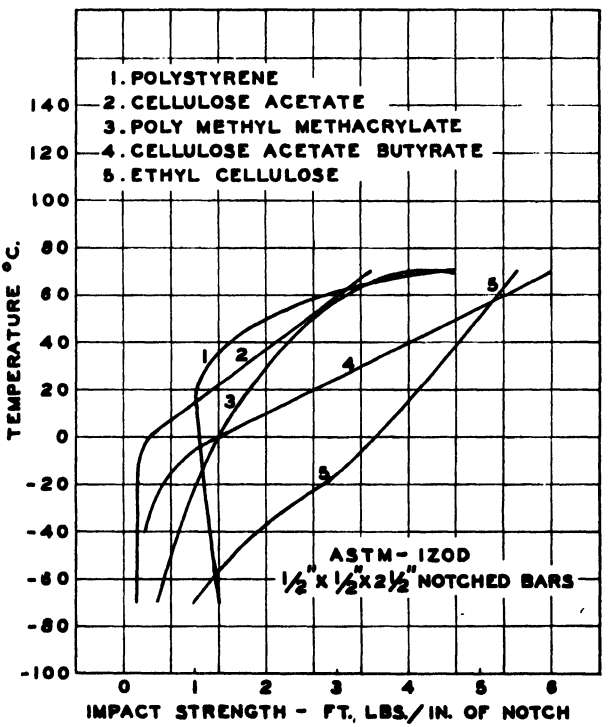

FIGURE 3. Effect of temperature on impact strength.

hot melts. They consist of blends of waxes and resins with sufficient ethylcellulose to give a coating that is materially tougher, harder and higher melting than common wax coatings.[73, 74, 75]

The presence of a minor quantity of ethylcellulose in a drying oil or oleo-resinous varnish provides initial film-forming properties that result in improved behavior of the coating during the drying period when a tough oleo-resinous film is in process of being formed by polymerization and oxidation of the oil.[76, 77] The improved behavior results in a shorter time of drying of the varnish to a tack-free condition, better "through drying" of the varnish film, and the possibility of applying thick coats without wrinkling.

The incorporation of a small amount of ethylcellulose into inexpensive lacquers improves the properties and widens the utility of these compositions. For example, addition of up to 25 per cent of ethylcellulose to pontianak or manila spirit varnishes improves their hardness, their abrasion, cold check, and moisture resistance.[78] Such modified spirit varnishes provide improved label and carton finishes and traffic paints of increased durability.

Typical of protective coatings containing substantial proportions of ethylcellulose are ignition cable lacquers. These are specialty finishes designed to prevent corona discharge over the surfaces of cotton-braided ignition cables of internal combustion engines. The coatings must be pliable, water-, oil-, and heat-resistant and provide good insulation under all conditions of use. Satisfactory coatings are made with ethylcellulose plasticized with a heat-resistant plasticizing resin.[79]

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Viscose

SANFORD A. MOSS, JR.

American Viscose Corporation

Viscose is one of the more extensively used and industrially important colloidal solutions. This orange-colored viscous liquid consists roughly of 7 per cent cellulose, 7 per cent sodium hydroxide and 2 per cent sulfur. The name is a condensation of the term *viscous cellulose,* and its industrial importance can be judged from the fact that in 1940 about 12,000,000 tons were manufactured. Since the reaction:

$$R_{Cell}—ONa + CS_2 \longrightarrow R_{Cell}—O—\underset{\underset{S}{\|}}{C}—SNa \qquad (1)$$

was discovered in 1892 by Cross, Bevan and Beadle [1] a great deal of work has been done on the subject. Many excellent papers on various phases have been published and many books on cellulose include comprehensive discussions. As well as the original researches of Cross and Bevan, it might be well to mention such authors as Reinthaler,[2] Dorée,[3] Marsh and Wood,[4] and Kline.[5] A huge amount of patent literature is available giving methods, theories, and explanations most of which is commercially useless and a great deal of which is downright misleading.

To manufacture viscose, cellulose is soaked in an 18 per cent NaOH solution to form alkali cellulose to which some investigators assign the formula $(C_6H_{10}O_5)_2 — NaOH$.[6] The sodium hydroxide solution is drained off and the cellulose is pressed until it is dry enough to be shredded and subsequently handled. In the shredded condition the alkali cellulose is allowed to age for about two days. During this aging period it depolymerizes. This fact is indicated by cuprammonium viscosity. Faust [7] showed that the hydrolysis number and copper number are not affected by the aging process and concludes that in the process a shortening of the chain and a reduction in micellar size occurs, but there is no further loosening of the structure. However, the necessity for the presence of air to cause normal aging [8] indicates that the depolymerization is due to oxidation.

Carbon disulfide is reacted with the alkali cellulose forming the sodium salt of the cellulose ester of dithiocarbonic acid, more commonly known as cellulose xanthate. This cellulose xanthate dissolved in dilute sodium hydroxide solution (approximately 3 per cent) forms the industrially important viscose. During the xanthation and subsequent dissolving, side reactions take place, giving by-products which impart to the cellulose xanthate and the viscose their characteristic orange color.

$$3CS_2 + 6NaOH \longrightarrow 2Na_2CS_3 + Na_2CO_3 + 3H_2O \qquad (2)$$

$$R_{Cell}—O—\underset{\underset{S}{\|}}{C}—SNa + 2NaOH \longrightarrow Na_2CO_2S + NaSH + \text{Cellulose} \qquad (3)$$

$$R_{Cell}—O—\underset{\underset{S}{\|}}{C}—SNa + NaSH \longrightarrow Na_2CS_3 + \text{Cellulose} \qquad (4)$$

Many other side reactions are possible depending on time, temperature and relative concentrations [9] but have little to do with the colloidal properties.

The viscose solution thus prepared is ripened at about 18° for a period of four to five days. During this period it is carefully filtered several times to remove bits of undissolved fibers, small gel particles and bits of foreign materials picked up during its passage. The viscose is then de-aerated and is ready for the regeneration of the cellulose during which process it is shaped into the form desired, principally rayon.

The formation of the alkali cellulose is a relatively rapid reaction, and the time of steeping (soaking) is determined by the time necessary for the NaOH to penetrate into the cellulose sheets (commonly used for viscose manufacture), solubilize the hemi-cellulose and other impurities, and diffuse out. If the cellulose is well opened, the operation may be completed in as little as 5 minutes.[2] However, with sheeted cellulose, steeping times of the order of magnitude of 1 hour are used. The electrolytes most effective in swelling cellulose are those with the most heavily hydrated ions. In adsorbing ions, cellulose also imbibes the water they carry, and therefore swells. Sodium hydroxide of 18 per cent concentration swells (mercerizes) cellulose but does not cause solvation.[3] The amount of hemi-cellulose present in the steeping liquor influences uniformity of reactions and subsequent colloidal properties and is consequently kept below a determined maximum. It is not economically feasible to discard the caustic after use, so a portion of the caustic which contains hemi-cellulose is sent through dialyzers where the caustic is recovered and returned to the process.[5] During the aging of alkali cellulose, the cellulose is depolymerized, as indicated by decrease in cuprammonium viscosity which is paralleled by the subsequent viscose viscosity. This lowered viscosity is desirable for the mechanical handling of the viscose in existing equipment. This limitation could be overcome, but the resistance of larger cellulose aggregates to subsequent shaping is so great that generally more is lost than gained.

When carbon disulfide is added to properly aged alkali cellulose the main reaction taking place is indicated by (1). Many side reactions occur, a few being indicated by equations (2), (3), and (4). Other possible and probable side reactions are discussed at length in much published data.[10] When alkali cellulose is xanthated, the cellulose xanthate formed imbibes a higher proportion of water, which in turn sets up such tensions that the cohesion forces holding the cellulose fibrils together are overcome.[3] Consequently, when dilute sodium hydroxide is added, dispersion (solvation) follows and the result is viscose.

Viscose is a highly viscous emulsoidal solution, as indicated by its viscosity, stability toward electrolytes, syneresis, weak electric charge, high conductivity, etc.,[5] and during the ripening period the first two of these properties undergo marked changes. It has been postulated that the colloidal changes are the predominating factor and that the chemical changes follow as a natural sequence,[11] but experience indicates the converse to be true.

The viscosity is governed by the degree of polymerization of the cellulose (controlled by type of pulp used and aging conditions of the alkali cellulose), per cent of cellulose and alkali, temperature, and ripening time. In plant practice viscoses range from 30 to 60 poises in viscosity. The actual viscosity is not as critical as is generally supposed, but is generally held within fairly close limits to match previously determined conditions of use. The finished products of the regenerated cellulose generally have a degree of polymerization of from 300-500 glucose units. The high viscosity of viscose is probably due to the fact that much of the water is present as envelop-water of the internal dispersed phase, and less of it in the continuous aqueous medium. If sodium hydroxide is added to the viscose, it raises the osmotic pressure of the external phase and thus attracts water from the envelop of the dispersed phase into the continuous phase, thus reducing the viscosity. Increasing the sodium hydroxide content from 4 to 6 per cent decreases the viscosity about 35 per cent.[5]

The degree of dispersion is the greatest, and the envelop-water and consequently the viscosity the lowest at a concentration of 8 per cent sodium hydroxide.[3] When cellulose xanthate is first dissolved, the viscosity of the solution rises—a fact probably due to an increase in the hydration of the cellulose. This period is so short that it is not generally detected and in many cases is over before mechanical mixing is completed. After this initial rise in viscosity, a curious colloidal phenomenon takes place; the viscosity begins to fall and continues to fall for from 1 to 2 days (depending on the temperature); at the end of this time it reaches a minimum and starts to rise. The viscosity continues to rise for about two weeks, at the end of which time the viscose gels. If the gel is allowed to stand, syneresis takes place. The first impression would naturally be that the initial fall in viscosity is due to depolymerization of the cellulose. However, while some degree of depolymerization occurs in every other step in the process (mainly in the aging of the alkali cellulose), practically none occurs during ripening.[12] The initial viscosity drop is probably due to the fact that, while the xanthate apparently dissolves during the mixing operation, the aggregates are quite large and very loosely held together. During the initial period these aggregates are subdividing (*i.e.*, forming more complete solution) and consequently the viscosity falls. Some authors attempt to explain this decrease in viscosity as the result of dehydration of the dispersed particles, that is, a decrease in the amount of water held by the dispersed phase due to osmosis;[11] but this does not seem likely. The subsequent increase in viscosity is due to desolvation. During the entire ripening time hydrolysis is taking place, as indicated by equations (3) and (4), and also

$$R_{Cell}\text{—O—}\underset{\underset{S}{\|}}{C}\text{—SNa} + H_2O \longrightarrow HO\text{—}\underset{\underset{S}{\|}}{C}\text{—SNa} + \text{Cellulose} \tag{5}$$

$$HO\text{—}\underset{\underset{S}{\|}}{C}\text{—SNa} \longrightarrow CS_2 + NaOH \tag{6}$$

are among other possibilities. The decrease in xanthate sulfur and increase in by-product sulfur can be readily followed. The cellulose thus regenerated is in an extremely hydrated form, but even so, its ability to retain envelop-water is far less than that of the xanthate, and coagulation is prevented only by the presence of the highly solvated xanthated particles which inhibit the association and aggregation of the cellulose. As hydrolysis continues, the viscosity increases until gelation takes place; even then it continues, and ultimately syneresis occurs. As would be expected, the higher the ratio of cellulose hydrate to cellulose xanthate the greater the ease of coagulation. The correct ratio of these two constituents coupled with the total amount of cellulose, sodium hydroxide and sulfur present controls the optimum degree of ripeness for subsequent handling, and is determined experimentally. Freshly prepared viscose is coagulated with relative difficulty and in general such extreme measures are necessary that the end product is adversely affected. Additional evidence of the colloidal nature of these changes is shown by the formation of structure during ripening,[13] and by the fact that the original viscosity may be restored (in fact, the whole ripening process may be reversed) by adding carbon disulfide to the viscose at any stage of the process.[5] The changes occurring during ripening can be represented in the following manner.[14]

$$\text{Na Cell} + CS_2 \longrightarrow \text{Na Cell Xan} \longrightarrow Na^+ + (\text{Micelle ion})^-$$

$$\text{Micelle ion, } \textit{i.e.}, \begin{pmatrix} \text{Cell Xan} \\ \text{NaCell Xan} \\ \text{Water imbibed} \\ \text{Cell reverted} \end{pmatrix} \longrightarrow \begin{matrix} \text{Cellulose} \\ + \text{NaOH} \\ + H_2O, \text{ etc.} \end{matrix} \tag{7}$$

At any period during ripening the cellulose can be precipitated as the above micelle ion minus much of the imbibed water by (1) acids weaker than dithiocarbonic acid, (2) methyl or ethyl alcohol, and (3) alkali and ammonium salts. This action is presumably one of dehydration of the dispersed phase. As the viscose grows older, lesser and lesser amounts of salt are required to cause precipitation, and it is by this means that the ripening of viscose is followed in most commercial processes. One method is to separate all the material that can be precipitated by salt and determine the ratio of sulfur in the precipitated portion (xanthate sulfur) to that in the unprecipitated portion (by-product sulfur). The more commonly used method is that of determining the concentration of salt required to cause a certain kind of precipitation; each manufacturer has his own method. These tests are for the most part empirical but are worthy of mention.

Salt Point. This test gives the concentration of common salt which just suffices to coagulate a drop of viscose allowed to fall into it. A small quantity of viscose is allowed to drop into a volume of the salt solution with stirring. There are many ways of carrying out the test, seven modifications being described by D'Ans and Jager.[15]

Ammonium Chloride Ripeness Test. This is the classic Hottenroth test which has been largely superseded by the salt point test. It is the volume of 10 per cent ammonium chloride solution required to coagulate the viscose under different conditions (20 g viscose diluted with 30 cc water). This depends on the degree of degradation of the cellulose, the number of xanthate groups still retained and the electrolytes in the solution, the temperature and the concentration of the sodium hydroxide.[16]

Other colloidal changes have been noted during ripening, such as change in turbidity, in conductivity, and in particle size, etc.,[17] but they are all a result of rather than the cause of the xanthate disintegration.

The greatest use for viscose is in the production of continuous filament rayon and rayon staple fiber. First the viscose is subjected to careful filtration during the ripening process, which removes undissolved fibers, foreign material introduced by the pulp, and to some extent gels that form during the ripening. Then the viscose is de-aerated under vacuum to prevent the escape of small bubbles during spinning. Formation of the actual filament is achieved by forcing the viscose through tiny orifices into a coagulating bath. This is called spinning. The spinnerettes are generally made of a platinum alloy and contain from 10 to 500 orifices for continuous-filament spinning and up to several thousand orifices for staple fiber spinning. The size of these holes ranges from 0.002 to 0.005 inch in diameter for various types of spinning.

The physical and chemical changes involved in coagulation are dehydration, which causes gelling, followed by the decomposition of the remaining cellulose xanthate. The first of these two changes occurs instantaneously when the viscose emerges from the orifice and largely determines the nature of the finished product. The second (chemical) change can be represented by the equation

$$2R_{Cell}\text{—O—}\underset{\underset{S}{\|}}{C}\text{—SNa} + H_2SO_4 \longrightarrow 2\text{Cellulose} + Na_2SO_4 + 2CS_2 \qquad (8)$$

which starts immediately but continues slowly for as long as several hours under usual conditions. Since so much depends on the instantaneous reaction when the viscose emerges into the coagulating medium, much work has been done on spinning baths.[12] The most generally used baths contain 7-13 per cent H_2SO_4, 13-25 per cent Na_2SO_4 and 0.5-1.5 per cent $ZnSO_4$. Organic materials like glucose are sometimes added to prevent formation of sodium sulfate crystals.[11] In some cases wetting or dispersing agents may be added.[20]

As the viscose enters the orifice it contains crystallites—rod-shaped particles dispersed at random. If in extrusion these crystallites were solidified in completely

parallel formation, a fiber of maximum strength and very low extensibility would be obtained. In actual practice this condition is, of course, not reached. The thixotropic recovery of the viscose solution is so rapid that apparently only the outer layer of each filament is frozen, an appreciable degree of parallelism being caused by passage of these rod-shaped crystallites through the tiny orifices. If the yarn was allowed to set up completely in this condition, as indicated in equation (8), the result would be a weak and very extensible product. However, before the filaments are completely set up, the drag on the thread by its passage through the spinning bath and over guides gives further orientation and the accompanying desirable tensile properties. Introduction of such orientation by a positive degree of stretch at the proper time during the regeneration was the subject of much consideration, and patents [26] and the literature [27] described this as an accomplished fact long before it was commercially perfected. It was not until the introduction of "double godet spinning" by Griffin [21] that this type of orientation could be most advantageously obtained. This is accomplished by wrapping the thread completely around a rotating wheel (godet) and from there passing it to a more rapidly rotating godet (wrapping the thread completely around the wheel one or more times) to give a positive degree of stretch, and thence passing the thread to a collecting device. When this stretch is applied at the proper time in the regeneration period a yarn of the desired tensile properties is obtained. Once this principle was definitely established, other methods of applying tension to the yarn in the plastic state by means of mechanical "braking" devices were introduced.[22] The yarn is then collected on a rotating spool or bobbin in the "spool" or "bobbin" process; or collected in the form of a "cake" by centrifugal force in a revolving bucket in the "bucket" or "pot" spinning process which is most generally used; or collected by a "cap twister" in the "continuous" spinning and purification process recently developed.[23] In the first two of these processes the yarn is subsequently washed, desulfided (with sodium sulfide), bleached (if required), finished (oiled or soaped) and then dried. By use of the right combinations of viscose, spinning bath, method and degree of stretch, finished products are produced ranging from textile yarns with a strength of 2.0 grams per denier (40,000 lbs/sq in) to high-tenacity yarns with a strength of 4.0 grams per denier (80,000 lbs/sq in), the latter for use in parachutes, tire cords, etc. Even higher strengths (up to 6.0 grams/denier) can be obtained by use of a strong (50-80 per cent) sulfuric acid [24] bath with subsequent quenching of the thread (which imparts a simultaneous coagulating and parchmentizing effect), but the finished product is so brittle that it has found no commercial application to date.

The manufacture of rayon staple fiber is substantially the same as that of continuous-filament yarn except that the main thread is much larger (up to 10,000 denier) and a number of them are gathered together and run through a cutter, after which the material is nearly always purified and dried in a continuous operation.

Cellophane, a transparent cellulose sheeting, is manufactured by forcing viscose through a long slit into a coagulating bath (casting). The thin wide sheet or film is then carried through various purifying and finishing baths, after which it runs over drying drums, the whole machine resembling a paper machine.

Sausage casings, etc., are extruded through an annular slot and the tube handled similarly.[25] Bottle-cap bands, etc., are made by coating mandrels with viscose and inserting them in coagulating baths, after which the structures are removed from the mandrels and subjected to the necessary purifying steps, as are other cellulose shapes. Artificial sponges are made by adding large crystals, *e.g.*, sodium sulfate, to viscose and then regenerating the cellulose. Subsequently the crystals are dissolved out leaving the interstices, thus forming the sponge structure. Viscose is used for sizing by coating the materials and then regenerating the cellulose on the surface.

The industrial importance of the process will be appreciated when it is considered

that in 1940 over 2,000,000,000 pounds of finished products, valued at approximately $750,000,000 were produced from viscose [5] in the United States.

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U.S. Patent 1,401,943 (Dec. 27th, 1921) illustrates an apparatus whereby the bundle of fibers, as extruded into the coagulating bath, is first wound about one cylinder (9) going at a slower speed, and then passes about another cylinder (10) revolving at a higher speed. "The stretching proper of the whole bundle of threads does not take place until they pass from the cylinder (9) to the spool (10), more meters being wound up per minute on the spool (10) than the cylinder (9) has conveyed out of the setting bath (11). For instance, when the number of revolutions of the cylinder (9) is such that it supplies forty meters per minute, while the spool (10) rotates at such a speed as to wind up fifty meters a minute, the plastic thread will be stretched twenty-five per cent." (page 2, lines 46-58). Claim 1 reads:

"The process of producing fine and uniform artificial threads, which consists in discharging the material of which the thread is formed from a plurality of fine openings, thereby producing capillary threads; coagulating such capillary threads and bringing them into a bundle, drawing the bundled threads by a positively driven drawing device; and thereafter, and as a continuing operation, winding the thread thus produced under a tension in excess of that exerted by the drawing device." J.A.

Phenolic Resins

A. J. WEITH

Director, Research and Development, Bakelite Corporation

Historical

The synthetic organic plastics industry began in 1868 with the development of cellulose nitrate, sold under the trade-mark "Celluloid," by John Wesley Hyatt. This product found many uses beyond the original aims of its inventor; but it soon became evident that other types of applications could be developed if a plastic were found to withstand higher temperatures and pressures, as well as more prolonged ageing. Such a material was announced by Dr. Leo H. Baekeland in 1909. It was a phenol-formaldehyde resin, and has been developed to a position of outstanding importance in the thermosetting plastics field. Phenol-formaldehyde resins retain commercial leadership and embody the largest amount of scientific data of any synthetic plastic. The introduction of this heat hardening type of material initiated what is now often referred to as the "Modern Plastic Era."

The products commonly accepted as synthetic resins are solid, or semi-solid, organic substances, partly or entirely amorphous, resulting from the chemical union of (usually) non-resinous materials. A substance is considered resinous because of its physical properties and physical structure rather than its chemical composition. Such materials have some properties resembling natural resins and are classed as resins because of these resemblances, which include amorphous structure, conchoidal fracture, and luster.

For about 100 years, organic chemists have been reporting certain reactions as giving "resinous bodies" rather than the crystallizable or distillable products they desired. Until the first decade of the twentieth century, these complex mixtures received scant attention from their discoverers, who were interested only in compounds that could be purified (as by crystallization or distillation) to a degree that would permit identification. Then the growing importance of natural resins in the manufacture of oil-resin varnishes caused a more critical examination of these synthetic resinous masses, and search for suitable substitutes for such natural resins as amber, copal, dammar, and shellac led to careful study of the more promising ones. Notable among these were the dark-colored transparent resinous mixtures resulting from the reaction between phenols and aldehydes, the resinous masses from petroleum oils, the resins formed from aldehydes in the presence of alkalies, and, later, the resin-like substance obtained by the reaction of glycerol with phthalic anhydride.

It was early recognized that phenols and aldehydes react to give more than one type of resinous product, and that, after heat-treatment, part of the reaction mixture might be found in a hard, infusible, insoluble form. The same chemical raw materials in slightly different proportions, when reacted under varying conditions, yielded either a product that could be melted and remelted as often as desired, or one that melted and then quickly hardened, while heated, to an infusible form. Since no one had learned to control the unpredictable reaction for yielding products that hardened with heat, the emphasis was placed on those products that would remain fusible and soluble in alcohols under heat.

It remained for Baekeland to show how to control the formation of the infusible substance, to elevate to real industrial importance the product of this reaction which had been studiously avoided. The synthetic resin industry resulted when he worked out methods of control for this refractory form, such that it could be industrially handled while still in the fusible, soluble, heat-sensitive stage. These controlled resinoid products were first described in the literature as three different reaction stages:[1] the "A" or fusible stage, the "B" or partially fusible stage, and the "C" or infusible stage.

It is fortunate for the plastics industry that Baekeland chose for study the phenol-formaldehyde reactions rather than other investigations. In the products of phenol-formaldehyde reactions, transformation processes occur rapidly at moderately high temperatures, but can be interrupted by cooling to room temperature. The fact that the maximum reaction point is well above normal temperatures permits storage of resinous compositions, thus contributing greatly to the development of practical plastic materials. But much more important was his disclosure that the proportions of the reacting materials and the character of the catalysts determine the course of the reaction, *i.e.*, determine whether the permanently fusible form or the form that may be hardened with heat would result, and, furthermore, that by a proper balance of heat and pressure, the hardenable product could be transformed in minutes, instead of weeks or months, into a dense, hard, infusible, insoluble product, superior for many industrial uses to any other resinous substance, natural or synthetic. Further development has perfected molding compounds that can be "cured" or hardened on a production basis in only a few seconds at proper elevated temperatures.

Since 1909, plastic materials have opened up entirely new industries—have enabled huge strides to be taken in already established industries. From the beginning, the phenol-formaldehyde—or phenolic—resins have maintained a leading part in this progress. Not only because of a given property, but, more often, because of an unusual combination of desirable properties, this class of materials has found many useful, divergent applications. Development has been along four major lines, so that today the phenolics are frequently classed in four groups: casting materials, molding compositions, bonding agents, and surface-coating resins.

Casting Materials

The cast phenolic resinoids were one of the first phenolic resins to become important commercially. They were cast into standard shapes in simple lead molds, and small articles—smoking pipe bits, cigarette holders, costume jewelry—were fabricated from these shapes with ordinary woodworking equipment. As molding and laminating processes were improved, the casting of phenolics gradually became eclipsed by these newer methods. In the middle 1930's, however, this process again came into commercial favor, as smaller runs of larger parts could be more economically cast in simple lead molds than in complicated compression-molding equipment. By this time many refinements in technique had helped improve quality and lower cost. Perfection of crystal-clear materials, in all colors, greatly enlarged the uses of the process for the production of many types of structural shapes, ornaments and costume jewelry; and development of a method for making two-color castings further increased the demand for materials for these applications. Use of permanent molds in place of individual lead molds—which must be stripped from the cast piece—has been successful on an experimental basis, and soon promises to become standard practice, a further contribution to lower cost and higher quality.

Molding Compositions

Molding occupies an extremely important place in the plastics industry, in many ways being analogous to the important position of "casting" in the metal industry. Molding materials contain a considerable percentage of synthetic resin as the bond-

ing agent, but also include several other ingredients to modify or accentuate the properties of the resin itself. Among the commonly used modifying ingredients incorporated into commercial molding materials are fillers, plasticizers, lubricants, dyes or pigments. Most important is the filler—wood flour, mica, asbestos pulp, macerated fabrics—which may greatly increase the strength and toughness of the molded piece. Plasticizers help in preventing brittleness and aid flow of material in the mold. Lubricants also serve this latter purpose and, in addition, facilitate removal of finished parts from the mold. Dyes and pigments produce the desired colors in the molded piece. These ingredients are blended with base resin in the desired proportions by the plastics manufacturer, and are furnished to the molder in the form of small granules, powders, preforms, or blanks.

From the start, the electrical industry has been one of the important consumers of phenolic molding materials. These plastics, because of their inherent characteristics, have a combination of properties long sought by makers of electrical equipment: high insulating value, good strength, superior dimensional stability, and ready moldability. As a result, they found countless applications in many types of electrical apparatus. For the first time, the electrical industry had at its disposal an insulating material that was tough, strong, non-warping, easily formed, and durable—especially in its resistance to solvents and oils. The communications industries (*e.g.*, radio) and the automobile companies, in particular, were quick to seize on these new materials, and their research and development work did much to speed the acceptance of the phenolics in related fields.

Uses of molding compositions soon became extremely numerous. Many of these diverse applications, however, had a requirement in common—either high heat resistance, exceptional shock resistance, extreme electrical properties, or, possibly, superior chemical resistance. Thus have emerged four major types of phenolic molding materials: general-purpose materials, shock-resistant materials, heat-resistant materials, and special materials.* Development of several different grades of molding compounds in each type has resulted in an extensive line of products that successfully meet the requirements of virtually any molding job. In general, phenolic molding materials display the following characteristics:

Dimensional Stability. Any slight change that takes place in dimensions of molded phenolic parts is not sufficient to give trouble on most uses where maintenance of accurate dimensions is essential. With the possible exception of polystyrene and vinyl chloride-acetate copolymers (thermoplastic materials) no other plastic has proved to be as dimensionally stable after molding as the phenolic materials.

Heat Resistance. The combination of properties inherent in molded phenolics makes them far superior for many heat-resistant uses. Even the general-purpose materials withstand higher temperatures than other types of thermosetting plastics.

Shrinkage. Phenolic plastics produce molded parts with very accurately predictable shrinkage.

Hardness. The surface hardness of molded phenolics is definitely better than that of other plastics.

Cold Flow. When a molded phenolic part is used under reasonable constant stress, there will be no cold flow with the proper type of material.

Moldability. From phenolics it is possible to mold parts in greater variety of sizes and shapes than with other types of plastics. Compression molding, either manual or automatic, is most commonly employed. Transfer molding † is also used extensively. Experiments under way with automatic injection molding indicate that this process may be practicable commercially in the near future. Heatronic molding [15] makes possible rapid cure and molding of hitherto impossible large sections.

* Special phenolics are grouped as follows: highly water-resistant; transparent; acid-resistant; low-loss; alkali-resistant; friction resistant; and closure type.

† See paper by C. B. Hemming in this volume.

Color. Colors available in phenolic molding materials range from light brown to black, in solid and mottled effects. Some bright transparent colors have also been developed.

Bonding Agents

One of the earliest uses of phenolic resinoids in solution was in the impregnation of paper and cloth for laminating. By 1912 the electrical industry was fabricating hundreds of insulating parts from sheets of laminated material. Development of radio gave this application a tremendous impetus, and to the present time this use has proved the largest for bonding resins. Tough, rugged, silent gears have long been made of stock laminated from cloth bonded with phenolic resins. By 1914 many durable cements based on these resins were being used in special applications throughout industry to resist moisture, steam, soaps, acids, solvents, and heat. One of the largest-volume uses was to cement incandescent light bulbs to their brass bases. Another, which put precision grinding in the metal-working industry on a mass-production basis, was resinoid bonds for abrasive wheels. A subsequently perfected application was a bond for plywood that was truly waterproof, producing a new material of construction, and expanding the plywood industry. Modifications, and similar urea-formaldehyde resin glues, have permitted plywood parts to be built up in varying thicknesses, and in complex shapes, an important contribution to the aircraft industry. Cements have been compounded to produce tough, tenacious bonds between hard, glossy materials, or soft, fibrous substances. Special insulating varnishes based on phenolic resins have been developed for saturating coils of electric motors and generators, where their high resistance to heat and moisture show particular merit.

Surface-coating Resins

Deficiencies in ordinary paints, enamels, and varnishes had not escaped attention of many of the early workers in plastics, so it is hardly surprising that considerable efforts were directed toward utilizing these recently developed inert materials in coating compositions. By 1912 lacquers based on phenolic resins were being used to protect brass beds and builders' hardware. Since that time an extensive line of heat-hardenable surface coatings has been developed to protect metals from attack by many strong chemicals used by industry. Another line of air-drying finishes, also based on phenolic resins, has found extremely wide application in protecting steel against rust in all sorts of uses—ship hulls, bridges, tanks, piping, chemical-processing equipment, waterfront structures, railway equipment, military machines—in short, any steel part that is exposed to the corrosive action of the atmosphere or chemicals. Their exceptional durability, moisture resistance, toughness, and flexibility make them of great value in protecting wooden surfaces, as in houses, boats, plywood airplanes, and the light metals aluminum, magnesium and their alloys.

Recent Developments

Definite progress has been made in laminating a variety of shapes and forms previously machined from thick, flat sheets. The widely publicized so-called plastic airplane is an outstanding example of the possibilities of processes of this nature. This process has tended to lessen the difference between the operation of the laminator and molder. Luminescent laminated material has been developed for many uses. Decorative effects achieved both by colors and by indirect fluorescent lighting produce beautiful products of excellent utility and distinctive design. Low-pressure molding (under 200 lbs per sq in) of impregnated paper and fabrics, and the post-heating of pressed sheet stocks into complex shapes have added appreciably to the expansion of applications.

An unusual use for molded-laminated stock is in the forming of asbestos shingles. Molds for this purpose are made of laminated phenolics. Allied with the laminating industry are plywood and impregnated wood. Phenolic resins continue to give the most moisture-resistant and serviceable plywood bonds. Development of planes, gliders, and boats has pointed the way to wide possibilities in this means of fabrication. Impregnation of wood with a suitable resin before bonding improves moisture resistance still further, and also increases strength across the grain. The resulting impregnated wood can be densified and laminated by hot-pressing. Thus an extremely strong piece can be obtained. Heavy sections can be made by bonding several thinner pieces, in much the same way that built up parts are made by gluing. The density of the finished articles may be varied widely by proper proportioning of the degree of impregnation and the pressure applied during curing.

In regular molding materials, there has been a shift toward the more impact-resistant products. As with laminated products, this has been because of their greater utility and the fact that they will withstand rough handling. There has been interest in using lignin, soybean meal, and rosin derivatives as extenders for phenolic resins.

Development of equipment continues. Automatic injection molding of thermosetting materials has reached a stage warranting commercial installations. High speeds of operation, along with good properties in the finished piece, are claimed. Somewhat along the same line is the much wider use of transfer molding, especially suited to impact-resistant materials. Here, also, improved speed, and better quality, are obtained. Intricate shapes, with many inserts, can be molded to close tolerances. Transfer molding, once considered only for specialty work, has reached an efficiency at which it often competes with regular compression molding.

Another development is the use of resin-impregnated paper or fabric-base board for molding. The excellent shock resistance of such materials is due not only to their long fibers, but also to the interlaced nature of these fibers. Sisal has also been employed as a filler for parts requiring extremely high shock resistance. Handles for a variety of instruments have been molded. Cutout forms—blanks punched from sheet stock composed of resins and fibrous fillers to brace weak sections of regular molded parts—are employed to great advantage. Points of high stress can be strengthened without recourse to an impact-resistant material, which, in many designs, would mean rebuilding the mold.

Glass fibers bonded with phenolic resins are finding extensive outlets in several fields due to their exceptional strength properties.

Chemistry of Phenolic Resins

The physical changes observable in the preparation of a phenolic resinoid, as the final reaction product is generally called, can follow either of two fairly well-defined courses. These are frequently referred to as the one-step, and two-step processes. The nature of the particular phenolic compound and aldehyde used, and the proportions in which they are present, as well as the conditions of reaction, determine which course is followed. With phenol itself, as well as with a number of substituted phenols, either the one-step or the two-step method is possible.

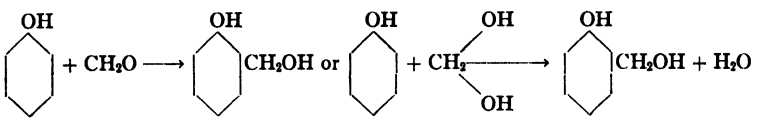
In the one-step process an alkaline catalyst is generally used, and more than one mole of formaldehyde is allowed to react with one mole of phenol. The reaction rate can be retarded at any point by lowering the temperature; and subsequent raising of the temperature causes it to proceed again, apparently as if no interruption had taken place. When the process is halted in the early stages, the product is called a *resole,* or "A"-stage resin; when it is allowed to proceed until an infusible product or resinoid is obtained, it is called a *resite,* or "C"-stage resin.

In the two-step process, the initial reaction is usually carried out in an acid reac-

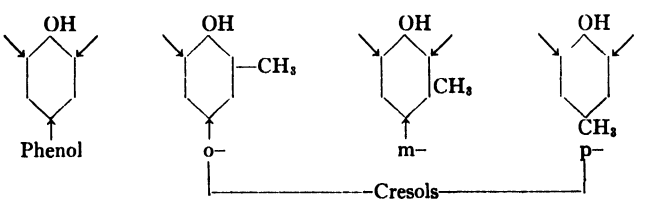
tion mixture, with the reactant ratio somewhat less than one mole of formaldehyde to a mole of phenol. The fusible intermediate product that remains after the removal of water and by-products bears some resemblance to rosin (colophony) and is termed *Novolak*. This is mixed with some other material, such as hexamethylenetetramine, capable of supplying more methylene groups. Fillers may also be added at this stage, and the mixture is converted to the infusible resinoid condition by the action of heat.

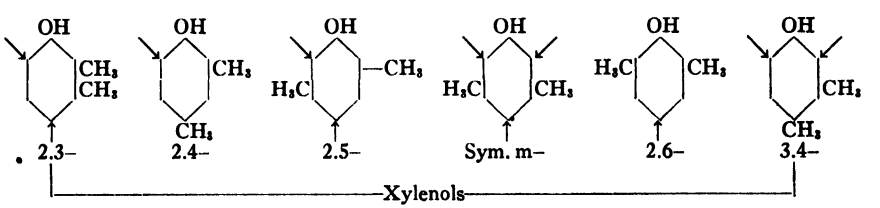
At the time of the commercial introduction of the phenolic resins in 1910, the principles of the chemical structure of high polymers were little known or understood. In fact, it was not until after 1925 that the work of Carothers, in the United States and Staudinger in Germany, on high polymers of many different types, paved the way for a sound understanding of the structural chemistry of large molecules. The earlier workers who investigated the chemistry of the phenolic resins were greatly handicapped by the lack of information on high-molecular weight compounds, and they found the complex behavior of the new products difficult to fit into a satisfactory theoretical pattern. They did, however, obtain much information, particularly about the nature of the intermediates formed, essential to the understanding of the problem as it has now been achieved. This early work has been reviewed by Baekeland [1] and by Ellis [2] and need not be described in detail here.

Two types of intermediate compounds can be shown to form in the reaction of a phenol with formaldehyde. The phenol alcohols, of which saligenin or *o*-hydroxybenzyl alcohol,

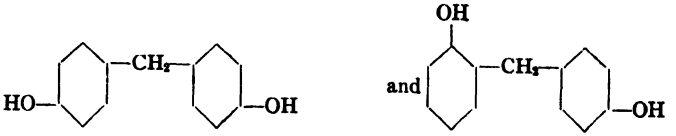


is the most familiar, were the first intermediates identified. These have been studied extensively by Granger,[3] who found that with phenol (C_6H_5OH) two monoalcohols, two dialcohols, and one trialcohol apparently are formed. This is in agreement with the suggestion of von Auwers [4] that phenol reacts with formaldehyde only in the positions *ortho* and *para* to the hydroxyl group. The reactive points for phenol, cresols and xylenols may be illustrated in the following formulas → indicating active position:

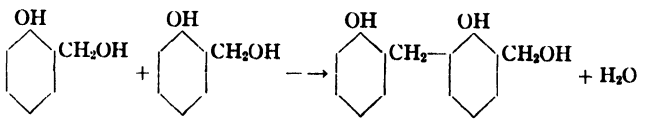




Formation of the second type of intermediate, the dihydroxydiphenylmethanes, in the acid-catalyzed reaction, was noted by Baekeland and Bender,[5] and by Megson and Drummond.[6] The compounds identified were the 4,4′ and 2,4′-dihydroxydiphenylmethanes

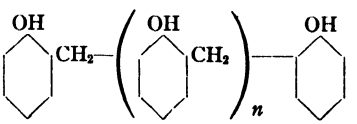


It is now evident that the behavior of these two types of compounds, the phenol alcohols and the dihydroxydiphenylmethanes, provide the key to understanding the one-step and the two-step processes. The phenol alcohols are readily formed in an alkaline reaction medium, and, when further heated, particularly in the presence of acids, undergo further condensation with elimination of water according to the following scheme:



This process, repeated over and over again by recombination of the products, rapidly leads to the formation of complex molecules consisting of phenol residues linked together by methylene groups. This is essentially what takes place in the formation of insoluble, infusible resinoid by the one-step process.

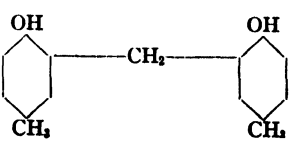
The two dihydroxydiphenylmethanes 2.4′ and 4.4′ are comparatively stable to heat, but when mixed with hexamethylenetetramine, or some other substance capable of supplying methylenes, they are also converted to resinoid. Actually in commercial practice, the Novolaks are not the dihydroxydiphenylmethanes themselves but their higher homologs of the general formula



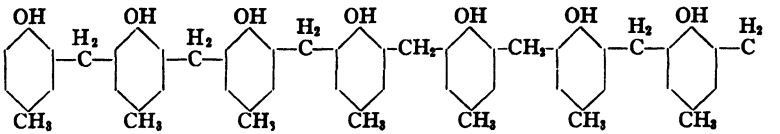
where n on the average has a value of about 4. The mechanism by which Novolak reacts with the methylene-supplying compound is not entirely clear, but there can be little doubt that the net result is not greatly different from that of the one-step process, namely, a mixture of large molecules of various shapes and sizes, consisting of phenol residues linked together by methylene groups.

The theory of the phenol-formaldehyde resin reaction as outlined above cannot be attributed entirely to any one investigator or group of investigators, but is rather a composite of the results of all those who have been active in the field. In addition to those already mentioned, Pollak and Reisenfeld [7] were among the later contributors whose results were helpful in establishing the idea of methylene linkages, but to Koebner should go a large share of credit for establishing a firm experimental basis for the explanation of the structure of the Novolaks.

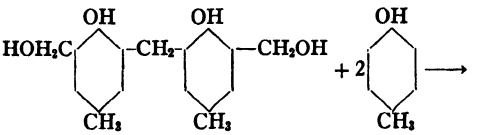
In a thorough study of the *p*-cresol-formaldehyde condensation, Koebner [8] has synthesized compounds varying from those possessing a binuclear structure thus,

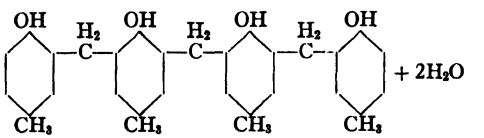


to those of heptanuclear structure,



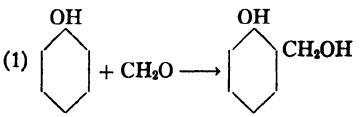
The general scheme for synthesis of these compounds is illustrated by the following reaction:



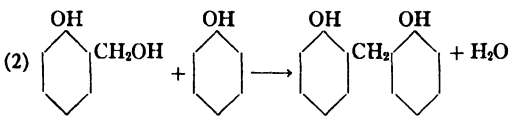


As a result of these investigations, Koebner concludes that the acid-catalyzed, permanently fusible cresol-formaldehyde resins (Novolaks) are mixtures of di-, tri-, tetra, and polynuclear compounds. The phenolic hydroxyl groups of these compounds are unchanged, and are difficultly soluble in dilute alkalies, owing to the formation of an insoluble sodium salt. Their resinous character may be due to the fact that they are mixtures of innumerable isomers and to the variety of large, and, in some instances, *extremely* large molecules.

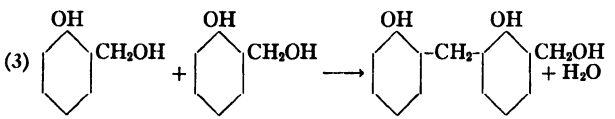
The great variety of reactions possible between phenol and formaldehyde either in neutral, acid, or alkaline solutions, and either with phenol or formaldehyde, in excess, is represented by Koebner by the following simple equations:



(alkaline reaction = phenol alcohol)



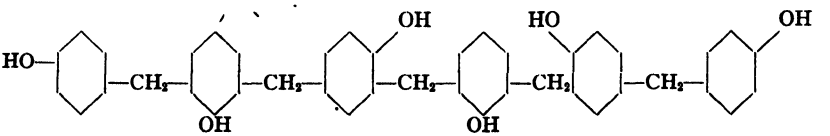
(alkaline or acid reaction = Novolak)



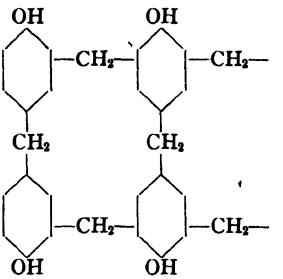
(alkaline reaction = Resol)

(4) Resol + Resol = Resit + water
(5) Novolak + formaldehyde = Resit + water
(6) Novolak + Hexa = Resit + ammonia

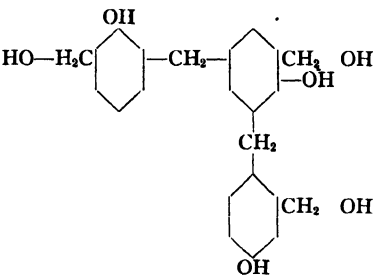
Equation (2) represents the formation of the simplest Novolak; equation (3) the formation of the simplest Resol. A typical Novolak molecule could be shown as:



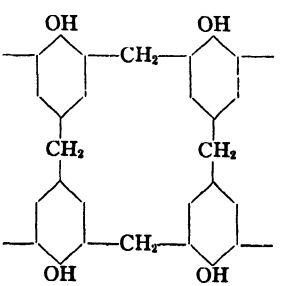
The complete hardening of this typical Novolak molecule follows the same general type of reaction which takes place in its formation and one part of such a three dimensional molecule might be



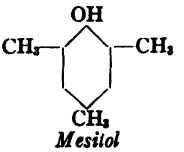
A typical Resole molecule could be



Two molecules of phenol in equation (2) react with 1.0 molecule of formaldehyde. As the ratio approaches 1 to 1, the chains that constitute the Novolak become longer, resulting in a resin of higher melting point, of lesser solubility in caustic or alcohol, and, finally, of infusibility and insolubility as the 1 to 1 limit is reached. This limit of 1 to 1 is reached only with *o*- and *p*-cresol, whereas phenol and *m*-cresol may combine with more formaldehyde, up to a ratio of 1 to 1.5, according to the following scheme:

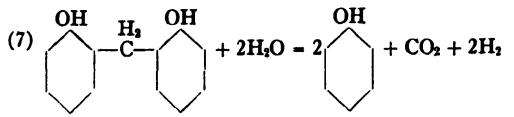


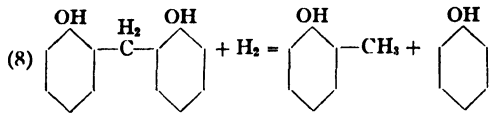
It is understood, however, that there is no regular arrangement of the chains in the final infusible form of a phenol resin, but rather a tangled mixture of various molecules whose structure is similar to that pictured above. In this connection it is interesting to note that Allen, Meharg, and Schmidt [9] reported the formation of mesitol from the degradation of a resin made from pure phenol and formaldehyde. It is difficult to see how this product could be formed except from a structure such as that shown above for the product of the reaction with the limiting ratio of formaldehyde.



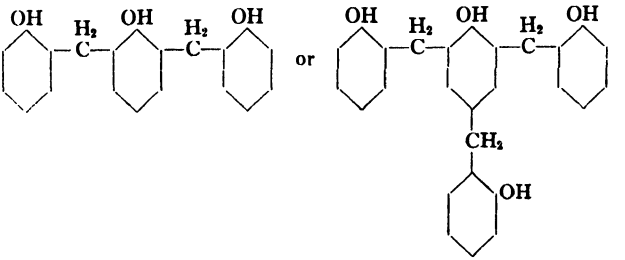
Mesitol

The mechanism of the degradation is not entirely clear and is probably somewhat involved. The net effects can be shown by equations in the following manner:





If in reaction (8) we take—

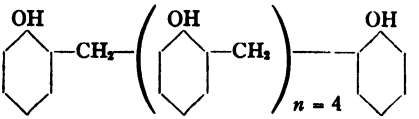


we might easily obtain xylenols and mesitol (sym-trimethylphenol) from a resin made with pure phenol and formaldehyde in harmony with the present views as to the structure of high polymers. As pointed out by Meyer and Mark [10] the tendency toward interlocking chains and three-dimensional structures is easily possible in the reaction of phenol and formaldehyde. If we substitute for phenol *o*- or *p*-cresol, in which one reactive position is blocked by a methyl group, such high-melting insoluble products are not obtained but rather compounds which belong to the chain polymers.

The constitution of Novolak has recently been the subject of an investigation by Wanscheidt, Itenburg, and Andrejewa [11] that provides convincing experimental evidence supporting the present view of its composition. They prepared a Novolak from phenol and formaldehyde in the presence of hydrochloric acid, removed free phenol with steam, then dried it by heating under vacuum. This product was fractionated by partial precipitation from alcohol solution. These fractions were examined by a number of different analytical methods with the results shown in the following table:

	Resin Fraction					
Analysis	I	II	III	IV	V	Unfractioned Resin
% of Total	10.7	37.4	16.4	19.5	16.0	....
Molecular Weight	210	414	648	870	1270	642
Polymerization Degree	1.1	3.0	5.25	7.3	11.1	5.2
% Hydroxyl	....	16.6	....	....	16.15	16.05
Average Melting Point (° C)	64	89	111	125	134	108
η_{sp} (30 per cent) in Alcohol	2.57	5.12	6.83	8.88	12.5	6.7

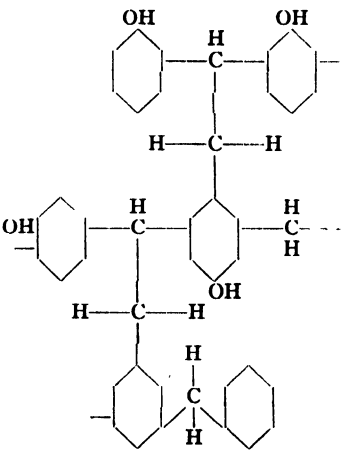
The regular increase in molecular weight, melting point, and specific viscosity shows clearly that the original Novolak is a mixture of polymer homologous compounds, and the hydroxyl values are in good agreement with the figure of 16.35 per cent calculated for a compound with the formula



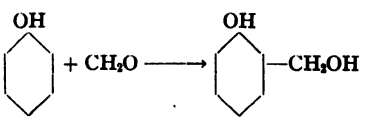
Such a compound would have a molecular weight of 624, which is close to the value of 642 found for the original sample before fractionation. The amounts in which the different fractions are found show, however, that only a small amount of the original resins would have the exact formula shown, and the greater part would consist of homologs with values of n greater or less than 4. It should also be mentioned that, in the formulas, all the points of substitution are made ortho to the hydroxyl. Actually ortho and para positions are both reactive, and the resin undoubtedly is a complex mixture of ortho and para derivatives.

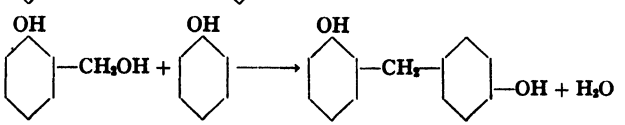
A late view of the sequence of steps by which a colloidal resin is produced involves some compromise between the views of three groups.[12, 13, and 14]

It is also conceivable methylene bridges, instead of connecting benzene rings, may exist between methylene bridges which already have formed.



In a study of the reaction products of phenols and aldehydes the following competing reactions should not be overlooked:

(1) 

(2) 

Alkaline catalysts tends to promote reaction (1), but are markedly less effective in stimulating reaction (2). Acids, almost opposite in effect, have a strong accelerating effect on reaction (2). They also promote reaction (1) but probably never at a rate exceeding the rate of reaction (2). The relative effectiveness of

the two types of catalysts explains largely the basic differences in the one and two step processes. It is well known that increase in temperature speeds these reactions but its relative effect on their rates has not been studied and no reliable information is available. These various factors account for the non-uniformity in molecular weight of the reaction products.

The following is the essence of the chaining mechanism: (a) The production of methylol compounds; (b) the union of these methylol compounds to form ethers; (c) the release of one of the formaldehyde residues to form free formaldehyde; (d) a resultant methylene-bonded polyphenol; and (e) the formation of a new methylol compound from the polyphenol which acts as a new phenolic starting material. The final resinous product consists of long polyphenol-methylene chains which terminate, according to conditions, in phenol or formaldehyde adducts. These chains are further cross-bonded with methylene residues from either formaldehyde or hexamethylenetetramine. Zinke [12] regards the chains as colloid molecules which have undergone the following process of growth: from methylol to dimethylol ether, and thence to diphenol methane by loss of formaldehyde. The diphenol methane acts as a starting phenol. Hultzsch [14] regards the methylene chains as the results of the polymerization of the unsaturated mono- and bis-methides. These polymers may, in turn, add formaldehyde, or react, by loss of water, to form extremely complicated structures.

Although the main points of structure and formation of the phenol-formaldehyde resinoids have now been cleared up, there still remains a wide field for further studies. There are almost limitless possibilities in the variations of properties brought about by changes in composition, modifications of reaction conditions, and use of new and different raw materials. Each of these factors may have an independent effect, and investigation will be needed to determine the extent and relation of such effects. It is therefore to be expected that research in the phenolic-resin field will lead to a better scientific understanding of plastics in general, and that, for many years, new and improved products will result.

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Coumarone-indene Resins

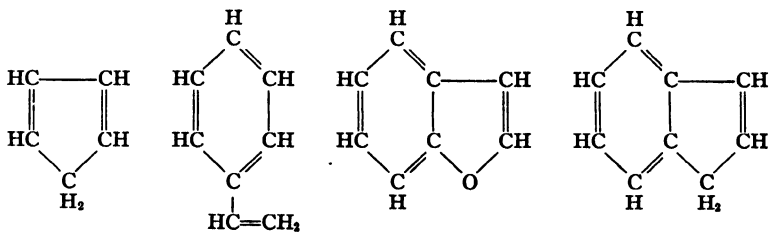
J. A. KENNEY

The Barrett Division, Allied Chemical & Dye Corporation

Coumarone and indene were first isolated in Europe from coal-tar distillates in 1890 by Kramer and Spilker, who demonstrated that these liquids could be polymerized to resinous bodies by the action of catalysts such as concentrated sulfuric acid.

Early commercial polymers were usually dark resins with variable composition and physical characteristics. The development of uniform commercial resins of the coumarone-indene type was purely an American enterprise inaugurated in the United States by the Barrett Company during World War I. The basic production methods were expanded to provide a variety of resin grades suitable for many commercial uses, including varnishes, rubber compounding, mastic floor tile, and adhesives. On this foundation there grew a flourishing industry. Today three manufacturers participate in this industry which, in 1940, produced over 24,000,000 pounds [1] and has since enjoyed considerable expansion.

The basic materials for the production of coumarone-indene resins are those bodies, usually hydrocarbons, obtained from the crude distillates recovered from by-product coke ovens or from the operation of water-gas plants. Among the most important resin-forming compounds occurring in these distillates are cyclopentadiene, styrene, coumarone-indene and homologous compounds. Typical structural formulas for these compounds are:



Cyclopentadiene *Styrene* *Coumarone* *Indene*

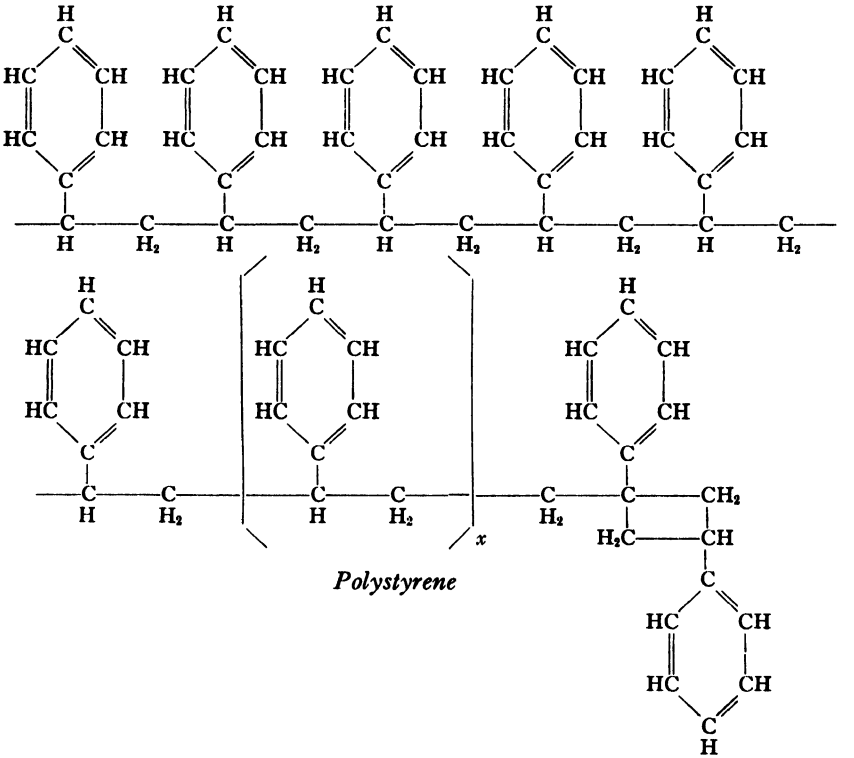
These bodies have one characteristic in common: each possesses one or more activated ethylenic linkages, to which their ready polymerizability may be attributed.

The fractions in which these compounds predominate are listed below: [2]

Cyclopentadiene and styrene	under 160°
Coumarone (B.P. 172°)	between 168-175°
Indene (B.P. 182°)	between 176-182°
Methyl coumarones	between 185-200°
Methyl indenes	between 200-210°
Dimethyl indenes	between 215-225°

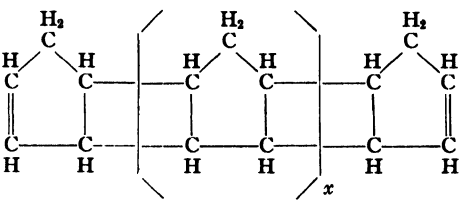
The mechanism of polymerization of this class of monomer has been considered to be a chain reaction by Staudinger and others, who have assigned typical structural formulas to these polymers.[4, 6, 7]

(5)



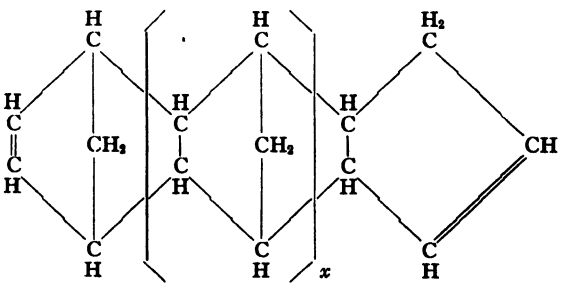
Polystyrene

(8)



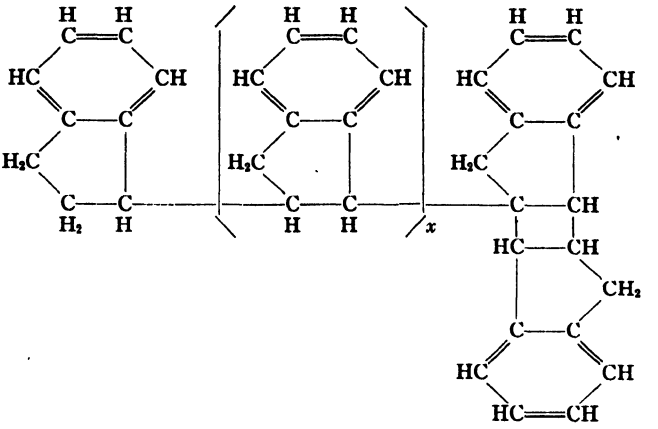
or

(9)



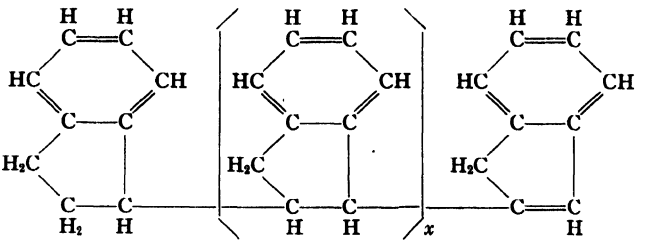
Polycyclopentadiene

(4)



or

(6)



Polyindene

The structure of the coumarone polymers is assumed to be a chain formation similar to that shown for polyindene.

These formulas aid in explaining the properties of the resinous bodies they represent and at the same time in reconciling these properties with the known constitution of the monomeric materials. Some investigators in this field have suggested that the final step in the chain reaction may involve cyclization of the chain [7] or a migration of the hydrogen to the terminal position.[5]

In the commercial production of the coumarone-indene resins the raw materials most widely employed are those coal-tar naphthas distilling in the approximate range of 150-200° which are rich in polymerizable constituents. It has not been found necessary to isolate the individual monomers or mixtures from them, for the resinification operation as the polymerization can be carried out by proper treatment of the naphtha in which these monomers occur in sufficient concentration. Heat, concentrated sulfuric acid, stannic chloride and antimony pentachloride are among the most active polymerizing agents.[3] According to the most widely applied manufacturing practice the naphthas are processed to remove acid and basic constituents, pretreated for further purification when necessary and dried.[3] The polymerization is effected by intimate admixture with small quantities of concentrated sulfuric acid. On standing, the acid settles and is removed and traces remaining are neutralized. Following the polymerization operation and removal of the catalyst, the resin is separated from the solution by distillation which eliminates the unreactive liquid hydrocarbons, leaving the molten resin in the still. The molten resin is then run to chipping equipment or, depending on the grade, directly into drums.

The quality and properties of the resin depend on the nature and derivation of the solvent naphtha fraction from which it is produced, the extent of purification or pretreatment of the naphtha and the method of polymerization employed.[3]

The diverse commercial requirements for the coumarone-indene resins have led to standardization of different forms of the resin to meet the specific properties demanded by the requirements of the different consuming industries. In Table 1 are given the specifications describing the most important of the coumarone-indene polymers and some of the special resins related to them.

Table 1. Coumarone-indene Resin Specification Chart

Type	Color Designation	Melting Range Cube-in-Mercury Method (° C)	(° F)	Ash (less than)	Form
High Melting	½, 1, 1½, 2, 2½	150-160	302-320	0.1%	Flake [10] or lump
Varnish	½, 1, 1½, 2, 2½, 3, 3½	127-137	261-279	0.1%	Flake
Medium Hard	1, 1½, 2, 2½, 3, 3½	115-125	239-257	0.5%	Flake
Rubber					
Rubber Hard	6 maximum	77-85	171-185	1.0%	Solid
Medium Soft	8 maximum	55-65	131-148	1.0%	Solid
Rubber Soft	8 maximum	45-55	113-131	1.0%	Solid
Plastic	2, 2½-8	20-30	68-86	0.1%	Viscous
	2, 2½-8	5-15	41-59	0.1%	Viscous
	2, 2½-8	*	*	0.1%	Soft Solids
Dark Grades	12 maximum	20-30	68-86	1.0	Viscous
	12 maximum	34-45	95-113	1.0	Viscous
	12 maximum	45-55	113-131	1.0	Solid
	20 maximum	75-85	167-185	1.0	Solid
	20 maximum	100-115	212-239	1.0	Solid
	20 maximum	125-135	257-275	1.0	Solid
Cycloparaffin	Waterwhite to Light Straw †	145-155	293-311		Lump
Cycloparaffin	Waterwhite to Light straw †	5-145 (in 10° Divisions)	41-293		Viscous to Lump
Alcohol Soluble	1-4	5-15	41-59		Viscous
		65-75	149-167		Solid
		85-95	185-203		Solid

* Other melting points available.
† Saybolt color determinations made on this resin in 50% solution (by weight) in petroleum benzine.

Standardization Methods

The specifications describing the standard grades of coumarone-indene resins are based on widely accepted test methods. Of most importance to the average commercial user are tests for color determination, melting point and oil solubility. Specific industrial applications occasionally require that a suitable grade of resin be selected by a test related to the process in which the resin will be applied.

Color Determination.[37] The color of the resins is determined by comparison of a solution of the resins in benzene with a set of colored solutions. The colorimetric solutions are prepared from suitable combinations of ferric chloride, cobalt chloride and hydrochloric acid to give arbitrarily fixed reproducible color standards. The color standards are sealed in standard one ounce (28 ml) square glass bottles. In making the test 2 grams of the resin are dissolved in 25 ml of benzene in a standard bottle identical with the test bottle.

The depth of color of the resin solution is compared with the standards by viewing the bottles by transmitted light. They should be held against a white background or daylight but not towards sunlight or artificial light. The colors are designated as C-½, 1, 1½, 2, 2½, 3, 3½, etc., in order of increasing color depth.

Melting Point Determination. The cube-in-mercury method is customarily used for determining the melting-point of coumarone-indene resins.

The assembly for this method is shown on Fig. 1. The resin is cast in the brass mold with the supporting rod in a central position. Low melting resins are cooled

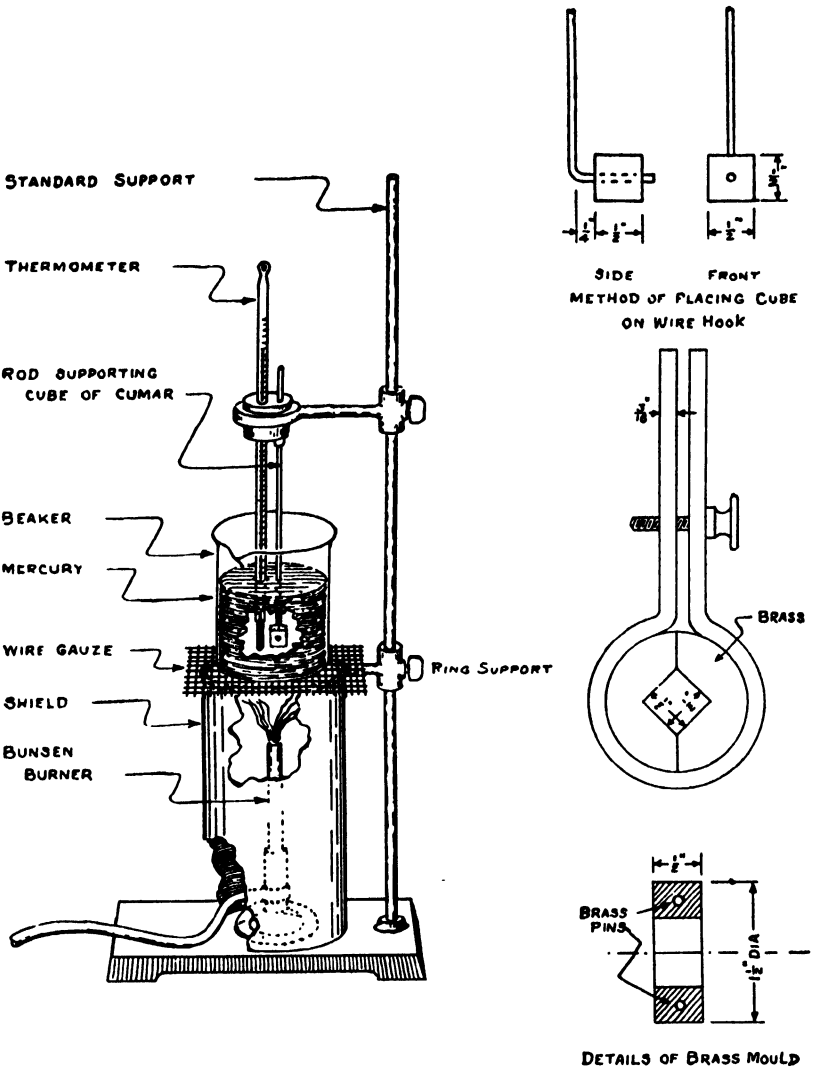


FIGURE 1. Assembly of test for Cumar * melting point cube-in-mercury method.

by surrounding the mold with ice. The cube is held under the surface of the mercury-bath as shown and the temperature of the bath raised at a uniform rate until the softened resin rises to the surface. The temperature (in degrees centigrade) at which this takes place is recorded and is converted to the corresponding air bath melting point by multiplying by 1.25 and adding 2°. This is the value usually given for resins of this type.

This air-bath melting point in ° C can be converted to the Ring and Ball melting point (A.S.T.M. D-46-26) by referring to the chart (Fig. 2).

* Registered trademark for coumarone-indene resins of The Barrett Division, Allied Chemical and Dye Corporation.

Solubility Test. This test is applied principally to the hard, pale grades to indicate resin particularly adapted for varnishes and kindred uses, and is made by blending 17.7 grams of resin with 18.2 grams of refined rapeseed oil at 140° and cooling in a test tube for one hour at 10°, 0°, and −10° while the tendency to cloud at each point is noted.

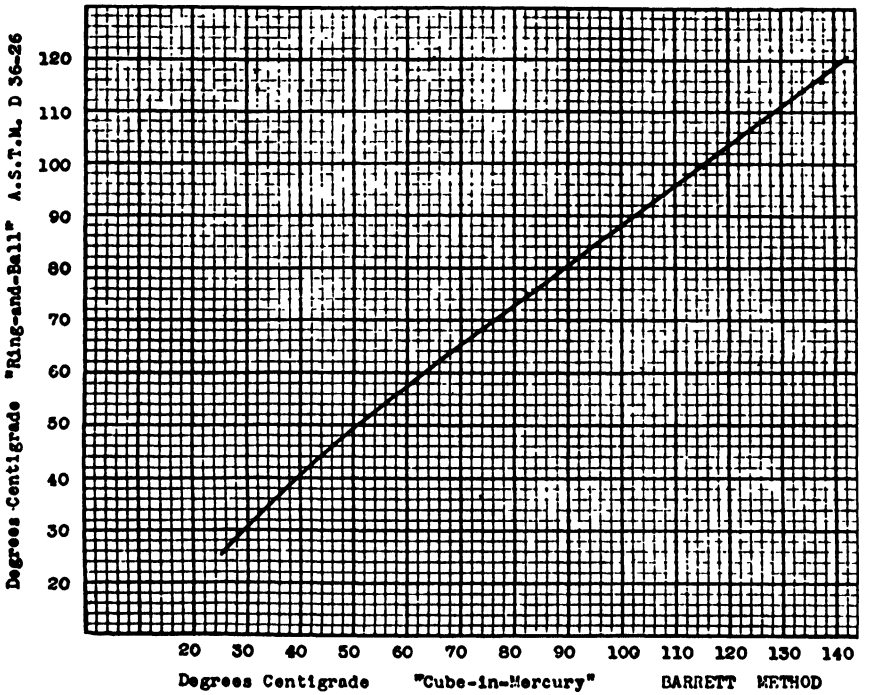


FIGURE 2. Determination of melting points approximate relationship of Barrett method to A.S.T.M. method D 36-26.

Properties of Coumarone-indene Resins

Coumarone-indene resins possess a combination of properties which make them attractive for a diverse number of industrial uses. They are strictly thermoplastic low molecular weight resins as a class and in some respects the properties of the soft or dark crude grades may differ from the hard, lighter grades. The general characteristics detailed below apply more particularly to the latter types.

Thermoplastic
Neutral and non-saponifiable
Resistant to acid, alkali, brine
Medium dielectric constant and low power factor
Low molecular weight
Optically inactive
Refractive index 1.617-1.645
Specific gravity 1.08-1.14

Thermoplasticity. Coumarone-indene resins are strictly thermoplastic and cannot be converted to an infusible stage by heating or other means.

Neutrality. The average hard grade of coumarone-indene resin has an acid number under 0.5 and is virtually non-saponifiable. These factors are of considerable importance in electrical insulation and compounds used in contact with metals and reactive metal oxides. There has been no evidence of any deteriorating effect on cellulose.

Corrosion Resistance. Alkalies, weak acids and brine have little effect on coumarone-indene resins, and their resistance to reagents of this type has brought these resins into use where this inertness is important.

Electrical Properties. Dielectric strength of the high melting grades (MP150-160°) of the coumarone-indene resins at 0.05 inch gap between electrodes (A.S.T.M. Method D-176-3ST has been determined as 490 volts per mil.

Power factors of the high-melting grades are: at 60 cycles at 80°, 0.5 to 1.0 per cent; at 1500 kilocycles at 21°, 0.04 per cent. Dielectric constant (depending on grade measured) is 2.42 to 3.45.

Low Molecular Weight. The various grades of resin differ in molecular weight, but determinations on commercial hard grades have revealed values ranging from 600 to 1000. Such resins melt to relatively low viscosity liquids and in true solvents show low viscosities at practical concentrations, a property which indicates their value for impregnation of porous substances.

Effect of Light. Coumarone-indene resins yellow and darken upon exposure to sunlight or ultraviolet light.

Effect of Heat. The low-melting, semi-liquid coumarone-indene resins flash as low as 160° and the high-melting grades up to 275°. Very slow decomposition of the higher melting coumarone-indene resins may take place at 300° but rapid decomposition is not apparent much below 340°.

Solubility and Compatibility of Coumarone-indene Resins

The following solvents will dissolve coumarone-indene resins in almost any concentration, limited only by high viscosity except where otherwise qualified:

(1) Aromatic hydrocarbon solvents, terpenes and their derivatives.
(2) Naphthenic hydrocarbons.
(3) Chlorinated hydrocarbons (a few very highly chlorinated derivatives excepted).
(4) Ketones.
(5) Ethers (soft grades will blend partially with ethyleneglycol monomethyl ether).
(6) Esters (hydroxylated esters and some polyhydric alcohol polybasic acid esters will blend only with the softer coumarone-indene resins).
(7) Cyclic, aromatic and terpene alcohols and ketones.
(8) Pyridine, aniline, some cyclicamines and nitrobenzol.
(9) Nitropropane (partial solvent).

Among the solvents in which the coumarone-indene resins are insoluble or sparingly soluble are:

(1) Alcohols (particularly lower aliphatic alcohols)
(2) Glycols and glycerine
(3) Aliphatic and some aromatic amines.

The phenol-involved coumarone-indene polymers or alcohol soluble types (see Table 1) are soluble in higher alcohols (butanol, etc.) and at high concentrations in the lower alcohols.

Petroleum Thinners. Aromatic type petroleum thinners will dissolve coumarone-indene resins, but those straight-run solvents with a low Kauri-Butanol number and high aniline point are not sufficiently effective to make stable solutions in all cases.

Accordingly, in practical use, these solvents are fortified by the addition of about 25 per cent of aromatic hydrocarbon or other stronger solvent.

The alcohol-soluble coumarone-indene resins and the cycloparaffins or highly hydrogenated types are more soluble in the aliphatic thinners.

Blends with Plasticizers, Resins and Modifying Materials

Coumarone-indene resins (high melting and plastic types) have been found to be compatible with a wide variety of materials of which the following are typical:

(1) Ester plasticizers.
(2) Rosin and resinates and non-fossil resins.
(3) Chlorinated resins and waxes (except highly chlorinated naphthalene or benzene).
(4) Oil-soluble phenolic resins.
(5) Chlorinated rubber.
(6) Polystyrene resins.
(7) Polyvinylacetal resins.
(8) Rubber and related gutta rubbers.
(9) Polymerized chloroprene (neoprene).
(10) Cottonseed pitch and straight run asphalts as well as gilsonite.[34]
(11) Long-oil alkyd resins.
(12) Coal-tar pitch.
(13) GR-S Synthetic rubber (Buna S).
(14) GR-A Synthetic rubber (Buna N).
(15) GR-I Synthetic rubber (Butyl).
(16) Ethyl and benzyl cellulose.
(17) Silicone resins.[11]

A majority of the vegetable oils will dissolve the coumarone-indene resins. Refined castor oil is an exception, although dehydrated castor oil will make suitable blends. If the oils are air-blown or highly polymerized (bodied) they do not blend completely.

Although in some instances coumarone-indene resins have been blended in small proportions with the following materials they have usually been considered to be incompatible:

(1) Shellac.
(2) Polyisobutylene.
(3) Polyvinyl acetate, polyvinylchloride and polyvinylidine chloride (Note 1).
(4) Molding type phenolic resins.
(5) Microcrystalline waxes.

Alcohol-soluble coumarone-indene (phenol involved) resins are more compatible with polyvinyl acetate.

There are numerous instances in which coumarone-indene resins have been used industrially (particularly in insulating compounds and paper coating) in blends with waxes, and laboratory tests have indicated the probable compatibility of these resins with a variety of neutral and synthetic waxes. However, blends made on a small scale do not always indicate conclusively the ability of large-scale mixtures to remain homogeneous at the slow cooling rates that obtain under such conditions. In some practical applications other resins or oils are used to maintain a satisfactory blend. Although paraffin wax will not remain blended in all proportions with coumarone-indene resins, experience has taught that the components may give stable blends when one is used with a large proportion of the other, *i.e.*, (a high ratio of paraffin to resin or the reverse). Certain of the cycloparaffins—(highly hydrogenated cou-

marone-indene resins) show much improved compatibility with paraffin or microcrystalline mineral waxes.

Industrial Applications

Coating Materials. Coumarone-indene resins have been long used in metallic paints particularly in vehicles for aluminum paints where neutral resins of this type are of particular value. These resins have been used in ready mixed, heat resisting paints and in aluminum vehicles of other types.

The good alkali-resistance of these resins has induced their wide use in alkali-resisting varnishes, concrete paints and concrete curing compounds. Various types of coumarone-indene varnishes and lacquers have been used for this purpose including blends with phenolic resins, chlorinated rubbers, ethyl cellulose and other resinous materials.

Coating technologists have taken advantages of the wide compatibility of coumarone-indene resins with many oils and other resins in developing special primers, baking finishes, ship paints, insulating varnishes and coatings for paper and fabrics.

Rubber Compounding. One of the earliest uses developed for coumarone-indene resins following their initial commercial production in the United States was in rubber compounding.[33]

Rubber technologists soon discovered that these resins were efficient softeners and tack producers which aided mill processing and imparted smooth flowing properties so essential in the production of wire insulation and other extruded and molded articles. Large quantities of the darker grades found extensive use in heel and sole stocks. In addition, both hard and soft grades were soon introduced in mechanical goods and adhesives of the solvent and latex type.

When polymerized chloroprene (neoprene) rubbers were introduced it was found that medium and soft grades of coumarone-indene resins were desirable compounding ingredients. In fact, their effects in compounding the synthetic resembled those attained with natural rubber.

Among the difficulties encountered during the rapid development of the compounding technique for GR-S (Buna-S) rubber was the necessity of utilizing channel black in order to attain suitable tensiles for use in many types of compounds. It was shown that the addition of coumarone-indene resin (M.P. 115-125° C) in GR-S (Buna-S) rubber compounds made with soft black as well as whiting, clay and other non-black fillers made possible the development of suitable physical characteristics. In this way these resins have become essential items in GR-S formulas for many rubber articles, such as wire insulations, water bottles and footwear.

Mastic Floor Tile Manufacture. The industrial production of mastic floor tile has enjoyed a rapid growth in the past ten years, and more than 60,000,000 square feet of these tiles have been laid in stores, hospitals, restaurants and industrial establishments in normal years. This tile consists principally of filler held by a binder composition made from asphalt in the case of the black tile and in the colored tile from a properly selected coumarone-indene resin plasticized with cottonseed or other fatty acid pitches or gelled oils. Coumarone-indene resins are particularly suited as they have low tinting effect and so permit economies in the use of pigment, the most expensive ingredient in colored tile. In addition, these resins are alkali-resistant and improve the resistance of the tile to alkaline cleaning powders and soap used in floor cleaning.

To produce the tile the resins are plasticized with various selected pitches derived from animal or vegetable oils to produce a binder with the desired physical properties and low coloring effect.[32] The binder, the fibrous and granular mineral filler and pigment are masticated on hot mixing rolls or in heated internal mixers of the Banbury type and subsequently are sheeted, while hot, through sheeting rolls. The sheet is passed through finishing rolls and is cut into square tile. Naturally the quality of

the tile depends not only on the raw materials but also on the technique of compounding.

Similarly plasticized coumarone-indene resins and fibrous or granular fillers have been mounted on and combined with a felt fibrous base.[12]

Molded Products. Although coumarone-indene resins are not tough and therefore not suited for high-strength molded articles, they have been used as binders for small parts and as modifying resins for other resinous binders. The good electrical properties, alkali resistance and mobility under heat have led to their use in certain molded specialties.

The coumarone-indene resins are generally modified with small proportions of other substances to increase toughness and to aid incorporation of fillers.[85] Conversely, coumarone-indene resins have been used in lesser proportions with other molding resins where their properties may improve the compound.

The value of these resins in the molding of commutator brushes and other molded electrical conducting carbons has been mentioned by McCoy.[13] Subsequent baking, first at low and then at very high temperatures serves to carbonize the resin, leaving a bonded conductor with its structure intact.

Preparation of molded electrical insulation materials from a pulp of asbestos or other fibrous material and a solution of coumarone-indene resin with tung oil in benzol has been disclosed. Premolding, expulsion of solvent and final hot molding and baking treatments have been employed.[14]

Incorporation of binder and filler without solvent by dry mixing or by wet grinding to avoid lumping has been suggested as a preliminary operation to molding.[15]

To produce impregnated articles of portland cement for insulators, etc., which could be rendered waterproof, it has been proposed to grind the cement and asbestos with coumarone-indene resin. After hydrating, molding and allowing the article to set, gradual heating is employed to cause the resin to flow and to seal the pores.[16] The treatment of molded articles of portland cement with molten resin has been suggested to effect absorption of the resin into the interstices of the material.[17] A similar treatment employing a molten combination of coumarone-indene resin and wax as a saturating medium for filling abrasive wheel voids to prevent loading during operation has been described.[18]

The use of these resins alone or in combination with tung oil has been proposed to increase the plasticity and flow in molding of products from phenolic resins.[19] Blends have been made involving highly polymerized oil (such as tung oil) with coumarone-indene resins and have been used as binders in compressed asbestos compositions.[20]

In the production of transcription records used widely in the radio industry, resins of the polyvinylacetal type have been used. Coumarone-indene resins have been used successfully as a flux with vinyl resins of this type to improve the milling and flowing properties and to aid the plastic in reproducing the fine contours of the master mold with fidelity. Records so produced are light in weight and have a minimum surface noise.

Paper Manufacture. That the value of coumarone-indene resins in the paper industry has been recognized is demonstrated by the diversity of uses in this field. Coumarone-indene resin alone and in blends has been used for stiffening fibre board and concurrently as a waterproofing agent. Application has been made in solution and as a beater size. In the latter case suspensions of the ground or powdered resin have been added to the beater and the resin entrapped in the felted fibres as the sheet was formed in the machine.[21] The full stiffening effect of the resin has been developed by raising temperature of the sheet above the flow point of the resin on the dry end of the paper machine or in a separate operation. Stocks produced by this method have demonstrated a unique workability in forming operations.

Coumarone-indene resins have been applied as extenders for oil-soluble phenolic

resins in combination with tung oil in making laminated paper goods. The resins have been applied to the sheets separately in solution. After drying the sheets between applications of each resin solution, lamination has been effected by heat and pressure.[22]

Fine packaging papers and semi-transparent glassine have been successfully coated and waterproofed with compositions containing coumarone-indene resins which add gloss and luster to the product.

An interesting composition involving coumarone-indene resin and amorphous petroleum wax has been mentioned as a waterproofing compound for container package walls.[23] The inventor uses blends of wax and high or medium melting coumarone-indene resin with ester gum as a non-volatile solvent. He claims that the combination of these materials gives a colloidal solution of the coumarone-indene resin which increases the plasticity and adhesion of the amorphous wax. He demonstrates the colloidal nature of the blend by showing the higher viscosity of the molten blend containing the coumarone-indene resin when compared with mixtures in which the resin is not used.

Miscellaneous. Blends of ethylcellulose with coumarone-indene resins, mineral oils and other modifying materials have been used in molten form for dipping metal parts. The hot melt, on cooling, forms a tough, closely clinging coat which protects the metal against corrosion during shipment even under conditions of high humidity. By making a suitable incision with a sharp instrument the coat can be peeled off when the protected article is to be used.

Adhesives. Coumarone-indene resins have been used with rubber in adhesives for many years.[36] Incorporation of the resin by milling into the rubber, addition to rubber solutions in hydrocarbon solvents and addition in emulsion form to rubber and GR-S latex are among the methods used for making suitable combinations.[80, 81] The resin has contributed tack and smoothness to the compound. More recently the high-melting grades have found advantageous use in adhesives in combination with GR-S (Buna S) rubber.

Some interesting blends of coumarone-indene resins with vinyl resins have been used in spreader coatings for cloth and in adhesives. Other adhesives based on blends of coumarone-indene resins and chlorinated rubber have been used.

Low-melting phenol or cresol-involved coumarone-indene polymers have been suggested as plasticizing or compounding agents for alcohol soluble corn-protein resins (zein).

Coumarone-indene resins have been emulsified successfully through the use of conventional emulsifying agents with or without the aid of colloid mills for stabilizing these emulsions. Typical methods for preparing such emulsions are given below:

Coumarone-indene resin (M.P. 25-50°)	22	parts	by	weight
Stearic acid	3	"	"	"
Water	74	"	"	"
Triethanolamine	1	"	"	"

Method: Melt the resin and stearic acid together and heat to 250°. Add the triethanolamine to the water and heat to 165°. Add the hot-resin melt to the water with high-speed agitation. Maintain the temperature indicated for each component until blending is finished.

Coumarone-indene resin (M.P. up to 100-110°)	38.2	parts	by	weight
Bentonite	3.0	"	"	"
Caustic soda (solid basis)	0.6	"	"	"
Corn oil fatty acid	1.9	"	"	"

Method: A jelly is prepared by stirring the bentonite into the water in which the caustic soda is dissolved. The corn oil fatty acid is added to the molten resin and the temperature of the melt is raised to a point substantially above its melting point. The bentonite jelly is heated to 80° and the molten resin is added with rapid stirring.

Special Derivatives

Phenol- or Cresol-modified Coumarone-indene Polymers. Reference has been made in this chapter to phenol-involved coumarone-indene polymers. These polymers are formed by polymerization of coumarone, indene and homologs in the presence of phenol or cresol and differ from the conventional coumarone-indene resins in their wider solubility and compatibility.[24, 25]

They are produced commercially in several melting points and colors, namely:

Viscous	5-15° C	¼-1
Soft	65-75° C	2½-3½
Hard	89-95° C	2½-3½

Unlike the standard type coumarone-indene resins, they are more readily soluble in aliphatic alcohols. They exhibit wider solubility in the higher than in the lower alcohols, although the concentrated solutions in ethanol are stable at low temperatures. They are more readily compatible with polyvinyl acetate, vinylacetate-vinylchloride copolymer resins, certain urea-formaldehyde resins, shellac, castor oil, arylsulfonamide-formaldehyde resins and in certain ratios with nitrocellulose and cellulose acetate.

Their resistance to alkalies and water is slightly less than that of the conventional coumarone-indene resins.

The phenol-coumarone-indene resins flash from 150-180° and above 200° give off fumes that are phenolic in nature. Some lots of these resins have been known to darken on standing. These resins have been employed in adhesives and special coatings.

Hydrogenated Coumarone-indene Polymers (Cycloparaffin Resins). By hydrogenating paraindene resins Staudinger [26] produced pale resins which he claimed were more heat-resistant than the original materials.

The commercial grades of these resins resulting from catalytic hydrogenation of coumarone-indene resins are water-white to pale straw in color.[27, 28, 29] Although the partly hydrogenated grades are more stable than the original coumarone-indene resins, they are slightly light sensitive. The completely hydrogenated resins do not undergo a color change in sunlight.

The commercial forms are produced in suitable steps in melting points from 10 to 155°. The hard grades are undecomposed up to 275° and flash between 275 and 350° F.

The resins are more readily soluble in petroleum naphthas and more compatible than the standard coumarone-indene resins in paraffin and other waxes. This high compatibility is more noticeable in the highly hydrogenated grades.

The cycloparaffin resins are used in pale coatings, paper coatings, wax adhesives and wax compounds.

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Polythene *

ALAN F. RANDOLPH

Plastics Department, E. I. du Pont de Nemours & Co., Inc.

The polymerization of ethylene and other olefins has been studied for some years past.[1, 2, 3] Earlier research led to the conversion of ethylene into various gases, liquids and resinous substances, or mixtures of them, which were shown to be, at least in large part, not simple polymers of ethylene, but rather the products of series of steps of splitting and polymerization,[1] which may be promoted by various catalysts.[2]

The simple straight-chain polymers of ethylene range, according to their molecular weight, from viscous liquids through gummy, sticky solids to solids of tough, flexible character which are suitable for use as plastics. The present paper is concerned only with those of the last-named type, to which has been given the generic name polythene.[4]

Polyethylenes of this type were first made by a process[5] patented by Imperial Chemical Industries Ltd., which involves heating ethylene gas under pressure. Admixture of a small percentage of oxygen[6] permits the polymerization to be conducted under lower pressures than would be necessary in its absence, but high pressures are required in order to bring about the polymerization at temperatures below that which would cause explosive decomposition to carbon and gases. The control of the operating temperature by adequate dissipation of the very large heat of polymerization, the design and construction of operative apparatus to withstand the high pressure, and the provision of reliable safety devices, have been obviously both important and difficult.[7]

General descriptions of this material appeared in several publications[8, 9, 10] at the time of its commercial announcement. A table of properties is given as an addendum to this paper.

Polythene is a thermoplastic resin, and as such can be molded, by either the compression or the injection method, and can be extruded into sheets, films, tubes, rods, filaments, and other shapes. It differs, however, from the conventional thermoplastics, such as the methacrylate resins and the cellulose plastics, in having a distinctly crystalline structure and a considerably greater coefficient of thermal expansion.

The mechanical and chemical properties of polythene, and their modification by changes in temperature, are influenced by the size of the macromolecules of polyethylene, which depends upon the conditions under which the polymerization has been carried out. The molecular weight will ordinarily be within the range 10,000-30,000. Both the average molecular weight and the distribution of molecular weights are of importance. The presence of a considerable proportion of polymer of low molecular weight is undesirable for some uses. On the other hand, a preponderance of polymer of very high molecular weight, although it promotes chemical resistance and the maintenance of flexibility at low temperatures, makes polythene rather difficult to process. Within the range of ordinary commercial material, a specimen can

* The word polythene was coined to be applied as a generic name to only those polyethylenes which are suitable for use as plastics. It is not a trade name.

be characterized well enough for most practical purposes by a determination of its viscosity in molten condition by the use of a standard orifice and under standard conditions of temperature and pressure.[7, 8]

The microcrystalline structure, which can be demonstrated by its diffraction of x-rays,[7] is responsible for the fact that polythene ordinarily exhibits a white, waxy translucence, but that, in thin sections, it can be made substantially transparent by being rapidly chilled from a high temperature, *e.g.*, by quenching in water.[11] Quenching also improves the flexibility, and the toughness at low temperatures.[8] The crystalline structure is responsible also for the ability of the resin to be cold-drawn,[12] with resulting considerable benefit to its mechanical properties through the orientation of its structure. A detailed examination of the structure by x-ray analysis has shown that the product consists of crystalline regions of orthorhombic symmetry, of unit cell dimensions $a = 7.40$ A, $b = 4.93$ A, $c = 2.53$ A (7).

The application to polythene, of any except the softer grades (*i.e.*, those of the lower viscosities),[8] of a gradually increasing tension, up to a certain critical value (of the order of 1,200-1,400 pounds per square inch), causes a gradual elongation in accordance with a modulus of elasticity of the order of 15,000. When the tension is increased beyond this point, the material yields abruptly and is stretched to four or five times its initial length before any appreciable increase in tensional stress can be developed in it.[7, 8]

This cold-drawing results in an orientation of the microstructure,* which is readily demonstrated by x-rays or by a polarizing microscope.[7] The tensile strength is increased greatly by cold-drawing, up to the neighborhood of 15,000 pounds per square inch of the reduced cross-section.

* "As in the case of other polymers of this kind, the orientation is clearly shown by examination under the polarizing microscope or by x-rays, which reveal a characteristic fibre diagram. It is now possible, in the case of crystalline polymers, to picture the change which takes place in the drawing process. Undrawn polythene consists of spherulitic aggregates of ordered regions or crystallites which can be seen under the polarizing microscope. The crystallites are to be regarded as ordered regions from which the chains project and are continued into nonoriented amorphous regions and into other crystallites. The sizes of the spherulites can be varied by thermal treatment; thus, by shock cooling, thin films can be made which are more transparent and flexible than ones which have been slowly cooled, and such films will cold draw more easily and at a lower stress. During the initial stages of stretching, orientation of the crystals takes place and can be detected by measurement of birefringence or by x-ray photography. On cold drawing, the crystallites are pulled into approximately parallel orientation, the long molecules becoming parallel to the direction of drawing; and during the process the crystals may be to some extent broken down to smaller ones. There may also be some reunion—in other words, recrystallization may occur.

"On heating at temperatures below the melting-point, this state of order tends to disappear, and the specimen will retract." (The shrinkage temperature of the oriented filament can be raised by a process of thermal conditioning[13]) "The orientation can, however, be completely removed only by heating above the melting point, although in the case of polythene of very high molecular weight, and therefore of very high liquid viscosity, extrusion or stretching produces some orientation of the molecules even above this temperature. It is of interest to compare this phenomenon with the stretching of rubber, where the rubber molecules themselves are oriented by stretching until crystallization takes place. This disappears on releasing the stress, because the freedom of rotation in unsaturated substituted chains is greater than in the saturated polythene chains at room temperature. However, rubber at low temperatures will crystallize and will also show the phenomenon of cold drawing.

"The x-ray diffraction pattern of polythene shows the presence of amorphous as well as crystalline regions; and the relative amounts of the two are of great interest, not only in the case of polythene but in the case of other crystalline polymers, since it has been found that slight changes can profoundly affect some of the more important mechanical properties. Examinations of the changes in physical properties (such as density and specific heat) with temperature indicate that there is a regular but increasingly rapid decline in the crystallinity of polythene as the temperature rises, the final traces of crystalline material disappearing at the melting point." [7]

The very low specific gravity of polythene, 0.92, is advantageous. It is about 13 per cent below that of polystyrene, 19 to 33 per cent below those of the ordinary vinyl ester copolymers, and more than 40 per cent below those of polyvinylidene chloride compounds.

In rigidity, polythene lies somewhere between the ordinary commercial categories of rigid and non-rigid. In thin sections it is pliable enough to resemble the non-rigid plastics such as plasticized vinyl copolymers and plasticized polyvinyl butyral, while in thick sections it may serve the purposes of a plastic of the rigid type.

Polythene is a notably tough plastic, and its toughness is not seriously impaired by low temperature. In the ASTM Izod impact test in a machine of 4 ft-lb capacity polythene is not broken at room temperature. At −57° C (−70° F) the Izod impact strength is 0.4 ft-lb. At −80° C (−113° F), a strip of polythene of a thickness of 0.075 inch is not broken by being folded double. In the British Avery impact machine with specimens of cross-section 0.5 by 0.5 inch, the softer commercial polythene absorbs 40 ft-lb of energy, and harder material as high as 200 ft-lb.[8]

Polythene absorbs practically no water. The amount absorbed under the conditions of ASTM test D570-42 is 0.01 per cent. Correspondingly, objects made of polythene are not subject to changes of dimensions with changes in atmospheric humidity, nor are the electrical properties of the material appreciably impaired by use in a damp atmosphere. The permeability to water vapor is very low. By ASTM test D697-42T the permeability is barely measurable. In a more severe test, the loss of weight of a container of water covered with the specimen and held for 24 hours in an air oven at 39.5° C gives figures for permeability such as

Thickness (mils)	Moisture Transmitted ($g/100m^2/hr$)
8.5	13.3
12.5	9.6
27.	3.9

In addition, polythene has remarkably high resistance to most chemicals and solvents. At high temperatures it is slowly decomposed by concentrated sulfuric or concentrated nitric acid, and swollen by concentrated acetic acid, but unaffected by concentrated hydrochloric acid and by the other acids in diluted form, or by aqueous solutions of salts. At room temperature, it is slowly attacked by strong nitric acid, but is unaffected by the other ordinary acids in any strength.

At room temperature, also, polythene is practically insoluble in all solvents. At temperatures above about 70° C it is dissolved to some extent by certain ordinary solvents and other liquids, including toluene, xylene, amyl acetate, trichloroethylene, petroleum ether, lubricating oil, paraffin and turpentine, and at temperatures above about 100° C (212° F) it becomes completely soluble in these. Even at elevated temperatures, however, it is insoluble in water, aliphatic alcohols, glycerin, ether, acetone, carbon disulfide and linseed oil. At room temperature it is not affected by chlorine, but absorbs fluorine, bromine and iodine, and at elevated temperatures it absorbs sulfur.

When heated in air, polythene is oxidized, but much less rapidly than rubber, and this oxidation can be almost entirely prevented, in the range of temperatures involved in fabricating operations, by the incorporation of certain antioxidants.[7, 8] If the conditions of manufacture or of service are such as to cause oxidation, an antioxidant should be used, since oxidation increases the power factor and also tends to stiffen the material so that it becomes difficult to process.[8]

The properties of polythene make it particularly adapted to the insulation of wires and cables. The electrical properties are excellent, particularly the low power factor, and these are not appreciably impaired by exposure to water or dampness. The resin is form-stable, tough, and pliable over a wide range of temperatures. In unmodified form or compounded with auxiliary ingredients, it is readily applied to

wire or cable in continuous lengths by extrusion. Another advantage of polythene in electrical applications is its comparative immunity to ozone; it is much less affected by ozone than is rubber.[7]

Polythene is compatible with certain resins, waxes, plasticizers and other modifiers, which may be found to alter its properties desirably for certain uses. Homogeneous mixtures with such ingredients can be made by kneading on mixing rolls or in a masticator mixer such as the Banbury. For such mixing a temperature between about 100 and 150° C (212 and 302° F) is usually required. The duration of the mixing operation should be held to a minimum both for reasons of economy and in order to mininize any damaging effects of heat and mechanical working upon any of the ingredients.

Incompatible ingredients such as pigments and fillers, as well as dyestuffs and antioxidants, may be incorporated by the same technique.

As plasticizers for polythene, certain non-resinous substances may be used, in manner analogous to the use of conventional plasticizers in other plastics. Plasticization can be effected also by incorporating polyisobutylene of high molecular weight, which does not impair the electrical properties of the polythene and improves its flexibility at low temperatures.[7, 14]

The coefficient of thermal expansion of polythene is relatively high and necessitates consideration in the design of equipment and technique for molding. Compression molds of flash type will seldom give satisfactory results with polythene because they are unable to maintain pressure upon the material as it cools and shrinks after the land surfaces have been brought together. Good results are obtained, however, with molds of positive type, in which pressure upon the article is maintained or increased [15] during its shrinkage. The cooling of the article in the mold, particularly if it is of thick section, must be relatively slow in order to minimize the strains which tend to develop by reason of the large coefficient of expansion. To be properly molded, uncompounded polythene must be heated to at least 120° C (248° F), but the use of temperatures above about 160° C (320° F) will cause the molded article to adhere to the mold. If necessary, adherence of the article to the mold can be prevented by coating the surface of the mold cavity with an external lubricant.

Polythene can be injection-molded in standard equipment. The temperature of the heating cylinder should be between about 175 and 260° C (347 and 500° F) in order to ensure adequate softening of the plastic. The temperature of the mold must be sufficiently below the softening temperature of the material to cause the molded article to harden in a reasonable time; but on the other hand too cold a mold must be avoided, since too rapid cooling will develop strains in the article and also interfere with maintaining adequate pressure upon the article as it cools. Usually good results will be had with a mold temperature of about 60° C (140° F), provided that the channels connecting the heating cylinder with the mold cavity are large enough to prevent premature hardening of their contents, with resulting failure to transmit pressure.

Stable aqueous emulsions [16] of polythene can be prepared by adding hot water to a hot solution of the resin in an organic solvent immiscible with water and containing a dispersing agent, and then volatilizing the organic solvent,[17] or by the incorporation of a dispersing agent, a protective colloid, and water.[16] Such emulsions may be used to impregnate textiles.

Coatings of waterproof and chemically resistant character may be deposited from solutions or dispersions, or by hot-melt technique or by flame-spraying.

Since no solvent is available for use at room temperature, the solution for coating with, *e.g.*, xylene as solvent must be applied hot. If the deposited layer of solution is allowed to cool, it gels, and the coating left after evaporation of the solvent is discontinuous and useless. Accordingly, either the coating must be maintained hot during evaporation of the solvent, in order to prevent gelling, or else the discon-

tinuous coating must subsequently be fused into continuity by being baked. Coatings deposited from emulsions require analogous treatments.

The hot-melt technique requires the use of material of relatively low molecular weight, and the incorporation of a suitable antioxidant to prevent oxidation during the prolonged heating.

Flame-spraying of suitably pulverized polythene containing antioxidants gives satisfactory coatings on materials which will tolerate the temperatures involved. Flame-spraying is done with a pistol which directs upon the work an adjustable flame of propane, oxygen and air. The velocity of these gases entering the pistol through an injector nozzle provides a steady delivery of finely divided polythene from a reservoir into the flame, which melts it and deposits it on the surface to be coated.[18]

Two pieces of polythene can readily be welded together by heat applied to the surfaces to be joined. Massive pieces can be joined without difficulty if care is taken to prevent oxidation during the exposure to heat. For welding and patching operations in which additional material must be supplied to fill a crevice or hole, this is preferably a mixture of polythene and polyisobutylene, rather than polythene alone.

Sheeting of polythene can be prepared by several techniques. The compound, softened by heat, may be extruded through a slit similar to that used in the preparation of continuous safety-glass interlayer of polyvinyl butyral resin, or the compound, heated and homogenized on mixing rolls or in a Banbury mixer, may be passed through a multiple-roll calender in the manner familiar in the case of rubber. The tension applied to extruded or calendered sheeting to carry it away from the point of its formation, or a higher tension deliberately applied, serves to orient the microscopic crystals of which the material is made up, and improves the mechanical strength of the sheeting. Sheeting can be made also by an adaptation of the block process heretofore used with the cellulose-ester plastics; a mass of the material is consolidated by heat and pressure into a block adhering to a bedplate, and sheets are cut from this by a planer.

Polythene is readily extruded, without solvent, to form continuous lengths of desired profile—fibers,[19] films,[20] tubes, rods, and the like—or as a covering for wires and cables. It can be extruded also in the form of a hot solution, into a hot nonsolvent which is miscible with the solvent used and serves to extract this solvent.[21]

For extrusion without solvent, equipment of the type used with other plastics is found suitable. As in any other operation of extrusion, the quality and uniformity of the results depend upon rational control of the factors involved. The compound arriving at the orifice must be homogeneous and heated to a suitable temperature, and all conditions throughout a run must be maintained constant.

The granular polythene fed into the screw is preferably not preheated. Sufficient heat to soften it and to facilitate its homogenization will be developed in its passage to the orifice; in fact, cooling of the screw may be necessary to prevent overheating and slippage. Screens should be placed at the breaker plate to hold back accidental lumps or foreign material. Optimum temperatures, once established for the throat, head and die, are kept constant by independent circulation of oil about each zone.

The extruded material is cooled so that it will hold its shape, but this cooling must be done slowly, rather than abruptly, by using first hot water and then cold water. Slow cooling is necessary, particularly in the case of material of thick section, because of the combination of poor thermal conductivity and high coefficient of thermal expansion. The decrease of volume of polythene in being cooled from 120 to 20° C (248 to 68° F) is about 12.5 per cent, and more than half of this occurs during a rapid crystallization between 120 and 80° C (248 and 176° F). If the material is cooled rapidly, the outside surface becomes relatively rigid while the center remains soft, and the decrease in volume resulting from the subsequent cooling

of the mass within this rigid shell usually results in the formation of voids and sometimes in the distortion of the cross-sectional shape. The incorporation of certain modifiers, such as polyisobutylene, which reduce the rigidity of the polythene, decreases this risk of voids or distortion, and extruded material of such a compound may safely be cooled more rapidly.

Polythene may be expected to find uses of wide variety, to which it is suited by its unique combination of properties. Probably of particular importance will be its use in electrical equipment, *e.g.*, the insulation of wires and cables, including coaxial cables for high-frequency work, where the power-loss must be small; molded cable-ends, high-voltage bushings, and dielectrics in condensers,[8] in wrapping and packaging, in gaskets and washers, in rigid piping and flexible tubing, in waterproof, chemically resistant coatings, in films and sheets for various uses, and in adhesives.[10]

Patents have disclosed the use of polythene as a binder for particles of magnetic alloys in the manufacture of cable cores, magnetic masses, etc.,[22] as insulation in high-frequency coaxial cables,[23] as interlayer for safety glass,[24] as a stiffening in collars,[25] as a casing for golf balls,[26] as a closure for containers,[27] as machine bearings,[28] as a lubricant of spinnerets in melt-spinning,[29] and as a coating of netting to provide a reinforced transparent sheeting.[30]

Polythene can be made in a porous, spongy form.[31] Admixed with specific auxiliary ingredients, polythene has been found useful for specific purposes. Thus the addition of 5 to 30 per cent of a synthetic rubber comprising the condensation product of glycerol alpha, gamma-dichlorhydrin and inorganic polysulfide improves the adhesiveness to fabric.[32] Polythene with urea-formaldehyde or phenol-formaldehyde has been proposed for the creaseproofing of fabrics.[33] Carbon black may be incorporated in polythene or chlorinated polyethylene to improve the strength and hardness of the resin and to increase its electrical conductivity.[34] It has been proposed to use certain inorganic fillers of good electrical properties.[35]

Halogenated polyethylenes are obtained by treatment of polyethylene, in solution or suspension in an inert liquid, with free halogen or a suitable halogenating compound. The properties of the product depend largely upon the content of halogen introduced, but also in part upon the conditions under which the reaction has been carried out.[36]

Chlorination has been effected to the extent of a chlorine content of about 70 per cent.[37] The character of the product changes with progressive increase in the content of chlorine. Up to about 30 per cent of chlorine, the chlorinated polymers are less rigid and more rubbery than the original polyethylene. Since the softness and pliability of such products are inherent, they may for that reason be preferable to resins with which similar characteristics are obtainable only by the addition of plasticizers, which may be gradually lost by volatilization, exudation or extraction. With further increase in content of chlorine, stiffer products are obtained, and finally a hard and brittle resin [7, 35] results.

Certain mixtures of halogenated polyethylenes of different halogen contents are said to have advantageous properties.[37] Halogenated polyethylene may be dehalogenated in order to effect a cross-linkage.[38] Part of the halogen in halogenated polyethylene can be replaced by ammonia-type nitrogen.[39]

The light-stability of halogenated polyethylenes may be improved by the addition of salicylates or of esters of aromatic acids with phenol.[40]

Sulfonyl chlorides of polyethylene are obtainable by simultaneous action of chlorine and sulfur dioxide.[41]

Processes have been described for the preparation of copolymers of ethylene with acetylene,[42] with cyclic amides,[43] and with other polymerizable organic compounds having ethylenic unsaturation.[44] It has been proposed also to dissolve polyethylene in monomeric styrene and then to polymerize the latter.[45]

Properties of Polythene

Property	Unit	Average Value [1]	Method of Test [2]
Specific gravity		0.92	D71-27
Index of refraction, n_D		1.5 at 25° C	
Tensile strength at −70; 77; 170° F	lb/in²	5000; 1900; 700 [3]	D638-42T
Elongation at −70; 77; 170° F	per cent	50; 50; 35 [3]	D638-42T
Modulus of elasticity at 77° F	lb/in²	14,600	D638-42T
Shear strength in thickness 0.040 in	lb/in²	990	Johnson shear jig
Tear-resistance in thickness 0.075 in	lb/in	440	D624-41T
Flexural strength at 77° F	lb/in²	1,700	D650-41T
Stiffness at 77° F	lb/in²	13,300	D747-43T
Impact strength, Izod	ft-lb/in	[4]	D256-43T
Hardness, Rockwell, at 77° F		R27	D229-43
Flow temperature	° C	104	D569-43
Deformation under load at 122° F	per cent	20	D621-43 [5]
Strain-release temperature	° C	75-80	du Pont
Yield temperature	° F	140	du Pont
Heat-distortion temperature, low-load	° F	122	[6]
Specific heat		0.5	
Coefficient of expansion per degree F		10.5×10^{-5}	D696-42T
Thermal conductivity	Btu/hr/ft²/° F/in	2.96	Cenco-Fitch apparatus
Dielectric constant at 60 to 10^8 cycles		2.3	D150-42T
Dielectric strength, short-time, in thickness 0.125 in	v/mil	475	D149-40T
Dielectric strength, step-by-step	v/mil	1000 [7]	
Volume resistivity	ohm-cm	greater than 10^{15}	D257-38
Power factor at 60; 10^6, 10^8 cycles		less than 0.0005	
Water-absorption	per cent	0.01	D570-42
Moisture-permeability in thickness 0.0085 in	g/100m²/hr	13.3	see text
Flammability in thickness 0.125 in	in/min	1.1	D635-41T
Effect of outdoor exposure		no discoloration, but	
Effect of accelerated weathering		in the absence of stabilizer the tensile strength and elongation decrease	
Basic color		white translucent [8]	
Resistance to solvents and chemicals		resistant to water, alkalis, acids and oxygenated solvents; at elevated temperatures not resistant to chlorinated solvents and aliphatic and aromatic hydrocarbons	

[1] For most of the properties the values obtained will be influenced by the method of preparation of the specimen.
[2] The numerical designations are those of ASTM methods.
[3] These values obtained on injection-molded test bars. Sheets of thicknesses 0.020 to 0.075 inch tested at 77° F by method D412-41, die C, gave tensile strength 1700-2400, elongation 200-600.
[4] At room temperature is not broken in a 4 ft-lb machine; at −70° F, 0.4 ft-lb.
[5] Test made with load of 1200 lb/in² since the 4000 lb/in² of the standard test was designed for more rigid plastics.
[6] Maximum fiber stress 66 lb/in²; proposed revised method D648-42T.
[7] Values obtained on early experimental material.
[8] Antioxidant added for electrical uses imparts a light brown color.

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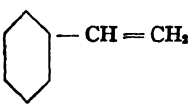
Polystyrene

IVEY ALLEN, JR., AND LAURENCE HUMPHREY

Research and Development Laboratories, Bakelite Corporation

A fertile field of organic chemistry has been opened up by the investigations of the past fifteen years on organic compounds of high molecular weight. Some beginnings had been made much earlier, particularly in the studies on cellulose and rubber, but it was the work of Carothers in this country and Staudinger in Germany on synthetic high polymers that really provided the scientific basis for the treatment of high-molecular-weight substances as a distinct class of organic compounds. The individual molecules are often so large that they show behavior normally associated with colloidal particles, which indeed they probably are. The properties of polystyrene clearly illustrate this fact.

Styrene, the monomer



is a mobile liquid boiling at 145° and having a refractive index of 1.5439 at 20°. On long standing at room temperature it gradually becomes more viscous and finally a hard, tough, glassy solid. Heat and certain catalysts cause the change to take place more rapidly. At any intermediate stage the viscous mixture can be shown to consist of a solution of polystyrene in unreacted monomeric styrene by pouring it into a solvent such as methanol which dissolves the monomer but not the polymer. Moreover, the polymer formed in the early stages of reaction can be shown to be not much different * in properties from that formed at any later stage; and, when the separated polymer is heated further at the polymerizing temperature in the absence of monomer, little change takes place.

The polymerization of styrene was reported in the literature as early as 1839[18] but received little attention until after Baekeland's work with the phenol-formaldehyde resins had shown the way to the commercial development of synthetic plastics. The characteristic property that most of the styrene polymers shared with other substances such as rubber and the soaps was the high viscosity of their dilute solutions in certain solvents. After McBain [10] had shown that soap molecules in solution associate to form large aggregates or micelles, and that the high viscosity of the solution was due to the presence of these micelles, there were a number of investigators [6, 8, 13, 15] who believed that the peculiar properties of the so-called highly polymerized compounds or neutral colloids such as rubber, cellulose, and polystyrene might be due to the same sort of effect. However, the work of Staudinger on polystyrene and other polymers of the vinyl type, and of Carothers on the condensation type, soon showed that it was primarily the large size of the individual polymer molecules and their manner of orientation that determined the properties of this class of substances.

* There is some evidence indicating a higher average molecular weight for polymer formed near the end of the reaction than for that formed at the beginning.[7]

By the polymerization of styrene under different conditions, a series of polymers showing a range of properties can be obtained. In one investigation [19] it was found that the product formed at 240° had a molecular weight of 3,500, was readily soluble in ether, could be easily powdered in the solid state, and dissolved in benzene without swelling, giving solutions of low viscosity. On polymerization at 15°, the product was almost completely insoluble in ether, and swelled greatly on dissolving in benzene. The solid was not friable, and the average molecular weight was much too high to be determined by the usual methods. When polymerization was carried out in dilute solutions in the cold with stannic chloride as the catalyst, the product had an average molecular weight of 2,500, and its properties were similar to those of the polymer formed at 240° without a catalyst. By the use of solvents it was separated into fractions varying in molecular weight from 1,100 to 13,000.

The higher-molecular-weight products give solutions that are extremely high in viscosity. It had been recognized by many investigators that some sort of relationship existed between molecular weight and viscosity, but quantitative information and a consistent theory on the subject were lacking.[22] Staudinger and numerous coworkers carried out an extensive investigation of this relationship for polystyrene as well as for several other such polymer homologous series, and concluded that within the limits of the usual methods for determining molecular weights the following relationship is valid:

$$\frac{\eta sp}{C} = Km\,M$$

Here ηsp, the specific viscosity, is given by the expression $\eta r - 1 = \eta sp$. The relative viscosity, ηr, is obtained by dividing the time of flow for the solution by that for the pure solvent. The concentration, C, is in terms of base moles per liter, that is, for polystyrene $C = 1$ for a concentration of 104 grams per liter of solution. M is the molecular weight and the constant, Km, was assigned the value of 1.8×10^{-4} by Staudinger. The relationship is applied only for dilute solutions where the viscosity-concentration relation is constant.

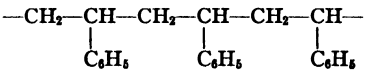
Ever since this equation was proposed it has been the subject of many investigations by others working in the field. It is now generally accepted as being a useful and convenient tool, subject to considerable limitation where rigorous accuracy is required.[9, 11]

The determination of molecular weight by the osmotic method is subject to much less limitation on theoretical grounds and has been used by Schulz for a study of the accuracy of the Staudinger equation. Schulz and Dinglinger [17] found that in general the values obtained by the viscosity method were too low when the Km value of 1.8×10^{-4} was used, and that the correct value depended on the conditions under which the polystyrene was prepared. According to their results, when the polymerization temperature is 20°, $Km = 1.5 \times 10^{-4}$ and decreases with increasing polymerization temperature to 0.48×10^{-4} for 140°. It was also found that when any particular polymer sample was separated by partial precipitation into fractions of different molecular weight, the different fractions all required the same Km value as the original unfractionated polymer. The variation in Km is considered to be a measure of the extent to which branching has occurred during the formation of the main polymer chain. The mechanism of branching is still the subject of investigation, as is that of the polymerization reaction itself. The two must be closely related.

The reaction mechanism has been investigated by a number of workers,[2] usually without adequate experimental results on which to reach definite conclusions. The most complete investigation on polystyrene, as distinguished from other polymers of the vinyl type, is that described by Schulz and his collaborators in a series of papers which have appeared in *Zeitschrift fur Physikalische Chemie* since 1936.

According to Schulz and Husemann [16] the reaction is of the first order up to at least 90 per cent conversion, and involves three distinct steps: (1) chain initiation, (2) chain propagation, and (3) chain termination. The rates of the second and third steps determine the average molecular weight. Chain initiation or activation is the slowest and hence the overall rate-determining process. These conclusions were reached on the basis of determination of the rate of conversion, the constancy of molecular weight throughout the reaction, and the shape of the polymer distribution curve. Although in disagreement with many other workers as to detail, the conclusions reached by Schulz agree in principle with those of most of the others, and probably represent the most useful hypothesis for the treatment of the styrene polymerization.

The original proposal of Staudinger as to the structure of the polymer was that the styrene units were linked together in such a way as to give the 1-3 configuration shown below.



This still appears to be the most probable form, although some evidence in support of a 1-2, 1-4 form has been presented,[14] and recently Barnes and Kropa [1] proposed a third possibility on the basis of infrared absorption studies that indicated the formation of methyl groups during polymerization.* Some recent work of Marvel and Moon [12] tends to support the 1-3 structure proposed by Staudinger, and that formula is also supported by the evidence obtained from destructive distillation of the polymer. Among the products formed in this process Staudinger and Steinhofer [20] reported 1,3-diphenyl propane, 1,3,5-triphenyl pentane, and 1,3,5-triphenyl benzene. Destructive distillation becomes evident when polystyrene is heated to 330-350° and is quite rapid at 360-375°. Experiments in the Bloomfield laboratories of Bakelite Corporation have shown that toluene and isopropenylbenzene are also products of the decomposition, and the formation of the latter compound is most simply explained on the basis of the 1-3 structure.

More information about the structure and chemical composition of polystyrene is desirable because of the direct relationship between these factors and the physical properties of the product. In particular, the flow characteristics or viscosity at various temperatures must be considered, because industrial applications of the material are largely dependent on the fact that it flows under pressure when hot and then hardens to a durable, rigid state on cooling. One of the industrial processes that exploits this property is called injection molding.†

Injection molding consists essentially of heating a thermoplastic material in a specially constructed chamber until it becomes plastic, then forcing it through a small orifice into a cool mold. The mold is kept closed until the plastic has cooled and hardened. It is then opened, the molded plastic piece removed, and the process repeated.

The temperatures involved in injection molding are usually much higher than those used in compression molding. There is considerable variation with different machines and different types of thermoplastics, but the temperature in the plastic at the point of injection usually falls somewhere in the range of 160-230°. The flow characteristics and the stability of the material at these comparatively high temperatures are therefore of prime interest in a practical way. A critical examination of polystyrene with regard to these two factors shows that it possesses flow properties

* This view now appears very doubtful, in the light of evidence presented by N. Wright at the Memphis meeting of the American Chemical Society, April, 1942.

† For a more complete and detailed discussion of injection molding, see "Molding Technic for Bakelite and Vinylite Plastics," Bakelite Corporation, New York, 1941.

that make it particularly well suited to injection molding and that its thermal stability makes it compare favorably with other thermoplastic resins.

Thermal stability has been studied under a variety of conditions, and it is necessary to draw a distinction between oxidation, which is promoted by heat, and true thermal degradation, which occurs in the absence of oxygen. The breakdown that occurs on prolonged heating above 100° but below the temperature of destructive distillation has been investigated, and the effects obtained at 135° and 160° were shown to be due to surface oxidation. The effect is negligible in the interior portion of the mass or when the heating is carried out under nitrogen. Even in air at 160° it develops slowly and takes several hours to become readily detectable. It has also been found that a rapid decrease in molecular weight throughout a molten mass of resin does not begin to occur until a temperature of about 250° is reached.

In one experiment polystyrene was molded in a familiar type of commercial injection-molding machine, equipped with a 2-oz cylinder, under conditions such that the temperature of the material at the injection orifice was about 240°. The material prior to molding gave a viscosity of 53.1 centipoises in 10 per cent toluene solution. With molding cycles up to 2 minutes, the molded pieces, when broken up and tested, showed viscosities practically the same as that of the original material. When a 4-minute cycle was used, the viscosity dropped from 53.1 to 42.8 centipoises. In practice the molding cycle is seldom more than 20 or 30 seconds, and the temperature reached by the material is rarely higher than 200-220°. Under such conditions the effect of the molding operation on the molecular weight of the material probably could not be detected.

With proper temperature control it is possible to extrude polystyrene by a variable-pitch screw without excessive degradation. The equipment used is similar to that long familiar in the rubber industry. Extruded rods and tubes are produced commercially in a wide variety of sizes. The mechanical work done on the polymer by the screw apparently is not an important factor in degradation, except as it serves to mix in atmospheric oxygen. There is still uncertainty concerning the relation between the three factors of heat, oxygen, and mechanical work as to the part each plays in molecular breakdown, but the indications are that mechanical work of itself is not particularly detrimental. The observations of Cotton [4] and of Busse [5] on the milling of rubber have not received sufficient attention in this connection.

In practice the viscosity or flow characteristics of a plastic may be expressed in several ways, but no single one is well adapted to cover the different types of behavior exhibited by polystyrene when heated from room temperature to injection-molding temperature. As it is heated, the resin changes from a hard, solid state first to a rubbery condition in which it is highly elastic, then gradually to what appears to be a true liquid of high viscosity. In the interests of clarity it is desirable to select certain points in terms best adapted to each particular state, with special consideration to the requirements of injection molding.

Polystyrene at room temperature is becoming familiar as a hard solid in the form of colorless transparent cast pieces or as molded objects in a variety of shapes and colors. The cold flow, or gradual distortion under heavy load, is extremely low at room temperature and does not become appreciable until about 60° is reached. It is also interesting to note that samples cooled in solid carbon dioxide have about the same impact strength as at room temperature. In the actual test, notched Izod compression-molded test bars were placed on a block of solid carbon dioxide for two hours and then broken in the normal way; an average value of about 0.275 foot-pound of energy to break was obtained. Injection-molded test bars under similar conditions give an average impact value of about 0.4 foot-pound energy to break.*

* This behavior has been studied in greater detail and was reported by Nason, H. K., and Hayes, R. F., American Chemical Society, Fall Meeting, Atlantic City, 1941.

The thermal softening point, as measured by the A.S.T.M. heat-distortion test, is about 80°. This is the point at which distortion under moderate load first reaches a small specified value. In the region of the thermal softening point, polystyrene shows behavior strikingly resembling that of crude rubber.[23]

The minimum temperature at which polystyrene (made by polymerization at room temperature) shows rubber-like elasticity is 65°. In one experiment a strip of polystyrene was heated to 95°, stretched to an elongation of 450 per cent, and immediately released. The strip contracted at once to an extension of only 50 per cent, and after 200 seconds it had returned to its original length. When the strip was held in the extended form for 10 minutes, the extension immediately after release was 175 per cent, and after 200 seconds was 75 per cent. This illustrates clearly the limited flow properties of the resin at 95°. As the temperature was increased above this point the properties of a true fluid gradually became more pronounced and the elastic property slowly disappeared.

The visible changes in polystyrene effected by heating the material above its softening point have been described by Weith, Turkington, and Allen.[21]

To demonstrate what takes place between 95° and the temperature of injection molding, granular samples of commercial polystyrene were heated in evacuated flasks at various selected temperatures. The flasks were heated in an oil bath for an hour, temperature being determined by a thermometer with the bulb in the interior of the resin mass. When the heating period was over, the polystyrene was allowed to cool and the resin removed by breaking the flask.

The product obtained by carrying out the above procedure at 135° looked somewhat like a loosely packed snowball with a thin coating of ice over its surface. The individual granules were clearly visible and appeared to be simply fused together at the points of contact as they existed in the original loosely packed granular material. Obviously there was little real liquid flow.

Increasing the temperature to 165° produced definite changes in appearance, although the opaque white character of a snowball was still retained. Some of the spaces between the particles assumed the shape of bubbles, indicating that the particles fused enough to form continuous walls around what were formerly the spaces between discrete particles, and the glassy or icy appearance at the surface appeared to go somewhat deeper into the mass. At 185° the fusion was practically complete, but the viscosity was so high that bubbles were trapped in the mass and gave it a white translucent appearance.

The products obtained at 210° and 225° presented a different appearance from those just described. Complete fusion had finally been obtained, and most of the bubbles or voids were eliminated, leaving the material with a clear, transparent, glass-like form. Even at these temperatures, however, the viscosity was found to be high, and the molten resin could not be poured out of the flask. The rate of flow was so low that the mass cooled before it moved more than a fraction of the way down the side of the container.

The behavior of the resin between 185° and 225° is of particular interest because this region is in the operating range of most commercial injection-molding equipment. For best results in molding it is necessary that the material be fairly fluid at the molding temperature so that the pressure applied will be transmitted throughout and will force the resin into all parts of the mold. On the other hand, if the viscosity is too low, the plastic will flow out between different sections of the mold to cause flash.* This makes necessary an expensive finishing operation on the molded piece. A third and most important consideration in the economics of injection molding is the time cycle required for the complete molding operation. Obviously this

* Flash is that portion of the charge which extrudes into the cracks between the sections of the mold and remains as a thin fin attached to the molded piece.

is a function of the time required to fill the mold and the time required to cool the resin to a state such that it can be discharged from the mold without deforming.

The description just given of the flow characteristics at various temperatures demonstrates that polystyrene is peculiarly adapted to the process of injection molding, combining as it does the factors that make for the production of clean, sharply defined molded pieces and for maximum speed of molding. This view is confirmed in practice in the production of a wide variety of molded objects.

Although the thermal stability and flow characteristics of the styrene polymers have been emphasized for their importance in injection molding, these resins also have other unique properties of great industrial significance. The excellent color and chemical stability of the resins early led to attempts to use them in protective and decorative coatings. Several such applications have been made successfully from solutions of high-molecular-weight polystyrene, usually plasticized with one of the chemical plasticizers such as tricresyl phosphate, dibutyl phthalate, or the like. High-molecular-weight polystyrene, however, is incompatible with most of the ingredients commonly used in paints and varnishes, particularly the drying oils—a fact that until recently has prevented them from being utilized widely for coating purposes. Recent work on the control of the styrene reaction has now made practical the production of styrene polymers of relatively low molecular weight which are readily soluble in the drying oils to produce oleoresinous varnishes.

When polystyrene first became available in commercial quantities, it was thought that the principal outlets would be in the electrical field. Actually, its use as a general-purpose injection-molding material has grown so rapidly that electrical applications, which develop more slowly, take at present only a relatively small proportion of the total output. Potentially, however, the electrical industry must still be considered as an important consumer. From the standpoint of electrical insulating properties alone, polystyrene has no serious rival among rigid synthetic resins.[5] *

It has a high dielectric breakdown strength and extremely high d c resistivity, even at temperatures near its softening point. Its low power factor at all frequencies rivals that of fused quartz, is better than that of many types of ceramic insulation, and is not greatly affected by temperature. Because of these properties and of the increasing interest in and demand for better insulating materials at ultra-high radio frequencies, polystyrene is assuming a new importance. Its use in high-frequency equipment to replace certain of the inorganic insulators that have been commonly used in the past will be limited principally by its thermoplasticity, its relatively high coefficient of thermal expansion, its comparatively low modulus of elasticity and other characteristics common to organic substances in general. Undoubtedly many of the objections to its use can be minimized or eliminated entirely by special attention to design.

Polystyrene film, now in use as a capacitor dielectric, is only one of a wide variety of possible applications in the communications field. The resin also has possibilities as a material for coil forms, stand-off insulators, insulating rods and bushings, coil-mounting strips, and insulating beads for co-axial cable, to mention a few. Other potential uses will be evident from the table of properties at the end of this chapter.

It is to be expected that, as more information is gained about the reaction mechanism of polymerization and the chemical structure of the products, further desirable modifications in properties will be made possible. A marked increase in flexibility would open up whole new fields of application. Likewise an increase in the thermal softening point without loss of good molding properties would have tremendous possibilities. These and other improvements should come with the growth of understanding of the basic chemistry of polymerization and the chemical structure of polymers.

* This may have been changed by subsequent developments. See, *e.g.*, paper on polythenes in this volume. J. A.

Properties of Polystyrene

	Specification
Product designations	Bakelite Polystyrene (Bakelite = Trade-mark) Monsanto Polystyrene (Lustron = Trade-mark) Dow Styron (Styron = Trade-mark)
Forms available	Films, impregnating varnishes, laminations, lacquers, molded articles, powder or granules, rods, sheets, tubes
A. *Physical Characteristics*	
1. Clarity	Colorless, transparent
2. Light transmission	88-90%
3. Refractive index	1.59
4. Dispersion	v
v value, $\frac{n_D - 1}{n_F - n_C}$	32
5. Color possibilities	Unlimited
6. Odor	Very slight to none
7. Taste	None
8. Effect of age	None
9. Effect of sunlight	Slight yellowing
10. Effect of H_2O	
Cold	None
Hot	None up to 60°
11. Specific gravity	
Unpigmented	1.054-1.056
Pigmented	1.054-1.070
12. Specific volume	
Unpigmented	26.3-26.2
Pigmented	26.3-25.9
B. *Working Qualities*	
1. Type plastic	Thermoplastic
2. Molding qualities	Excellent
3. Recommended molding method	Injection
4. Metal inserts	
Chemical effect on	Inert
Use in molded articles	Poor to good
5. Compression ratio	2.0-2.3
6. Injection molding	
a. Temperature	300-500° F
b. Pressure	10,000 lb/sq in and up
c. Mold shrinkage	0.002-0.008 in/in
7. Machining qualities	Fair to good
8. Methods of forming	Blowing, extrusion, injection molding, compression molding, transfer molding
C. *Mechanical Properties*	
1. Injection-molded	
a. Tensile strength	5,000-9,000 lb/sq in
b. Transverse strength	14,000-19,000 lb/sq in
c. Elongation	2-5%
d. Modulus of elasticity	
Tension	$1.7\text{-}2.0 \times 10_6$ lb/sq in
Transverse	$3.9\text{-}4.7 \times 10_5$ lb/sq in
e. Impact (ASTM D256-38)	0.35-0.50 ft-lb
f. Hardness	
Rockwell Superficial	15X 89-92
Rockwell H	51
Rockwell L	100
Rockwell M	87-90
D. *Electrical Properties*	
1. Volume resistivity	$10^{17}\text{-}10^{19}$ ohm-cm
2. Dielectric strength	0.005 in thick = 3,500 volts/mil 0.015 in thick = 2,200 volts/mil 0.125 in thick = 500-700 volts/mil

	Specification
3. Dielectric constant	
a. 60 cycles	2.5-2.6
b. 1,000 cycles	2.5-2.6
c. 1,000,000 cycles	2.5-2.6
4. Power factor	
a. 60 cycles	0.0001-0.0002
b. 1,000 cycles	0.0001-0.0002
c. 1,000,000 cycles	0.0001-0.0004

E. *Thermal Properties*

1. Burning rate	Slow
2. Specific heat	0.32 cal/° C/g
3. Thermal expansion	6-8 × 10^{-5}/° C (tent)
4. Heat distortion	75-85° C 162-180° F
5. Cold flow tendency	Very slight

F. *Chemical Properties*

General resistance to:	
1. Water	Excellent
2. Water absorption, 24 hr at 25°	0.07% Max. @ 25°C
3. Mineral acids, weak	Excellent
4. Mineral acids, strong	
Non-oxidizing	Excellent
Oxidizing	Discolors slightly
5. Alkalies, weak	Excellent
6. Alkalies, strong	Excellent
7. Alcohols	Excellent
8. Ketones	Swells
9. Esters	Soluble
10. Hydrocarbons, aromatic	Soluble
11. Hydrocarbons, aliphatic	Fair to good
12. Oils, mineral	Poor to excellent
13. Oils, animal	Poor to excellent
14. Oils, vegetable	Poor to excellent

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Styrene and Polystyrene

J. Lawrence Amos

Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan

Styrene monomer and its polymers and copolymers have acquired great significance in the rubber and plastic industries because of the properties which may be achieved by their use and the improved methods of producing these compounds cheaply and in large quantities.

Monomer

Methods of Manufacture of Monomeric Styrene. Monomeric styrene (phenylethene) is a water-white unsaturated hydrocarbon of the formula $C_6H_5 - CH = CH_2$.

Ethylene, benzene, and a catalyst such as aluminum chloride are the raw materials used in the manufacture of ethyl benzene.[4, 45, 88] The major portion of the styrene manufactured is produced by the dehydrogenation of ethyl benzene to styrene.[5, 19, 59, 79, 83, 90] Certain methods for preparing styrene from alpha chloroethyl benzene by removing hydrogen chloride from the side chain of the latter are also known.[19, 59, 77, 89] Some of the other methods for producing styrene which are only of academic interest have been reviewed by Ellis [19] and Stanley.[59]

Styrene is being recovered as a by-product, from gas condensates and tar oils produced in the manufacture of artificial gas and coal-tar distillates, with difficulty because of the purification problem.[85-88]

Properties of Monomeric Styrene. Pure monomeric styrene is a colorless liquid having the following physical and electrical constants:

Boiling point: 145° 760 mm Hg [16]
Melting point: −30.61° [16]

Density $\frac{25}{25}$: $0.9050\ {}^{16}D_{(t)} = 0.9240 - 0.000918t$ [49]

Index of refraction $\frac{25}{25}$: 1.5440 [16]

$$N_{D(t)} = 1.5583 - 0.00056t$$ [49]

Specific heat: 0.316 [16]
Viscosities in millipoises:

50° F	9.0
100° F	6.0
180° F	3.8 [16]

Latent heat of evaporation: 85.0 cals/gm [16]
Critical pressure: 23.0 atm [16]
Critical temperature: 373.0° [16]
Flash point: 31.° [16]
Fire point: 34.° [16]
Coefficient of expansion ° C: 0.857×10^{-3} [16]
Heat of polymerization: 20,000 cals/gm mole [59]
Vapor pressure: In mm Hg

$$\text{Log } P = -1649.6\frac{1}{(t + 230)} + 7.2788$$ [49]

1000 cycles:	Dielectric constant	2.36
	"Q" factor	5300
	% Power factor	0.019
10^6 cycles:	Dielectric constant	2.35
	"Q" factor	6460
	% Power factor	0.0155
D.C. specific resistivity		1.07×10^{13}

Limits of Inflammability and Ignition Temperature of Styrene in Air. The limits of inflammability of styrene by volume in dry air at laboratory pressures and temperatures ranging from 29.3° to 65.2° are 1.10 per cent for the lower and 6.10 per cent for the upper limit. All mixtures falling within these limits are inflammable.

Styrene has ignition temperatures of 490° in air and 450° in oxygen.[29]

Electrical Properties at 25°:[16]

Inhibitors and Antioxidants. Monomeric styrene polymerizes when exposed to sunlight, the rate depending upon the temperature and various other factors. Styrene exposed to air oxidizes slowly, giving benzaldehyde, peroxides and other products, which affect its polymerization rate. To lessen and in some cases to prevent the low-temperature polymerization and oxidation of styrene during storage, inhibitors and antioxidants may be added. The following are examples of inhibitors and antioxidants which have been used: hydroquinone,[75] pyrogallol, guaiacol,[21] various sulfur compounds,[47] sulfur,[76, 80, 84, 188] catechol derivatives,[81, 94] chloranil,[99] and benzoquinone.[100, 120, 114]

Uses for Monomeric Styrene. The major uses for monomeric styrene are for the production of the thermoplastic polystyrene[19, 59] and "GR-S," a synthetic rubber.[18, 67] Styrene is being used in the production of its copolymers[19] and intermediates in the manufacture of compounds for perfumes, varnish resins, etc.[91, 102, 117]

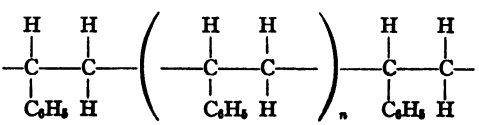
Polymerization. Polystyrene is one of the oldest known synthetic resins, having been prepared by Simon in 1839 by the application of air and heat to monomeric styrene. It was not until about 100 years later that polystyrene was made commercially available in the United States as a clear transparent product.

Styrene can be polymerized to its dimer[8] and to higher polymers of molecular weights which may exceed 1,000,000. In most instances the molecular weight of the polymer produced varies inversely with the temperature of polymerization, and is lowered by use of a catalyst.[10] Most of the polystyrene made commercially for molding purposes has a mean molecular weight of 35,000 to 200,000. The polymers below this range find applications in dielectric compositions,[11] varnishes, and coatings.

The theoretical aspects of the polymerization of styrene are presented by Mark in Vol. 5 of this series.[8] The commercial considerations in the polymerization of styrene have been discussed by Stanley[59] and Ellis.[19] See also[115, 116, 127].

Constitution of Polystyrene

Staudinger[65] teaches that polystyrene consists of a large number of styrene monomer units which are connected through their vinyl groups in the form of a linear macromolecule. His conception of the macromolecule can be shown by the following formula:



He bases the above molecular structure upon chemical, physical, and x-ray data, as well as on the structure of the products obtained when polystyrene is decomposed above 300° (monostyrene, 2-4-diphenyl-1-butene, 1-3-diphenyl propane, and 2-4-6-triphenyl-1-hexene).

De Boer[14] has investigated the positions of the benzene rings in polystyrene. He

SCHEME A

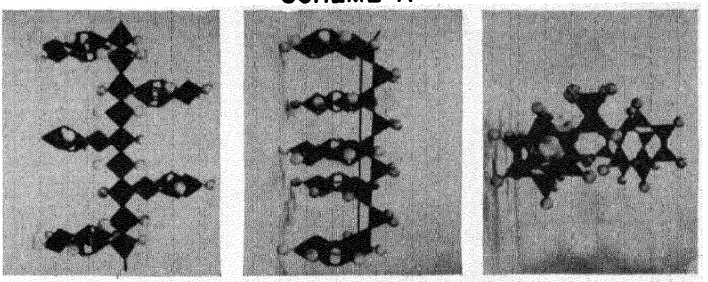


FIG. 1 EDGE VIEW FIG. 2 SIDE VIEW FIG. 3 TOP VIEW

SCHEME B

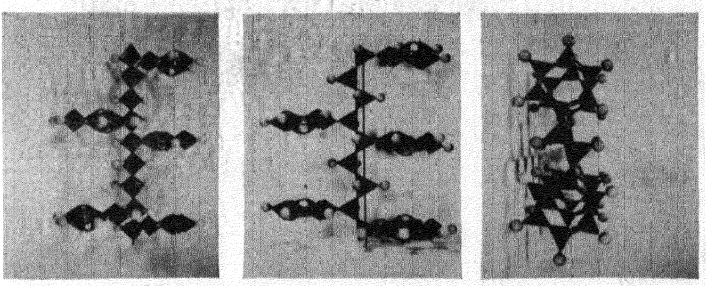
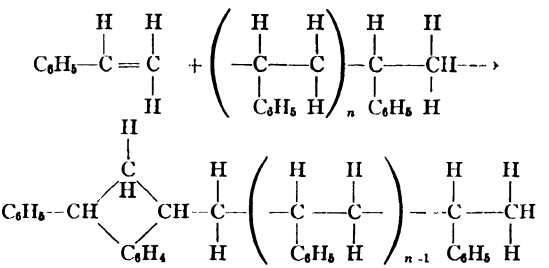


FIG. 4 EDGE VIEW FIG. 5 SIDE VIEW FIG. 6 TOP VIEW

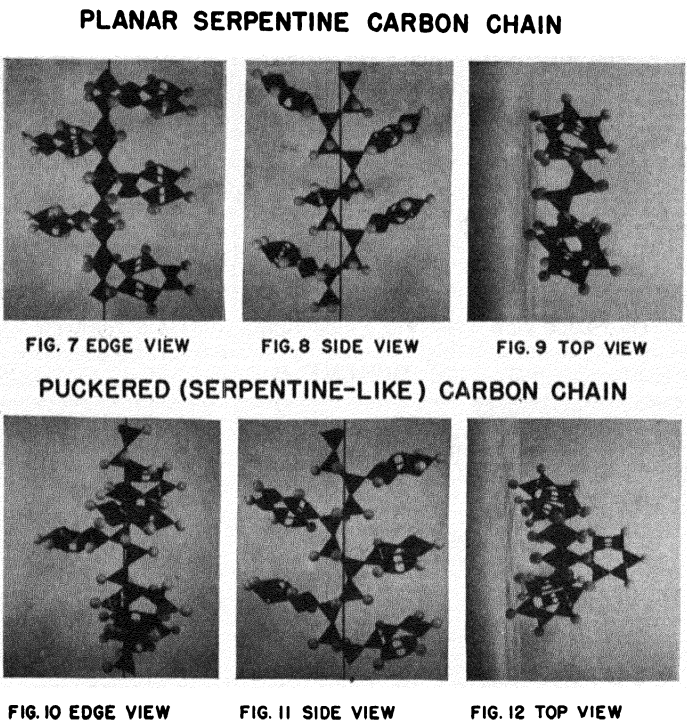
FIGURES 1-6. Molecular configurations for Polystyrene. Normal straight paraffin carbon chain.

of the various chain configurations. The C—C and C—H distances were taken as 1.55 Å and 1.07 Å, respectively.

Staudinger [63] as well as Whitby,[70] by using the bromination method of McIlhiney,[72] have shown that low molecular weight polystyrene produced catalytically at low temperatures shows olefin linkage. This test, however, does not show unsaturation in higher molecular weight polymers. It has been suggested that the unsaturation in the higher polymers is rendered inactive by the size of the polystyrene molecules (steric hindrance), or is removed by cycling the two vinyl groups with the production of an indane ring, as shown by the formula:



Recent investigations in this country and in Europe have emphasized the fact that polystyrene consists of a mixture of macromolecules of different molecular weights, different chain lengths, different internal structure of the chains, and possibly even different end groups.



FIGURES 7-12. Molecular configurations for Polystyrene.

In order to show that polystyrene consists of a heterogeneous mixture of molecules, two methods are available. First, the ultracentrifuge can be used to separate small quantities of polystyrene into several different molecular weight fractions. The objections to the use of this instrument are that it is too expensive, and that the size of the samples analyzed is so small that the different fractions collected cannot be subjected to mechanical tests.[32, 56, 58, 69] The second method is called fractional precipitation, which consists in adding to a solution of polystyrene some non-solvent in sufficient amount to precipitate out the least soluble (highest molecular weight) fraction, which can be collected, weighed, and analyzed. Addition of more non-solvent will precipitate the next lowest fraction, and so on.

The results of a fractionation experiment of Mark [35] are shown on a ternary phase diagram in Fig. 13. A polystyrene sample was prepared by polymerizing pure styrene at 125° with benzoyl peroxide as the catalyst. This polymer had a P_w number (number of monomer units per polymer molecule) of 950.

The line *PS* shows a swollen gel in the upper part and in the lower part a homogeneous solution (polystyrene in methyl ethyl ketone). Along the line *SM* there exists complete solubility between methyl ethyl ketone and methanol. Along the line *MP* polystyrene appears both swollen and dissolved in methanol.

The experiment was conducted at a constant temperature with the slow addition of methanol to a solution containing two per cent by weight of polystyrene dissolved in methyl ethyl ketone. The numbers 1 to 10 on the horizontal axis represent the points at which the different fractions were taken. Their corresponding P_w values (polymerization degree) are tabulated below the line *SM*. The numbers along line *SP* indicate the concentration of polystyrene in methyl ethyl ketone. When the tenth

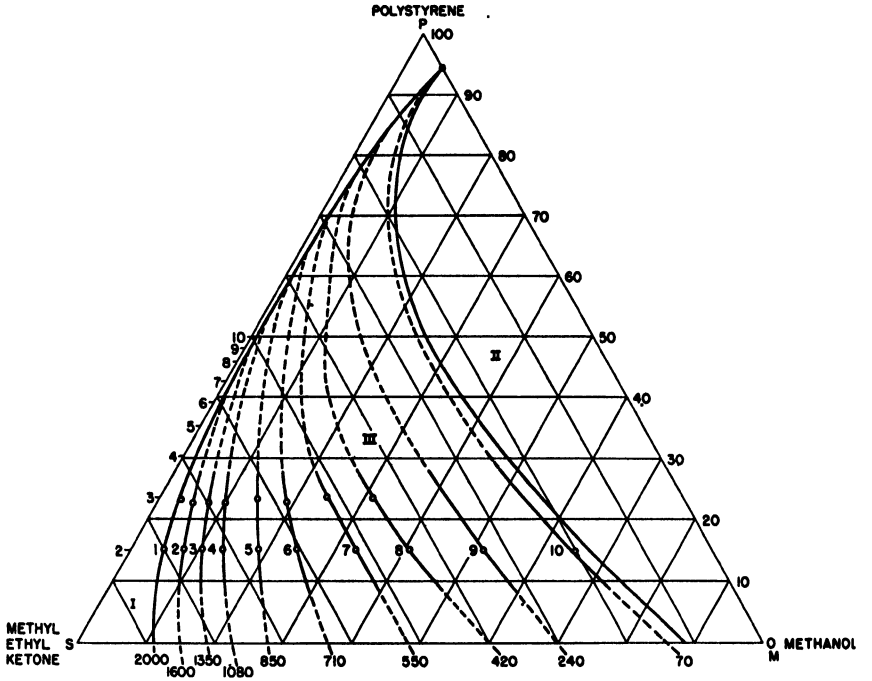


FIGURE 13. Ternary diagram describing the fractionated precipitation of a polystyrene sample. *Courtesy Dr. H. Mark.*

fraction was recovered, further addition of methanol gave no precipitate of polymer, although about 1.5 per cent of the original weight of the polymer was still in solution. This shows that the low molecular weight polystyrene is soluble in methanol.

The ternary diagram shows the following:

(1) In the area designated as I a homogeneous solution of polystyrene exists in methyl ethyl ketone of a low methanol content (1-phase system).

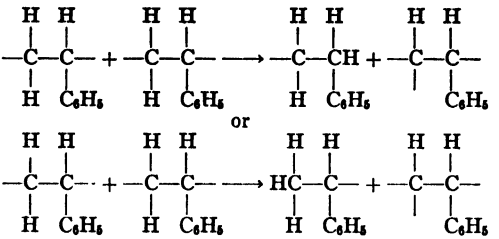
(2) There exists in the area designated as II a solution of low molecular weight polystyrene in a liquid of high methanol content (1-phase system).

(3) In the area designated as III there exist together swollen high molecular weight polystyrene and a methyl ethyl ketone solution of low molecular weight polymer and medium methanol content (2-phase system).

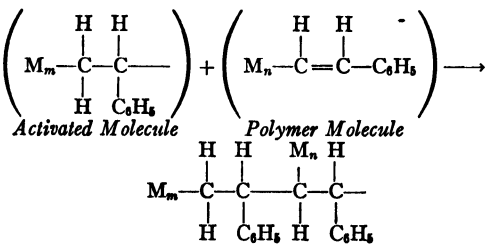
(4) As the points 1, 2, 3, etc., depart from each other along the fractionation line of nearly constant polymer concentration, the resolving power of the two solvents becomes higher with respect to fractionation.

Staudinger and Schulz,[68] through viscosity and osmotic measurements, have shown that polystyrene polymers are not simple chains but are more or less extensively branched. Their findings have been confirmed by Signer's [55] double refraction measurements of polystyrene under flow.

Schulz [61] has investigated branching and cross-linking in polymers. He claims that branching occurs during the formation of the long chains because a special step creates two free valences on one chain end, thus making it possible for the chain to grow in two independent branches. It is not known which reactions lead to the formation of branching. According to Schulz, the collision of two nuclei with their active ends probably leads to a branching center according to the following scheme:



Flory [20] presents the following formula to show how the branched chain polymers may be formed:—



Schulz [51] investigated the branching of styrene during polymerization. The K_m constant (Staudinger's constant) for unbranched polystyrene is about 1.8×10^{-4}, while the values for polystyrene (Schulz) polymerized at 20, 60, 100, 132, and 220° are 1.18, 0.79, 0.57, and 0.42×10^{-4}. These values show that the unbranched polystyrenes are more capable of forming solutions of higher viscosity at a given concentration than are branched polymers of the same mean molecular weight. This investigation shows that the higher the temperature of polymerization the more branched the polystyrene; furthermore the greater the degree of branching in polystyrene, the lower its rate of solubility will be. The average degree of branching was determined for each of the above five polystyrene samples and was found to be 1.5, 2.3, 3.5, and 4.3 respectively (average number of branched chains per polystyrene molecule). The average lengths of the main chains (number of monomer units) were 2,600, 2,000, 1,200, 550, and 350.

Properties of Polystyrene

Physical and Mechanical Properties. Many variations in the properties of polystyrenes may be attributed to differences in their mean molecular weight, degree of branching, and non-uniformity of molecular weight. These are dependent chiefly upon the purity of the monomeric styrene and the conditions of polymerization. The electrical properties of polystyrene are not influenced much by the above variables. However, many of the mechanical, and physical properties are changed to a great extent. Thus while the low molecular weight solid polymers are brittle and have low softening points, the higher molecular weight polymers result in improved heat resistance and mechanical strength.

Polystyrene has remarkable dimensional stability under prolonged heating. Fig. 14 compares the dimensional change of polystyrene with that of other commercial plastics at 50 and 70°.[22] In making the test, samples 1.75″ × 2.50″ with a thickness of 0.10″ were used. To determine the dimensional change the width and length of each specimen were measured. All samples were conditioned at 25° and 50 per cent relative humidity before measuring. Dimensional changes in polystyrene on ageing are slight, because of the low water absorption of the polymer and freedom of the plastic from added plasticizers. Moore [46] has compared the various properties of polystyrene with other plastics.

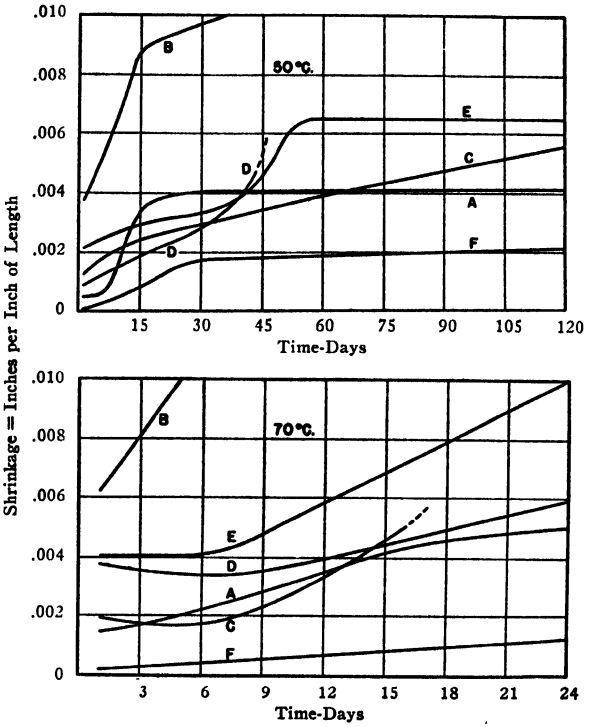


FIGURE 14. Dimensional stability of plastics at 50 and 70° C. A. Phenol Formaldehyde general purpose resin; B. Cellulose Acetate; C. Cellulose Acetate Butyrate; D. Methyl Methacrylate; E. Ethyl Cellulose; F. Styron* (Dow Polystyrene). The 70° C test was concluded at the end of 25 days because of the abnormal distortion of some samples.

Staudinger and Stanley [64] review the effects of solvents and plasticizers upon polystyrene. Plasticizers usually are not added, because of the lowering of the softening point, their effect on the dimensional stability on ageing, and their effect on exposure to prolonged heating of the molded article.

Effect of Temperature on Properties of Polystyrene. One will note after studying Figs. 15, 16, 17, and 18 that a critical transformation occurs at 80° to 85° for the polystyrene tested. (Patnode and Scheiber [49, 180] show that a similar transformation occurs in the density and temperature relationship for polystyrene at about 80 to 85°).[96] At this temperature polystyrene changes from a hard, glass-like solid to a soft, rubbery plastic. Whitby,[70] Meyer, Susich, and Valko [41] and Carswell, Hayes and Nason [12] have described how polystyrene above its transition range has elastic properties somewhat similar to those of rubber in regard to extensibility, elastic-after-effect, set, etc.

When the temperature is reduced below the transition range, the tensile and flexural strengths, elongation and flexural deflection of injection-molded polystyrene pieces increase, and this trend continues to about −30°. Most thermoplastics show reduced elongation and reduced flexural deflection as the temperature is lowered. This tendency of polystyrene to become tougher at sub-zero temperatures in conjunction with its low moisture absorption, and good dimensional stability, has led to its use where low temperatures are encountered, such as in interior parts for refrigerators.

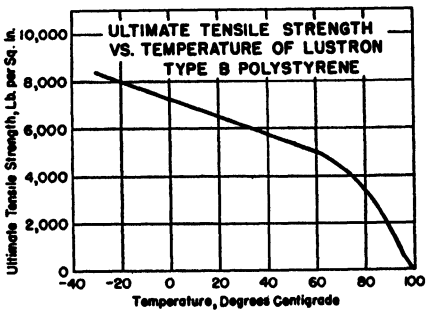
*Trade Mark Reg. U. S. Pat. Off.

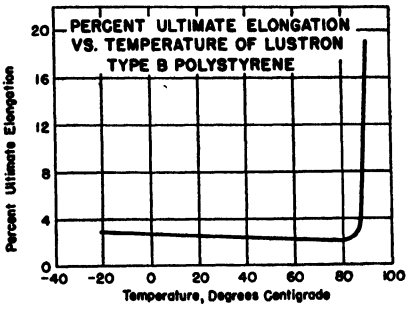
Table 1. Working Conditions and Mechanical Properties of Molded Commercial Polystyrenes [18, 113]

Injection molding temperature, (° F)	375-500
Injection molding pressure (lbs/sq in)	10,000-30,000
Injection mold shrinkage (in/in)	0.002-0.008
Tensile strength (lbs/sq in)	5,000-9,000
Elongation (per cent)	2-5
Modulus of elasticity, tension (lbs/sq in)	$1.7\text{-}2.6 \times 10^5$
Compression ratio	2.0-2.3
Compressive strength (lbs/sq in)	11,500-15,000
Flexural strength (lbs/sq in)	8,000-19,000
Impact strength (ft-lb/in of notch $\frac{1}{2} \times \frac{1}{2}$ in notched bar, Izod Test	0.3-0.5
Brinell hardness (2.5-mm ball, 25-kg load)	20-30
Rockwell hardness (A.S.T.M.)	M75-M90
Thermal Properties [18]	
Thermal conductivity (10^{-4} Cal/sec/sq cm/° C/cm)	1.9
Specific heat (cal/° C/gm)	0.32
Thermal expansion (per ° C)	$6 \text{ to } 8 \times 10^{-5}$
Softening point (° F)	220-240
Distortion under heat (° F) (A.S.T.M.)	170-180
Electrical Properties	
Volume resistivity (ohm-cms) (50% R.H. and 25°)	$10^{17}\text{-}10^{20}$ [16]
Dielectric strength, short time, (volts/mil, $\frac{1}{8}$-in thickness)	500-700 [40]
Dielectric constant (60 cycles per sec)	2.5-2.6 [16]
(10^3 cycles per sec)	2.5-2.6 [16]
(1 megacycle per sec)	2.5-2.6 [16]
(60 megacycles per sec)	2.6 [14]
(120 megacycles per sec)	2.5 [14]
Power factor (60 cycles per sec)	0.0001-0.0002 [16]
(10^3 cycles per sec)	0.0001-0.0002 [16]
(1 megacycle per sec)	0.0001-0.0004 [16]
(60 megacycles per sec)	0.0005 [44]
(120 megacycles per sec)	0.0007 [44]
General Properties [16, 18]	
Specific gravity	1.054-1.070
Specific volume (cu in/lb)	26.3-25.9
Refractive index	1.59
Water absorption, immersion 24 hrs.	0.00 to 0.05
Tendency to cold flow	Slight
Burning rate	Slow
Effect of age	Practically Nil
Effect of sunlight	Slight
Effect of weak acids	None
Effect of strong acids	Attacked by oxidizing acids
Effect of weak alkali and strong alkali	None
Effect of organic solvents	Soluble in aromatic and chlorinated hydrocarbons
Machining qualities	Fair
Color possibilities	Unlimited
Optical Properties [18]	
Light transmission is 88-90 per cent in the visible region (4000-7000 Å). An interesting property of the material is the manner in which it transmits light through rods or sheets, carrying it around curves and bends, and emitting it only at edges, ends or at points where the surface is roughened.	

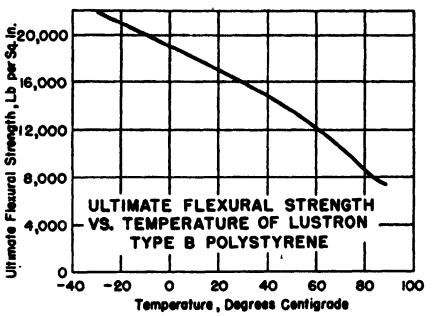
Electrical Properties. Polystyrene possesses outstandingly low electrical power factor, high dielectric strength, great arcing resistance, high surface and volume resistivity, and low water absorption (Table 1).

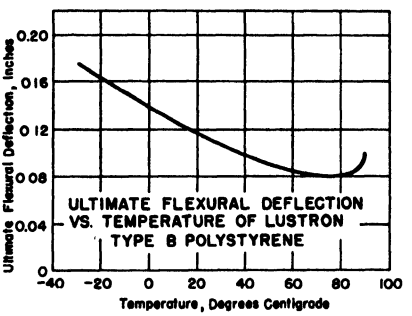
Blount [6] compares the electrical properties of polystyrene with other plastics. He shows the ratio of the resistivities of polystyrene to phenol low-loss to be 1000 to 1





FIGURES 15 AND 16. Tensile strength and elongation determined simultaneously over a range of temperatures with injection-molded, dumbbell-shaped test specimens of ¼ in. × ¼ in. cross-section on a screw type tensile strength testing machine.





FIGURES 17 AND 18. Flexural strength and deflection at various temperatures as determined by test on a 2 × ½ × ¼ in. test specimen.

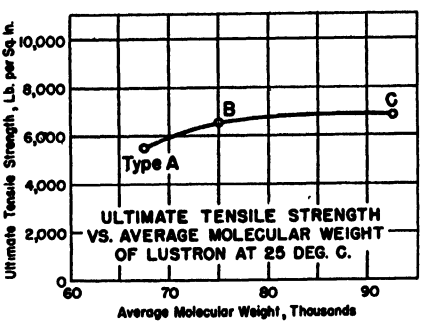


FIGURE 19. Strength increase with molecular weight.

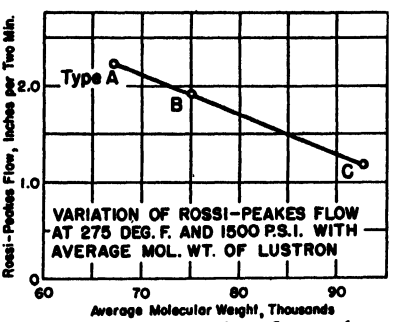


FIGURE 20. Rossi-Peakes flow values showing flow decrease with increase in molecular weight. *Courtesy Monsanto Chemical Co.*

and that of polystyrene to general purpose phenolics 10,000,000 to 9. The loss factor (power absorbed by insulation at 60 cycles) comparison gives polystyrene a rating of one, low-loss phenolics 458, urea 740, and general purpose phenolics 10,000. Loss factor becomes more important as frequency increases.

Polystyrene in the cast, molded, and solution forms as well as monomeric are used in the electrical industry. The use of monomeric styrene to form high-voltage cable joints, plugs and insulation has been well described by Scott and Webb.[54] The elec-

trical applications of polystyrene have been discussed by Matheson and Goggin.[40]

X-ray and Orientation Properties. Katz [30] shows that both styrene monomer and polystyrene give amorphous x-ray patterns. The monomer gives a single ring while polystyrene gives a second smaller concentric ring in the x-ray pattern, which Katz has called the "polymerization ring."

Rubber and some plastic materials, when stretched, show crystallinity by x-ray patterns. Stretched polystyrene does not show this crystallization phenomenon.

Hühnemörder [37] observed orientation in stretched polystyrene by x-ray patterns. Katz and Fuller [30] observed orientation in stretched polystyrene by a similar method. Their x-ray pattern for stretched polystyrene shows the polymerization ring split into two equatorial maxima.

Preferred orientation can readily be shown in stretched polystyrene by measuring its birefringence, (double refraction), which is a direct measure of the degree of orientation in the polymer.[48] A birefringence study of polystyrene, which has been stretched within the proper temperature range and then cooled while in the elongated state, shows that orientation increases directly with increase in the amount of stretch, and that the impact strength, elongation, and flexibility of the stretched product increases with increased orientation. See also [118 and 154]

Muller [48] shows the relationship between elongation (stretch) and birefringence (orientation) of polystyrene stretched at 100°, 120°, and 150°. His data (Fig. 21) show that orientation in polystyrene at 100° increases rapidly with elongation. He teaches that rolling, stretching and molding polystyrene produce orientation effects which influence the tensile strength, bending strength, folding strength, and fibering of the fabricated article. He considers stretched polystyrene as a material with frozen highly elastic tension. The density of polystyrene changes about two per cent with the maximum degree of orientation.

Jenckel and Lagally [28] show that the tensile strength of polystyrene filaments possessing molecular orientation reaches a pronounced maximum at 50°. This temperature does not coincide with the solidification temperature of polystyrene, which is about 85°, and is believed to be a second solidification temperature.

Certain fabrication procedures are used to impart orientation to threads, tubes, rods and sheets of polystyrene so as to improve the impact strength and flexibility of the fabricated object.[25, 78] Staudinger and Stanley [64] produced threads of 0.6 to 1.5 deniers by extruding a polystyrene solution into heptane and then orienting the molecules in the polymer by stretching at a speed six to ten times as great as the speed of extrusion. Blythe and Hofmann [7] as early as 1845 showed that polystyrene softened by heat can be drawn out into very fine threads which have the greatest similarity to spun glass. See also [96 and 137]

Effect of Impurities upon Polystyrene Properties. Liquid impurities left in polystyrene have a great influence on the physical properties of the polymer. The outer surface of polystyrene articles containing considerable volatile impurities gradually appear opaque or covered with a white coating. Upon observing this coating with a microscope the sample will appear to be covered with a network of small cracks. This effect, called "crazing," is due to the impurities evaporating from the surface of the polymer sample, thereby causing a contraction in volume. The surface film contracts and, not possessing sufficient elongation, develops numerous small cracks. The impurities which cause "crazing" in polystyrene impart a lower softening point, poor ageing characteristics, and eventually poor physical and mechanical properties to the polymer. Aleksandrov [1] and Korzhavin [81] have disclosed the above reason for "crazing" in polystyrene and have suggested methods of preventing it, *i.e.*, purer monomeric styrene, polymerization of the pure styrene more completely, addition of plasticizers, and application of vacuum to the heated polymer. Water included in polystyrene gives it an opaque appearance. Upon exposure to air, this gradually evaporates from the surface of the polymer and finally gives a glass-clear polymer.

Many impurities in polystyrene impart to it color which generally becomes more pronounced upon ageing. Volatile impurities produce bubbles in polystyrene. This difficulty can be overcome by removing the volatile compounds from the styrene monomer before polymerization. See also [181, 182, 183, 185].

Colloidal Properties. Staudinger [60] classifies the polymers of styrene into three groups of molecular colloids, according to different lengths of the fiber-molecules. The first group, called hemicolloids, contains polymers with molecular weights up to 10,000. The length of the chain-molecules range from 50 to 250 Å. These polymers do not show pronounced colloidal properties because they dissolve without swelling, their solutions have a low viscosity, the solids are powdery or gluey masses, and filaments prepared from them have low tensile strength and are very brittle.

The second group, called mesocolloids, contains polymers with molecular weight range of about 10,000 to 100,000 and chain lengths from 250 to about 2500 Å. The properties of this group are intermediate between those of the other two groups.

The last group is called eucolloids; it contains macromolecules whose mean molecular weights exceed 100,000 with chain lengths greater than 2500 Å. These polymers show characteristic properties of lyophilic colloids because their dissolution is accomplished by great swelling, their solutions are highly viscous, their flow phenomena are not those of a normal liquid and they do not obey Einstein's Law (formula for the viscosity of spherical particles). The solid polymers are tough, hard, and can be fused to form filaments or films of high elasticity. Commercially the most important polymers belong to this group.

Staudinger [60] teaches that a dilute solution of polystyrene is a molecular dispersion and not a micellar dispersion. (Micellar particles are those held together by van der Waals' attraction forces; molecular materials are those held together by normal covalent linkage.) His views have been confirmed by Dobry's [15] work on molecular weights and viscosity measurements of polystyrene solutions. Further evidence is the work of Signer and Gross [57] in showing that the partial specific volume (volume occupied by one gram of polystyrene) of a dissolved polystyrene in various solvents has the same value:

$$V = 0.92 \pm 0.03$$

which value is the same as that for the dry polymer. Additional support by Signer [57] shows that the sedimentation velocity of a definite polystyrene in centrifugal fields of high intensity in most of the solvents considered, when corrected for the difference in apparent gravity and in viscosity, is practically independent of the solvent liquid.

Mark [86] teaches that the shape of polystyrene molecules in dilute solution appears to be neither compact (more or less sphere-like clusters), nor extended stiff (rod-like) fibers with elastic vibration, but are rather in a bent shape, though not rolled entirely together (ball-shape). He points out that his view is in fairly good agreement with data obtained by Staudinger's viscosity equation, sedimentation-velocity and double-refraction measurements.

Molecular Weight Determination

Viscometric Method. Since the colloidal and the other properties of polystyrene depend so much upon the size of the polymer molecules, it soon became very necessary to have methods to determine the molecular weight. Staudinger,[61] through a great number of viscosity measurements of dilute solutions of a series of homologous products, showed that there exists a linear relationship between the specific increase of the viscosity and the molecular weight of the dissolved substance. He expressed this relationship by the following equation:

$$\frac{\eta_{sp}}{C} = K_m \cdot M$$

In this equation C is the concentration of the solution, which can be expressed in grams per cubic centimeter or "basic molar units" per liter (a solution has a concentration of one "basic molar unit" when it contains in one liter the weight of one structural unit in grams). η_{sp} is the specific viscosity (viscosity of solution of polymer divided by viscosity of solvent minus one), K_m is a constant, a characteristic of the type of polymer being investigated, and M is the molecular weight of the polymer. After K_m is known, one can calculate M by measuring the specific viscosity at a certain low concentration. Staudinger used the K_m constant value of 1.8×10^{-4} for linear polystyrene, and recommended using a specific viscosity not greater than 0.4 (viscosity measurements made at 20° with benzene as the solvent). The viscometric method for determining molecular weights has been subjected to considerable criticism because of the error caused by branched chains in polymers such as high molecular weight styrene.[61, 42] This method of determining the molecular weights of polystyrene is simple, rapid, and convenient, and especially good for a large number of measurements. See also [119].

Schulz [53] has recommended the determination of the K_m constant for Staudinger's equation osmotically by separating polystyrene into about ten fractions and then determining the molecular weight of two or three of the fractions osmotically and their respective specific viscosities in dilute solution. Knowing the molecular weight and the specific viscosity of each fraction, its K_m constant can then be determined by Staudinger's equation. Schulz used the arithmetical average of the K_m constants for the fractions as the K_m constant for the polystyrene under investigation. Table 2 from Schulz's paper shows how the K_m constant determined by osmotic and viscosity

Table 2. Characteristic Constants for Polystyrene Thermally Polymerized under Nitrogen

Polymerization Temperature (° C)	$\frac{\eta_{sp}}{C}$ gm	$K_m \cdot 10^{-4}$	$\overline{K}_m \cdot 10^{-4}$	$\overline{P}$
20	131.	1.5	2.15	5900
80	30.7	0.61	0.87	3400
100.5	17.2	0.57	0.815	2020
132	11.3	0.51	0.73	1490
140	9.2	0.48	0.69	1280

measurements on fractions, as well as the $\overline{K}_m$ constant determined in a similar manner on the polymerizate varies with polymers produced by different polymerization conditions. $\overline{P}$ is the polymerization degree of the different polymers.

Schulz [52] showed that molecular weights determined osmotically on polystyrene fractions are two, three, or four times higher than those determined by the viscosity method. This difference is attributed mostly to the effect of branched chains in the polymer. This method is claimed to be the best for determining the molecular weight of polystyrene. Its objectionable features are the difficulties of obtaining membranes which will give duplicate check results and the diffusion of the lowest molecular constituents in the original polymer through the membrane gives molecular weight values that are too high.

Ultracentrifuge Method. This method for determining the molecular weight of polystyrene is reliable, but slow, expensive and complicated.[68] Signer and Gross [57] used a Sveberg centrifuge in determining the composition of polystyrene of the mean molecular weight of 80,000 (See Table 3, and Appendix 3).

Elastic Properties

Houwink [26] demonstrated the thermo-recovery property of polystyrene by stretching strips of the polymer 450 per cent at 95° and retaining them at this extension for different lengths of time before releasing them. The extensions for the various time intervals are shown in Table 4. These data show that permanent set increases the

Table 3. Ultracentrifuge Method for Determining the Molecular Weight of Polystyrene

Molecular Weight	Content (%)
25,000 to 45,000	1.9
45,000 to 65,000	12.0
65,000 to 85,000	43.8
85,000 to 105,000	30.6
105,000 to 125,000	9.3
125,000 to 145,000	2.2

longer the 450 per cent extension period of the polystyrene is maintained, and that the plastic flow (flow produced by a deformation which does not completely disappear when the stress is removed) is considerable at this elongation.

Houwink [26] has shown that the amount of thermo-recovery in polystyrene is inversely proportional to the amount of monostyrene present in the polymer. He carried out experiments by compressing polystyrene samples, and then recording the recovery after the compression load had been removed. With 50 per cent styrene monomer in the polymer, no thermo-recovery took place, and it is suggested that the high monomer content permitted complete relaxation during compression.

According to the kinetic theories developed by Kuhn,[34] Guth,[24] Mark,[37, 38] and others, the deformation under the action of an external force in an elastic polymer is of two types, ordinary elastic (which occurs in polystyrene at temperatures below

Table 4. Relaxation of Polystyrene above its High-Elasticity Temperature *

Time of extension of 450%	Extension immediately after release (%)	Extension 200 seconds after release (%)
Instantaneous release	50	0
5 minutes	150	55
10 minutes	175	75
90 minutes	300	150

* Temperature at which a small stress imparts a large elastic deformation.

about 80 to 85°) and highly elastic deformation. In the case of ordinary elastic deformation, external forces change the equilibrium of the material under the internal forces of repulsion and attraction, and alter the mean distance between the particles. This results in an accumulation of elastic energy, which, with the removal of the external forces, reverts the system to its original minimum energy state. In the case of highly elastic deformation, application of external forces causes a regrouping of the particles (molecules) which leads to irreversible transposition (plastic flow) and reversible transposition (elastic flow), the result of which is a preferred orientation of particles in the material. Upon the removal of the external forces, while the sample is still hot, it will return to its original unoriented state. The amount of recovery depends upon the amount of flow that takes place during the action of the external forces. The less the plastic flow (irreversible transposition), the greater the recovery. Above 80 to 85° highly elastic deformation of polystyrene occurs in which the orientation of the molecules plays a great part. The restoring forces are furnished by the tendency of the oriented chains to return to their equilibrium in a random kinked condition. Aleksandrov and Lazurkin [2] have also made a study of the elastic properties of polymers.

Gurevich and Kobeko [23] have shown that during the molding of polystyrene highly elastic deformation takes place; this is retained on cooling, because at room temperature the velocity of reversible deformation of polystyrene is insignificantly small. The presence of these strains may be detected by inspection between crossed Polaroid sheets. These authors claim that the time during which about one-half of the complete elastic deformation of polystyrene would appear or disappear at room temperature is of the magnitude of hundreds of thousands of years. At temperatures above

100° the time interval is in seconds, and polystyrene returns rapidly to the original form. Thermoplastics whose elastic deformation appears at temperatures not too far above room temperature may after a comparatively short time show reversible deformation of commercial importance. This reversible deformation causes buckling and shrinking in molded articles above their useful temperature range.

Plastic Properties

Houwink [26] teaches that polystyrene of a mean molecular weight of 100,000 shows only quasi-flow (stress versus rate of flow relationship not linear at beginning of flow) when tested over a temperature range of 80 to 120° in a Williams plastometer.

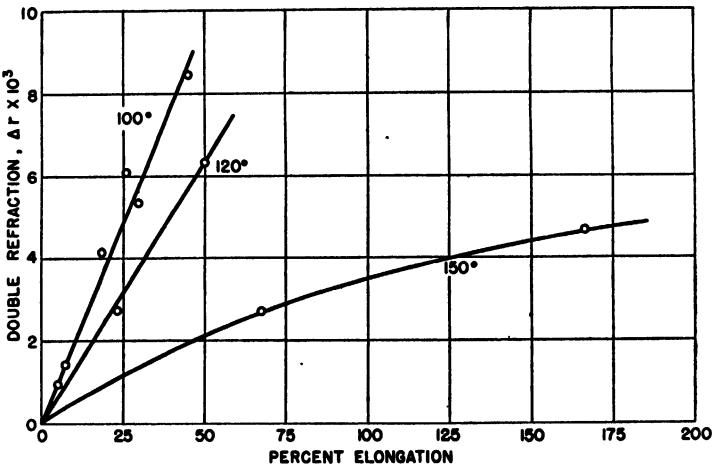


FIGURE 21. Double refraction of polystyrene stretched at different temperature.

He attributes this behavior of polystyrene to the tangled, fibrous structure of its molecules. The stretching out, disentanglement, and orientation of these long fibers (molecules) may result in quasi-flow.[110] See also Appendix 3.

Polystyrene granules [16] uniformly distributed in a flat die and molded with a low flow (the granules only soften and stick to one another) produce a molding with low strength and low toughness (low-flow Figs. 22 and 23). When a sample of the same polystyrene is preformed and allowed to flow in the die (1¼-inch preform placed in end of 2½ × 1¾ × 1/10-inch die and the end of molding with highest flow used for impact and tensile testing), the preform is forced to change shape, and the polymer molecules tend to become oriented in the direction of the flow, thereby producing a stronger and tougher article (high-flow Figs. 22 and 23). Low molding tempera-

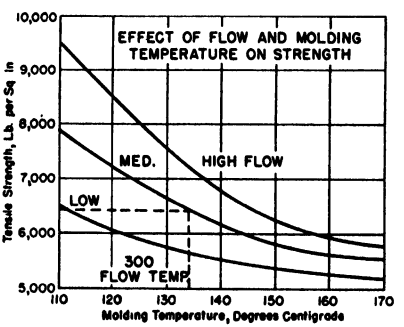


FIGURE 22

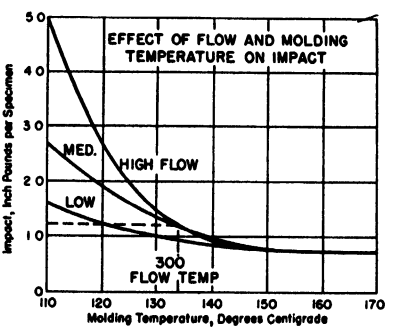


FIGURE 23

tures facilitate this distortion and orientation, while high temperature, due to the greater fluidity of the polymer, will allow these particles to draw partly back to their original shapes, thus somewhat nullifying the orientation that the flow is producing. These two counter effects, of course, are taking place simultaneously. When polystyrene is molded with medium flow in the die (7.2 grams, 1¼-inch preform placed in center of 2½ × 1¾ × ⅒-inch die), the strength and toughness of the molding varies inversely as the molding temperature [84] (see Figs. 22 and 23).

In making the study of the effect of flow upon the mechanical and physical properties of compression molded polystyrene, a modified Williams plastometer [78] was used. It consists of two flat, polished, steam-heated plates between which is placed a 1¼-inch diameter molded disc of three grams of polystyrene. The plates are then forced together with a 744-pound weight for 5 minutes, while the temperature is maintained constant. The polymer flows out beyond the upper two-inch diameter plate so that the only material being worked is the two-inch disc of polymer between the two plates (Fig. 24). This final thickness of the two-inch diameter disc of polystyrene in ten

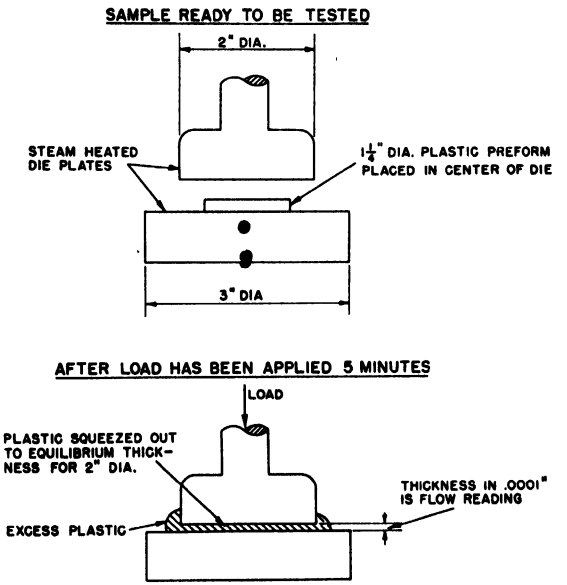


FIGURE 24. Flat plate flow tester.

thousandths of inches is used as the flow value. Fig. 25 is a typical flow curve of polystyrene which shows that at "300 flow" (.03") the flow temperature is 134°. The impact and tensile strength of this polystyrene at "300 flow temperature" are shown in Figs. 22 and 23.

Compression moldings of polystyrene made with high flow in the die show that the strength and toughness in the direction of the orientation are greater than that at right angles to the direction of orientation. Fig. 26 shows that the tensile strength and impact are increased somewhat in both directions. Plastics, when molded at temperatures that produce the same flow, will show practically the same ease of molding in the ordinary types of dies. If a polymer was found satisfactory for producing a certain molded article at a given temperature and at a good production speed, another polymer with higher "flow temperature" would require a higher molding temperature to produce this satisfactory production rate, while a polymer with a lower "flow temperature" could be molded at a lower temperature and still give this satisfac-

tory production rate. The strength and toughness of polystyrene increases with lower compression molding temperatures (see Figs. 22 and 23). In order to obtain the best properties for compression-molded thermoplastics, they should be molded at as low a temperature as possible, while still maintaining a good production rate.

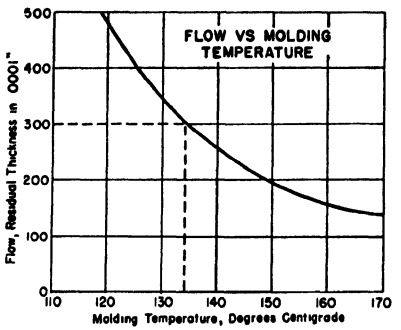


FIGURE 25

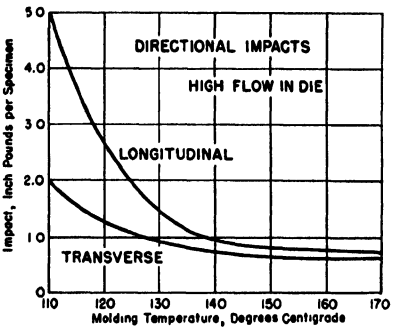


FIGURE 26

In comparing the mechanical properties of compression-molded samples of different styrene polymers, the samples are molded at temperatures corresponding to their respective "300 flow." This flow value was chosen because its "300 flow temperature" represents about the lowest practical temperature for compression molding polystyrene in average commercial dies while still obtaining good commercial production rates.

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References 91-138, together with some additions to this paper will be found in Appendix III at the rear of this volume. Some of these references have a bearing on the main paper, and, where possible, their numbers have been inserted.

Editor.

Dichlorostyrenes and Their Polymers

J. C. MICHALEK AND C. C. CLARK

The Mathieson Alkali Works

The nuclear chlorinated styrenes, more particularly the dichlorostyrenes, polymerize and copolymerize to give high molecular weight resins and elastomers of excellent heat resistance. Thus, the adverse effect of high temperature on polystyrene plastics and on styrene-butadiene rubber has been largely overcome by the substitution of dichlorostyrenes for styrene.

The isomers of dichlorostyrene, the properties of which are listed in the accompanying table, have pleasant odors, particularly the 3,4 isomer, which has an odor resembling geraniums.

Dichlorostyrene Isomer	N_D^{25}	B P. (° C)		Density 25/4
2,6	1.5724	59	at 2 mm	1.280
3,5	1.5745	53.5	at 1 mm	1.237
2,5	1.5788	74	at 3 mm	1.245
2,4	1.5812	69	at 2.5 mm	1.246
2,3	1.5780	61	at 1 mm	1.264
3,4	1.5840	76	at 3 mm	1.243

The monomeric dichlorostyrenes are very active. Highly purified samples have been observed to polymerize virtually to completion in 3 to 4 hours at 60° to 70° with methanol-extractable residues running as low as 0.1 per cent by weight. In spite of this rapid polymerization, it is possible, by working with cross-sections of less than 0.5 inch, to keep the temperature of the reaction below limits which would be injurious to the polymer.

The polymerization reaction is affected by impurities, although not always adversely. Sulfur as SO_2, introduced into the monomer in small amounts, seems to aid in the growth of long chains, whereas sulfur as H_2S has the opposite effect. Figure 1 shows the effect of temperature on the average molecular weights obtained by polymerizing the dichlorostyrene monomer alone and with small amounts of SO_2 or H_2S. Polymerization occurs in spite of the presence of 0.1 per cent of *p*-tertiary-butyl catechol, although at a reduced rate.

The polymers obtained from the isomers described above are all hard, transparent, colorless substances which resemble polystyrene in chemical resistance, solubility and general appearance. An interesting exception is the 3,4 isomer, which is insoluble in toluene, although it is a linear polymer. Only slight swelling occurs at the boiling point. It is insoluble also in carbon tetrachloride and in carbon tetrachloride-toluene mixtures, but is completely, although slowly, soluble in methyl ethyl ketone.

In addition to mass polymerization, dichlorostyrene can be polymerized in true emulsion to give a latex-like product before coagulation and very finely powdered

* From an article published in *Chemical and Engineering News*, September 25, 1944. Further information on Mathieson's rubber, as in the case of other synthetic rubbers, will probably not be divulged for the duration of the war.

resins after coagulation. The monomer may also be dispersed in water using conventional stabilizers, and polymerized as beads or pearls.

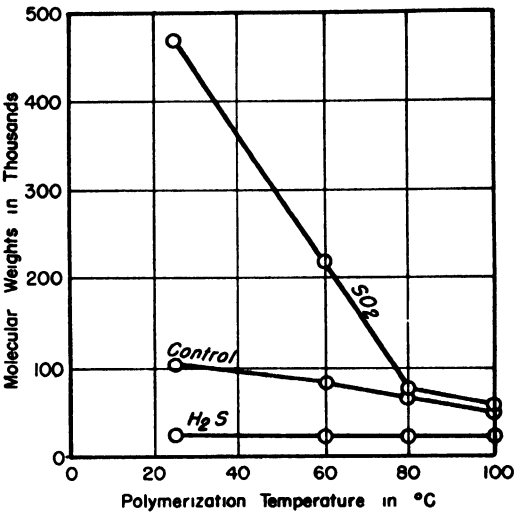


FIGURE 1. Effect of SO_2 and H_2S on molecular weight of dichlorostyrene polymer.

Polydichlorostyrene Plastic

Under conditions of high purity and careful control of the polymerization reaction, dichlorostyrene polymerizes to give a plastic with a distortion temperature of 240° to 265° F, which is higher than that for any plastic which combines excellent electrical characteristics with good strength, machinability, and moldability.

The tensile and flexural strengths of this plastic are above the range usually obtained for polystyrene, and its impact strength is substantially superior to that of polystyrene. It does not become brittle at naturally occurring low temperatures. Hardness is retained to a high degree at temperatures of 200° F and above. Resistance to water absorption is good, even at elevated temperatures. The polymer is self-extinguishing, according to ASTM-D-635-41-T. The products of pyrolysis include carbon dioxide, water, soot and hydrogen chloride.

Polydichlorostyrene is very stable. Since the chlorine is attached to the styrene nucleus, the tendency to split off hydrochloric acid is negligible, so that the addition of stabilizers is unnecessary. The plastic is resistant to a variety of chemicals, being unaffected by strong acids and alkalies at room temperature or by lower alcohols, aliphatic hydrocarbons, glycols, and vegetable oils. It is soluble in aromatic hydrocarbons, chlorinated hydrocarbons, some esters, some ethers, methyl ethyl ketone and some higher ketones.

Compatibility with conventional plasticizers is superior to that of polystyrene. The highly plasticized polymers have an interesting application in the composition of cements and pressure-sensitive adhesives.

Polydichlorostyrene plastics may be molded by conventional methods, although some modifications in injection molding and extruding technique are required because of the high distortion temperature and melting point.

Copolymers of Dichlorostyrene

Dichlorostyrenes are very readily copolymerized with other unsaturated substances, either by mass or emulsion polymerization methods. True copolymers are formed with: styrene, alpha-methyl styrene, methyl acrylate, methyl methacrylate,

acrylonitrile, vinyl acetate, dimethyl furane, piperylene, quinine, 2-methyl-pentadiene, dimethylbutadiene, butadiene, maleic anhydride, isoprene, cyclopentadiene, indene, and chloromaleic anhydride. Many of these copolymers are rubber-like products.

Dichlorostyrene Rubber

When dichlorostyrene copolymers are compounded in a formula of the GR-S type, a rubber of greatly improved heat resistance is obtained. Dichlorostyrene rubber shows superiority over GR-S in tensile strength, oil resistance, elongation, tear and modulus at 300 per cent, both at room temperature, and at 212° F. The effect of aging at 212°F for 48 hours is much less marked on this rubber than on GR-S. It also compares favorably with natural rubber in hot tensile strength, resistance to heat aging, and water absorption, and excels in oil resistance. Dichlorostyrene rubber shows low permeability to hydrogen, helium, and carbon dioxide. Excellent resistance to flex-cracking is demonstrated by flexometer and road tests. The rubber also has excellent milling characteristics.

Best performance is obtained when the rubber contains 12 to 16 per cent chlorine, equivalent to 30 to 40 per cent dichlorostyrene. Hardness can be controlled by varying the dichlorostyrene content of the crude rubber, as well as the sulfur in the formula.

Table 1. Properties of Mathieson Plastic [a]

Characteristic	Mathieson Plastic	Polystyrene [a]	Cellulose Acetobutyrate [a]
Molding qualities	Good	Excellent	Excellent
Compression molding temp., ° F	350 to 425	275 to 375	260 to 360
Compression molding pressure, lb/sq in	2000 to 5000	1,000 to 10,000	500 to 5,000
Injection molding temp., ° F	475 to 525	325 to 500	340 to 420
Injection molding pressure, lb/sq in	10,000 to 30,000	10,000 to 30,000	8,000 to 30,000
Specific gravity	1.39 to 1.40	1.054 to 1.070	1.15 to 1.23
Refractive index, N_D	1.62 to 1.64	1.59	1.47 to 1.49
Flammability, in/min (ASTM-D-635-41T)	Self-Exting.	0.75 to 1.50	2.50 to self-ext.
Tensile strength, lb/sq in	4600 to 7460	3,000 to 8,500	2,500 to 6,700
Modulus of elasticity, lb/sq in $\times 10^5$	5.0 to 7.0	1.7 to 4.7	0.6 to 2.0
Flexural strength, lb/sq in	14,000 to 19,000	4,800 to 19,000	2,100 to 12,700
Impact strength, ft lbs/inch of notch (ASTM-D256-41T)	1.0 to 1.5	0.26 to 0.4	0.5 to 7.5
Hardness, Rockwell	>M100	M55 to M95	M23 to M72
Distortion under heat, ° F	240 to 265	165 to 190	117 to 214
Dielectric strength, volts/mil	370	500 to 700	250 to 400
Dielectric constant	2.55 to 2.65	2.5 to 2.7	3.5 to 6.4
Power factor (per cent)	<0.1	0.01 to 0.08	1.0 to 6.0
Water absorption, 24 hours (per cent)	.02	0.04 to 0.06	1.6 to 2.1
Effect of weak acids	None	None	Slight
Effect of strong acids	None	None	Decomposes
Effect of weak alkalies	None	None	Slight
Effect of strong alkalies	None	None	Decomposes
Effect of organic solvents	Soluble in aromatic and chlorinated solvents	Soluble in aromatic and chlorinated solvents	Soluble in ketones and esters
Effect on metal inserts	Inert	Inert	Inert
Clarity	Transparent	Transparent	Transparent
Color possibilities	Unlimited	Unlimited	Unlimited

[a] From "Technical Data on Plastic Materials," by Plastic Materials Manufacturers' Association.

Table 2. Compounding and Properties of Mathieson Rubber

Mathieson rubber	100 parts by weight
Bardol	5
Zinc Oxide	5
W-6 Black	50
Sulfur	2
Captax	1.5

Table 2. Compounding and Properties of Mathieson Rubber—*Continued*

Curing temperature	280° F			
Chlorine in crude rubber, %	8.8	12.5	16.2	23.2
Curing time, minutes	70	70	70	80
Tensile, psi	2,530	3,490	3,960	2,400
Elongation, %	490	735	745	560
Modulus at 300% elongation	1,230	690	840	....
Durometer hardness (Shore)	65	61	60	73
Set, %	13	28	31	38

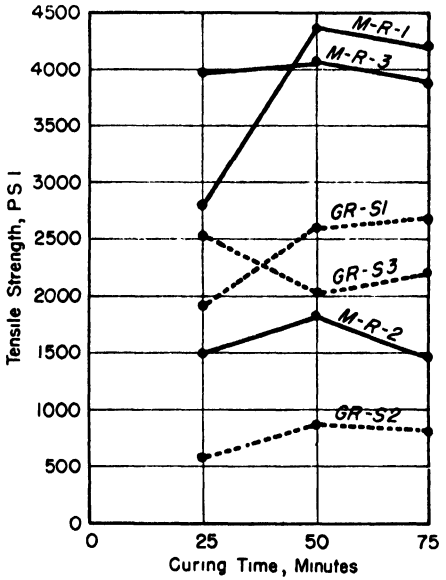


FIGURE 2. Tensile strength of Mathieson rubber (12.9 per cent chlorine). The data in this figure are from tests made at room temperature and the curves numbered 1 represent unaged samples, 2 represent the samples tested at 212° F, and 3 represent samples aged for 48 hours at 212° F.

Polyvinyl Resins

G. C. MILLER

General Sales Manager, Thermoplastics Department
Bakelite Corporation, New York

In contrast to the manufacture of phenolic, urea and alkyd resins by a condensation type of reaction, vinyl resins are prepared by polymerization. As a result, each polyvinyl resin molecule consists of a linear chain in which the monomers have reacted with one another at the double bond to form high-molecular-weight polymers. This reaction can be brought about by irradiation with ultraviolet light or by the addition of a small amount of peroxide, ozone, or lead tetraethyl.

The properties of the resulting resin are closely associated with its molecular weight and with the relative quantities of the various polymer bands of which the resin is composed. Certain characteristics of polyvinyl resins vary with the average molecular weight, while others seem almost completely independent of it. Tensile and impact strengths, abrasion resistance, and viscosity in solution increase with the molecular weight; while water absorption, refractive index, hardness, and electrical properties remain practically constant throughout the range of molecular weights. The solubility in organic solvents rises with decrease in molecular weight.

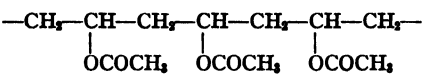
COMMERCIAL VINYL RESINS

Four principal types of polyvinyl resins are produced today. These are:

Polyvinyl Acetate
Polyvinyl Chloride
Copolymerized Vinyl Chloride and Vinyl Acetate
Polyvinyl Butyral

Vinyl Acetate, the monomer, is a clear liquid, having a boiling point of 73 deg. C., and the following structure:

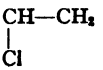
The polymerized resin, polyvinyl acetate, is a linear-chain compound, a portion of which can be shown as follows:



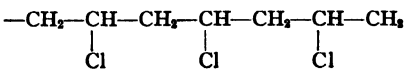
When properly compounded, polyvinyl acetate resins exhibit such excellent adhesive qualities that they are employed extensively as adhesives for bonding cellophane, cloth, paper, cardboard, porcelain, metal, mica, stone, leather, wood, glass, and certain plastic sheets and films. However, their range of application is not restricted to the adhesive field. Other commercial uses include high gloss and oil resistant paper coatings, leather finishes, and sizes for textiles, felt, and straw. Because of their stability on storage, these resins form the base for non-tarnishing

metallic inks and lacquers. Their clarity, gloss, and adhesion recommend them as ingredients in nitrocellulose lacquers. In emulsion form, they are used to modify latex emulsions, and as highly filled compounds they are used for molding.*

Vinyl Chloride is a gas under normal conditions, having a boiling point of −14 deg. C. Its structure is:

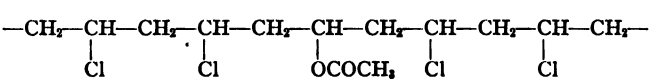


When polymerized in an autoclave, a linear-chain compound is formed as follows:



This resin is usually plasticized for use. When compounded with a suitable pasticizer, it can be extruded, molded, or sheeted into any of a variety of useful forms. When plasticized and dissolved in a suitable solvent, it results in formulations useful for coating cloth or for stop-off lacquers for electroplating equipment.

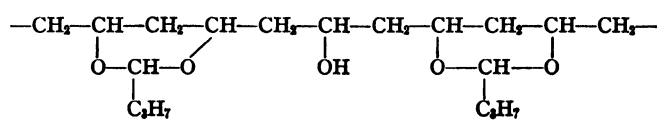
Vinyl Chloride-Acetate Copolymer. If, prior to polymerization, vinyl chloride, vinyl acetate, and a catalyst are mixed together with or without a solvent, and the charge treated in somewhat the same manner as for polymerizing the vinyl acetate alone as described above, the result is a copolymer, in which, theoretically, the two monomeric materials have reacted with themselves and with each other at the double bonds. The structure of this conjoint polymer probably approximates:



In such a copolymer, the chloride: acetate ratio can be varied over a wide range to produce resins of grades suitable for specific applications. The commercially important copolymers at present, however, are in the range of 80 to 95 per cent chloride.

As mentioned above, the properties of these polyvinyl ester resins are also closely associated with the resin's average molecular weight and with the relative quantities of the polymer bands of which the resin is composed. To suit best the requirements of individual applications, copolymers of vinyl chloride and vinyl acetate are made whose average molecular weight is a definite value within the range of 41,000 (for surface-coating resins) to 161,000 (for textile fibers). Approximate intermediate values, as typical examples, are 51,000 for resins to be used for calender-coating paper or for injection molding, 74,000 for compression-molding compounds, 102,000 for rigid sheet stock, and 152,000 for plasticized elastic sheeting and wire insulation.

Polyvinyl Butyral can be prepared by dissolving polyvinyl acetate in an alcohol, introducing the solution, together with an acid catalyst, into a reaction vessel, then hydrolyzing and condensing with butyraldehyde. The material is next precipitated, washed, and dried. The structure of the final resin is complex, due to a possible cross-linking of aldehydes and hydroxyls. A typical structure may be somewhat as follows:



This is the resinous material which, mixed with plasticizer and sheeted, forms the strong, adhesive interlayer used in high-test safety glass.

* The emulsions generally contain protective colloids. When mixed with plasticizers, *e.g.*, dibutyl phthalate, they give flexible adhesives. See this volume, p. 258.

Uses Depend on Characteristics

As can be seen, each of these four types of resins possesses distinctive properties which lead to specialized uses. The polyvinyl acetate resins are used principally as thermosealing adhesives. Polyvinyl chloride resins, in the plasticized form, have rubber-like characteristics but much better chemical resistance than does rubber. They are used to form molded articles and also for waterproof and stainproof cloth coatings. Polyvinyl butyral is used principally for the interlayer of automotive safety glass.

A majority of all other uses of vinyl resins is taken care of by the copolymers, which are truly versatile resinous materials. There are many varied products which copolymer resins have made possible. End uses for these resins are myriad. As rigid molding materials they are used for printing plates, radio recording, and molded floor tiles; as elastomeric molding materials they are used for distributor cap nipples, grommets, and other automobile parts; in their rigid extruded form they become architectural trim and corrosion-resistant piping; as elastomeric extruded materials they are utilized for tubing weather stripping, and wire and cable insulation. When produced as rigid sheets they are employed as dictation records, electrotype molds and navigational and calculating instruments; as flexible sheeting they are fabricated into shoes, handbags, and unholstery. Flexible films produced from these resins are used for shower curtains, raincoats, industrial protective clothing, electrical insulating tape and laminating film. Formulated into coating solutions, these resins are used in the coating of cloth and paper, the protection of metal and other surfaces. Cloth so coated is used for upholstery, paper as cap liners, and surface coatings for storage tanks and containers of all types.

As synthetic fibers and textile yarns these versatile resins become hosiery, shirts, and fish-nets. As rigid monofilaments they are applied as window-screening and brush bristles.

In many of these applications, polyvinyl resins are used because they alone of all materials have the necessary physical chemical characteristics. In some instances, freedom from warpage is important; in others, a superior polished finish is desirable directly from the mold; and in still others, extreme resistance to alkalies, acids, alcohol or grease is necessary. Further advantages of copolymer resins are extremely low water absorption, low moisture-vapor transmission, freedom from odor and taste, lightness in weight, high strength, non-toxicity, good adhesive properties, thermoplasticity, non-flammability, and the availability of a variety of light colors.

Compounding the Copolymers

All the monomeric materials—the bases of the polyvinyl resins—are derived from plentiful raw materials, natural gas, salt, coal, water, and air. The monomeric materials are converted to polymeric form by the polymerization process, and the resins can then be used with or without compounding. Compounding the resins is carried out by first hot-mixing them with the proper lubricants, stabilizers, opacifiers, plasticizers, or coloring materials, then fluxing and milling.

The resulting resinous material is a homogeneous mass which, while still hot, appears and acts very much like a colored or transparent dough. This resin "dough" can next be calendered by itself, extruded, calendered directly onto paper or cloth, sheeted and ground into molding compounds of various colors, or extruded into various forms. The fluxing, milling, and calendering operations are accomplished with heated mixers and rolls in much the same manner as is rubber compounding. Because there is no deterioration whatsoever with these resins, they can be produced and molded the same day or the powder can be stored indefinitely before molding. Also, the finished products never need any treatment to preserve them in any way.

Many Uses Developed

Developments in all these resins have been numerous, particularly in the copolymer resins which are now produced in plasticized form, resulting in an entirely new, colorful, and even transparent elastic plastic. All the resins, however, are well founded in their diversity of applications.

Polyvinyl acetate, as an example, is used most widely for sealing various types of food packages. The sealing of milk cartons, hot-drink cups, viscose film packages and other similar adhesive applications is well established in the food packing industries.

In the form of calendered tape, polyvinyl acetate is an excellent heat-sealing material for paper. This development—an extremely difficult one indeed—has resulted in a product which can be laid between sheets of paper to fasten them by a simple heat-sealing operation.

Polyvinyl acetate is also used as the "holding" material in small photoflash bulbs. The insulating qualities of the resin keep hot particles of metals from touching the glass, help to prevent the glass from being weakened, and reduces breakage. The resin layer because of its adhesive qualities also strengthens the glass, increasing impact resistance.

Modified polyvinyl acetate adhesive is also used for bonding impervious materials such as glass and metals. In some cases this bonding agent simplifies the assembly of small electrical devices, particularly where precision assembly of stamped parts is important. The material's use in the manufacture of loud-speaker housings and phonograph motors are outstanding examples.

Polyvinyl chloride is used extensively for impregnating fabrics—both industrial and domestic. Industrial applications include fabrics used for wrapping underground pipe lines to prevent corrosion, while domestic fabrics, particularly silk, are impregnated with a polyvinyl chloride solution to be made into raincoats, tobacco pouches, and curtains, because the impregnated material is both waterproof and stainproof.

Plasticized polyvinyl chloride compounds—both extruded and sheeted—have also gained wide acceptance. Extruded material is used for coating wire, while sheeted material is used principally for its high chemical resistance, such as in electroplating tanks. The toughness, lack of taste or odor, and high resistance of polyvinyl chloride to many corrosive agents all combine to suit it well for these applications.

Copolymerized vinyl chloride and vinyl acetate is the basis of several new and unique extensions of the plastics industry. Two of these developments have opened entirely new fields for plastics—as synthetic fibers, and flexible elastic materials in sheet form.

When spun from an acetone solution on equipment similar to that used for making acetate rayon, copolymer vinyl resin produces a textile fiber of high strength and outstanding chemical resistivity. These materials have already entered the industrial field as filter fabrics for chemical processing and as the bonding agent in new industrial felts. Industrial sewing thread and marine twine are also made of this material in large quantities because of its high strength and retention of strength when wet.

Highly plasticized calendered sheeting is an unusual material having many of the advantages of leather and rubber yet capable of being made transparent or in any of a wide variety of colors. It will not oxidize and can be made waterproof, oilproof and greaseproof, or non-flammable. It can be stretched to as much as 2½ times its normal length and always returns to its original size and shape. This material, first made into belts, suspenders, and garters, has been widely accepted and is now being used either by itself or in conjunction with other materials for women's and children's footwear, raincoats, wristwatch straps, wallets, waterproof pouches and rifle covers, and life-saving kits.

In unplasticized sheet form, copolymer vinyl resins are used for transparent packages, airplane windows and frost shields, watch crystals, radio dials, and many types of drawing, calculating, and navigating instruments. The uses of vinyl copolymer resin sheet are many because the material combines many advantageous properties not obtainable in other thermoplastic sheets. Its ease of fabrication, low moisture absorption, together with high strength and enduring permanence of dimensions, fit it admirably for these and other uses.

Some of the molded parts made of these resins are combs, toothbrush handles, glass cleaner sprayers, and various ornaments. Radio transcriptions are compression molded of the compounded resin, while most other articles are injection molded. The injection molding of highly plasticized material has finally been made commercially feasible, and articles such as smoking-pipe bits made of the flexible transparent plastic have created a definite demand.

Vinylidene Chloride Polymers

ROBERT C. REINHARDT

The Dow Chemical Co., Midland, Michigan

Although vinylidene chloride (1,1-dichloroethylene) has been known for more than one hundred years, extensive work on the polymers of this compound has been limited to the last decade. This work resulted in the introduction to the plastics industry in 1939 of a family of thermoplastics based on vinylidene chloride and known as "Saran." These new polymers now occupy a distinctive position in the widening field of synthetic plastic materials.

Regnault [18, 19] in 1838 reported the formation of a white, non-crystalline precipitate from a liquid boiling between 35° and 40°, which was apparently an impure 1,1-dichloroethylene. He considered this precipitate merely an isomeric modification. The liquid was prepared from trichloroethane by reaction with alcoholic potassium hydroxide, a method used by Kraemer [14] and Bauman.[1] In 1872 the latter described the formation of a white substance when dichloroethylene was exposed to sunlight. Ostromislenski [17] found that vinylidene chloride polymerized in light to a white amorphous mass insoluble in many solvents.

Feisst,[7] together with Staudinger [28] and Brunner,[22] investigated polydichloroethylene in greater detail. A portion of the polymer used was prepared from an apparently impure dichloroethylene fraction from commercial trichloroethylene. Other studies were made on polydichloroethylene formed as a by-product in the Rheinfelden works of the I. G. Farbenindustrie. It was found that this polymer was completely soluble in warm tetrachloroethane, decalin, and tetralin, partially soluble in benzene, chloroform, and carbon disulfide, and insoluble in ethers and alcohols, which permitted a separation of molecular weights by fractional solubility. The major part of the work involved reactions of the polymer with aniline, resorcinol, quinoline, pyridine, trimethylamine, and hydrazine, and studies of the products formed. The formation of high molecular weight hydrocarbons when the polymer was reduced with hydrogen iodide and phosphorus was reported as evidence that polydichloroethylene was composed of thread-like molecules.

The relation of vinylidene chloride to other polymerizable compounds is noteworthy. The effect of unsymmetrical substitution in ethylene compounds is well illustrated by comparing vinylidene chloride with its two isomers, *cis* and *trans* 1,2-dichloroethylene, which polymerize only with great difficulty. Ellis [6] and Brooks [4] have commented on the unsymmetrically substituted ethylenes prepared by early investigators. Sawitsch [20] observed that 1,1-dibromoethylene polymerized to a white solid. Denzel [5] and Biltz [3] made 1-chloro-1-bromoethylene, the polymer of which was found to be insoluble in many solvents. In general, 1,1-disubstituted ethylenes appear to polymerize more easily and form less soluble polymers than the vinyl compounds.

Polymerization

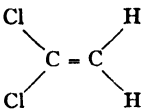
Monomeric vinylidene chloride, 1,1-dichloroethylene, is a colorless liquid with a mild characteristic odor. Important properties are given in Table 1. The most

convenient source of this compound is the reaction of 1,1,2-trichloroethane with aqueous alkali.

$$2CH_2Cl\,CHCl_2 + Ca(OH)_2 \xrightarrow{90^\circ} 2CH_2 = CCl_2 + CaCl_2 + 2H_2O$$

Although this general reaction was used by many early investigators, it has been the subject of a number of recent patents.[67, 71] 1,1,2-Trichloroethane may be made from petroleum and brine by well known reactions involving ethylene and chlorine. Other methods for its preparation are those based on bromochloroethane,[11] trichloroethyl acetate,[13] tetrachloroethane,[72] and catalytic cracking of trichloroethane.[24]

Table 1. Properties of 1,1-Dichloroethylene

Molecular formula	
Molecular weight	96.95
Boiling point	31.7° at 760 mm
Freezing point	−122.1°
Density	1.2129^{20}_{4}; 1.2085^{25}_{25}
Index of refraction	$n^{20}_{D} = 1.4249$

Carefully purified vinylidene chloride free of oxygen polymerizes very slowly. As ordinarily prepared, however, vinylidene chloride polymerizes readily at temperatures above 0° to form a polymer which is insoluble in the monomer and precipitates as a white powder.[85] The presence of dissolved oxygen which reacts to form acid chlorides and peroxides catalyzes the polymerization. Vinylidene chloride is not a vinyl compound, but much of the technique of vinyl chloride polymerizations is applicable to it. The many chemical catalysts for polymerization which have been used successfully [39-41, 44, 56] may be classified into five groups: organic peroxygen compounds, organometallic compounds, organic carbonyl compounds, inorganic salts, and inorganic acids. Benzoyl peroxide in concentrations of 0.05 to 2.0 per cent has been used frequently in laboratory work,* and a typical polymerization curve is shown in Figure 1. The straight-line nature of these curves is characteristic, and is evidence that the reaction is of zero order.

The benzoyl peroxide-catalyzed polymerizations have little, if any, induction period above 30°, but usually show a lower polymerization rate for the first few per cent conversion. This behavior is illustrated by the enlarged portion of the curve (inset in Figure 1).

The use of other catalysts or combinations of catalysts causes wide variation in polymerization rates, but in general does not change the shape of the curves. Thermal polymerization of vinylidene chloride without added catalyst usually does not occur at a rate sufficiently high to be useful, but photopolymerization has been successful both with and without auxiliary chemical catalysis. Light of wave length less than 4500 Å causes polymerization at temperatures as low as −35°.

Many inhibitors of the polymerization of vinylidene chloride have been described in patents.[26-34, 49]

A solid phase appears during the polymerization of vinylidene chloride, since the polymer is not soluble in the monomer. In mass or bulk polymerizations, where only monomer and catalyst are present, the polymer is flocculent precipitate below about 10 per cent conversion; between 10 and 20 per cent conversion the slurry becomes

* Unless otherwise credited, the source of data and information is The Dow Chemical Company.

solid; above 20 per cent no liquid is visible and the porous solid becomes harder with increasing polymerization. With proper choice of conditions the reaction reaches 100 per cent conversion to polymer, and results in the evolution of about 20,000 gram calories per gram mole of monomer. In order to control the polymerization rate and the physical characteristics of the product, it is often desirable to add to the monomer a solvent or an immiscible liquid and conduct the polymerization in solution, emulsion, or other dispersed system.[42, 43] The products of different polymerization methods differ only in minor details.

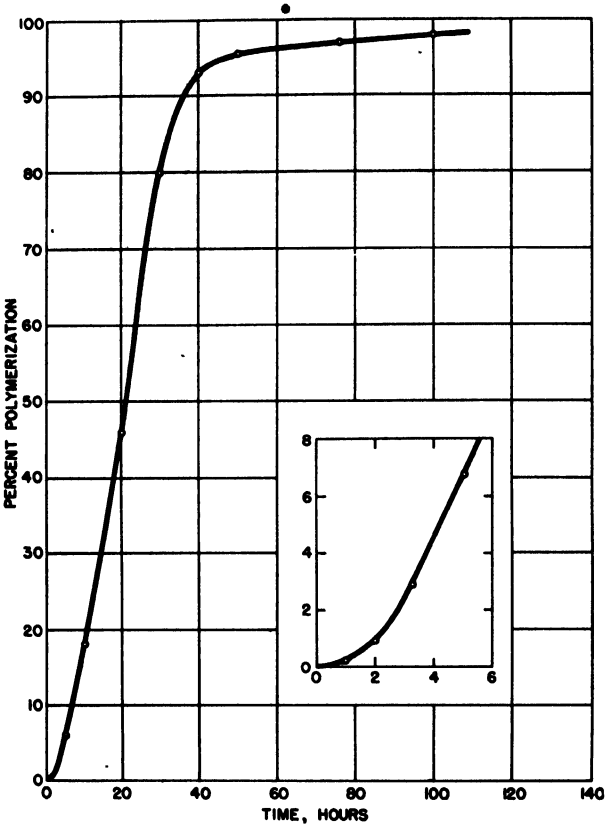


FIGURE 1. Polymerization of vinylidene chloride. Catalyst, 0.50 per cent benzoyl peroxide; temperature, 45° C.; dark.

Polyvinylidene chloride is a white porous powder with a softening range of 185-200° and a decomposition temperature of about 225°. When fused and cooled, the polymer is colorless and nearly transparent. In either form, polyvinylidene chloride possesses two outstanding characteristics—crystallinity, as determined by x-ray diagrams, and insolubility. These will be discussed later in detail.

The distinctive properties of polyvinylidene chloride are given in Table 2. The utilization of the polymer as a plastic material in the ordinary sense is difficult because of its high softening range, its tendency to evolve HCl at the temperatures required for plastic working, and its incompatibility with usual plasticizers. These obstacles, not necessarily disadvantages, are characteristic of the molecule, but despite them, polyvinylidene chloride can be worked by special methods to produce a

Table 2. Properties of Polyvinylidene Chloride

Molecular formula	$(-CH_2-CCl_2-)_n$
Molecular weight	10,000-100,000
Softening temperature	185-200°
Decomposition temperature	210-225°
Density	1.875 gm/cc at 30°
Index of refraction	1.63
Flammability	Nonflammable
Solubility	Insoluble in all organic solvents at temperatures below 100°
Reactivity	Unaffected by all common reagents at temperatures below 100°

unique plastic material. For general use, the properties of the polymer are best modified by copolymerization.

Copolymerization

Vinylidene chloride forms copolymers with many substituted ethylenes, particularly the common vinyl compounds, with dienes and their derivatives, and with a number of other unsaturated compounds. Specific examples are described in many patents; important copolymers of vinylidene chloride are those with vinyl chloride,[37, 61, 63, 68] vinyl acetate,[37] styrene,[38] esters of acrylic and methacrylic acids,[50, 69] and vinyl cyanide.[62] Other compounds which are known to copolymerize with vinylidene chloride are butadiene and its derivatives,[25, 57, 70] various unsaturated esters,[45-47, 51] unsaturated ethers [48] and halogen-substituted propenes.[52]

In general, when vinylidene chloride is copolymerized, each mixture of monomers has a different polymerization rate and produces a polymer of different composition. Usually the product contains a larger proportion of vinylidene chloride than the original monomer composition, and the rate of polymerization is slower than for

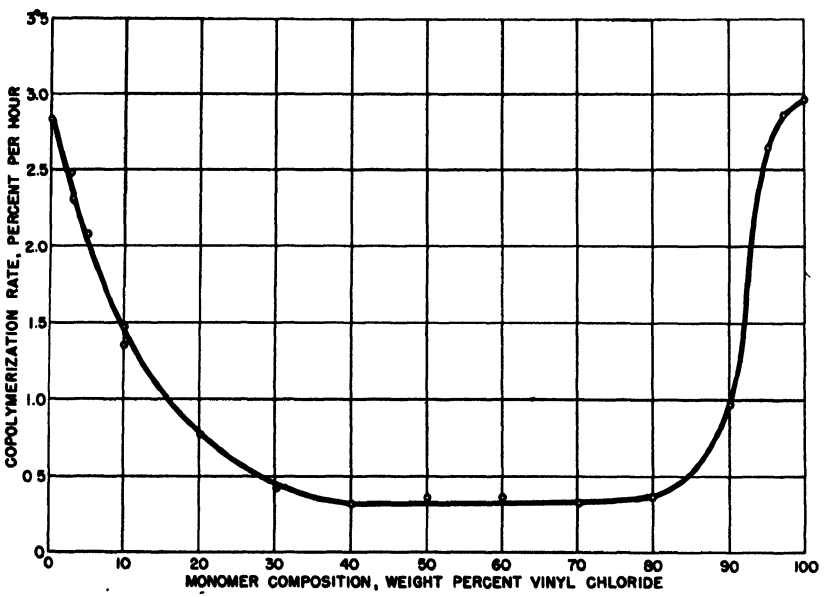


FIGURE 2. Copolymerization rate of vinylidene chloride and vinyl chloride as a function of monomer composition. Catalyst, 0.50 per cent benzoyl peroxide; temperature, 45° C.; dark.

either monomer alone. Except in rare cases the products are true copolymers and contain little or none of the individual polymers.

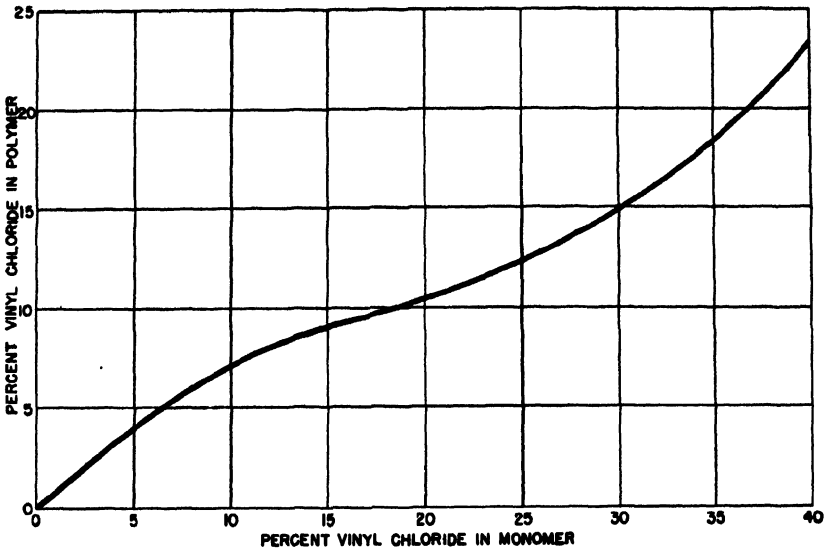


FIGURE 3. Copolymerization of vinylidene chloride and vinyl chloride. Catalyst, 0.50 per cent benzoyl peroxide; temperature, 45° C.; dark; approximately 50 per cent polymerization.

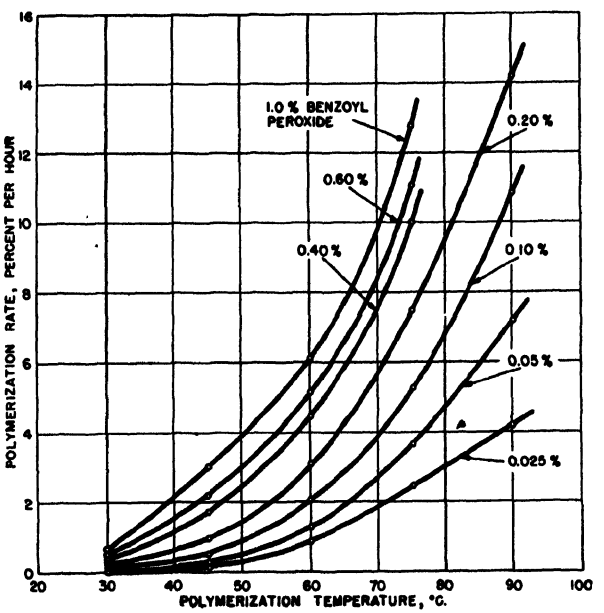


FIGURE 4. Copolymerization rate of vinylidene chloride and vinyl acetate as a function of polymerization temperature and catalyst concentration. Monomer composition, 85 per cent vinylidene chloride, 15 per cent vinyl acetate; temperature, 45° C.; dark.

A typical case is illustrated by Figure 2. Although vinylidene chloride and vinyl chloride have nearly identical polymerization rates with 0.5 per cent benzoyl peroxide at 45°, mixtures of the two monomers may have but one-tenth the polymerization rate of either component. Figure 3 shows the average polymer compositions produced from a number of monomer mixtures. Since the polymer contains more vinylidene chloride than the monomer, the vinyl chloride concentration in the monomer increases as the polymerization progresses; consequently, the product of such a polymerization contains a wide distribution of copolymer compositions in addition to the distribution of chain lengths.

The thermal and peroxide catalysis of copolymerization is illustrated in Figure 4 with an 85 per cent vinylidene chloride, 15 per cent vinyl acetate monomer composition. Increased temperature is preferable to higher catalyst concentration as a means of increasing the polymerization rate. The relation of chain length to polymerization temperature for these copolymers is shown in Figure 5.

The methods used for polymerizing vinylidene chloride are applicable with certain changes to the formation of its copolymers. However, the widely varying polymerization rates and the heterogeneous copolymers introduce important complications in the study and development of both process and products.

Analysis of vinylidene chloride copolymers may be done by standard methods. Determination of the per cent chlorine is usually sufficient to give the average composition, although, as mentioned by Berger,[2] the results obtained by this method may be in error by several per cent. Comparative measurements of chain lengths are made by the determination of solution viscosity, but due to the extremely limited solubility of certain copolymers, it is often necessary to use only the best solvents at temperatures of 120° or above.

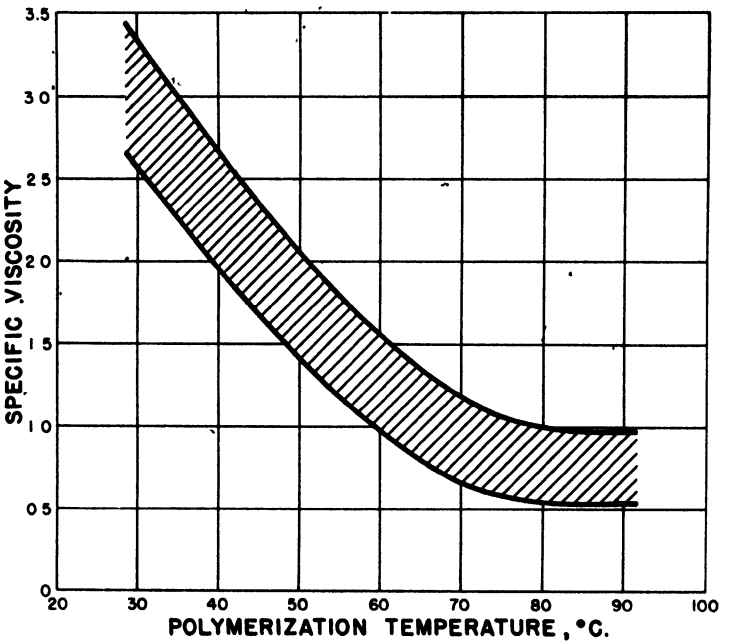
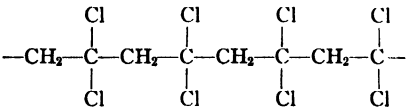


FIGURE 5. Specific viscosity of vinylidene chloride-vinyl acetate copolymers as a function of polymerization temperature. Monomer composition, 85 per cent vinylidene chloride, 15 per cent vinyl acetate; catalyst, 0.50 per cent benzoyl peroxide; dark; solution, 2 per cent in *o*-dichlorobenzene at 120° C.

Structure

A most important and fundamental property of polyvinylidene chloride, *i.e.*, crystallinity, was first noted by Feisst,[7] after x-ray diagrams had been made by Hengstenberg and Sauter. Further comments were made by Staudinger,[21] who assigned to polyvinylidene chloride the head-to-tail configuration



and attributed its crystallinity to its regular molecular structure. Natta and Rigamonti [16] studied a number of polymers by electron diffraction and found polyvinylidene chloride to be highly crystalline. Subsequent work of a more accurate and detailed nature has resulted in a fairly complete picture of the fine structure of polyvinylidene chloride and its copolymers.

The examination of representative polymers and copolymers of vinylidene chloride by means of x-rays results in patterns of which Figures 6 and 7 are typical. From

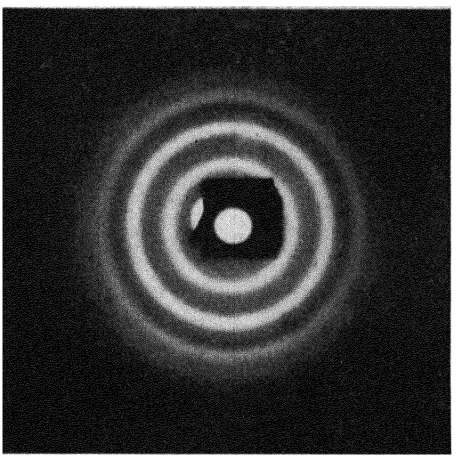


FIGURE 6. Polyvinylidene chloride (powder). MoK_α radiation; specimen to plate distance 6.5 centimeters.

these it may be said that (1) the well defined rings indicate a high degree of crystallinity; (2) the background scattering indicates an appreciable amount of amorphous material; and (3) polyvinylidene chloride is more crystalline than its copolymers. If, for example, a polymer or copolymer of vinylidene chloride is completely fused at a temperature above its melting point and cooled rapidly to a low temperature, it becomes amorphous, and an x-ray pattern such as that of Figure 8 results. Storage of amorphous polymer at suitable temperatures permits gradual recrystallization. Severe mechanical working (*e.g.*, stretching) of either completely amorphous or partly crystalline polymers produces orientation, as shown in Figure 9. Polyvinylidene chloride and copolymers which are largely vinylidene chloride can, therefore, be said to exist in three modifications:

(1) Crystalline: the normal "as polymerized" state, giving a sharply defined x-ray pattern but also known to be partly amorphous.

(2) Amorphous:* soft, easily deformed material obtained by fusing and rapidly cooling crystalline polymer; reverts to the crystalline form under suitable conditions.

(3) Oriented crystalline: tough, strong, showing characteristic x-ray fiber pat-

* Some substances classed as amorphous may contain or even consist of crystals or other aggregates of colloidal dimensions, which tend to make larger crystals. J. A.

tern; produced by plastically deforming either partly crystalline or amorphous material.

Accurate measurement and analysis of the x-ray diagrams, together with these considerations, led to a concept of the structure of polyvinylidene chloride which is adequate to explain observed physical phenomena.

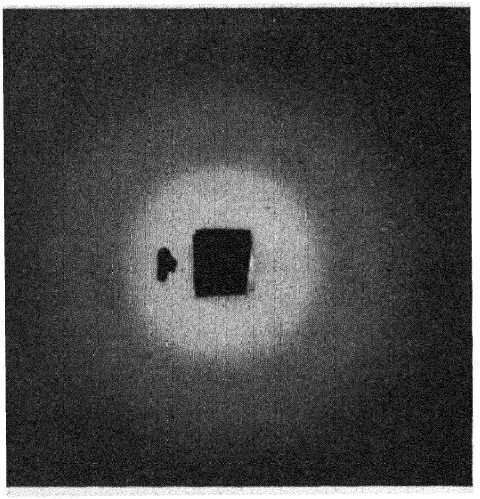


FIGURE 7. Amorphous copolymer of vinylidene chloride and ethyl acrylate. MoK_α radiation; specimen to plate distance 6.5 centimeters.

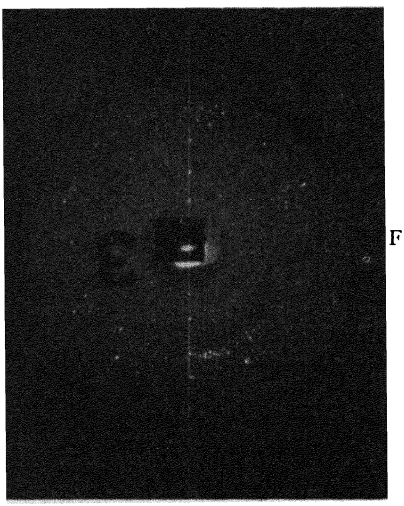


FIGURE 8. Normally crystalline vinylidene chloride-vinyl chloride copolymer, amorphous. MoK_α radiation; specimen to plate distance 6.5 centimeters.

A single chain of polyvinylidene chloride is believed to have the structure shown by the model, Figure 10, and dimensions drawn in Figure 11. Monomer units are joined head-to-tail, with a serpentine configuration of carbon atoms. With a carbon valence bond angle of 120° and a carbon-carbon distance of 1.55 Å, an identity period of 4.67 Å results.

This structure is in better agreement with the observed reflections than those given by Fuller,[8] who suggested a zig-zag arrangement of carbon atoms with the chain shortened by partial rotation.

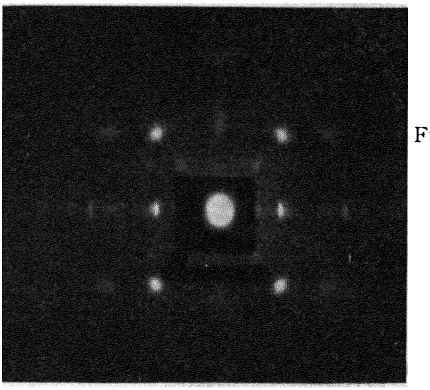


FIGURE 9. Normally crystalline vinylidene chloride-vinyl chloride copolymer, oriented; fiber axis vertical. MoK_α radiation; specimen to plate distance 6.5 centimeters.

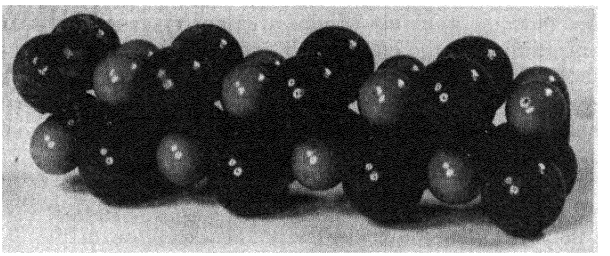


FIGURE 10. Scale model of a portion of the polyvinylidene chloride chain.

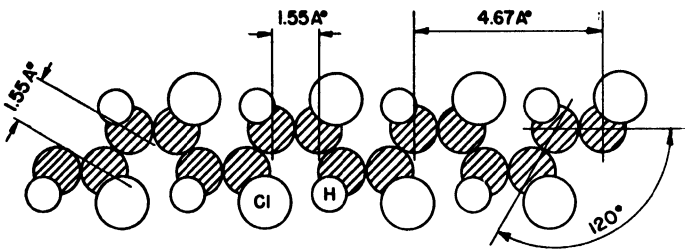


FIGURE 11. Chain configuration of polyvinylidene chloride (scale of interatomic distances expanded with respect to that of atomic radii).

Solution viscosity and osmotic pressure measurements indicate a range of chain lengths of 100 to 1000 monomer units. As with other high polymers, the chain length is an inverse function of the polymerization temperature and the catalyst concentration. Determination of the branching coefficient, n, by the method of Houwink [12] gives $n = 1$. This unusually low value and the marked tendency to crystallize are strong evidence that the chains are not branched. In the amorphous state, they are randomly distributed and probably highly curled. Crystallization involves the movement of portions of such molecules into a macromolecular lattice which has no well defined boundaries.

The unit cell of polyvinylidene chloride is monoclinic and contains four $—CH_2—CCl_2—$ units. Its dimensions have been determined accurately as follows:

$a = 13.69 \pm 0.015$ Å
$b = 4.67 \pm 0.01$ Å
$c = 6.296 \pm 0.010$ Å
$\sin \beta = 0.8212 \pm 0.015$
Volume of cell = 330.6 Å

The dimensions of the "crystallite" are believed to be about 20-30 Å parallel to the chain axes and about 200-500 Å at right angles. In the crystalline portions, the chains are essentially parallel, although the long-chain molecules undoubtedly traverse both crystalline and amorphous regions. The comparatively low proportion (20-40 per cent) of crystalline regions in fused and recrystallized polymer and the high ratio of length to diameter of the molecules indicate that the amorphous regions are probably the continuous phase. Such a picture is not one of mesomorphic arrangement, nor of a crystalline modification dispersed in an amorphous one, but rather a continuous transition between crystalline and amorphous material. Both modifications share in determining the ultimate physical properties.

Copolymerization introduces units in the chain which tend to destroy its regularity, and consequently its ability to crystallize, although the introduction of small amounts of other monomers merely results in minor discontinuities in the crystalline regions. The magnitude of the effect varies somewhat with the structure of the copolymerizing molecule, but in general, copolymers which contain less than about 70 per cent vinylidene chloride are essentially non-crystalline. Other effects of copolymerization which are related to the decreased crystallinity are reduced softening temperature and increased solubility in organic solvents.

Phenomena Associated with Crystallinity

Crystalline polyvinylidene chloride (with the exception of the "as polymerized" powder) is hard, tough, and resembles ordinary plastic materials in many respects. Amorphous polyvinylidene chloride is soft, rubbery, capable of being mechanically worked, and tends to crystallize on standing. The oriented modification is very strong, tough, and exceedingly flexible. In general these statements are true also for crystalline copolymers; and in fact, the copolymers which fall in this range are those which possess a most advantageous combination of properties for commercial molding and extrusion.

A very narrow softening range is characteristic of the crystalline polymers and crystalline copolymers of vinylidene chloride. A few degrees above the softening range these polymers have a sharp, reproducible crystalline melting point, observed by the change in light transmission of a sample heated between crossed "Polaroids." This temperature probably corresponds to the melting of the most stable crystalline regions. The process of melting is comparable to the solid-liquid transitions of lower molecular weight crystalline compounds. At higher temperatures the molten polymer may be quite fluid. The flow data given in Figure 12 illustrate the sharp softening point of a crystalline vinylidene chloride—vinyl chloride copolymer as compared with polystyrene.

When a normally crystalline copolymer is heated to a temperature sufficient to melt the crystalline portion and then cooled below the crystalline melting point in a manner such that no recrystallization occurs, it is amorphous and is said to have been supercooled.[55] When it is so treated, the tendency to crystallize is a function of many variables, the most important of which are the copolymer composition, the time and temperature of storage, and the presence of addition agents such as plasticizers. Figure 13 shows the wide variation with temperature of the induction time which elapses before recrystallization begins. This induction period, as measured between crossed "Polaroids," is a reproducible quantity for any copolymer composition and treatment. In Figure 13 the area below either curve denotes the conditions under which the supercooled polymer may be produced and stored. Above about

110° the crystallization induction period is increased by the relatively high thermal energy of the polymer chains; below about 60° the increase is due to the high internal viscosity. The effect of certain plasticizers in reducing the crystallization induction period, as shown in curve B, may be attributed to the increased mobility of the chains. The short induction period at the lowest portion of the curves illustrates why rapid cooling of a fused polymer is usually necessary to produce samples which are amorphous at room temperature.

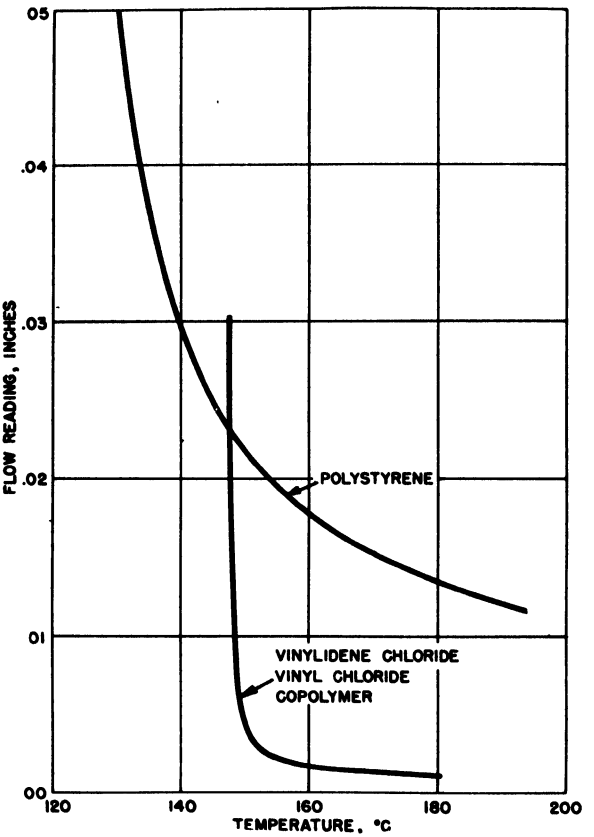


FIGURE 12. Typical flow curves of a crystalline vinylidene chloride-vinyl chloride copolymer and polystyrene. "Flow reading" is the equilibrium thickness attained by a film of plastic subjected to a constant load between parallel polished plates heated to the temperatures shown.

When crystallization has started, several marked changes occur in the physical and mechanical properties of the polymer. The most important of these are:

(1) A gradual development of a typical crystalline x-ray diffraction pattern.
(2) An increase in hardness.
(3) An increase in the force required to produce deformation.
(4) An increase in density.
(5) Evolution of about 3.4 gram calories per gram of polymer as heat of crystallization.
(6) Variations in electrical properties.
(7) An increase in resistance to the action of solvents.

Amorphous polyvinylidene chloride and amorphous copolymers of vinylidene chloride prepared from normally crystalline copolymers bear a similarity to natural rubber in two respects other than those already mentioned. For very low elongations, a filament of such amorphous polymers exhibits nearly perfect elasticity until crystallization occurs. Also, if a supercooled filament is stretched to an elongation of 150-250 per cent and allowed to crystallize further, it will elongate slightly without application of load.

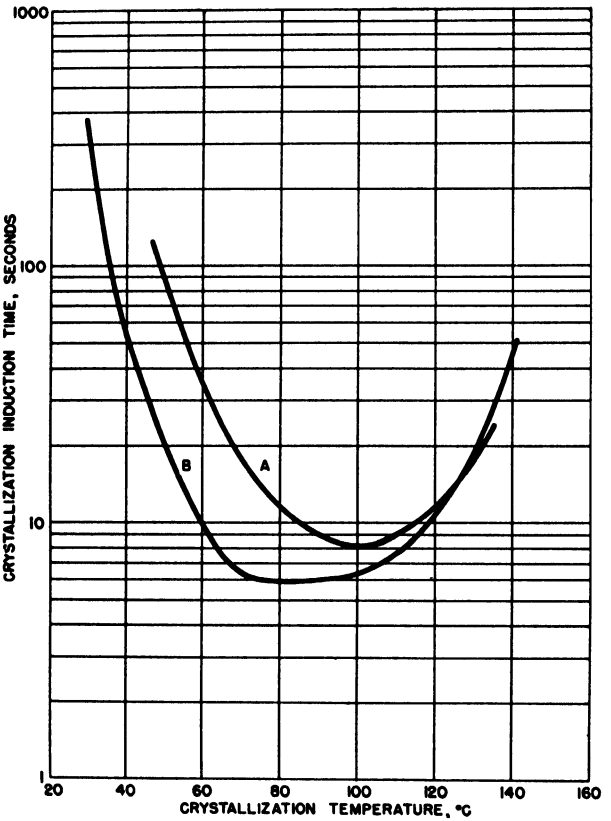


FIGURE 13. Typical crystallization induction period curves for a normally crystalline vinylidene chloride-vinyl chloride copolymer. Curve A—no plasticizer; curve B—7 per cent plasticizer. Specimen thickness 0.050 inch.

Orientation

Vinylidene chloride polymers and copolymers exhibit orientation when either the crystalline or amorphous modifications are mechanically worked, but the degree of orientation produced may vary, depending on the polymer composition and treatment. If a filament of polyvinylidene chloride is stretched at a temperature somewhat above the polymer crystalline melting point, and quickly cooled, the strand will show some slight orientation. Crystalline polyvinylidene chloride may also be stretched, with the application of comparatively high loads, and a filament so treated will exhibit orientation, together with increased strength and flexibility. However, if a similar filament is supercooled, and stretched before crystallization begins, a

high degree of orientation results. The x-ray pattern (Figure 9) is characteristic of this treatment, which may be used to produce fibers of exceptionally high strength and flexibility.[60] The load-elongation curve for a supercooled filament (Figure 14) shows that the force required for plastic deformation is nearly constant below 300 per cent elongation; but after orientation has occurred, elastic elongation requires a relatively high load. Supercooled filaments may be stretched to an elongation of 350-400 per cent, depending on previous treatment, and the greatest increase in tensile strength is found to occur with the last few per cent of stretch. Tensile strengths of 100,000 pounds per square inch have been obtained with optimum stretching conditions, but with the sacrifice of other desirable properties.

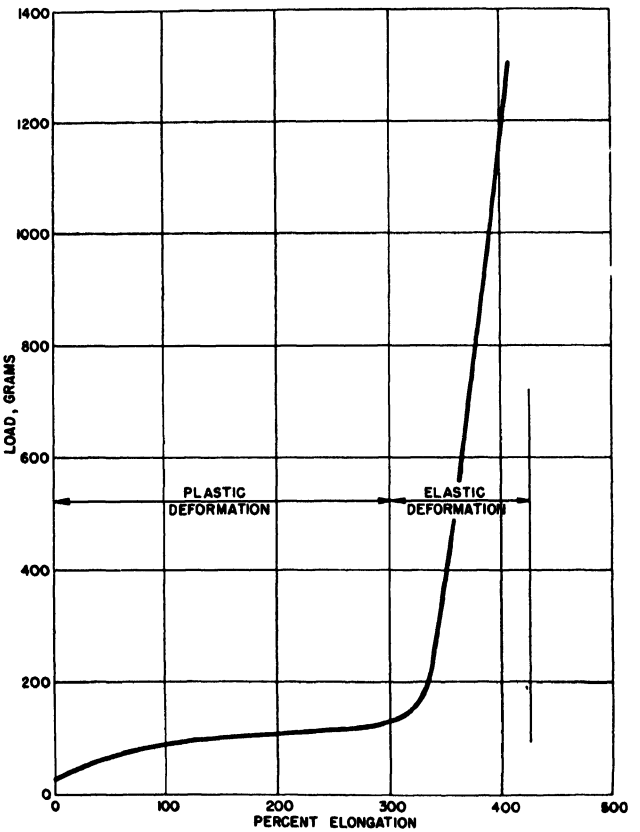


FIGURE 14. Typical load-elongation curve for a supercooled filament of a normally crystalline vinylidene chloride-vinyl acetate copolymer, plasticized. Temperature of test, 20° C.; Scott IP2 testing machine; final diameter of filament 0.011 inch.

Fabrication

Certain vinylidene chloride polymers and copolymers may be fabricated by the methods commonly used for thermoplastics, but in order to take advantage of the unique properties resulting from the crystalline structure, additional methods have been developed. The high softening point and relative thermal instability of polyvinylidene chloride have largely excluded it from the industrial fabrication procedures for which the copolymers of lower softening temperatures are more adapt-

able. The copolymers now available require special technique in their fabrication. Important considerations are the use of inert metals in hot zones, minimum heating times, and the incorporation of a satisfactory plasticizer and heat stabilizer.

The remarkable properties of oriented filaments of vinylidene chloride copolymers have stimulated the development of extrusion processes. Modification of the screw-type extrusion machines to permit streamline plastic flow and uniform heating, together with the use of entirely new types of stretching and winding machinery, have resulted in the production of a wide variety of extruded articles. Cordage (0.010-0.100-inch diameter filaments) and tubing have gained industrial prominence, and intensive work on textile fibers is continuing.

Injection moldings of vinylidene chloride copolymers possess unusual toughness and durability, since the molding cycle may be modified to produce finished articles which are partly oriented. The use of cold dies results in supercooled articles suitable for further treatment, while heated dies permit crystallization, desirable for rapid cycles and dimensional accuracy of the finished piece. Economic considerations usually favor injection molding over compression molding, although the latter may be accomplished quite satisfactorily.

Vinylidene chloride copolymers may be fabricated by a variety of new methods, in that the combination of thermoplasticity with crystallinity permits operations such as cold or hot rolling,[54] forging, blowing, stamping, and welding.[58]

Physical Properties

The relative insolubility and unreactivity of polyvinylidene chloride was noted by a number of early workers. This characteristic is not greatly altered by increasing copolymerization until the copolymer contains less than about 85 per cent of vinylidene chloride; consequently, the commercially available copolymers are resistant to the action of all but a very few common materials. At temperatures above 100°, compounds of the type of dioxane,[64] *o*-dichlorobenzene,[65] and cyclohexanone [66] show some solvent action, but true solutions may not be obtained in many cases. At room temperature, high vinylidene chloride copolymers are substantially unaffected by both aliphatic and aromatic hydrocarbons, alcohols, esters and ketones. Inorganic acids and alkalies have little or no effect, with the exception of concentrated sulfuric acid, sodium hydroxide, and ammonium hydroxide, which cause discoloration. Resistance to water is exceptional, ASTM tests showing 0.00 per cent absorption in 24 hours, and less than three grams per square meter per 24 hours water vapor transmission at 45°.[10]

In view of the low compatibility of crystalline vinylidene chloride polymers and copolymers with other materials, it is not surprising that a very limited number of plasticizers offer any advantages.[30, 53, 59] Plasticized and stabilized copolymer compositions are available as molding powder or in fabricated shapes under the name of "Saran." Heat and light stabilizers, dyes, pigments, fillers and lubricants have been developed specifically for many applications.

Detailed tabulations of the properties of "Saran" which are of interest to the fabricator and the user have been given by Goggin,[9] Goggin and Lowry,[10] and the annual plastics properties charts of *Modern Plastics*.[15]

Uses

"Saran" has found wide use in fields new to plastics because of its fortunate combination of chemical inertness, strength, and toughness. Extruded and oriented, it has found application in heavy textiles, ropes, braids, belts, and in tapes for furniture and transportation seating. Extruded "Saran" tubing, rods, and other structural shapes are used as process piping and for a variety of mechanical parts. Injection and compression moldings of "Saran" have solved many difficult molding and application problems where its superior mechanical and chemical properties are essential. A number of basic fabricated forms are illustrated in Figure 15.

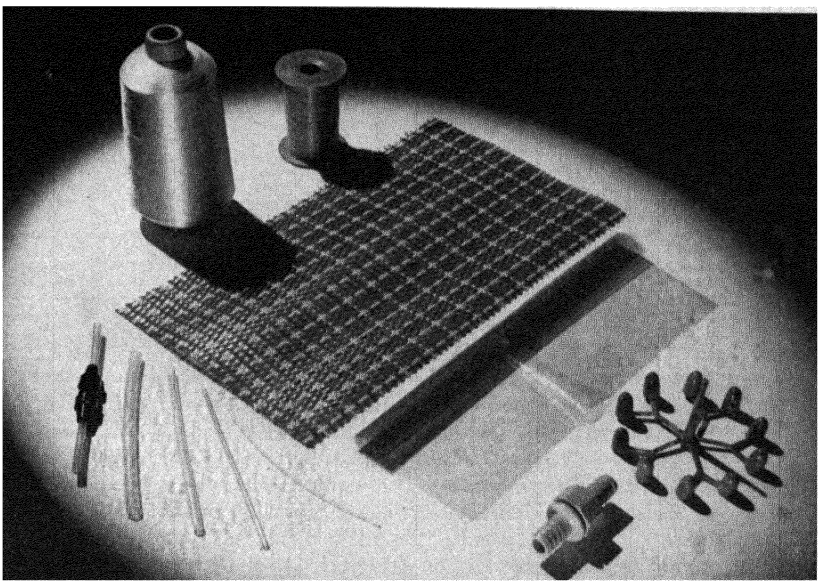


FIGURE 15. Basic fabricated forms of Saran—cordage, rattan, tubing, textile filaments, foil, and injection moldings.

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62. U S P. 2,238,020.
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69. British P 525,048
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72 French P. 786,803.

Urea-Formaldehyde and Related Resins

GEORGE BARSKY

Barsky & Strauss, Inc., New York

As with phenol and formaldehyde, the reaction between urea and formaldehyde was known to take place long before the development of useful products. C. Goldschmidt [1] obtained a white insoluble material on reacting urea and aqueous formaldehyde. This white amorphous material was also obtained by other early workers and was known as "Goldschmidt's Compound." Other early investigators of the reaction were Dixon,[2] Hölzer,[3] Ludy,[4] Einhorn,[5] and Einhorn and Hamburger.[6]

John was probably the first to attempt the manufacture of commercial products from the urea and formaldehyde. His first United States patent [1,355,834 (1920)] described the preparation of adhesives and impregnants for fabrics. John used relatively large proportions of formaldehyde to urea (molar ratio more than 2:1), and removed water by distillation. His products were not exploited successfully.

The advent of cheap urea as a result of the extensive development of the fixed nitrogen industry during and after World War I stimulated experimental work on urea resins. Early investigators were concerned with the preparation of cast resins, the water-soluble reaction product being concentrated and poured into molds to cure. It is possible in this way to obtain clear, glass-like objects of great brilliancy; but on aging, cracking and crazing take place as the water of the gel structure evaporates.

Pollak [7] and his co-workers in Austria are generally considered to be the first to have prepared molding powders of commercial possibilities. Carleton Ellis [8] and his staff were active in the United States at about the same time. Curiously, the industry started in the United States first along the lines of mixed urea-thiourea-formaldehyde products in 1929, the original process being that developed in England. The urea moldings then known were affected too much by contact with water. The English investigators found that substitution of thiourea for a part of the urea gave superior water resistance. However, the cost of thiourea was high and it caused corrosion and staining of molds. Gradually the properties of the all-urea molding compounds were improved and the mixed thiourea-urea compound was abandoned.

The use of urea resin molding has grown steadily and has undoubtedly contributed greatly to the demand for light-colored and decorative plastics. In general, developments parallel those of the phenol-formaldehyde resins. Subsequent to the establishment of the molding powders on a firm commercial basis came the coating resins, that is, resins soluble in organic solvents, miscible with film-forming materials and thus suitable for use in varnish and enamels. In the case of phenol-formaldehyde resins, the oil solubility is obtained by reaction of an intermediate with another reactant, or by reaction of the phenol alone with another reactant to form a substitute phenol before reaction with formaldehyde. In the case of urea-formaldehyde, oil solubility is obtained by reaction of an intermediate with butanol or similar alcohol.

Production of Urea Molding Resins

In the production of urea resins for molding, urea and formaldehyde solutions are reacted under controlled conditions of pH, temperature, etc. The resulting solution is mixed with a high-grade cellulose filler and dried under carefully controlled conditions. The dried product is ground with pigments and an accelerator if desired, and comes on the market in the form of powder. Accelerators speed up the cure during molding and consist of compounds which generate small amounts of acid during molding.

For certain molding operations it is more desirable to have a material denser than the fluffy powder. Densification is accomplished by means of densifying and agglomerating machinery such as the Banbury mixer. The powder or granulated material is sold to molders who form pieces of various shapes by pressing the molding material in steam-heated molds under pressure obtained hydraulically.

For laminating, water solutions are used. These are of several grades, of different concentrations. Urea and formaldehyde may be used, or mixtures of urea and thiourea with formaldehyde. The laminator buys these solutions, impregnates and dries cloth or paper sheets. He then presses bundles of such sheets between steam-heated platens in hydraulic presses.

Properties of Urea Molding Resins

Urea resins are thermo-reactive, that is, they set to a hard mass when hot in the mold. They do not discolor with light or time. The base resin is transparent and colorless, and with the white filler always used, very light shades are obtainable. It is tasteless and odorless. With the light colors small amounts of dirt in the molding powder show readily in the finished piece, and great care must be taken to avoid such contamination. In addition, due to the translucency of the finished moldings, slight defects such as entrapped air and flow lines are easily noticed. The final molded resin contains a small percentage of water, the evaporation of which on exposure causes a slight distortion of shape. However, this distortion is not objectionable in many cases. Urea resins are affected by changes in atmospheric humidity, contracting somewhat in low humidity and expanding in high humidity. This results in warping or cracking with some shapes, especially where metal inserts are used, or where, as in containers for materials containing water, different portions of the same piece are under different conditions of humidity. Continuous exposure to temperatures over 170° F will also cause cracking. Machining of urea resins cannot be done satisfactorily as a general rule. The cured resin does not burn on exposure to free flame but chars and emits disagreeable odors, due to the formation of amines.

Manufacture of Urea Coating Resins

These resins are soluble in organic solvents, principally the higher alcohols and mixtures of these alcohols with coal-tar hydrocarbons. The resin itself is a reaction product of formaldehyde, urea and butanol. In the manufacture of these resins, 2.5 moles or more of formaldehyde are condensed with 1 mole of urea under slightly alkaline conditions. A small amount of acid is then added and, after further condensation, an excess of the alcohol. The water is then removed by azeotropic distillation in the presence of excess alcohol. Finally a good part of the excess alcohol is removed by adding a higher boiling coal-tar hydrocarbon and continuing the distillation.

Thiourea or melamine may be substituted for urea.[9]

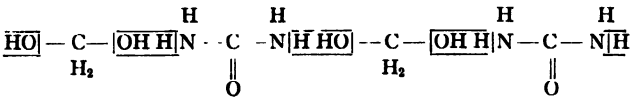
Uses for the Coating Resin

This resin is used for the manufacture of industrial enamels, such as are used as finishes on automobiles, household refrigerator exteriors, metal furniture, etc.

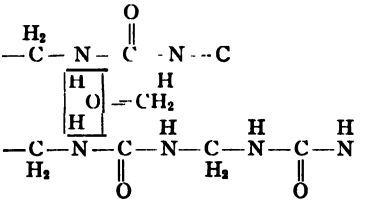
The resin is water-white [10] and perfectly transparent, even after baking. It is heat-hardening, and baked films of it are hard when hot, as when removed from the oven. Baking time is about one hour at 250° F, or two to three hours at 200° F. When cured the resin is hard and brittle, but deficient in adhesion. Blended with alkyd resins, it produces excellent coating films, imparting hardness and gloss, and improving the color and baking characteristics over the alkyd. It exhibits no yellowing on age or light exposure. After baking it is resistant to almost all organic solvents. Solutions are somewhat difficult to grind with pigments. The resin is neutral and does not react with ordinary basic pigments.

Reactions

According to its conventional carbamide formula, urea has two amino groups and is therefore capable of reacting with formaldehyde (methylene glycol) to form compounds of high molecular weight



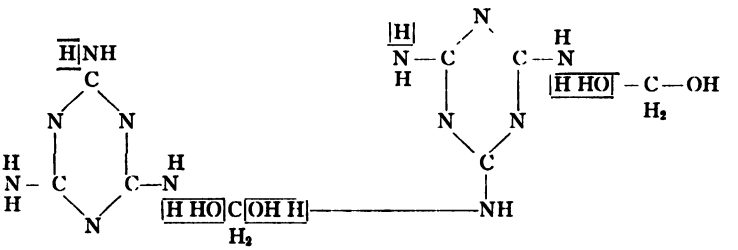
In addition to the formation of long chains, as shown in the above formula, cross linkages from chain to chain or across the same chain can be formed by the reaction of additional formaldehyde:



Probably a mixture of linkages is formed during the manufacture of the resin with additional cross linkages formed during molding. The completion of additional cross linkages is the probable reaction taking place during thermosetting. There are two points in favor of this theory. First, commercial urea molding powders and moldings have approximately 1.3 moles of formaldehyde per mole of urea. As the ratio of formaldehyde is lowered, it becomes increasingly difficult to obtain moldable products. On the other hand, with higher ratios, the water-resistance and thermosetting properties decrease. The 1.3 ratio apparently provides the optimum of cross linkages.

The second point is that water is formed during the molding operation to the extent of about 9 per cent of the actual resin present. This indicates that a condensation reaction forming water is responsible for the final thermosetting.

Thiourea reacts similarly to urea, but melamine is quite different in that it has three amine groups and therefore can form a three-dimensional structure more readily than the two ureas. Each of its three amino groups is the same in reactivity:



Defects of Urea Resins

The principal defect of the urea molding resins has been the effect of water, both liquid and vapor, and research efforts have been directed to improving this weakness. The action of water produces a swelling effect similar to that of water on proteins. The use of thiourea results in improved water resistance, probably because of the more hydrophobic character of the C = S linkage compared to that of the C = O group. The incorporation of a small amount of water-soluble salts in a urea resin lowers its water resistance markedly.

In the last five years attention has been turned from urea to related diamine compounds in the hope that these might, like urea, yield resinous products but of superior water resistance. Despite many attempts, dicyandiamide, the dimer of cyanamide, has not proved to be a fruitful raw material. On the other hand melamine, the trimer of cyanamide, has proved to be very useful. The melamine resins have shown very interesting properties, and when the manufacture of melamine is developed to a point of lowering its cost, these resins will become a very important addition to the plastics family.

Comparative Physical Properties

Properties	Urea	Melamine
Water absorption 24 hrs. (25° C) (%)	0 75-3.0	0 35
Specific Gravity	1.45-1.55	1 45-1.55
Flexural Strength (p.s i)	10000-16000	10000-16000
Impact, Izod (ft lbs)	0 24- 36	0 24-0 35
Tensile Strength (p.s i)	6000-13000	.
Compressive Strength (p s i)	24000-30000	. .
Modulus of Elasticity (p s i)	$1\ 5 \times 10^6$	.
Resistance to heat (° F)	180	210
Distortion under heat (° F)	260	. .
Mold Shrinkage	0 005 0 011	..
Volume Resistivity	10^{13}	10^{12}
Dielectric Strength, Short Time, 1/64" thick disc	650-720	610
Dielectric Strength, Short Time, 1/8" thick disc	350-370	320-350
Dielectric Constant, 60 cycles	7 0-8.0	9 0-9 5
" " 10^6 "	6.4-7.5	7 5-8 0
Power Factor, 60 cycles	0.035-0 045	0 06-0 09
" " 10^6 "	0 025-0 040	0 03-0 04
Loss Factor, 60 "	0 24-0 36	0 54-0 85
" " 10^6 "	0 16-0 30	0 22-0 32
Arc Resistance (seconds)	140	.....

(Data on unconditioned samples)

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See also review of amino resins by J. Hofton, Chemistry and Industry, Dec 2nd, 1944.

According to J. E. Lynn (Am. Dyestuff Reporter, 33, 554 (1944) the shrinkage and felting of wool can be effectively controlled by a resin condensate based on melamine. See U. S. P. 2, 329, 622 to E. P. Johnstone and W. Van Loo.

Acrylic Resins

D. S. FREDERICK

Vice President, Rohm & Haas Co.

Acrylic compounds have been known for some time, but only during the last fifteen years have they found practical application. Their commercial development has been due largely to the efforts of the late Dr. Otto Rohm, who published his doctorate thesis on these compounds in 1901, and then continued his work on the acrylic derivatives for many years.

Chemical Constitution. The acrylic resins are polymerized derivatives of acrylic acid, $CH_2 = CHCOOH$. Although resins may be made from all types of derivatives, polymers containing salts of acrylic acid, acrylate esters, acrylonitrile, and esters of alpha-methyl acrylic acid are of principal commercial importance.

Methods of Preparation. Since the acrylic resins are all polymers, the first step in their preparation is the manufacture of the monomers. The acrylate esters may be synthesized from ethylene cyanohydrin by the following reaction:

$$CH_2OHCH_2CN + ROH + H_2SO_4 \rightarrow CH_2 = CHCOOR + NH_4HSO_4$$

(R represents an alkyl group)

The esters of alpha-methyl acrylic acid, commonly called methacrylic acid, may be prepared by the following reactions:

$$(CH_3)_2CO + HCN \rightarrow (CH_3)_2C(OH)CN$$

$$(CH_3)_2C(OH)CN + ROH + H_2SO_4 \rightarrow CH_2 = C(CH_3)COOR + NH_4HSO_4$$

(R represents an alkyl group)

Acrylonitrile can be conveniently synthesized by the dehydration of ethylene cyanohydrin.

The monomeric acrylic and methacrylic esters are colorless, mobile liquids which are polymerized under the influence of heat, light, or oxygen-yielding compounds such as peroxides, to give the polymeric resins. Antioxidants such as hydroquinone act as polymerization inhibitors. The acrylic monomers may be polymerized singly, or may be copolymerized with each other or with other unsaturated compounds, such as vinyl chloride, styrene, etc.

The monomers may be polymerized in aqueous dispersions, in organic solvents, or without the addition of non-polymerizable materials. Consequently, the resins are available in the form of aqueous emulsions, solutions in organic solvents, or as solid polymers.

Properties. The acrylic polymers vary in properties from soft, sticky semi-liquids to tough, hard solids. They are all characterized by colorless transparency and excellent resistance to ageing, sunlight, oxygen, and ozone. Most of them are thermoplastic. Their outstanding property is their crystal clarity, as they possess the maximum theoretical light transmission for transparent materials having their range of refractive indices.

The acrylate esters are softer and more extensible than the corresponding methacrylate esters. Thus, methyl acrylate is a soft, tacky solid, whereas methyl methacry-

late is the hardest of the common acrylic plastics. In general, lengthening the alcohol chain in the ester group causes softening of the polymer and lowers the heat-distortion temperature. Branched-chain alcohols yield harder resins than do straight-chain alcohols containing the same number of carbon atoms. As is to be expected, the solubility of the polymers is greatly affected by the number of carbons in the alcohol chain. For example, methyl methacrylate is insoluble in petroleum hydrocarbons, whereas esters in which the alcohol group contains four or more carbon atoms are, in general, soluble in paraffinic hydrocarbons. Solubility, toughness, and heat-distortion temperature of the polymers of any specific derivative are dependent on the molecular weight of the polymer. In general, solubility is decreased, toughness is increased, and heat-distortion temperature is raised, with increasing molecular weight.

As the temperature of polymerization, catalyst concentration, and polymerization solvent all influence the molecular weight of the resulting polymers, by carefully controlling polymerization conditions, it is possible to control the properties of the polymerized resins. Furthermore, because of the wide variation in the properties of the individual polymers, and of the possibility of copolymerizing the acrylic monomers with each other and with other unsaturated compounds, it is possible to make resins possessing a wide variety of characteristics. Thus, the addition of plasticizers which may impart undesirable qualities of taste, odor, or lack of permanent flexibility or ageing properties can be completely eliminated in the manufacture of acrylic resins.

Applications. The acrylic monomers, while not resins themselves, are employed for copolymerization with other materials to yield useful products. Acrylonitrile, whose polymer is not generally used alone, as it is an insoluble powder, is copolymerized with butadiene to give the highly oil-resistant synthetic rubbers of the Perbunan type.

Sodium polyacrylate, which forms highly viscous aqueous solutions, is used as a thickening agent.

Aqueous dispersions of acrylic resins are employed in the textile field as permanent finishes, stiffening and increasing the tensile strength and wear resistance of the impregnated fabrics. In the leather field, these dispersions are used in finishing genuine leather. In this application, the adhesion and permanent flexibility of the softer acrylic polymers are of great importance. In addition, they do not detract from the natural "feel" and appearance of the leather.

Solutions of acrylic polymers are used as protective coatings, as adhesives, and as binders in the manufacture of laminated glass. In these fields, their flexibility, elasticity, adhesion, chemical resistance, and excellent ageing characteristics are important. As coatings, they are employed on metals, textiles, artificial leather, rubber, glass, porous surfaces and containers. They are used as adhesives for wood, metals, textiles, rubber, plastics, and glass.

The most important form of the acrylic resins from the practical standpoint is the solid thermoplastic type. Polymers of methyl methacrylate in the form of rods, sheets, and molding powders are most widely used. Since these polymers are thermoplastic, they may be fabricated by heating and forming into the desired shape, or they may be machined by ordinary woodworking methods.

Rods, which are manufactured by casting in rod form direct from the monomer, or by extruding from molding powder, are employed in the manufacture of fountain pens, display fixtures, "cold-light" surgical instruments, architectural trim, furniture, battery and radio parts, and novelties.

Sheets, which are manufactured chiefly by casting from the monomer, are at present very widely used in the windshields, cockpit enclosures, gun turrets, landing light covers, windows and noses of aircraft. The flat sheets are heated to a temperature of 220° — 275° F and then formed to the desired shape by the use of male or female dies. The formed shapes are cemented and machined to the desired finished parts. Sheets are also employed in the manufacture of instrument and gauge covers, gun-slit

covers for military tanks, display fixtures, furniture, drafting instruments, decorative articles, and boat windshields and portlights.

Molding powders are supplied for both compression and injection molding. They are used in making articles such as automobile radiator ornaments, instrument covers and dials, hair brush backs, reflectors, decorative articles, knobs, artificial jewels, dentures, lenses, refrigerator parts, drafting instruments, and cosmetic containers.

Polymers of the higher methacrylate esters have been found to be outstanding as pour-point depressants and viscosity index improvers for use in petroleum oils.

Properties

Plexiglas is an acrylic thermoplastic and therefore its properties will be found to vary with the temperature of the material. The values given apply for 25° to 30° (77° to 86° F).

Optical Properties

Clarity	Light Transmission—91-92% Scattering Effect—Practically nil
Refractive Index N_d	1.488-1.489
Dispersion	.008

Physical Properties

Specific Gravity	1.18-1.19
Hardness Mohs	2-3
Vickers	18-20
Brinell	18-20 (500 kg 10-mm ball)
Tensile Strength	7,000-8,000 lbs/sq in
(Elongation at failure)	5-15%
Flexural Strength	14,000-16,000 lbs/sq in
Compressive Strength	10,000-12,000 lbs/sq in
Impact Resistance	0.3-0.5 ft lb (A.S.T.M. Charpy notched bar)
Modulus of Elasticity	4-6 × 10^5 lbs/sq in
Coefficient of expansion	8 × 10^{-5}/° C
Water absorption by Weight.	
24 hrs	0.3%
48 hrs	0.4%
500 hrs	1.2% (Equilibrium)

Electrical Properties

Dielectric Constant (60 cycles)	3.4 to 3.6
(1,000,000 cycles)	2.5
Power Factor (at 60 cycles)	5 to 6%
Volume Resistance	10^{15} ohms/cm³
Dielectric Strength (short time test)	500 volts/mil
(one minute stepwise)	400 volts/mil

Chemical Properties

(Approved test of the Committee on Plastics of the American Society for Testing Materials.)

Pieces of Plexiglas 1″ × 3″ × .125″ were totally immersed in the following twelve chemical solutions for 192 hrs at 25° and the absorption measured.

Immersion Solution *	Weight Gain (%)
30% Sulfuric Acid	0.6
3% Sulfuric Acid	1.0
10% Hydrochloric Acid	0.7
10% Sodium Hydroxide	0.8
1% Sodium Hydroxide	1.0
10% Nitric Acid	0.9
5% Acetic Acid	1.0
2% Sodium Carbonate	1.0
10% Sodium Chloride	0.9
10% Ammonium Hydroxide	0.9
3% Hydrogen Peroxide	1.0
100% Distilled Water	0.9

* All concentrations given in % by weight in distilled water.

A gain in weight of 1% or less is considered negligible except in unusual applications. None of the above solutions appreciably affect the appearance or strength characteristics of Plexiglas.

Alkyd Resins

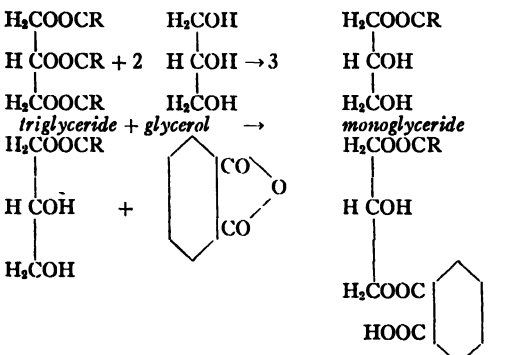
JAMES R. PATTERSON

General Electric Co., Schenectady, N. Y.

The resinous esters of polyhydric alcohols and polybasic organic acids or their anhydrides, and modifications of these esters are known as alkyd resins. The modifications usually are mixed esters with monobasic acids. Occasionally the mixed ester contains some monohydric alcohol. Other modifications are simple mixtures and reaction products with lesser quantities of other resins and fatty oils. Some of the polybasic acids or anhydrides used are phthalic, maleic, sebacic, adipic and the addition products of maleic anhydride with unsaturated compounds, such as certain terpenes hydrocarbons, rosin and cyclopentadiene. Examples of monobasic acids are rosin and fatty acids from animal and vegetable oils. Glycerol, pentaerythritol, mannitol, sorbitol and the glycols are suitable polyhydric alcohols.

Glyceryl phthalate is a common unmodified alkyd. However, because of its brittleness and poor solubility in low-cost solvents and drying oils it is not widely used. Rosin-modified glyceryl phthalates are much more soluble but offer no improvement in flexibility. They can be used to impart hardness to other film-forming materials. Rosin-modified alkyds can be softened and made more flexible by replacing a part of the rosin with long-chain fatty acids.

The most extensively used alkyd resin is the so-called oil-modified glyceryl phthalate type. Actually this type could be more correctly described as oil acids-modified. Since glyceryl phthalate is insoluble in most drying and non-drying oils, these alkyds are not made directly with the oil. One way of making them is to use the fatty acids derived from the oil. Glyceryl phthalate is soluble in the acids and when a portion of the phthalic anhydride is replaced a mixed ester is formed. Another way is to react the oil with the glycerol by alcoholysis before combining with the phthalic anhydride. The alcoholysis reaction and the formation of the alkyd may be demonstrated as follows:



monoglyceride + phthalic anhydride → monomeric alkyd

This monomeric alkyd could have been illustrated as being a neutral ester with both phthalic carboxyls combined with both monoglyceride hydroxyls. However, because of the different reaction rates of the primary and secondary hydroxyl groups, and the first and last carboxyl groups to combine, it is doubtful that the neutral ester is formed. Also, the neutral ester would not be polyfunctional and thus would not be polymerizable. Prolonged heating of the polyfunctional monomer results in chain growth and resinification by further esterification between two or more monomers. If the fatty acid radical is saturated the monomer is difunctional and its polymers will be non-drying and non-curing. With unsaturated fatty acids the monomer is trifunctional and its polymers will air-dry and cure or gel.

Castor oil is an exception to other oils in its miscibility with glyceryl phthalate. Since it is a hydroxylated oil, homogeneous resins can be made by direct reaction of the oil with glycerol and phthalic anhydride. Identical resins can be made with castor oil acids, so it is probable that considerable ester interchange occurs. The truly oil-modified alkyd is an oil-acid or rosin modification to which oil has been added. Depending on the temperature and time of heating, this oil may combine with the resin through ester interchange or may remain as a solution.

The practical range for the fatty acids content of alkyds is between 25 and 75 per cent. The degree of modification is expressed as oil length. A tabulation of the terms used in describing varying oil lengths and the approximate content of fatty acids follows:

Oil Lengths	% Fatty Acids
Very short	Less than 35
Short	35-45
Medium	45-55
Long	55-65
Very long	More than 65

Often the long and very long oil-length alkyds are made by extending with oil the short or medium oil-length types. Also sometimes intermediate oil lengths are produced by blending longer and shorter varieties. Usually it is not desirable to use these methods, but such properties as brushability and flow characteristics may be improved by doing so. Other properties, such as drying speed and general durability, may be poorer.

Most of the characteristics of alkyds vary with the oil length. For example, solubility in low-cost solvents increases with the oil length. Uncured resins from medium to very long oil lengths are soluble in aliphatic solvents. Short modifications require aromatics, and for very short ones mixtures of aromatics, alcohols, esters or ketones are used. Cured or gelled alkyds are insoluble in these solvents but may be swelled by the stronger ones. Some of the characteristics of cured alkyd films are charted in comparison with oil length in Fig. 1.

The choice of fatty acids used in alkyds depends on the desired characteristics. For non-curing types saturated acids such as lauric, myristic, palmitic, and stearic are suitable. Oleic acid and castor oil modifications might be termed semicuring; they can be cured at elevated temperatures but are not satisfactory for drying at room temperatures. Linoleic types are used where color retention, through drying and resistance to exterior exposure are of paramount importance.

The term "through drying" is used in contrast to "skin drying," which is a condition in film formation wherein the surface of the film hardens, leaving the inner portion in a soft and plastic state. Linolenic types offer improved hardness and gloss but provide poorer color retention and have a tendency to skin-dry. Examples of products containing large amounts of linoleic and negligible amounts of linolenic acids are the fatty acids of soya, walnut and dehydroxylated castor oils, a portion of the unsaturated groups in the latter being in conjugated positions. Other suitable

materials are made by fractionating natural and tall oil acids. Linseed and perilla acids contain large proportions of linolenic acid.

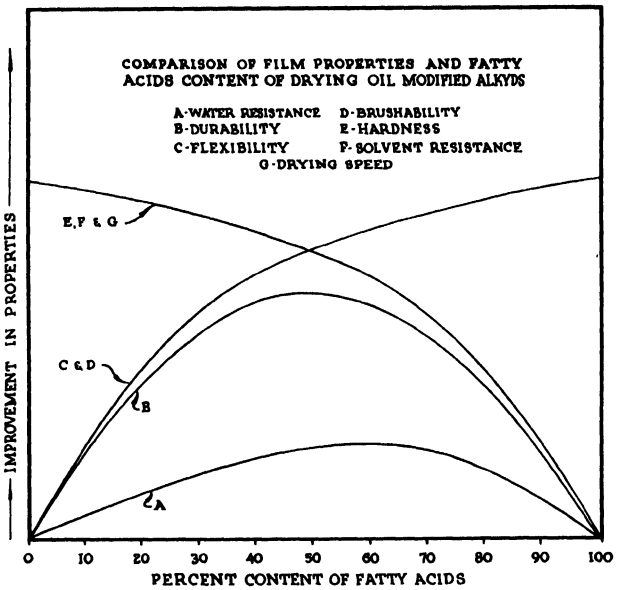


FIGURE 1

Fatty acids with three unsaturated groups in conjugated positions, such as in tung and oiticica oil, are used to provide maximum drying speed, hardness, and water resistance. However, because of their tendency to polymerize to too great an extent before esterification is completed, their full value is not realized. Still greater unsaturation is found in clupanedonic acid, and some fish oils offer excellent drying speed, hardness and gloss, but are lacking in outdoor durability. Also, unless properly polymerized, alkyds made with them skin-dry to such an extent that wrinkled films result. This is a distinct advantage when a wrinkled film is desired.

Replacing a portion of the fatty acids with rosin produces a faster and harder-drying resin and imparts greater water resistance, gloss and solubility. Rosin- and oil-modified alkyds retain their color very well. Their chief disadvantage is decreased exterior durability. Nevertheless, they are widely used in many types of outdoor coatings. Phenol-formaldehyde resins are sometimes added to further increase hardness, drying rate, and water resistance. Similar additions can be made to other types of alkyds for the same purpose.

Maleic anhydride is used several ways in alkyd resins. Many oil acid-modified glyceryl phthalates contain small percentages of it to shorten manufacturing time and increase viscosity. Because of its much greater reactivity and tendency toward gelation before sufficient esterification has been completed, it is seldom used as an entire replacement for phthalic anhydride. Some of its addition products with certain types of unsaturated compounds are less reactive, and are used in place of phthalic anhydride for special applications. It can be used with the glycols in long-chain polymers having some resemblance to drying oils.

The largest use of maleic anhydride in alkyds is in conjunction with rosin. Its addition product with rosin is a tribasic acid with a higher melting point than rosin. When esterified with polyhydric alcohols, high-melting, light-colored resins are formed which have found extensive use in oleo-resinous varnishes and nitrocellulose

lacquers. Glycerol is the most generally used alcohol. To prevent gelation and to avoid insolubility in drying oils, the amount of maleic anhydride used is considerably below the theoretical quantity required to saturate the rosin. This type of alkyd could be considered to be a rosin-modified glyceryl ester of a tribasic acid; it is generally known as maleic-modified ester gum. Nitrocellulose lacquers containing these alkyds are characterized by quick release of solvent, good color, gloss and hardness, and easy sanding and rubbing. Oleo-resinous varnishes made with them are light-colored and dry very well; they do not retain their color at elevated temperatures nor are they as resistant to outdoor exposure as oil acids-modified glyceryl phthalate resins.

An alkyd similar to the varnishes made with maleic modified ester gum is the oil acids modification of the glyceryl ester of the tribasic acid formed when rosin is combined with an equivalent amount of maleic anhydride. This type of alkyd dries faster and is more durable than the varnishes of corresponding oil length.

Permanently flexible film-forming plasticizing alkyds are made with the long-chain aliphatic dibasic acids like adipic and sebacic. Their glycol esters are straight-chain polymers whose characteristics are considerably dependent on their molecular size. With high molecular weights they are elastomers with many rubber-like characteristics. Those of less molecular size are viscous liquids. The glycol esters are not heat-convertible or curing. The esters of polyhydric alcohols containing three or more hydroxyl groups are heat convertible because of the cross linking between the chains owing to the greater functionality. These offer more film strength and toughness than the glycol esters. To avoid the heat-curing, which may destroy flexibility, a portion of the third hydroxyls in glycerol, for instance, can be blocked off with a monobasic acid. A typical example is the mixed ester of glycerol, sebacic acid, and castor oil acids. This alkyd is compatible with many harder film-forming materials and to them it lends permanent flexibility, toughness, and elasticity over a wide range of temperatures. Also this type of alkyd serves as an excellent binder for permanently flexible, oil, water- and weather-resisting putties, caulking products, and filling compounds.

Polyhydric alcohols other than glycerol and the glycols are becoming more prominent in alkyd manufacture. Sorbitol and the pentaerythritols have been restricted to special applications by limited availability and cost. Now that they are available at a cost more comparable with glycerol they should be extensively used, especially since they provide faster and harder drying, more water resistance and better durability. However, because of the greater number of hydroxyls per molecule, control of their esterification is difficult. In short oil length alkyds it usually is necessary to employ a large excess of hydroxyls in order to obtain low acid values. This results in sacrificed water resistance and hardness. Also, unless a sufficient number of the hydroxyl groups are blocked off with monobasic acids, a part of the resin may be insoluble.

As must be apparent from this discussion, the principal use for alkyd resins is in film-forming applications. The chief use is in protective and decorative coatings for metals, wood, paper, and textiles. Uses other than those previously mentioned are in adhesives, printing inks, rubber compounding and floor coverings. The characteristics responsible for the extensive use of alkyds in protective and decorative coatings are excellent durability or retention of initial appearance after long exposure to severe conditions of weather, plus heat resistance, color retention, toughness, adhesion, flexibility, ease of application, versatility and moderate cost. They can be specially designed for specific uses. Short oil lengths are best for baking, medium and long oil lengths for air-drying and brushings. There are alkyds made specifically for architectural finishes, printing inks, water-thinned paints, nitrocellulose lacquers, urea-formaldehyde enamels, aluminum vehicles, bulletin colors, grinding vehicles, marine paints, electrical insulation, and many other uses. They are supplied in a variety of solvents to make them adaptable to application by spraying, dipping, brushing,

flowing, or roller coating. They are compatible with a wide variety of pigments, and disperse and suspend them very well. They are miscible with some varnishes and oils, making it possible to formulate many intermediate products. They can be made to close specification of viscosity, acid number and color, and they retain their characteristics to a remarkable degree during long storage.

Alkyd solutions are usually supplied without driers, permitting the user to fit them more closely to his requirements. For high-temperature baking no drier is needed. For low-temperature baking from 0.02 to 0.1 per cent cobalt or manganese is desirable. Often from 0.3 to 1.0 per cent zinc or 0.2 to 0.4 per cent calcium is added to prevent wrinkling of thick films. For air-drying about 0.03 to 0.1 per cent cobalt plus 0.5 to 1.0 per cent lead is suitable. However, in some dark colors, to avoid loss of drying speed on storage, a portion of the cobalt, one-third to one-half, should be replaced with manganese. In some instances it is advantageous to replace the lead with 0.2 to 0.4 per cent calcium. Lead drier should not be used in clear finishes because of the possibility of the precipitation of lead phthalate. This precipitation has a negligible effect on drying, but it is unsightly. Satisfactory drier combinations for clear alkyd finishes are 0.02 to 0.05 per cent cobalt plus a similar content of manganese, or 0.03 to 0.1 per cent cobalt plus 0.2 to 0.4 per cent calcium. These contents of drier are percentages of metal based on the amount of resin solids, and the metals should be in the form of the usual soluble driers.

In nitrocellulose lacquers alkyd resins may function as an additional film-forming ingredient or as a film-forming plasticizer. Rosin-modified types are used to impart hardness and higher solids, short oil alkyds provide durability, toughness, gloss, adhesion and additional solids. Medium oil, adipate and sebacate types act as film-forming plasticizers. Short non-drying oil alkyds are used where durability and non-lifting by succeeding coats of lacquer are of prime importance. When adhesion is of more importance than non-lifting, oxidizing oil modifications are employed. The average composition of these lacquers is about equal parts of resin and nitrocellulose plus the required amount of plasticizer. With medium oil length drying or semi-drying oil alkyds excellent lacquers are made by using from one to three parts of resin to one of nitrocellulose with no additional plasticizer. Lacquers possessing an unusual combination of hardness and flexibility are produced with about equal parts of nitrocellulose and sebacate alkyd.

The toughness, adhesion, flexibility, and gloss of urea or melamine formaldehyde enamels are enhanced by use of a properly selected alkyd resin. Short non-drying oil types provide the best color retention at high temperatures but are deficient in toughness, adhesion, and gloss. Short to medium drying oil resins offer the best toughness, adhesion, and gloss but may lack satisfactory color retention. Semi-drying oil modifications are used when a compromise in characteristics can be tolerated. The normal range of composition in these enamels is from 90 to 50 per cent alkyd and 10 to 50 per cent urea or melamine formaldehyde resin.

The equipment required to manufacture alkyd resins of good and uniform quality is rather complex and should handle batches of several tons of material for economical operation. The reaction kettle should be of closed construction, fitted with a reflux condenser and made of a corrosion-resisting metal such as stainless steel or aluminum. Good mixing is necessary and provision must be made for blanketing with an inert atmosphere or cooking in solvent. Close temperature control is of utmost importance. Liquid and vapor heat-transfer systems and electric heating have proved very satisfactory. A method for rapid cooling is also required.

Since most alkyds are used in solution, a mixing tank should be located at a point convenient to the reaction kettle. Then when the batch has reached the desired end point it can immediately be pumped or dropped by gravity into the solvent. The sudden chilling stops the reaction at the chosen end point. The mixing tank should be equipped with a stirrer, cooling coils and a condenser to return volatilized solvent.

In addition, facilities for accurate weighing, filtering, bending, storage and control testing are necessary.

Before World War II, alkyd resins had been in use for a relatively few years. However, their quick drying and general durability fitted them so well to finishing military equipment that they were specified for most ordnance, automotive, aircraft and Naval protective and camouflage finishes. The laboratory groups employed in preparing these specifications and developing new resins for special requirements have discovered new compositions and better and more economical methods of manufacture. This knowledge, plus newly available raw materials and the expected increased use should mean that alkyd resins in the near future will be improved in durability, hardness, drying speed, color retention, water resistance, gloss and gloss retention without much increase in cost.

Furan Resins

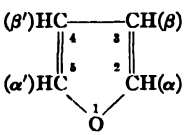
A. P. DUNLOP AND F. N. PETERS, JR.

The Quaker Oats Company, Chicago, Ill.

Introduction

From a laboratory standpoint, furan compounds have been known for many years. Furfural (*2*-furylaldehyde), the most widely known compound of this series, was obtained accidentally in 1832 by Dobereiner [1] while preparing formic acid by the action of sulfuric acid and manganese dioxide on sugar. It was named furfurol (*furfur*, bran, *oleum*, oil) by Fownes,[2] who obtained it by distillation of bran with sulfuric acid. Later work established the presence of the aldehyde group, and the compound became known as furfuraldehyde, now abbreviated to furfural.

Investigation of the structure of furan compounds has occupied the attention of numerous investigators. The formula for furan, the parent compound, is now generally accepted as:

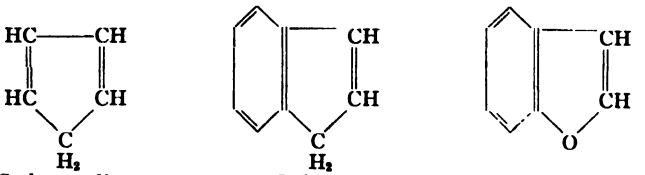


Baeyer [3] and Marckwald [4] established the position of the aldehyde group in furfural as being in the 2 or α-position. Excluding rearrangements, it follows that compounds derived from furfural by addition and condensation reactions involving the aldehyde group are likewise α-substituted furans. For a discussion of the position assumed by groups introduced by nuclear substitution reactions, the reader is referred to the excellent paper by Gilman and Wright.[5] The effect of various substituents on the stability of furan compounds has been studied extensively by Gilman and his co-workers. It is concluded that so-called negative substituents (nitro, carboxy, etc.) stabilize the ring, whereas relatively positive groups labilize the nuclear hydrogen atoms and tend to weaken the ring. For example, furfuryl chloride is quite unstable and resinifies readily.[6] Furoic acid (2-carboxy furan), on the other hand, exhibits a rather high order of stability. Data on the thermal stability of furfural have appeared in the literature,[7] and as expected this aldehyde is less readily affected by heat and acids than its reduction product, furfuryl alcohol.

The chemical activity of furan compounds is a function of both the unsaturated heterocyclic ring and the group or groups attached to the ring. In connection with the former, a study of ring compounds which are similar in their structural aspects may be of assistance in ascertaining the mechanism by which various furans undergo changes to complex forms.

Selecting furan itself, the parent compound, for purposes of illustration, we may consider it as a cyclic diene oxide, in which the double bonds 2,3 and 4,5 are conjugated. Comparison with cyclopentadiene, indene, and coumarone (benzofuran), and their polymeric derivatives suggests some interesting possibilities. For instance,

Bruson and Staudinger [8] propose the structure shown in Fig. 2 for the lower poly-



Cyclopentadiene *Indene* *Coumarone*

Figure 1

mers of cyclopentadiene, since measurement of unsaturation indicated the presence of two double bonds in each polymer isolated.

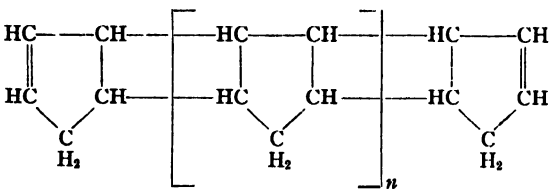


Figure 2

On the other hand they found that rubber-like polymers of this diene contained a double bond for each C_5H_6 unit and the following structure was assigned (Fig. 3):

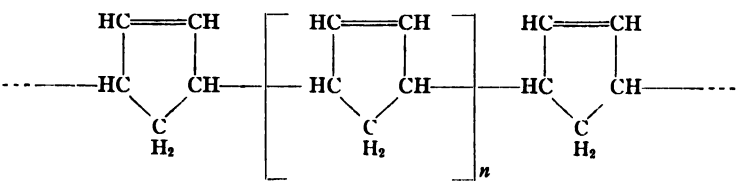


Figure 3

In the case of indene, polymerization occurs readily, and apparently involves a chain mechanism through the 4,5 double bond, as shown by Whitby and Katz [9] (Fig. 4). A similar structure has been assigned to polycoumarone.

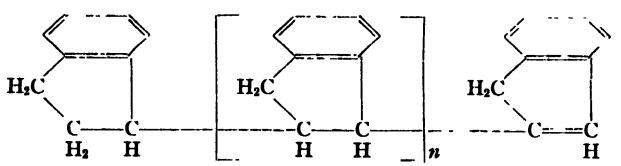
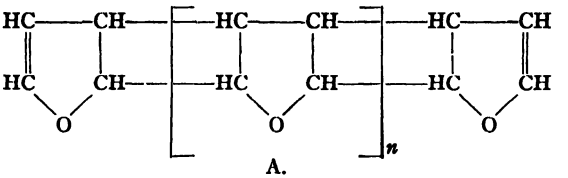


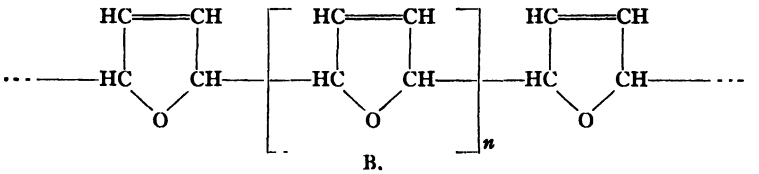
Figure 4

Mechanisms such as those illustrated may apply to furans, and it is altogether possible that all of them take place. Theoretically, then, polyfuran may have one of the structures given in Fig. 5, or more probably a combination of them leading to three-dimensional polymers (Fig. 6). Structures A, B and C have also been suggested recently by Penn [10] and, in addition, structure B was proposed earlier by Gilman and Hewlett.[11]

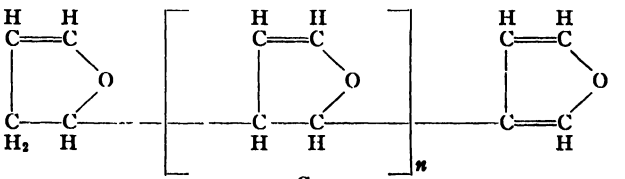
Indirect evidence in support of the B type of polymerization is found in the condensation of ethylene with furan to form 3,6-epoxycyclohexene.[12] This involves addition at the α-positions in furan with a resulting shift of unsaturation to the β-furan carbon atoms (Fig. 7).



A.



B.



C.

Figure 5

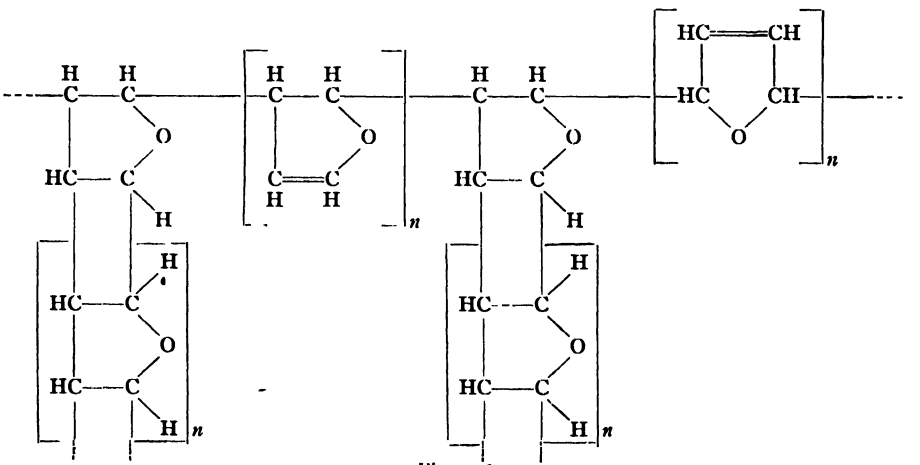


Figure 6

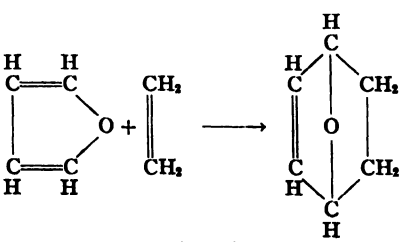


Figure 7

A similar mechanism is proposed for the formation of 3,6-endoxo-Δ^4-tetrahydrophthalic anhydride by condensation of furan with maleic anhydride.[13] In addition, in their studies on nuclear substitution of furan types, Gilman and Wright [5] suggest that the first step involves addition in the 2,5 position with a shift of unsaturation.

Thus far we have considered only polymerization reactions involving the nuclear double bonds. In addition to this we must also discuss two other factors which influence the resinification mechanism of furan compounds, and which add to the complexity of the resulting products. These involve the contributions offered by (1) ring substituents such as aldehyde, alcohol, etc., and (2) the active nuclear hydrogens which can in some instances lend themselves to intermolecular condensations. In the first instance, little information is available, but some evidence has been accumulated relating to the latter. For instance, investigation [14] of the lower molecular weight condensation products obtained by the action of heat and/or acid catalysts on furfuryl alcohol has demonstrated that intermolecular dehydration takes place to yield compounds of the type illustrated in Fig. 8.

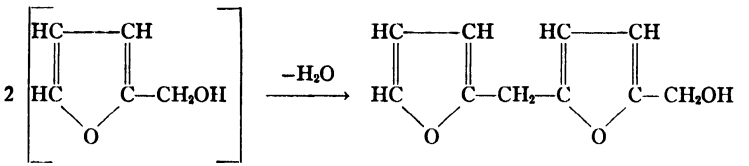


Figure 8

In addition to this, it has been shown [15] that ethyl furoate, in which the nuclear hydrogens are less labile than those in furfuryl alcohol, can be condensed under acidic conditions with formaldehyde to yield resinous products, with the probable structures shown in Fig. 9.

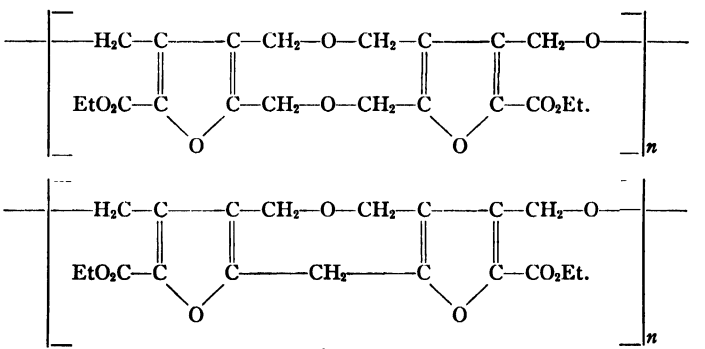


Figure 9

This work demonstrates the important point that, while the β hydrogen atoms are less labile than those in the α position, they are nevertheless active enough, under acidic conditions, to enter into condensation reactions of the type illustrated. This offers one more means by which furan compounds can become thermosetting, since condensation through the β hydrogens might be accomplished in such a manner as to yield cross linkages. For example, in the pyrrole series, Tronov and Popov [16] condensed α,α'-dimethylpyrrole with acetone to yield a product, $C_{15}H_{20}N_2$, which they believed resulted by condensation through the β hydrogen atoms with the elimination of water. They assigned to it the structure shown in Fig. 10.

Summarizing, it is evident that furan compounds are polyfunctional and that they may resinify in the following ways:

A. Polymerization
(1) Through the 2,5 and 3,4 positions (Fig. 5A).
(2) Through the 2,5 positions (Fig. 5B).
(3) Through the 2,3 or 4,5 positions (Fig. 5C).
(4) By a combination of any two or all of the first three (Fig. 6).

It is perfectly obvious that ring substituents, and also the nuclear hydrogen atoms, may exert a profound influence so that resinification may also occur by:

B. Condensation
(1) Involving the ring substituents.
(2) Involving the nuclear hydrogen atoms.

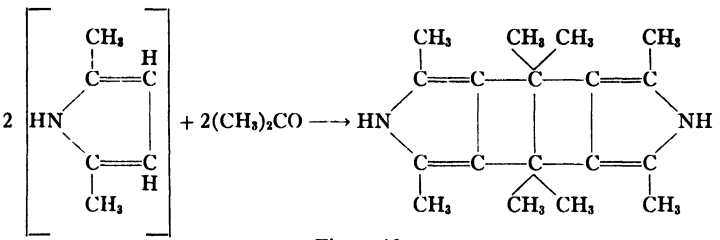


Figure 10

Furfural Resins

Furfural is obtained commercially by the acid hydrolysis of the pentosans in oat hulls, cottonseed hull bran, and corn cobs. When pure it is a colorless liquid (d_4^{20} 1.1598; b. 161.7° [17]) which darkens in color on storage, a change involving only a minute quantity of the aldehyde under normal conditions. The stability of furfural has been much maligned. This is indicated by its successful use, in enormous quantities with minimum losses, in a variety of commercial applications, some of which entail exposure to relatively high temperatures. This misconception of the stability of furfural arose through the use, in the early days of furfural manufacture, of a product containing considerable amounts of acetic acid and sometimes acetaldehyde and possibly traces of ketones. Furfural as made today is a very pure product and test data show that, even as high as 230°, several hours' exposure are necessary to produce detectable changes in its physical properties.[7]

Table 1. Furfural

Specific Gravity (20/20)	1.161
Refractive Index (n_D^{20})	1.5261
Flash Point (open cup)	56°
Boiling Range (99%)	157-167°

In its aldehyde reactions, furfural resembles benzaldehyde. Thus, treatment with KCN leads to the formation of furoin, $C_4H_3O \cdot CO \cdot CHOH \cdot C_4H_3O$, the furan analog of benzoin. With alkalies, furfural undergoes the Cannizzaro reaction to give furfuryl alcohol and furoic acid. It condenses with ammonia to yield hydrofuramide, which is transformed into the isomeric furfurin under the influence of heat or alkalies.

The resin-forming properties of furfural were early noted by a number of investigators. On standing exposed to air it is very slowly transformed into a resin, a change accelerated by heat and catalysts. Vacuum-distilled furfural sealed in a glass ampule for 24 years shows no visible change except darkening in color, even though it has been exposed to ordinary daylight throughout that period. Trickey and Miner [18] accomplished the resinification, at 100°, using catalysts such as ferric and aluminum chlorides to obtain initially an acetone-soluble, viscous resin, which on further heating changed to an infusible solid. Finely divided metals,[19] sulfuric acid,[20] and hydrochloric acid [21] have also been employed catalytically to induce resinification.

Alkaline resinification of furfural was described by Meunier [22] and by Mains and Phillips.[23] The aldehyde was heated with aqueous alkali, after which the reaction mixture was acidified to produce the resin. There is little doubt that the resin is, for the most part, due to the action of the acid on furfuryl alcohol formed by the Cannizzaro reaction in the first step.

The resins prepared by the self-condensation of furfural have found little use in the industry. Condensation of this aldehyde with a variety of other compounds, however, has led to the development of a number of interesting resin types.

Reaction with Phenols. Both acid and alkaline catalysts have been used for the reaction of furfural with phenolic compounds, and in addition the condensation has been carried out in the absence of added catalytic agents. Using dilute acids, it has been shown [24] that the aldehyde group reacts initially with phenol to yield a mixture of *o*- and *p*-hydroxyphenyl-furyl-carbinols (Fig. 11).

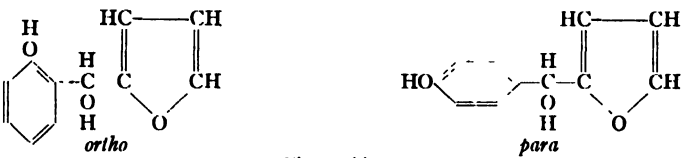


Figure 11

As more phenol and furfural condense, resinous products are formed, and presumably the conjugated double bonds in the furan ring play an important part in providing a network of cross linkages leading to thermosetting resins of a more complex nature than the corresponding phenol-formaldehyde products.

The early work of Beckmann and Dehn [25] on the reaction of furfural with hydroxyaromatic compounds was followed by a number of other investigations. Probably the most important commercial applications are represented by patents to Novotny [26] and Miller.[27] Ordinarily furfural-phenol resins do not go through the A, B and C stages so characteristic of the phenol-formaldehyde types. The rubbery, nonflowing B stage is avoided, and the resins maintain their flow characteristics over relatively long periods at temperatures slightly above those required to induce plasticity.[28] Molding compositions from potentially reactive furfural-phenol resins have been exposed to heat and pressure for as long as 45 minutes, and, during this period, have remained sufficiently plastic to allow continuous injection molding.[29] On the other hand, furfural-phenol resins cure very rapidly when the reacting temperature is reached, and molded articles of high strength and chemical resistance can be made in a short over-all molding cycle. Applications for these resins include the preparation of laminating varnishes, lamp and radio tube cements, and the production of bonded abrasive articles, combat helmet liners, instrument cases and the like. Typical properties of furfural-phenol resin products are listed in Table 2.

Reaction with aldehydes and ketones. Like other aldehydes, furfural will condense with substances which have a hydrogen atom in the α-position to a carbonyl group. This reaction takes place in both acid and alkaline media, with loss of water, to yield unsaturated side chain compounds (furylethylene derivatives). For example, acetaldehyde condenses with furfural to yield β-2-furylacrolein, and acetone reacts to give mono- or difurfural-acetone (Fig. 12).

Furylpolyene aldehydes and ketones are formed by further condensation reactions involving these compounds. The products obtained by reacting furylacrolein with acetone [30] and with ethyl methyl ketone and furfural-acetone [31] in dilute alkaline medium have been isolated. One is immediately struck with the system of conjugated double bonds existing in these compounds, as illustrated in Fig. 13 for bis-furylacrolein-acetone (1,9-bis-furyl-5-oxo-1,3,6,8-nonatetraene).

Table 2. Furfural-Phenol Resin Products *

Property	Pure Resins	Molding Compounds Fillers: Wood Flour	Molding Compounds Fillers: Asbestos	Molding Compounds Fillers: Fabric	In Laminated Products Fillers: Paper	In Laminated Products Fillers: Cloth
Molding qualities	Fair	Excellent	Good	Good	Limited	Limited
Molding range:						
Temperature (° F)	250-450	330-400	330-360	300-360	290-350	290-350
Pressure (lbs/sq in)	0-500	1000-3000	1500-4000	2000-4000	1000-2000	1000-2000
Compression ratio	1.5-2.0	2.5-3.0	2.5-6.0	4.0-7.5	1.5-3.0	1.5-3.5
Specific gravity	1.2-1.3	1.3-1.4	1.6-2.0	1.3-1.4	1.3-1.4	1.3-1.4
Specific volume (cu in/lb)	23.1-21.3	21.3-19.8	17.3-13.9	21.3-19.8	21.3-19.8	21.3-19.8
Mold shrinkage (in/in)		.005-.007	.002-.004	.004-.006		
Colors and mottles	A	V	Bl. and Br.	Bl. and Br.	V	V
Transparency	Translucent	Opaque	Opaque	Opaque	Opaque	Opaque
Machining qualities	Good	Fair	Poor	Fair	Good	Good
Thickness 1/1000 in	10 up	20 up	20 up	20 up	10 up	10 up
Tendency to cold flow	None	None	None	None	None	None
Tendency to unmold	None	None	None	None	None	None
Effects of:						
Sunlight and	Prolonged exposure darkens light colors slightly.					
Ultraviolet light	Dark colors and especially black and brown are very permanent.					
Aging	Improve with age both electrically and mechanically.					
Acids						
Weak	None	None	None	None	None	None
Strong	Decomposed by HNO_3 and H_2SO_4	Decomposed	Decomposed	Decomposed	Decomposed	Decomposed
Alkalies		Slowly	Slowly	Slowly	Slowly	Slowly
Weak	None	Softened	Softened	Softened	Softened	Softened
Strong	Disintegrated	Disintegrated	Disintegrated	Disintegrated	Disintegrated	Disintegrated
Alcohols	None	None	None	None	None	None
Ketones	Slight	Slight	Slight	Slight	Slight	Slight
Esters	None	None	None	None	None	None
Hydrocarbons	None	None	None	None	None	None
Oils: Animal, mineral and vegetable	None	None	None	None	None	None
Water:						
Cold	VR [1]	SI [2]	VR	SI	SI	SI
Hot	VR	MR [3]	VR	MR	MR	MR
** Water Absorption (% by Weight)						
Gain after 48 hours	0.05	0 3-0 6	0.10-0.26	0 8-1.4	0.3-2.0	0.92
Gain after 96 hours	0.06	0 6-1 0	0.19-0.40	1 2-2 0	0.4-4.5	1.04

A = all except white Bl = Black
V = large variety dark shades Br = brown

Heat: Resistance to—° F	300	280	350-500	280	250	250
Effect of:	Slight shrinkage and hardening.			Improves electrically.		
Specific heat—Cal/° C	0.32-0.37	0.30-0.40	0.30-0.40	0.30-0.40	0.30-0.40	0.30-0.40
** Distortion under:		131°	136°			
Burning rate	EL [4]	EL	PI [5]	EL	EL	EL
Coefficient of expansion per ° C		0.00003	0.00002			
Hardness—Brinnell—500 Kg. load		35-40	44-46	30-35		
Thermal conductivity						
10^{-4} cal/sec Cm ° C	3.0-3.5	3.5-5.0	10 0-20.0	5.0-8.0	5.0-8.0	5.0-9.0
** Tensile strength—lbs/sq in	5000-9000	5000-12000	4000-12000	5000-10000	10000-20000	9000-12000
Kraft paper:						
Across grain					13000-20000	
With grain					18000-25000	
Tensile split, kraft paper—lbs/sq in					180-310	
** Flexural strength—lbs/sq in	10000-12000	10000-16000	8000-14000	10000-16000		
Kraft paper:						
Across grain					25000-30000	
With grain					20000-24000	
** Compressive strength—lbs/sq in		28000-36000	24000-36000	26000-30000		
Kraft paper						
Edgewise					15000-20000	
Flatwise					30000-40000	
** Impact strength—ft lbs/in sq	0.4-2.7	1.0-6.5	1.0-6.0	20.0-39.0		
** Breakdown voltage, 60 cycle-volts/mil						
Room conditions	400-1100	400-600	200-500	200-500	900-1800	300-700
At 120° C		170-190				
After 48 hours in water		380-590				
** Power factor—% radio frequency	0.5-1.0	1.0-6.0	6.0-15.0	5.0-8.0	1.5-4.8	4.1-6.4
** Surface resistance—megohms						
After 96 hours at 95° and 90% humidity	4560+	4560	500	200	1500	200

* Courtesy Durite Plastics, Inc , Philadelphia
** A.S.T.M. Standard or Tentative Test Method.
[1] VR = Very resistant
[2] SI = long immersion impairs slightly
[3] MR = More rapid impairment
[4] EL = Extremely low
[5] PI = Practically incombustible

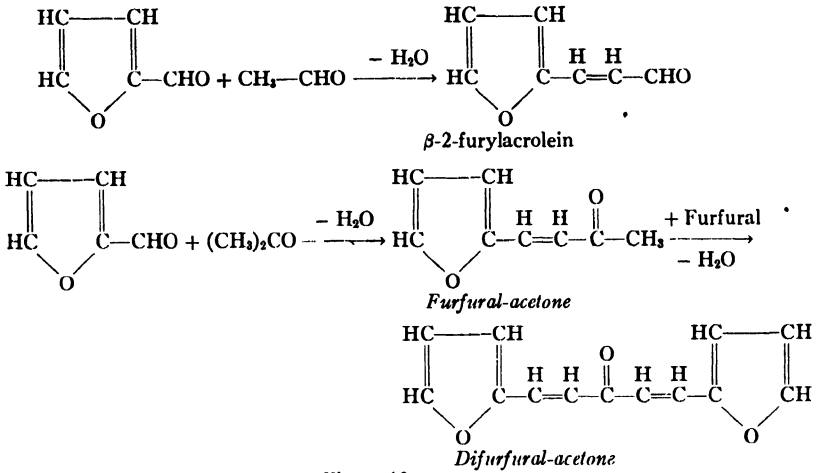


Figure 12

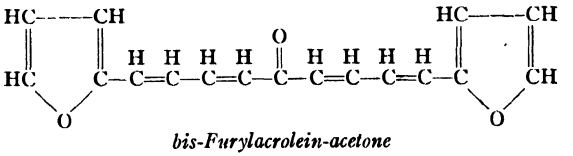


Figure 13

Koenig [32] observed that furylacrolein and its homologs tend to resinify on exposure to light to yield alcohol-insoluble resins. Kappeler [33] condensed furfural with various aldehydes using an acid catalyst to obtain solid products, resembling ebonite, which were insoluble in the common solvents, and resistant to the action of acids and alkalies.

Meunier [22] prepared varnish resins by condensing furfural with acetone, as did Mains and Phillips,[23] who also worked with ethylmethyl ketone. The use of a furfural-acetone resin, admixed with fillers, for the production of molded articles is the subject of a patent to Richardson.[34] In this process the initial condensation is carried out with an alkaline catalyst, which is removed prior to mixing the resin with non-alkaline fillers, and curing with heat and pressure in the presence of naphthalene sulfonic acid. Other investigators [35] have worked with furfural-ketone condensation products, either alone or incorporated with other materials, for a variety of applications.

Reaction with ammonia, amines, and amides. When condensed with ammonia, furfural yields hydrofuramide, which is converted by heat or the action of dilute alkali into the secondary base furfurin.

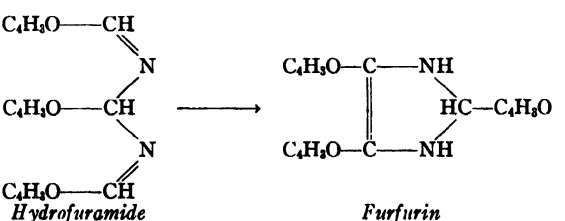


Figure 14

The furfurin so obtained is an alcohol-soluble resinous mass, which on prolonged heating yields a hard, lustrous product. Probably the resins obtained by Meunier [22] and by Mains and Phillips,[23] by heating furfural and ammonium hydroxide, were furfurin resins. Bruins [36] prepared black resinous substances by treating a 20 per cent solution of furfurin in furfural with a variety of catalysts. In this case it is probable that one step in the resinification involves condensation of furfural with furfurin. A furfurin-formaldehyde resin is the subject of a patent to Berliner.[37]

Under suitable conditions, furfural condenses with primary amines with the elimination of water to form the corresponding aldimine ($RCH = NR'$).[38] In some cases, however, the reaction can be highly complex and may involve cleavage of the furan nucleus.[39] For instance, treatment of furfural with aniline in the presence of hydrochloric acid yields a black product to which has been assigned the following probable structure: [40]

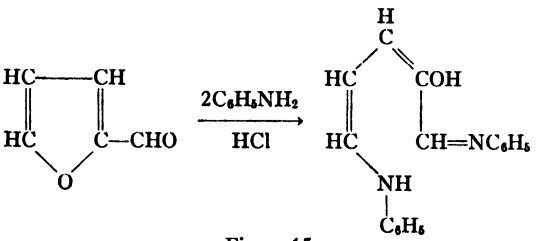


Figure 15

A study of the condensation of furfural with various amines was made by Mains and Phillips,[23] who found hydrochloric acid to be an effective catalyst for the formation of both fusible and infusible resins. An acetone-soluble resin, compatible with cellulose acetate, has been prepared by merely heating equimolecular proportions of furfural and aniline at 170°, for a period of 1 to 3 hours.[41]

Beebe *et al.*[42] condensed furfural with various amines, such as aniline, and prepared a solution of the condensation product together with an iodine-containing catalyst. When this solution is coated on a metal surface, and the solvent evaporated, the remaining film is light sensitive. Printing plates have been made for years by this process. Cold-molding compositions, for the manufacture of insulators, using a mixture of a furfural-aniline resin and a phenol-aldehyde resin are described by Huxham.[43] Cherry and Kurath [44] have patented wax substitutes and plasticizers formed by reaction of furfural, an amine, and an organic acid. A variety of other furfural-amine resins for a miscellany of applications are described in patents to Kistler,[45] Winterkorn,[46] and Goodhue.[47]

The reaction of furfural with amides was investigated by Beaucourt.[48] Acetamide gave a low yield of a crystalline material, whereas only resinous products were obtained with formamide. Schiff [49] and Biginelli [50] studied the condensation of this aldehyde with urea. Using an excess of urea, in aqueous medium, the latter worker obtained a product to which he assigned the following structure:

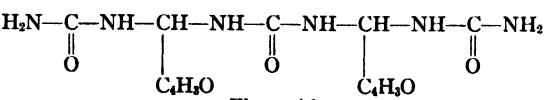


Figure 16

Acid condensation of furfural with urea results in the formation of black, lustrous resins.[51, 52] The reaction can also be carried out using heat alone, or with a basic catalyst, as proposed by Novotny and Johnson.[53] D'Alelio [54] describes resinous compositions, suitable for the production of molded articles, by reaction of furfural, a urea, and malonic diamide. Two recent patents [55] are concerned with the formation

of resinous products from furfural and thiourea and from furfural and a urethane. Equimolecular proportions of furfural and *p*-toluenesulfonamide, when heated at 150° for 8 hours with an alkaline catalyst, yield a resin suitable for use in lacquer compositions.[56]

Furfuryl Alcohol Resins

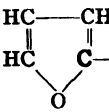
Hydrogenation of furfural[57, 58] gives furfuryl alcohol,  . The commercial product is a yellow to dark amber liquid with the properties shown in Table 3.

Table 3. Furfuryl Alcohol

Specific gravity, (25/25)	1.130
Refractive index ($n^{25}D$)	1.4840
Flash point (open cup)	75°
Boiling range (95%)	167-177°

Normally miscible with water, furfuryl alcohol undergoes a gradual change on storage to become incompletely soluble. This change is greatly accelerated by heat and acids, and is retarded by a large variety of both inorganic and organic basic substances.[14] This suggests that where syntheses involving the alcohol are concerned, they be done in a basic medium. With this precaution, furfuryl alcohol can generally be used in reactions typical of a primary alcohol. For example, it is virtually impossible to esterify furfuryl alcohol using acid catalysts, but the reaction proceeds smoothly by using the Schotten-Baumann reaction. This sensitivity to acids, particularly mineral acids, is increased by the presence of moisture.[59] On the other hand, it is difficult to maintain anhydrous conditions due to the ease with which furfuryl alcohol undergoes intermolecular dehydration. In such cases the use of calcium carbide or a non-acidic drying agent may be beneficial.

The resinification mechanism of furfuryl alcohol is quite complicated. Initially, condensation products of the type shown in Fig. 8 are formed along with difurfuryl ether. As resinification proceeds, formaldehyde is split out yielding difurylmethane, both of which have been identified as reaction products.[60, 61] The formaldehyde then re-condenses, probably in a manner akin to that in the pyrrole series,[62] to yield methylene and ether cross-linkages involving the β-furan carbon atoms (Fig. 17). Inasmuch as an increase in titratable acidity is observed on resinifying furfuryl alcohol, it is also possible that ring-splitting occurs, to a limited extent, with the

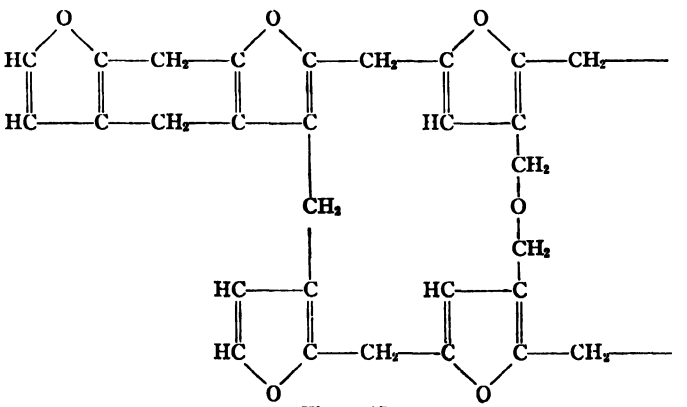


Figure 17

formation of levulinic acid.[63] The final structure of the resin is probably further complicated by polymerization reactions through the nuclear double bonds, as described previously.

The literature makes frequent reference to furfuryl alcohol resins prepared by the action of a wide variety of catalysts.[64] Some of the recently available Duralon resins are manufactured from this product. For the most part the resins are used for the purpose of forming protective coatings and for impregnation of various materials. Resin formation by condensation of furfuryl alcohol with aldehydes, has been claimed by a number of investigators. An early patent to Trickey and Miner [65] stipulates furfural as the aldehyde, and more recently, Delmonte [66] has described resins useful as bonding and laminating agents which are derived from a combination of these two furan compounds. A resistant finish, by acid resinification of a mixture of furfural and furfuryl alcohol with a copolymer of vinyl chloride and vinyl acetate, is the subject of a patent to Lewis.[67]

Formaldehyde and furfuryl alcohol condense in an acidic medium to yield resins [68] which are suitable for varnishes and the preparation of molded articles. A similar type of resin is described by Harvey,[69] involving the preliminary step of partially resinifying furfuryl alcohol prior to condensation with formaldehyde.

Phenolic compounds react with furfuryl alcohol to yield resins having excellent mechanical strength and chemical resistance. The reaction is accelerated by acid catalysts,[70] but may be carried out through the agency of heat alone.[71] A detailed study of the application of a furfuryl alcohol-phenol resin for the preparation of paper-base laminates has been reported.[72] The physical properties of the laminates are listed in Table 4, which for purposes of comparison includes the corresponding data for various other resins. A resin suitable for coating paper may be prepared by the reaction of furfuryl alcohol with a lignin-sulfonic acid or a salt of such an acid.[73] Molding compositions comprising furfuryl alcohol and hydrolyzed lignocellulose adjusted to pH 3 to 6 are claimed by Katzen *et al.*[74]

Condensation of furfuryl alcohol, urea and formaldehyde yields a resin suitable for use in coating compositions.[75] A series of patents to Humphrey and Borglin [76] is concerned with the formation of furfuryl resin esters which are condensed with maleic anhydride. The products may be hydrogenated to reduce unsaturation at various stages in the process to yield substances useful in coating formulations. Other furfuryl esters which have been used for the preparation of resins include the formate,[77] crotonate [78] phthalate [79] and the silicate.[80]

Miscellaneous Furan Resins

Casein [81] or aluminum caseinate [82] mixed with furfural and wood flour may be molded into products suggested for use as insulators or as substitutes for ivory and horn. Other molded products were made by Sweeney and Arnold,[83] using various agricultural materials with urea or phenol condensed with furfural. A resin, suitable for brake linings or clutch facings, prepared by condensation of furfural with the distillation residue of cashew nut shell liquid is claimed by Caplan.[84]

A series of alkyl-furyl-carbinols was prepared by Peters and Fischer.[85] All the products resinified on exposure to light and air, or under the influence of a variety of catalytic agents.

The use of furfural as a starting material for the preparation of synthetic rubber through piperylene has been investigated by Guinot [86] and by Berkenheim and Dankova.[87] The process involves the hydrogenation of furfural to methyl tetrahydrofuran, followed by catalytic dehydration to piperylene (1-methyl-1,3-butadiene), which yields a rubber on polymerization. Butadiene itself has been prepared by passing tetrahydrofuran, in the vapor phase, over a phosphate catalyst at 250-450°.[88] Polymerization products of 1-(α-furyl)-1,3-butadiene are also described in the patent literature.[89] Vinyl furan, the furan analog of styrene, may be prepared by decar-

Table 4. Comparison of Laminates Made with Various Resins on Mitscherlich Paper [72]
(F = Flatwise; E = Edgewise)

Resin type	Phenolic		Urea		Melamine J			Polyvinyl Butyral	
Laminating pressure (psi)	100	1000	100	1000	100	500	1000	100	1000
Resin content	40	40-43	60	57	60-62	60-61	61-62	38-40	38-45
Specific gravity	1.34	1.41	1.35	1.47	1.47	1.49	1.49	1.15	1.27
Ultimate tensile strength (psi)	23,700	25,200	13,300	18,200	16,500	17,400	17,800	13,100	13,200
Flexural strength (psi) F	27,400	29,500	16,900	23,300	20,000	21,600	23,400	13,500	13,100
E	26,000	27,200	17,900	20,500	16,600	18,000	18,100	15,400	15,600
Compressive strength (psi) F	44,600	43,000	33,800	39,000	37,700	42,800	46,300	32,600	29,400
E	21,500	22,600	19,100	21,600	23,600	21,800	23,900	6,600	8,700
Johnson shear (psi) F	10,900	11,600	6,600	9,500	7,900	7,400	7,700	6,700	6,800
E	11,500	12,400	10,500	12,000	9,800	11,300	12,600	6,100	6,400
Charpy impact, (ft-lb/inch notch) F	5.39	6.78	1.72	1.93	1.51	1.30	1.67	11.8	11.7
E	0.63	0.86	0.47	0.45	0.47	0.42	0.49	1.48	1.30
Bonding strength (lbs)	760	800	735	800	870	850	930	300	375
Water immersion 24 hours at 77° (% increase in weight)	1.52	1.44	1.98	2.16	2.43	2.18	1.51	14.00	11.02

Resin type	Allymer		Furan		Ethylcellulose
Laminating pressure (psi)	1-5	1-5	100	1000	300-600
Resin content	40	40-44	39-41	41	60
Specific gravity	1.43	1.43	1.38	1.42	1.20
Ultimate tensile strength (psi)	20,900	25,800	25,300	25,100	13,000
Flexural strength (psi) F	20,600	27,700	29,700	26,900	16,000
E	20,700	25,900	26,100	27,000	9,500
Compressive strength (psi) F	39,400	40,400	43,800	. . . .	22,800
E	9,900	13,400	17,800	. . .	5,500
Johnson shear (psi) F	9,900	11,600	. . . . .	. . .	6,300
E	9,300	12,100	. . .	. . . . .	5,900
Charpy impact, (ft-lb/inch notch) F	7.93	7.75	5.18	5.12	9.52
E	0.93	0.84	0.68	0.71	1.48
Bonding strength (lbs)	535	510	555	640	335
Water immersion 24 hours at 77° (% increase in weight)	7.52	6.27	3.53	4.29	4.73

boxylation of furylacrylic acid.[90] On polymerization in the presence of oxygen-yielding catalysts, it yields latex-like and rubber-like substances which can be vulcanized.[91] The preparation and polymerization of furyl vinyl ketone and furyl isopropenyl ketone are described by Barnes.[92]

Catalytic oxidation of furfural in the liquid phase yields furoic acid, some of the esters of which have been found to be useful in the resin field. Borglin [98] prepared the fenchyl and bornyl esters in high yields, which he used as plasticizers in coating compositions. Allyl furoate, when heated for several hours at 130-140°, yields a brown-colored, glassy resin resembling acrylic ester resins.[94]

Tetrahydrofurfuryl alcohol forms esters having interesting properties. The phthalate is reported to be a good plasticizer for polyvinyl chloride, and the oleate has been used in a similar capacity with Koroseal. Claborn [95] described the preparation of tetrahydrofurfuryl acrylate from the lactate, and indicated that this ester may be used for the preparation of coatings and the manufacture of molded articles.

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Allyl Resins

ALPHONSE PECHUKAS

Director of Research, Columbia Chemical Division, Pittsburgh Plate Glass Co.

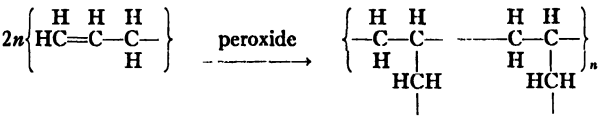
There exists a generic class of resin-forming synthetics which is as yet unnamed. These substances, typified by the allyl resins, are similar in chemical behavior to those from which the numerous synthetic thermoplastic resins are derived; but their polymers resemble more closely in properties the substances usually considered as thermosetting resins. In general, synthetic thermoplastic resins are formed by the peroxide-catalyzed polymerization of unsaturated organic compounds, while the thermosetting resins are formed by acid- or alkali-catalyzed polycondensations occurring between such substances as phenol or urea and formaldehyde. This third class of synthetic resin-forming substances is also resinified by polymerization under the influence of peroxidic catalysis; but while the synthetic thermoplastic resins will dissolve in solvents and flow at high temperatures, the resins typified by the allyl polymers resemble the conventional thermosetting compounds in that they are resistant to solvents and will not flow appreciably at high temperatures.

Derivation

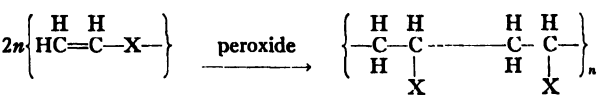
The allyl resins, formed principally by esterification reactions from allyl alcohol, stem fundamentally from petroleum sources. One of the conventional methods for the production of allyl alcohol is the chlorination of propylene at elevated temperatures to yield allyl chloride, which may then be hydrolyzed to allyl alcohol. Allyl alcohol may then be esterified by several methods to form the monomeric forms of the allyl resins. These allyl resin-forming substances usually contain two or more allyl radicals in a molecular unit.

Polymerization

The formation of resinous bodies from the allyl substances depends upon the peroxide-catalyzed reaction of the unsaturated grouping, which may be represented by the equation:



This reaction is similar to the formation of thermoplastic resins from substances containing the vinyl grouping, represented by the equation:



However, the allyl resins, containing at least two unsaturated groupings in a molecular chain, polymerize not to linear polymers but to three-dimensional networks.

The formation of the three-dimensional lattice is strikingly reflected by the behavior of the allyl resin monomers upon heating in the presence of peroxide catalysts.

Whereas with the thermoplastic-forming monomers the molecular weight of the polymers increases in well-ordered fashion as the reaction proceeds, the increase in molecular weight of the allyl resin monomers is much more abrupt. In Figure 1

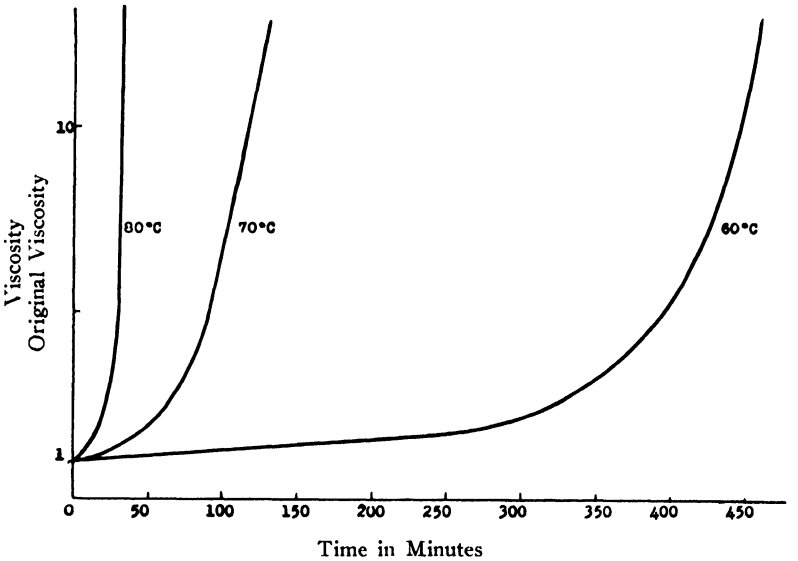


FIGURE 1. Changes in viscosity of allymer CR-39 upon heating with benzoyl peroxide.

are plotted the viscosities, on an arbitrary scale, of a typical allyl resin monomer * upon heating with benzoyl peroxide at various temperatures.

Gelation of the polymerizing substance thus occurs when only a small proportion of the substance has polymerized. This is due to the formation of a loose, three-dimensional lattice by random polymerization of the monomeric substance, leading to rapid cross-linking of growing chains. A true gel is formed initially, comprising the insoluble, highly polymeric substance "swollen" with unpolymerized monomer or with low molecular weight polymers. As a further example, Figure 2 illustrates

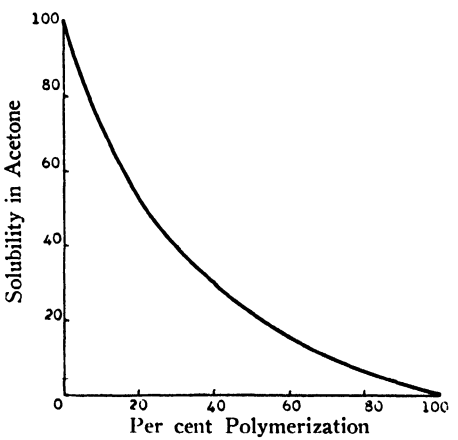


FIGURE 2. Solubility of polymer with degree of polymerization.

*Allymer CR 39, produced by the Columbia Chemical Division, Pittsburgh Plate Glass Company.

data typical of that obtained upon extraction of the low molecular weight substances from the partially cured gel with a suitable solvent. It will be noted that the rate of insolubilization is initially much more rapid than would be predicted upon a straight-line relationship between the degree of polymerization and the insolubility of the polymeric material. This is to be expected from the very rapid growth of chains early in the polymerization, because of the addition of low polymers to one another. In general, gelation of the substance occurs when approximately 20 per cent of the monomeric material has disappeared.

Properties

The allyl resin-forming monomers, in general, are clear, colorless liquids or semi-crystalline solids which rapidly decrease in viscosity as the temperature is raised. They are stable at ordinary temperatures for prolonged periods of time, but upon heating in the presence of peroxide catalysts they increase in viscosity and form friable gels. On further heating these gels form strong, hard, insoluble, infusible, colorless to slightly yellow, solid resins. The conversion of the monomer into the hardened resin occurs without the evolution of water, ammonia or other volatile by-products, because of the nature of the polymerization processes. The ready flowability of the monomers makes it possible to use these resins in processes where the use of solutions of highly polymeric substances would be detrimental.

The initial stages of polymerization, resulting in the formation of friable gels, give rise to relatively weak products because of the presence of a large amount of unpolymerized or slightly polymerized material. However, at this stage the friable gel may be crushed and will reknit by polymerization of additional material upon further heating. In Table 1 are listed a number of the interesting physical properties of a few of the pure, fully hardened polymers which may be obtained by variation of the molecular structure of the resin-forming monomers.

Table 1. Typical Properties of Clear Allyl Resin Polymers *

Density (g/cc)	1.30-1.35
Rockwell hardness	M 95-M 117
Tensile strength (psi)	5,000-13,000
Compressive strength (psi)	22,000-27,000
Flexural strength (psi)	9,500-31,000

* All properties were measured at 25°.

While initially the monomers are soluble in a number of organic solvents, the solubility decreases markedly as polymerization proceeds, and the fully cured polymers are essentially insoluble. In general, most solvents which can be used for the dilution of the monomeric substances separate from the mass as polymerization proceeds. Thermoplastic resin-forming monomers, such as vinyl acetate do not exhibit this behavior because of copolymerization of the vinyl grouping with the allyl compounds.

The fully cured polymers show most of the characteristics of a completely thermosett resin, but in one respect they exhibit a very interesting behavior. Upon heating the clear polymers to elevated temperatures, a decrease in the modulus of elasticity occurs, and thus at high temperatures under load the polymers may be distorted to a considerable extent. This behavior is illustrated in Figure 3, showing the distortion of a clear polymer under a constant load applied in flexure. Within specific temperature ranges, some 30 to 40° in extent, the modulus of elasticity changes quite rapidly with temperature, but again reaches a fairly constant value at much higher temperatures. This appears to result from a relaxation in the gel structure of the fully cured polymer. When these polymers are cooled after deformation at high temperatures, the distortion induced by the load may be "frozen." However, the resin is under strain in this condition and exhibits a remarkable "memory."

When the load is relieved, the distorted section retains its shape at low temperature. If, however, the polymer is reheated to the temperature range at which the modulus decreases, a very rapid transformation to its original shape will occur.

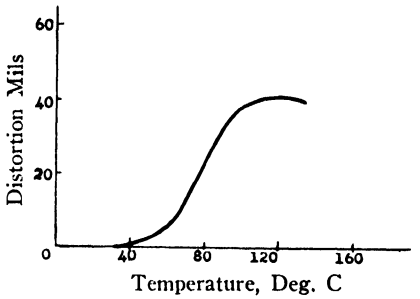


FIGURE 3. Distortion of polymer under constant load.

Presumably due to this apparent "memory," the abrasion resistance of the polymers of the allyl materials is very high, particularly toward a wearing type of abrasion. This is not because of an actual flow of the surface of the resin under abrasion, but because of the distortion of the surface of the resin specimen under the pressure of the abrasive particle, followed by a quick recovery to its initial state in the resin surface.*

Applications

Since polymerization of the allyl resin-forming materials occurs without the evolution of gaseous by-products, exceptionally clear transparent materials may be obtained. The polymers themselves, therefore, find application in practically all glazing uses where good visibility is essential. Because of the thermosetting nature of the polymers, the clear substances will withstand high temperatures. The peculiar characteristics of the polymers also lend themselves to applications where abrasive conditions are encountered. Their extreme insolubility is beneficial where severely stressed parts are exposed to solvent action. Thus when subjected to stress, substances soluble in the surrounding medium tend to craze because of absorption of solvent by the polymeric material. The allyl polymers, being extremely resistant to solvent action, are not affected in this manner. A similar application, in which resistance to solvents is of paramount importance, is in the manufacture of transparent tubing for use with aromatic solvents such as are present in aviation gasoline. The clear polymers have been applied in airplane cockpit enclosures, in gauge glasses for aromatic fuels, in optical systems, electric-light bulb protectors, inspection windows, gas-mask lenses, and similar items.

A second type of application of great importance in the use of the allyl resin-forming materials is the impregnation of fibrous substances, followed by polymerization of the resin. Since no gaseous by-products are formed during the cure, low pressures may be used throughout the operations of forming the various complicated shapes demanded for structural and semi-structural uses. When reinforced by suitable fibrous fillers, very high strengths may be developed in the polymers. In Table 2 are listed the properties of a typical material produced by plying layers of fabric made of glass fiber, impregnating the composite with allyl resin, and polymerizing the allyl-containing substance.

Strong, light-weight materials produced in this fashion find application in many instances where high strength and relatively decreased weight are important. Besides the advantage of very low pressure conditions during fabrication, large sec-

* Abrasion resistance is commonly measured by embedding abrasive particles in a matrix (*e.g.*, rubber) and passing such a composite, under definite load, over the surface to be tested.

tions may be conveniently produced from these resins. Typical of the applications which have been made of materials of this type are fairings,* switch boxes, flooring, bulkheads, ducts, doors, shock boards, etc., particularly for aircraft, and tanks for water, fuel, and similar substances, as well as tubing, name-plates, and various light-weight tools.

Table 2. Typical Properties of Fiberglas * Laminated with Allymer CR 149 †

Resin content	41%
Specific gravity	1.75
Rockwell hardness	M 117
Tensile strength (psi)	53,400
Flexural strength (psi)	100,000
Edgewise compressive strength (psi)	54,400

* OC-64 Fiberglas fabric produced by the Owens-Corning Fiberglas Corporation, heat-treated
† An allyl compound produced by the Columbia Chemical Division, Pittsburgh Plate Glass Company.

* Fairing is an engineering term applied to a member or structure primarily designed to produce a smooth outline and reduce drag, as in aircraft J. A.

Fumaric and Maleic Acid Resins

C. KINGDON DOSCHER

Chas. Pfizer & Co. Inc., New York.

Fumaric and maleic acids have become of increasing importance among the newer raw materials used by the resin industry. Since their original application to the manufacture of alkyd resins, where their growth was most rapid, many other types of resins have been developed from them. Most promising of these recent products are preparations suitable for molding, casting, and laminating.

Being stereoisomers, fumaric and maleic acids are very similar in many of their chemical properties, yet the polymerides formed by reacting them with identical substances have varying physical properties which in many instances are quite different. Maleic acid, normally used as the anhydride, is stronger than its isomer, and usually reacts faster and at lower temperatures. Because of its *trans* structure, fumaric acid does not form an anhydride. In general, those products of fumaric acid which are thermoplastic by nature have a higher softening temperature than similar products made from maleic acid. In manufacturing operations, fumaric acid has been found to be less corrosive to resin kettles and equipment than maleic acid, and, in addition, is not lost as readily by sublimation. Fumaric acid fumes are much less toxic.

The most important resinous products of fumaric and maleic acids are obtained by esterification or condensation with various types of alcohols, followed by polymerization. Resins are also produced by the diene synthesis involving addition of the maleic radical to other unsaturated compounds. As the polymers and the resulting resins differ in their physical properties according to the type of alcohol or diene with which the acids are reacted, they may be most simply classified as follows:

I. Esters of saturated alcohols
  A. Monohydric alcohol esters: Neutral esters of methyl, ethyl, propyl alcohols, etc.
  B. Polyhydric alcohol esters (condensation products): Glycerol and glycol esters.
II. Esters of unsaturated alcohols
  A. Monohydric alcohol esters: Neutral esters of allyl and methallyl alcohols; geraniol esters; propargyl esters.
III. Mixed esters of saturated and unsaturated alcohols
  A. Monohydric alcohol esters: Neutral vinyl-ethyl ester.
IV. Addition products of diene synthesis (Diels-Alder)
  A. Terpene-maleic adducts
  B. Higher polyene adducts: Abietic acid and its esters; eleostearic acids.

Polymerization

The mechanism of polymerization by which certain compounds of fumaric and maleic acids attain the resinous state may be most readily interpreted by the illuminating work of Carothers,[7] Kienle,[18] and Bradley,[2, 3, 4] on natural and synthetic polymerides. An important contribution of these men has been the postulation of the

functionality theory, an analysis of polymer formation based on the reactivity of the combining molecules.

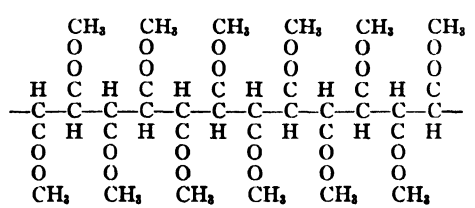
As defined by Carothers, polymerization is an inter-molecular combination functionally capable of proceeding indefinitely; condensation is a special type of polymerization characterized by the elimination of reaction products, usually water. Kienle expressed the reactivity or functionality of polymerizing molecules by the number of reaction points in each molecule. Thus, fumaric and maleic acids have a potential functionality of four, each carboxyl group counting as one and the carbon-to-carbon double bond as two. Monohydric saturated alcohols are assigned a functionality of one; dihydric saturated alcohols, having two hydroxyl groups, are bifunctional; glycerol has a functionality of three, etc. Longer-chain saturated and unsaturated alcohols, acids, and esters have varying degrees of functionality depending not only on the number of reactive groups but also on their relative position in the molecule and the conditions of reaction. When a potentially functional group in a molecule is for some reason unreactive or can act only intramolecularly, then it has zero reactivity with respect to polymeride formation.

By applying this nomenclature to reacting systems it has been established [18] that when one reactant has a functionality of one and the other a functionality of N, where N can be any integer, a pure compound results except when steric hindrance or the presence of isomerides prevents crystallization, in which case, if a solid forms, that solid will be non-crystalline. When the interacting molecules each have a functionality of two, a linear thermoplastic polymeride will result. If the reactants have a functionality of (N,M), where N is two or greater, and M is three or greater, a thermosetting polymeride will be formed.

When using this method of analysis it is important to distinguish between bi- or bi-bi-functional polymerizations and the more polyfunctional systems, not merely because of the essential difference in the character of the polymerides, but mainly for the reason that in the first case polymerization proceeds without the accumulation of unreacted or potentially functional groups, whereas in the latter case there develops an accumulation of unreacted groups with every step of the polymerization. Furthermore, in a system involving the interaction of polyfunctional molecules, the progress of polymeride formation is such that as each intermediate polymeric molecule is formed the functionality of the intermediate product must be considered, as far as further reaction is concerned, as if the newly formed molecule were a monomeride.

Esters of Saturated Alcohols

Monohydric Alcohols. The esterification of fumaric and maleic acids with monohydric saturated alcohols in which the reacting system has a (1,4) functionality, proceeds in a straightforward manner to the production of definite chemical compounds. The resulting esters are monomeric and have a potential functionality of only two. At room temperature dimethyl fumarate is a solid; the ethyl, propyl, and butyl esters are liquids of increasing viscosity. Under normal conditions the pure esters polymerize extremely slowly, but when the carbon-to-carbon double bonds become activated by an oxidizing catalyst,[9] a linear thermoplastic polymeride is formed which probably has the following structure:



These chain-like polymers are soft, sticky resins that are of value in coating compounds as modifiers or copolymers. Somewhat more solid, non-sticky polymerizates are said to be obtained when these esters are polymerized in the presence of small amounts of acid-producing catalyst in aqueous dispersion in a closed vessel.[12] This polymerization technique is believed to produce longer-chain, higher molecular weight polymerides, which consequently have a higher softening point.

The addition of small amounts of other easily polymerizable substances, such as butadiene, acrylic nitrile, or vinyl choride, has a promoting effect on the polymerization of these esters. Larger amounts of copolymer have the effect of changing the character of the resulting polymeride from soft, rubbery resins to solid, glassy ones. For example, when diethyl fumarate is copolymerized in aqueous emulsion with nearly equal proportions of butadiene and acrylic nitrile, an easily worked polymerizate is produced which can be vulcanized to a rubber claimed to be stable to gasoline.[14] By copolymerizing in a similar manner diethyl fumarate with an equal weight of a mixture of isobutylene and styrene a product is obtained which can be worked into shaped articles by pressing or injection molding.[15] Similar moldable products are obtained when these esters are copolymerized with vinyl chloride.[16]

Dykstra [9] has shown that interpolymerization products of fumaric and maleic acid esters with other polymerizable substances such as vinyl acetate were true copolymerizations, and that the resulting copolymers had characteristics distinctly different from mechanical mixtures of the two substances separately polymerized. From this it may be deduced that the chain-like molecules or polymerides contain units of fumaric ester and copolymer united by primary valence bonds, the number and type of copolymer units determining the characteristics of the resulting resin. When copolymers having a functionality greater than two are used, such as butadiene, the possibility of forming three-dimensional polymers or cyclic polymers increases. If the chains become sufficiently long to contain at least two butadiene units, the possibility of cross linking between chains is apparent. This variation of molecular structure affords the opportunity of preparing polymers of distinctive characteristics.

Polyhydric Alcohols. When fumaric or maleic acid is reacted under oxygen-free conditions with dihydric alcohols, such as ethylene glycol or diethylene glycol, the reacting system, which has a (2,4) functionality, proceeds first to the formation of essentially linear polymers. The initial step of the reaction is the formation of a half ester:

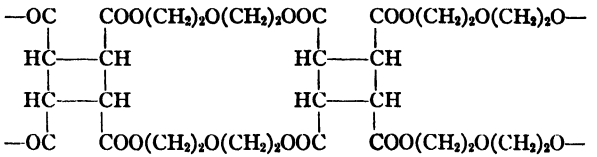
$$\begin{matrix} & \text{CHCOOH} & & & & \text{CHCOO(CH}_2\text{)}_2\text{O(CH}_2\text{)}_2\text{OH} \\ & \| & & & & \| \\ \text{HOOCHC} & & + \text{HO(CH}_2\text{)}_2\text{O(CH}_2\text{)}_2\text{OH} \longrightarrow & & \text{HOOCHC} & \end{matrix}$$

On further heating condensation occurs with the formation of a linear polyester:

$$\begin{matrix} \text{CH=CH} & & \text{CH=CH} & & \text{CH=CH} & \\ | & & | & & | & \\ \text{HOOC} & \text{COO(CH}_2\text{)}_2\text{O(CH}_2\text{)}_2\text{OOC} & & \text{COO(CH}_2\text{)}_2\text{O(CH}_2\text{)}_2\text{OOC} & & \text{COO(CH}_2\text{)}_2\text{O(CH}_2\text{)}_2\text{O—} \end{matrix}$$

If the reactants are used in molecular proportion, the resulting polyester may be expected to contain three types of molecules, some of which are dihydroxy or dicarboxylic esters, while others are balanced molecules with terminal carboxyl and hydroxyl groups. By titrating the total acidity, the degree of condensation and the average molecular weight can be calculated.

It is apparent that the longer the chain the greater will be the number of unsaturated linkages per molecule. Chains having two or more unsaturated linkages per molecule have a potential functionality of four or more, and therefore are capable of conversion to infusible and insoluble resins. Oxygen, being an active catalyst for addition polymerization, activates the ethylene bond of the maleic radical so that cross linking occurs to form a system, one unit of which may be qualitatively represented by:



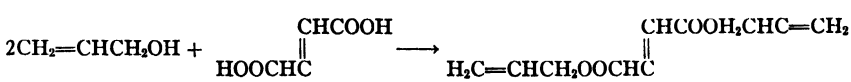
Rust,[22] working with maleic polyesters, and Doscher,[8] using fumaric polyesters, have shown that rapid-curing casting resins may be prepared from glycol condensation products by the incorporation of a suitable oxidizing catalyst. The use of small amounts of copolymer has been found advantageous in speeding the curing of the resin. Vinyl acetate, styrene, methyl methacrylate, and similar substances have been found to be of value in this connection. A typical diethylene glycol fumarate casting resin containing 5 per cent vinyl acetate and 0.1 per cent benzoyl peroxide will cure to a hard resin in 24 hours. The resulting resin is insoluble in common organic solvents, and is resistant to moderate concentrations of most organic and inorganic acids; strong alkalies, however, will attack it. The Rockwell hardness of the cured resin varies from L 50 to L 110. Using pure materials, diethylene glycol fumarate or maleate castings can be made in light colors or water-white if desired, with good color stability. As they have a high refractive index, these castings can transmit light around curves in a manner similar to quartz.

When a longer-chain glycol, such as hexaethylene glycol, is condensed with fumaric or maleic acid until an acid number of about 70 is reached, a linear polyester is obtained which is soluble in water.[5] Upon subsequent polymerization by oxygen conversion a resin insoluble in water is produced. This type of product is of particular value in the preparation of coating, impregnating or adhesive compositions. After application of these solutions to suitable surfaces, they are dried and the resin is rendered insoluble in water.

The reaction of fumaric or maleic acid with saturated alcohols containing more than two hydroxyl groups, such as glycerin, usually results in the formation of an insoluble gel. Such gels have a high acid number, indicating that gelation occurs shortly after the start of the reaction and before any appreciable condensation takes place. Because of this high reactivity, fumaric and maleic acids are not generally used without modification in the production of oil-soluble glyceride resins, but are commonly used in conjunction with phthalic anhydride, serving to modify the properties of the glycerol phthalate.

Esters of Unsaturated Alcohols

Monohydric unsaturated alcohols have a functionality greater than two and hence react with fumaric or maleic acids to form esters which may be polymerized to thermosetting resins. Diallyl fumarate is an example of this type of ester. Allyl alcohol may be esterified with fumaric acid either in the usual manner or by ester interchange[20] to form a normal monomeric ester:



These esters, which have three unsaturated carbon-to-carbon linkages, may be polymerized by oxidizing catalysts or actinic light. The polymerization is exothermic and if not carefully controlled may occur with violence, causing the polymer to char. The resulting polymeride is a glass-clear solid having an extremely low tensile strength. Because of this inherent weakness the resin is of very little practical value in itself. However, when used as a copolymer with other esters, such as diethylene glycol fumarate, the diallyl esters have the effect of decreasing the time of curing.

Longer-chain unsaturated alcohols, such as geraniol, which contains two carbon-to-carbon double bonds, may be esterified with fumaric or maleic acids to give high-boiling liquids [20] which may be polymerized to hard, tough films by heating after the addition of benzoyl peroxide. These products appear to be of value primarily as modifiers of coating compounds designed for baking.

Propargyl alcohol, $CH \equiv C—CH_2OH$, reacts with diethyl fumarate to form dipropargyl fumarate by ester interchange. This product is of interest as an example of a short-chain alkynyl ester. Upon treating with benzoyl peroxide and heat, the ester is said to polymerize slowly to a hard, brittle, insoluble resin.[21] These maleic and fumaric esters may be interpolymerized with other polymerizable substances such as vinyl esters, acrylic or methacrylic esters, butadiene, etc., to form products useful in either coating or molding applications.

Mixed Esters of Saturated and Unsaturated Alcohols

The monoethyl ester of fumaric or maleic acid may be treated with acetylene in the presence of a catalyst consisting of a mixture of mercuric oxide and borontrifluoride-acetic acid to produce a neutral vinyl-ethyl ester.[19] These clear, colorless liquids may be easily polymerized by the usual methods to hard resins, and are of value as copolymers.

Diels-Alder Reaction Products

The Diels-Alder diene synthesis illustrates one of the few reactions in which the behavior of fumaric acid is entirely dissimilar to that of maleic acid. The α, β-enal grouping ($—C=C—C=O$), which is essential to the diene synthesis, occurs in both these acids, but is far more reactive in the maleic anhydride molecule than in the fumaric acid molecule. Although fumaric acid has been found to react slowly with various conjugated terpenes, such as levo-α-phellandrene, yielding resinous acids,[6] it is substantially unreactive with unconjugated terpenes. Maleic anhydride not only reacts exothermally with conjugated terpenes at low temperatures, but also reacts readily with unconjugated terpenes at higher temperatures. By means of this synthesis maleic anhydride forms a series of valuable reaction products.

The inactivity of fumaric acid toward unconjugated terpene hydrocarbons may be overcome by the addition of solubilizing and reactive alcohols, such as triethylene glycol, to produce balsam-like polyesters. The presence of a small amount of stannic chloride accelerates the reaction. This product differs from the maleic-terpene adduct in that it is an ester of a complex organic acid formed during a reaction that apparently involves unsaturation of both the terpene and the fumaric acid. Products of this nature have found utility as resinous plasticizers for cellulose derivatives.

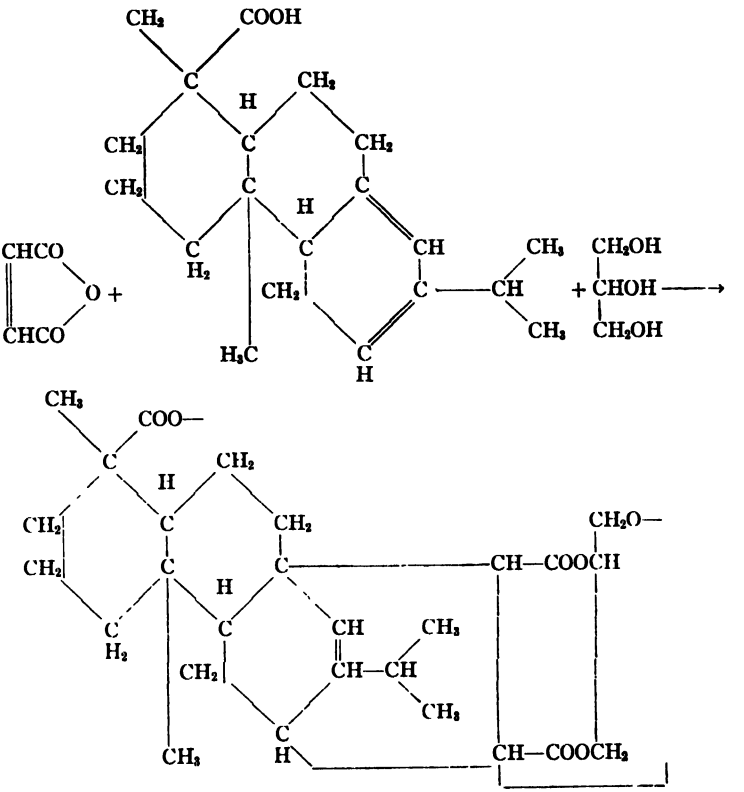
Perhaps the most important diene reaction of maleic acid occurs in the combination of the anhydride with abietic acid.[1, 18, 17] Glycerol is added to the reaction to esterify the carboxyl groups, giving a polymer, one unit of which may be assigned the provisional formula which appears on p. 1073.

Large quantities of maleic anhydride are used commercially for this reaction in the production of "Amberol" and "Beckacite" maleic resins, which have found wide application in the paint and varnish industry.

Maleic anhydride also reacts readily with tung, linseed, and other drying oils,[10] serving to modify their properties. As these adducts contain carboxyl groups, they may be esterified with alcohols to produce additional modifications. Alkalies also react with these carboxyl groups to form salts which may be either soluble or insoluble in water, depending upon the alkali used.[11]

It has frequently been stated in the literature that fumaric acid may be substituted for maleic acid or anhydride in the preparation of various diene reaction products, and equivalent results obtained. This assumption has apparently been based on the

belief that fumaric acid is converted to maleic acid at the elevated temperatures at which these reactions take place. However, Bradley [6] has shown that upon heating fumaric acid at 200° for eleven hours no detectable amount of maleic acid is formed, and even at 250° less than 0.25 per cent of maleic acid is formed. As these temperatures are above those generally employed for the diene synthesis it does not appear likely that any appreciable rearrangement occurs.



Although the resinous products derived from fumaric and maleic acids have been only briefly described, it is apparent that their potential field of application is very broad. The production of resins derived from maleic anhydride alone has grown from 3,432,887 pounds in 1938 to 6,476,883 pounds in 1940, as reported by the U. S. Tariff Commission, and will no doubt increase further as new products are developed after the war. A new fermentation process for the manufacture of fumaric acid from carbohydrates has recently opened a source of supply of this acid at a price low enough to encourage large-scale consumption. The combination of these factors should make fumaric and maleic acids of increasing prominence in the expanding plastics industry.

Diethylene Glycol Fumarate

Compression molding temperature	130-140°
Compression molding pressure	2,000-3,000 lbs/sq in
Curing temperature (castings)	50-60°
Shrinkage	1-2%
Refractive index	1.44-1.46
Tensile strength	5,000-7,000 lbs/sq in
Specific gravity	1.3-1.4
Hardness (Rockwell)	L-50-L-110
Water absorption, 24 hrs.	1-3%
Effect of acids	Resistant
Effect of alkalies	Attacked
Effect of organic solvents	Resistant
Machining qualities	Good
Clarity (unfilled)	Transparent

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20. Rothrock, H. S., U. S. Patent 2,221,663 (Nov. 12, 1940)
21. —, U. S. Patent 2,221,662 (Nov. 12, 1940).
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Selected List of Patents of Fumaric and Maleic Resins

Patent No.	*Patentee*	*Abstract*
U. S. 1,945,307	H. Dykstra Ass'd. to duPont	Resinous products derived from copolymerization of fumaric and maleic esters with vinyl esters
U. S. 1,993,027	E. G. Peterson Ass'd. to Hercules	Alkyd resins containing terpinene-maleic anhydride-glycerol adducts suitable for coatings
U. S. 2,025,947	I. Humphrey Ass'd. to Hercules	Alkyd-type resins produced by reacting maleic anhydride with esters of abietic acid
U. S. 2,063,540	C. Ellis	Modified alkyd resins, suitable for coatings, made by reacting maleic anhydride with rosin and tung oil.
U. S. 2,160,940	E. C. Britton, C. W. Davis, F. L. Taylor Ass'd. to Dow	Acid resistant diallyl fumarate-vinylidine chloride copolymers.
U. S. 2,166,542	T. F. Bradley, Ass'd. to American Cyanamid	Water soluble resins derived from hexa-ethylene glycol fumarate or maleate.
U. S. 2,182,316	H. Hopff, G. Steinbrunn, Ass'd. to I. G.	Copolymerization of diethyl fumarate and isobutylene to produce lacquer raw materials
U. S. 2,195,215	S. S. Kistler, C. E. Barnes, Ass'd. to Norton Co.	Fumaric or maleic modified alkyds used as binder in grinding wheels.
U. S. 2,195,362	C. Ellis	Method of preparing condensation products of fumaric or maleic acid with glycol derivatives.
U. S. 2,206,171	C. Ellis	Glycol derivatives condensed with fumaric or maleic acid and used to modify drying oils in coating compounds.
U. S. 2,220,621	C. Ellis	A printing ink containing diethylene glycol fumarate or maleate, non-drying at room temperature but drying rapidly under heat.
U. S. 2,220,854	H. R. Slagh Ass'd. to Dow	Preparation of dimethallyl maleate and digeranyl maleate.
U. S. 2,220,855	H. R. Slagh Ass'd. to Dow	Preparation of diallyl fumarate.
U. S. 2,221,418	A. Weihe, Ass'd. to Gen'l Aniline & Film Corp.	An elastic resinous product derived from the condensation of maleic anhydride with dithio-dibutylene-glycol.

Patent No.	Patentee	Abstract
U S. 2,221,662	H. Rothrock Ass'd. to duPont	Hard brittle resin formed by polymerization of propargyl fumarate
U S. 2,221,663	H Rothrock Ass'd. to duPont	Resinous products derived from dimethallyl maleate; resinous fumaric esters of tiglyl alcohol, allene carbinol, 1-hydroxy-3-chlorobutene-2, methallyl isopropenyl carbinol, isopropenyl ethynyl carbinol, geraniol, and other unsaturated alcohols.
U. S. 2,224,035	J H. Long Ass'd. to Hercules	Adhesive composition containing glycol esters of terpinene-maleic anhydride condensates adapted for the lamination of flexible sheet material.
U. S. 2,230,230	J K. Boggs, Ass'd to Hercules	Aqueous dispersions of terpene-maleic-diethylene glycol adducts suitable for coating compounds.
U. S. 2,234,958	T. F. Bradley W. B. Johnston, Ass'd. to American Cyanamid	Useful resins produced by the reaction of fumaric acid with a non-conjugated terpene, such as pinene, and glycerol.
U. S. 2,235,447	T. F. Bradley, W. B. Johnston, Ass'd. to American Cyanamid	Resinous products produced by the reactions of fumaric acid with non-conjugated terpenes
U. S. 2,238,030	T F. Bradley, Ass'd. to American Cyanamid	Diallyl fumarate-vinyl acetate copolymers suitable for casting resins and coating compounds
U. S. 2,249,768	E. L Kropa Ass'd. to American Cyanamid	Preparation of allyl esters of fumaric and maleic acids.
U. S. 2,251,765	B. E. Sorenson, Ass'd. to duPont	Preparation of diallyl maleate in presence of aluminum.
U. S. 2,253,681	T. F. Bradley, W. Johnston, Ass'd. to American Cyanamid	Resinous products produced by the reaction of fumaric acid with conjugated terpene.
U. S. 2,254,382	H. T. Neher, Ass'd. to Rohm & Haas	Preparation and polymerization of methallyl acid maleate and fumarate; copolymerization with methacrylate and styrene
U. S. 2,255,313	C. Ellis	Casting and molding resins derived from diethylene glycol fumarate and maleate
U. S 2,266,794	W. Pannwitz, B. Ritzenthaler, H. Hopff, G. Steinbrunn, Ass'd. to I. G.	Rubberlike products from interpolymerization of diethyl or dibutyl fumarate with butadiene.
U. S 2,273,891	M. A. Pollack, I E. Muskat, F. Strain, Ass'd to Pittsburgh Plate Glass	Molding compounds derived from methallyl esters of maleic and fumaric acids.
U. S. 2,276,267	T F. Bradley, Ass'd. to American Cyanamid	Coating compositions containing dodecaethylene glycol fumarate or hexamethylene glycol maleate.
U. S. 2,280,256	D. G. Patterson, Ass'd to American Cyanamid	Polymerization of fumaric or maleic acid—linseed oil fatty acids ethylene glycol allyl alcohol resin suitable for coatings or molding compounds.
U S. 2,280,862	B E. Sorenson, Ass'd to duPont	Diallyl maleate–linseed oil coating composition.
U. S. 2,281,394	B. E Sorenson, Ass'd. to duPont	Preparation of diallyl and dimethallyl maleate by ester interchange in presence of metallic magnesium
U S 2,286,251	H. W. Arnold, Ass'd to duPont	Preparation of light and heat stable copolymers of diethyl or dimethyl fumarates with acrylates.
U. S 2,290,674	G. F D'Alelio Ass'd. to General Electric	Resinous products formed by the condensation of maleic diamide with aliphatic aldehydes.
U S 2,294,226	G. F. D'Alelio Ass'd to General Electric	Preparation of granular polymers by dispersion in water containing a water-soluble salt of a polymeric fumaric acid.
U S 2,295,513	T. F Bradley, Ass'd to American Cyanamid	Diallyl fumarate.
U. S. 2,296,823	M A. Pollack, A G. Chenicek Ass'd. to Pittsburgh Plate Glass	Preparation of methallyl esters of fumaric and maleic acids from methallyl halides
U. S. 2,300,880-1	D. R. Erickson, P. J. Thoma Ass'd to Michigan Research Labs.	A printing ink derived from fumaric and maleic terpene-rosin adducts.
U. S. 2,311,327	T. F. Bradley Ass'd to American Cyanamid	Resinous products from diallyl fumarate.
U. S. 2,319,575	M. C. Agens, Ass'd. to General Electric	A resinous product derived from the esterification of glycerol, tetrahydrofurfuryl alcohol and fumaric acid.
U. S. 2,322,542	D. G. Patterson, Ass'd. to American Cyanamid	Fumaric acid floor covering composition.
U. S. 2,323,706	G. F. D'Alelio, Ass'd. to General Electric	Resinous products derived from copolymerization of diethylene glycol fumarate or maleate with di(buten-1-yl-3) succinate.

Patent No.	*Patentee*	*Abstract*
U. S. 2,329,456	W. E. Campbell, Ass'd. to Carbide & Carbon	Coating compound containing vinyl chloride, vinyl acetate and monoethyl fumarate.
U. S. 2,337,873	G. F. D'Alelio Ass'd. to General Electric	Oil soluble alkyd resin containing polyhydric alcohol fumarate suitable for flexible coatings.
U. S. 2,337,874	G. F. D'Alelio Ass'd. to General Electric	Shock resistant casting resins containing diethylene glycol fumarate or maleate, copolymerized with phenol aldehyde condensation products.
U. S. 2,340,110-1	G. F. D'Alelio Ass'd. to General Electric	Diallyl fumarate and maleate resins used for removing cations from liquid media.
B. 355,281	J. Johnston Ass'd. to I. G.	Process for the manufacture of modified alkyd resins, using maleic anhydride.
B 407,957	R. S. Morrell, S. Marks, H. Samuels	Coating compound derived from the reaction of maleic anhydride with β-elaeostearin.
B. 466,898	G. Johnston, Ass'd. to I. G.	Molding powder prepared by copolymerization of maleic esters with vinyl chloride in aqueous dispersion.
B. 476,727	G. Johnston Ass'd. to I. G.	Molding compounds produced by copolymerizing fumaric esters and vinyl chloride in aqueous emulsion.
B. 498,414	S. Saunders Ass'd. to Pinchin, Johnson & Co.	Modified alkyd resins derived from the reaction of maleic anhydride with monoglycerides.
B. 501,669	G. Johnston Ass'd. to I. G.	Resins suitable for coatings or adhesives formed by copolymerization of fumaric esters with isobutylene in aqueous emulsion
B. 512,703	G. Johnston Ass'd. to I. G.	Rubber-like products formed by copolymerization of butadiene hydrocarbons and fumaric or maleic acid esters in aqueous emulsion.
B. 17248/43	Ass'd. to du Pont	Light and heat resistant fumaric ester-vinyl chloride copolymers.
C. 390,208	O. Nicodemus, et al Ass'd. to I. G.	Process for the preparation of vinyl-ethyl esters of fumaric and maleic acids. These esters polymerize to resins of great hardness.
C. 419,131	Donald G. Patterson Ass'd. to American Cyanamid	Terpene-fumaric-polyhydric alcohol adduct suitable for surface covering.
G. 684,017	K. Wolf, F. Grom	Adhesive product produced by the reaction of maleic anhydride with castor oil.
G. 699,445	H. Hopff, C. W. Rautenstrauch, Ass'd. to I. G.	Fumaric acid esters polymerized in aqueous dispersion to produce granular molding compounds.

The Colloid Aspects of Nylon

J. B. NICHOLS

Chemical Department, E. I. du Pont de Nemours & Co. Wilmington, Delaware

Historical

Nylon is "a generic term for any long-chain synthetic polymeric amide which has recurring amide groups as an integral part of the main polymer chain, and which is capable of being formed into a filament in which the structural elements are oriented in the direction of the axis." Two common types are polyamides prepared by (1) the interaction of a diamine and a dicarboxylic acid and (2) the condensation of aminocarboxylic acids. They have the following structural arrangement:

$$\text{—CO—R—CO—NH—R'—NH—CO—R—CO—NH—R'—NH—} \quad (1)$$
$$\text{—CO—R—NH—CO—R'—NH—CO—R—NH—} \quad (2)$$

where R and R′ may represent alkylene chains containing different numbers of methylene groups. For the most part, the discussion which follows will be limited to 4 and 6 methylene groups for R and R′ respectively. This example is the so-called 66 polymer, made by the interaction of hexamethylenediamine and adipic acid. In general, therefore, nylon consists principally of hydrocarbon chains linked together by amide groups. The ends of the chains may contain free amino or acidic groups, and in fact their estimation serves as a means for determining the average chain length.

In 1928 polymerization was one of the great unmapped regions of organic chemistry. With this in mind, Carothers and a group of co-workers in the laboratories of the Du Pont Company initiated a comprehensive study of the field of polymerization. Carothers has stated:[1] "Our studies of polymerization were first initiated at a time when a great deal of skepticism prevailed concerning the possibility of applying the usually accepted ideas of structural organic chemistry to such naturally occurring materials as cellulose; and the primary objective was to synthesize molecules of known structure by strictly rational methods."

Dr. E. K. Bolton in his Chemical Industry Medal address[2] summarized the research steps leading to the synthesis of polyamides with outstanding fiber-forming properties. Carothers found that linear polyesters with molecular weights above 10,000 could be formed by means of a molecular still and that fibers could be drawn from these products. These initial fibers did not appear suitable for textile purposes, however, because of their solubility characteristics and low melting points. Even mixed polyester-polyamide substances exhibited similar shortcomings. The first polyamides investigated appeared to be too refractory for use in preparing fibers. However, the observation was made that 9-aminononanoic acid could be polymerized to form a polyamide with a melting point of 195° suitable for spinning into fibers, which, after cold drawing were equal to silk fibers in strength and pliability. Following this observation, Carothers prepared polyamides from a variety of amino acids and also from dibasic acids and diamines.[3]

Early in 1935 polyhexamethylene adipamide was synthesized from hexamethylenediamine and adipic acid and was called 66 polymer, the first digit indicating the number of carbon atoms in the diamine and the second the number of carbon atoms in the

dibasic acid. In common with the polyesters first studied, fibers could be formed from this polyamide by melt spinning and also by spinning from a solution of the polyamide in phenol. Also, as was found for the polyesters, undrawn polyamide fibers became very strong and elastic after cold drawing. Cold-drawing is the remarkable permanent-stretch phenomenon shown by polyamide and some other linear polymer fibers when stress is applied to an unoriented specimen in suitable temperature range. Instead of breaking apart, it stretches into two sections of different diameters, with a sharp junction between. Practically all the reduction in diameter occurs at this junction. During the drawing operation, the shape of this boundary does not change; it merely advances along the thicker section until the latter is exhausted. The thinner section has become highly oriented. At elevated temperatures the fiber is reduced uniformly without the occurrence of "necking down." On the other hand, at rather low temperatures breaking occurs without appreciable drawing.

Nylon may be formed into fibers, bristles, sheets and other shapes. Its first commercial uses have been in yarn for full-fashioned hosiery and other textile applications, surgical sutures, fishing leaders, and bristles of all kinds to replace hog bristles. Supplies of the latter have become more and more uncertain because of disturbed world conditions, and their resistance to abrasion and water is definitely inferior to that of nylon.[4] Other uses will become apparent as more of the polymer becomes available.

Early in 1940 the first large-scale commercial production of nylon was begun. For the first time the supremacy of silk in the full-fashioned hosiery industry is threatened. Nylon as a textile yarn offers the fabric designer the possibility of creating fabrics of far greater wearing qualities than heretofore obtainable with silk or any other fiber. It makes possible, moreover, the construction of fabrics where sheerness is an important characteristic.[5]

Preparation

One method of preparing nylon and fabricating it into yarn is as follows:[6] For the type of nylon under discussion here, adipic acid and hexamethylenediamine are combined to form a salt which is charged into an autoclave where polymer formation is carried out at elevated temperature and pressure. In the autoclave the salt is polymerized to a long-chain linear polymer with a molecular weight in the neighborhood of 10,000 or higher. The molecular weight and viscosity of the product are controlled by the use of suitable stabilizers. The molten nylon is then extruded as a ribbon onto a chilled roll and the ribbon is cut into small pieces or flakes.

To fabricate the yarn, the nylon flakes are charged into the hopper of the spinning unit where melting takes place on a specially designed heating grid. The molten mass is then pumped through special filter packs and forced through the spinneret to form fine filaments. It is necessary to blanket the molten nylon with an inert gas to prevent any degradation by oxygen at elevated temperature. The filaments which are formed by extrusion through the spinnerets freeze rapidly on striking the air below the spinneret and are wound up on bobbins.

At this stage the filaments are in a substantially unoriented condition. By the application of a suitable force, however, the nylon filaments are drawn out to about four times their original length. During this process the fiber becomes highly oriented and develops extremely desirable textile properties, namely a tensile strength higher than that of any of the commonly used textile fibers and a considerable degree of true elasticity. After the drawing, the regular textile operations may be carried out to introduce twist and to put the yarn into form suitable for weaving.

Physical Properties

The various polyamides which comprise the nylon family are "crystalline" in structure in the same sense that cellulose and stretched rubber frequently are said to

be "crystalline"; that is, a well defined x-ray pattern is produced. Nylons possess rather sharp melting points when protected from the air by an inert atmosphere. For example, the melting point of polyhexamethylene adipamide is 264°, of the 6-10 polymer,* 238°, and of the 10-10 polymer, 202°. The heat of fusion of the 66 polymer is about 22 calories per gram. Its average specific heat from room temperature to the melting point is 0.55 calorie per gram and above the melting point, 0.64 calorie per gram. The refractive index of the 66 polymer is 1.54 and its density 1.09 to 1.14, depending on its thermal and mechanical history.

Solubility. 66 nylon is insoluble in most reagents. Phenol, meta-cresol, formic acid and the halogen-substituted lower fatty acids are active solvents, but all the common dry-cleaning solvents are inactive. Strong mineral acids act as solvents, but there is considerable tendency toward degradation, especially if heat is applied. Fairly concentrated solutions of alkalies have little effect below the boil.[7]

Cold-drawing. As mentioned previously, the most interesting physical property of nylon is its ability to be cold-drawn. Depending on the nature of the polyamide, a fiber may be drawn from 4 to 7 times its original length. A well drawn, highly oriented nylon fiber possesses high tenacity and elasticity and therefore is well suited for manufacture of fine hosiery, which requires both properties.

Water Absorption. 66 nylon absorbs much less water than cotton, rayon or silk, and its fibers are nearly as strong when wet as when dry. 66 nylon bristle immersed in water at 26° absorbs 7.6 per cent of water.

Microscopic Appearance. Molten 66 polymer when slowly cooled develops large spherulites easily visible under the microscope, which show a characteristic cross between crossed Nicols. However, when the polymer is cooled sufficiently rapidly, it is optically clear. These spherulites disappear when the temperature is raised above 250°. Drawing elongates these spherulites into cylinders.

Optical Properties. Polyamides have a relatively high ultraviolet light absorption below a wave length of 2550 Å, with a moderate absorption up to 3400 Å. Examination of the infrared absorption spectrum indicates that nylon possesses a large amount of hydrogen bonding between the amide groups of neighboring chains. An undrawn yarn possesses little double refraction, but a completely drawn yarn possesses as much double refraction as ramie, for example.

Electrical Properties. The dielectric constant and power factor of bone-dry 6-10 polymer are respectively 3.5 and 2 per cent at ordinary temperatures. At temperatures above 100°, however, the values are much higher and are comparable to those of polar, hydrogen-bonded liquids such as alcohols, whereas an insulator of the non-polar type is not appreciably affected by temperature. The high power factor and low resistivity of nylon at elevated temperatures probably arise from increased ionic conductance. Dry 66 nylon has a volume resistivity of 4×10^{14} ohms per centimeter at 18 per cent relative humidity. When saturated with water, its electrical resistance decreases to about 5×10^{9} ohms per centimeter.

Electrokinetic Properties. Harris [8] has investigated the surface electrical properties of unoriented and of highly oriented 66 nylon fibers by a microelectrophoretic technique. Both types of fibers showed reversals of charge, the unoriented fiber at a higher pH value, 3.9, than the oriented, pH 2.7. Since nylon consists essentially of hydrocarbon chains connected by amide groups, Harris considers that the reversal of charge is principally dependent on the presence of the amide groups, because pure hydrocarbons do not exhibit reversals of sign of charge under comparable conditions. The difference in the pH mobility curve obtained may be greater or less than Harris found, depending on changes in orientation produced during the pulverization of the nylon preparatory to the measurements of mobility. However, similar differences have been noted for the electrophoretic properties of other substances, such as viscose rayon [9] when studied in unoriented and oriented condition.

* Based on diamine having 6 carbon atoms and dibasic acid with 10 carbon atoms.

Chemical Properties

Nylons are hydrolyzed by strong mineral acids and alkalies at elevated temperatures and by superheated water. At 85°, however, nylon yarn may be left in contact with 10 per cent sodium hydroxide for 16 hours without appreciable drop in tenacity.[7]

Physiological Action. Biologically, nylon is inert. It appears to be harmless to the skin and is finding increasing use for surgical sutures. Nylon itself will not support the growth of mildew and mold, and is not ingested by moths.

Yarn Properties

Table 1 gives comparative yarn properties for 66 nylon, silk, viscose process rayon, acetate rayon and wool.[10] The outstanding tenacity, both wet and dry, of nylon is evident, also its remarkable elastic recovery. Its water absorption at 60 per cent R.H. is the lowest of the fibers tabulated.

Table 1. Comparative Yarn Properties

Yarn	Tenacity g /denier Dry	Wet	Elastic Recovery from 4% Stretch	Water Absorption 60% R.H
Nylon	4.5-8**	4-6.5**	100%	3.5%
Silk	4.7	3.8	50	11 *
"Cordura" rayon	3.5	2.2	40	—
Viscose rayon	1.8	0.9	30	12 *
Acetate rayon	1.5	1.0	50	6.5
Wool	1.3	0.9	100	13 *

* Wilson and Fuwa, *Ind. Eng Chem*, **14**, 913 (1922).
** Depending upon the type of nylon.

Setting. One of the most interesting properties of nylon fabric (hose) is its ability to take a permanent shape or set by means of a simple treatment with boiling water or steam. This phenomenon is similar to that which takes place in the pressing of cotton, wool, or silk garments, but these operations on the natural fibers are much more easily reversible than with nylon.[10]

Dyeing. Nylon shows some affinity for a wide range of dyes, but the best results thus far on nylon 66 hosiery have been obtained with the class of dyes especially developed for cellulose acetate yarns and fabrics, and with acid colors.[11] It is likely, however, that 66 nylon can be modified to acquire enhanced dyeing characteristics.

Sensitivity to Light, Air, and Heat. Nylon possesses at least as much resistance to sunlight as silk. In general, the undrawn fibers are more sensitive to both light and heat in the presence of oxygen than the drawn fibers. Fig. 1 is given to show the effect of drawing on the sensitivity of 66 nylon yarn to air at elevated temperatures. The undrawn portion became a reddish brown whereas the drawn portion remained nearly white. The impurities tending to produce this darkening may be removed by extraction with dilute alkali.[12]

Toughness. Oriented nylon fibers are also extremely tough, that is, they wear well. Bristles made from large oriented nylon monofilaments possess very marked abrasion resistance. Also the loop strength, which is a common measure of toughness, is about the same for nylon yarn as for silk and nearly three times that of viscose textile rayon.

X-Ray Structure

According to Fuller,[13] drawn polyhexamethylene adipamide yarn gives a fiber pattern which indicates that the chains are arranged in planar, zigzag parallel formation. The observed fiber period is 17.0 Å. Comparison of the fiber pattern with that of natural silk is given on page 157 of the same article. The most highly ordered regions of 66 polymer may be assigned a monoclinic or triclinic unit cell. However, it should be stressed that at the present time the ideology and the terminology of the

x-ray structure of high polymers are in a state of flux. Until precise methods of characterization have been established it seems better to speak of "states of order" and avoid too free use of the term "crystallinity." Detailed x-ray investigations in progress by Fuller at the Bell Telephone Laboratories have dealt mainly with quenching and drawing phenomena in an attempt to elucidate the structural and mechanical features involved.

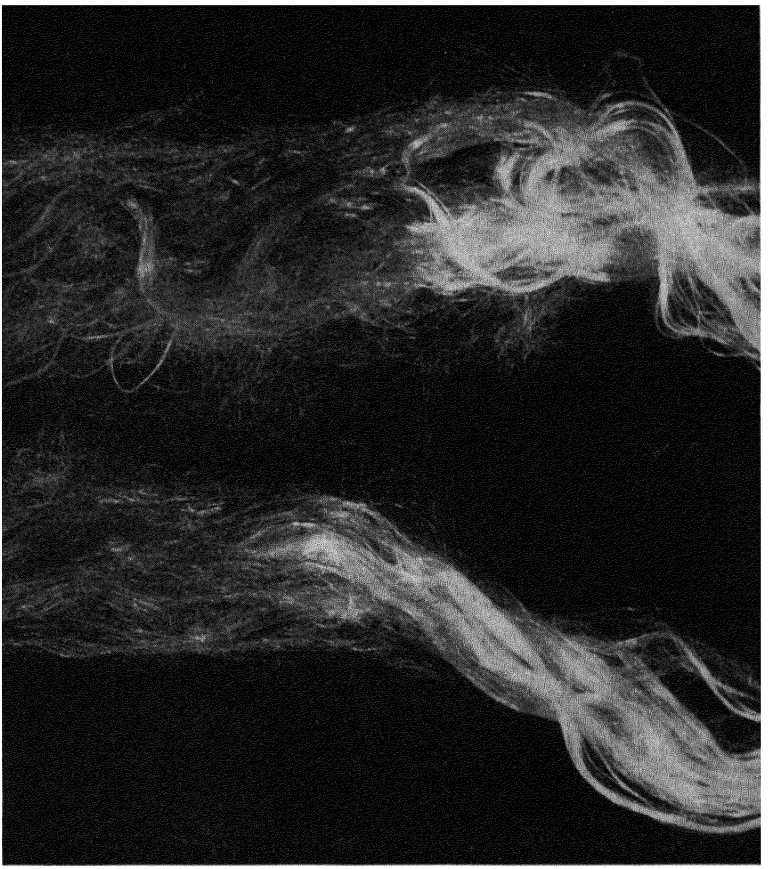
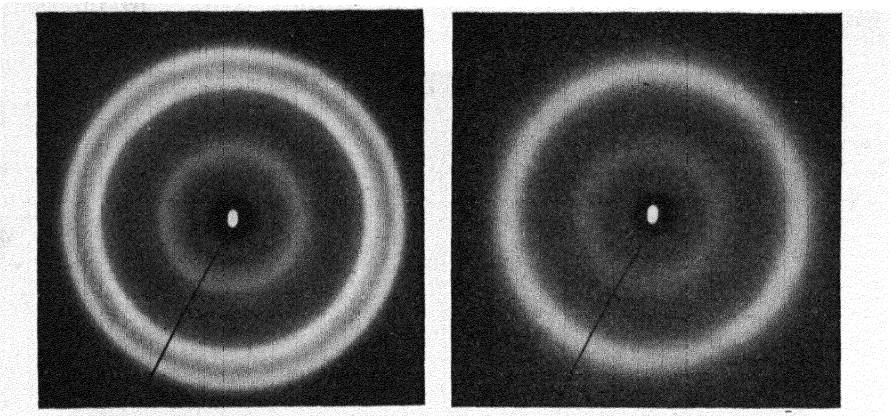


FIGURE 1. Photograph showing the effect of drawing on the sensitivity of 66 nylon yarn to air at elevated temperatures. Portion at left is undrawn, while portion at right is drawn ca. 300 per cent.

Quenching Phenomena. The rapid cooling of molten nylon produces a ductile material of which the x-ray diffraction pattern for 6-10 polymer (Fig. 2b) is represented by a single diffuse ring. This is produced by small crystallite size, lateral disorder of the chains, lattice distortion or any combination of these. Slow cooling of a nylon melt, however, yields a translucent, fairly non-ductile product characterized by a "crystalline" x-ray pattern with two sharp rings representing spacings of approximately 3.7 and 4.4 Å (Fig. 2a).

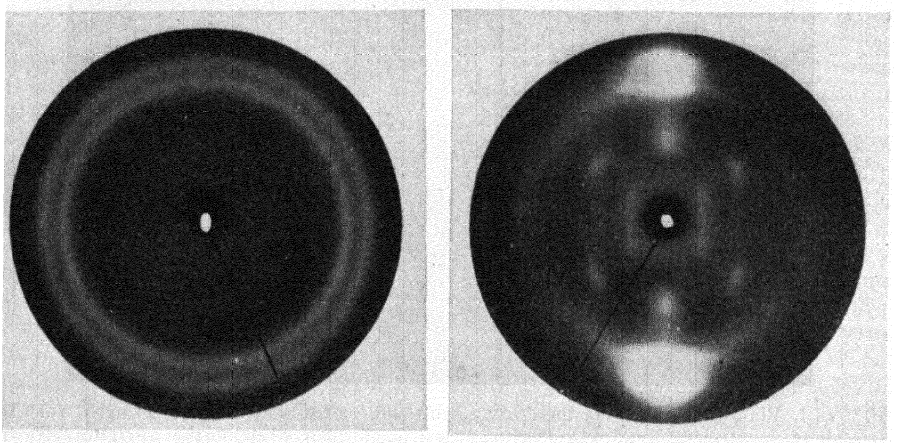
In quenched nylon each amide group is hydrogen-bonded to a neighboring amide group, from infrared data.[14] At intermediate rates of cooling considerable freedom of rotation is possible for the chains, and chain segments have a chance to fit together

and make ordered areas. Some rotational melting and rearrangement occurs during conditioning or annealing of a quenched product, but the extent of "crystallinity" is not as marked as when the sample was originally slowly cooled to the same elevated temperature.



a b

FIGURE 2. X-ray diagrams of 6-10 nylon fibers. a, cooled slowly to 25 C.; b, quenched to 25 C.



a b

FIGURE 3. X-ray diagrams of 66 nylon fibers. a, undrawn; b, after drawing 400 per cent.

Effect of Heat Treatment. In a detailed experimental study, Fuller, Baker and Pape [15] attempted to relate changes in the crystalline nature of linear polyamides to their elastic properties as a result of quenching and annealing. They investigated polyhexamethylene adipamide (66 polymer) with an intrinsic viscosity of 0.97 in *m*-cresol at 25° and polyhexamethylene sebacamide (6-10 polymer) of intrinsic viscosity 1.02. They carried out two types of heat treatment: (1) quenching the molten materials at different rates and (2) annealing previously quenched samples. X-ray patterns showing the effect of these treatments may be found in the original article.

They present considerable evidence that the kinetic unit in linear polymers is a chain segment.[16]

At the melting point a statistical unit containing a certain average number of repeating units behaves as the center of crystallization. If cooling is slow enough, these units form crystallites or highly ordered areas of a certain average size. With rapid cooling, however, the rate of loss of kinetic energy may exceed the rate of ordering and the segment may be frozen in the position occupied at the melting point. During annealing the intermolecular forces are sufficiently weakened to allow rotational motion of the molecule, resulting in more complete lattice formation. This chain mobility in the solid state shown by linear polyamides is proposed by Fuller as the reason for the independence of melting point and molecular weight of high polymers.

The chain segment or molecular freedom in solid polyamides probably also permits solid-state reactions like further condensation.[17]

According to Fuller, the elastic behavior also furnishes information on the increase of "crystallinity" with increased annealing temperature of a quenched sample or slower rate of cooling of a melted sample. Young's modulus was found to decrease rapidly for polyhexamethylene sebacamide as the temperature of quenching was lowered from 180° to 90°, below which point the filaments possessed considerable elasticity.[18]

Drawing Phenomena. As indicated earlier, satisfactory yarn properties of polyamides are not developed until the originally unoriented yarn is stretched or drawn. Fig. 3 gives the x-ray diffraction diagrams for an undrawn 66 nylon fiber and the same sample after drawing 400 per cent.

Viscous Behavior

The viscous behavior of polyamides, especially the intrinsic viscosity, has been used as one of the main guides in following the polymerization process.[19] Intrinsic viscosity is defined mathematically as $[\eta] = \frac{\ln \eta_r}{c}$, where c is the concentration of the substance in g/100 ml, and η_r is the viscosity of the solution relative to that of the solvent. This expression is valid over a somewhat wider concentration range than the original Staudinger form $[\eta] = \frac{\eta_r - 1}{c}$, which is really the first term of a logarithmic series. According to Fordyce and Hibbert,[20] Flory and Stickney,[21] and Baker, Fuller and Heiss,[22] the equation accurately reproduces data on relative viscosities of linear polymers up to 1.5 and molecular weights up to about 30,000.

Staudinger's conclusion that intrinsic viscosity of linear polymers increases directly with the chain length provides a very convenient relative method for measuring molecular weights, provided it can be calibrated by some absolute method. The methods used for the calibration will be considered in the next section. Because of the relative constancy of the proportionality constant for different polymeric materials when molecular size is expressed in terms of chain length, Staudinger believes that linear polymers are fully extended in solution. On the other hand, hydrodynamic analysis indicates that rod-like particles would increase the intrinsic viscosity as the square of the length.

Recently, however, Kauzmann and Eyring,[16] on the assumption of spontaneous kinking of flexible molecules under the influence of thermal energy, have been able to derive Staudinger's relation. The fundamental equation may be written $[\eta]_v = KZ + BZ^{1/2}/R + F$, where $[\eta]_v$ is the volumetric intrinsic viscosity, Z the length of the chain, R the gas constant, and K and F constants. For large values of Z, $[\eta]_v = KZ$, Staudinger's relation. This analysis also predicts that the natural logarithm of the relative viscosity divided by the concentration should approach a constant value at moderately low concentrations, that is, the intrinsic viscosity.

Dilute Solutions. Various solvents have been used for determining the intrinsic viscosity of polyamides. Among the most common are *m*-cresol, concentrated hydrochloric acid, and 90 per cent formic acid. The intrinsic viscosity varies considerably with the solvent used. For example, the values determined in 38 per cent hydrochloric acid average approximately 0.4 of those obtained in *m*-cresol; in 90 per cent formic acid and in dichloroacetic acid the values are approximately 0.9 of those in *m*-cresol; and with 30 per cent phenol-chloroform the values are about 1.3 times those in *m*-cresol. For the most part these differences may be related to differences in degree of kinking in the various solvents rather than to degradation. For example, when the polymer is precipitated from hydrochloric acid solution and redissolved in cresol its original viscosity in cresol is reproduced.

It is of interest that the intrinsic viscosity passes through a maximum as the chloroform content of the phenol solvent is increased. This would indicate that a better solution was being obtained. For solutions containing greater than 70 per cent of chloroform, the intrinsic viscosity falls off rapidly until at approximately 95 per cent chloroform the value is only ½ that at 70 per cent. On the other hand, addition of chloroform to dichloroacetic acid reduces the intrinsic viscosity to about ⅔ the value in dichloroacetic acid alone, probably corresponding to a poorer solution and greater kinking.

Concentrated Solutions. The viscous behavior of concentrated solutions of polymeric materials is usually of more industrial significance than that of the very dilute solutions described above, usually 0.5 per cent or less. Spinning and extrusion operations are carried out on solutions up to 25 or 30 per cent concentrations or even on molten polymers (spinning). Accordingly it is desirable to know whether changes occur in the more concentrated solutions and to use the greater sensitivity of viscosity measurements on concentrated solutions to characterize the chain length of the materials, in order to predict and control the physical properties of the finished products. Solutions of polymers up to 25 per cent in formic acid were examined in capillary viscometers and found to be viscosity-stable over a period of several days, and reproducible.

Of the various empirical formulas which have been developed to show quantitatively the effect of concentration upon viscosity,[23] Fikentscher's relation [24] has proved most satisfactory for extrapolating to infinite dilution. According to Fikentscher, $\log \eta_r = \frac{75k^2}{1 + 1.5\ kc} + k$, where η_r is the viscosity of the solution relative to that of the solvent, c is the concentration of the solution in g./100ml., and k is Fikentscher's viscosity constant. By means of a chart on which a series of curves is plotted of $\frac{\log \eta_r}{c}$ against k for different concentrations, the curve representing zero concentration may be obtained by extrapolation. If then the ordinates of this curve are multiplied by 2.303, the curve representing Fikentscher intrinsic viscosity $[\eta]_F$ vs. Fikentscher k is obtained.

The following table is representative of results obtained by the extrapolation.

Table 2. Fikentscher Intrinsic Viscosity of Concentrated 66 Nylon

Polymer	Concentration (g./100 ml)	Relative Viscosity η_r	$[\eta]_F$
A	0.5	1.45	0.75
	10	24.6	0.468
	25	370	0.465

It is evident that solutions of polymers over a considerable range of concentration exhibit the same viscous behavior but give an extrapolated value of intrinsic viscosity roughly ⅔ that measured in dilute solution. These extrapolated values of $[\eta]_F$, how-

ever, are proportional to the directly measured intrinsic viscosities over a considerable range of molecular sizes.

Viscous Behavior in Molten Polymer. The viscosity characteristics of molten polymers have also been examined in connection with the spinning operations. The determination of viscosity at elevated temperatures, for example 285°, is subject to a number of difficulties such as (1) the reduction of viscosity by a small amount of water, (2) oxidative degradation unless the system is carefully protected by an inert atmosphere, and (3) the presence of variable amounts of easily volatile or sublimable low molecular weight material. Under properly controlled conditions, however, the melt viscosities and intrinsic viscosities are in satisfactory agreement, and as will be shown in the next section, the melt viscosities may be used to calculate the degree of polymerization through an empirical relationship obtained by Flory.

Molecular Weight

All synthetic polymers consist of mixtures of chemically similar molecules. The manner in which the different sizes are distributed about an average has considerable effect on the physical properties of the material. Methods which have been investigated for determining an average molecular weight are the ultracentrifuge, end-group titrations, and osmotic pressure measurements. Of these methods, only the first gives a weight-average molecular weight, M_w, and information on the distribution of molecular weights, and the latter two a number average, M_n. The weight-average molecular weight is also yielded by the intrinsic viscosity when properly calibrated. The intrinsic viscosity is only proportional to M_n when there is a constant ratio between M_w and M_n. Flory [25] has shown theoretically that the ratio should be 2 for a linear condensation polymer formed by the reaction of bi-functional compounds.

Ultracentrifugal Analysis. An ultracentrifuge study of 66 polymer was carried out by Nichols [26] to establish the correlation between weight-average molecular weight and intrinsic viscosity. However, difficulties were encountered in obtaining solvents with suitable differences in density and refractive index, low viscosity, and low corrosive action on the centrifuge cells. Good solvents such as *m*-cresol have the same refractive index—and formic acid nearly the same density—as the polymer. It was therefore necessary to resort to mixed solvents with all the uncertainty introduced thereby. A sedimentation-velocity determination in a 10 per cent phenol-chloroform solution on a sample with a cresol intrinsic viscosity of 0.75 gave a molecular weight of about 20,000. Sedimentation-equilibrium determinations on the same sample in 10 per cent and 33 per cent phenol-chloroform solvents gave average molecular weights of 28,000 and 22,000, respectively. On the other hand, sedimentation-equilibrium runs of similar polymers in a 30 per cent dichloroacetic acid-chloroform solvent gave average molecular weights of approximately 6,000.

It seems likely that the molecular weight in the phenolic solvent was somewhat too high, and that in the acid solvent considerably too low, because of the formation of a complex between the polymer and the active part of the solvent. Therefore, until solvents better suited for ultracentrifuge analysis have been uncovered, little information will be available as to the heterogeneity of nylons. Initial attempts to fractionate material by adding non-solvents to cresol or formic acid solutions were not fruitful either, because precipitation occurred in too narrow a range of non-solvent concentration.

Osmotic Pressure Measurements. In view of the difficulties experienced with ultracentrifuge measurements, the main reliance has been on osmotic pressure measurements in a solvent consisting of 90 per cent formic acid containing 0.1*N* sodium formate to improve the membrane conditions. The osmometer used was patterned after that described by Herzog and Spurlin [27] and was constructed of KA2SMo stainless steel to provide sufficient resistance to formic acid solutions. Cellophane mem-

branes were found satisfactory to separate the solution from the solvent. Equilibrium was reached in an average of from 2 to 4 days with reproducibility of the order of 1 to 3 per cent. By this method, number-average molecular weights may be estimated from about 2,000 to 20,000 (Table 3), the lower limit being fixed by the permeability of the membrane to low molecular weight polymer.

Amine End-Group Titration. Flory has shown that the determination of the amine end-group content (strictly speaking the titratable base) will give an estimate of the number-average molecular weight, providing the amount of stabilizer used and the amine loss during the preparation of the polymer are known. The titration may be carried out in *m*-cresol or a *m*-cresol-chloroform solution, using *m*-cresol sulfonic acid as the agent and *m*-cresol purple as the indicator. The molecular weight is then calculated from the formula.[28]

$$\text{M.W.} = 113 \left(\frac{1+r}{1+r-2rp}\right)$$

where r is the ratio of the deficient reactant to the reactant present in excess, that is, 99.8/101 for a system containing 1 per cent of acid as stabilizer and which lost 0.2 per cent amine during the reaction. The symbol p represents the extent of reaction, that is, 1 — (mole per cent NH_2/100); 113 is the molecular weight of a segment, or ½ of the repeating unit of hexamethylene adipamide. The range of usefulness of this method is from 100 per cent NH_2 (monomer) to about 0.2 mole per cent NH_2 corresponding to about 12,000 in molecular weight. On the basis of the amine end-group titrations, Flory developed the following relation between number-average molecular weight and intrinsic viscosity in *m*-cresol,

$$DP = 158[\eta] - 29$$

where DP is the number of segments of molecular weight 113 in the chain.

Table 3 gives data for a range of 66 polymers which indicate that the end-group titration is practically as reliable as the osmotic pressure method for estimating molecular weights. For molecular weights less than 4,000 the amine titration seems to be more reliable owing to the permeability of the membrane to material of molecular weights less than 1000. The molecular weights calculated from osmotic pressure and amine end-group titrations serve to calibrate the intrinsic viscosity measured in *m*-cresol and in formic acid, shown in Table 3. Since the relation is linear over a considerable range, Flory's prediction of a constant relation between weight-average and number-average molecular weights for the polymerization of bi-functional reactants is substantiated.[25] The relation for formic acid was obtained from 10 per cent solutions of the polymer as described in the previous section on viscous behavior.

As a still further check on the correctness of Flory's considerations, the molecular weights calculated from the viscosity of molten polymer at 285° are given in Table 3. If the chains are not linear and if the distribution curve is not of a similar form for the series of polymers, one would expect a greater deviation here, since the method is at least five times as sensitive as the others. According to Flory's findings [29] the following relation is valid for 66 polymer at 285°:

$$\text{M.W.} = 113 \left(\frac{\log \eta_{285°} + 1.57}{0.427}\right)^2$$

where $\eta_{285°}$ is the melt viscosity in poises at 285°. The satisfactory agreement between the molecular weights calculated from melt viscosity and osmotic pressure data supplies the final verification of the correctness of Flory's assumptions.

In summary, 66 nylons of different degrees of complexity are essentially linear and have the same type of distribution curve. Osmotic pressure measurements and amine end-group titrations give a reliable estimate of the number-average molecular

Table 3. Comparison of Molecular Weights of 66 Polymer from Osmotic Pressure, End-Group Titrations, and Melt-Viscosity Determinations.

Sample Designation	Stabilizer	Melt Viscosity	[η] Sodium Formate Formic Acid Solvent	[η] 10% Soln. Formic Acid	[η] Cresol	Amine Loss (Mole %)	Mole % Amine Titrated	Number Average Molecular Weight From NH_2 Titration	Melt Viscosity	Osmotic Pressure
A	None	—	0.10	0.106	ca 0.2	—	13.9	810	—	(3100) *
A-W	Water extracted	—	—	0.117	—	—	8.8	1290	—	(3100) * 0
B	Acid	20±	0.30	0.32	0.48	0.1	0.09	5700	5100	5600
C	Alkali	67	0.38	0.37	0.63	0.9	3.16	7200	7150	6800
D	Acid	330	0.47	0.43	0.75	ca. 0.2	0.25	9900	10400	9700
E (yarn)	Acid	360	—	0.48	0.84	ca. 0.2	0.27	ca. 10000	10600	ca. 11000
E (chip)	Acid	420	—	0.49	0.86	ca. 0.2	0.265	ca. 10000	10900	—
F	None	1000	0.70	0.65	1.16	ca. 0.3	0.61	14100	13000	13000

* Membrane permeable to a considerable portion of the sample.

weight. Ultracentrifuge measurements, although rendered uncertain by the reaction with a solvent of unsuitable characteristics, give weight-average molecular weights of the proper order of magnitude in a phenol-chloroform solvent. However, until fractionation techniques are developed, the only information on the distribution of molecular sizes present in nylon polymers is that furnished by Flory's theoretical treatment.[25]

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Borated Resins

ERNEST P. IRANY

Plastics Division, Celanese Co. of America

It has been known for a long time that boric acid has a very pronounced tendency to form complex products with polyhydroxy compounds. Definite proof of the constitution of these products and of the mechanism of their formation is not yet possible, but it is reasonable to assume that they are ester-like compounds which may remain at some initial stage of molecular addition or reach a more advanced equilibrium in the form of hydrated esters.

True boric acid esters of monohydric alcohols exist and are definitely identified substances which can be easily prepared. They show, in the pure state, no acidic properties; upon hydrolysis with water, pure boric acid is produced. Esterification of polyhydric alcohols with tribasic boric acid may be expected either to result in the formation of cyclic compounds or to yield high-molecular polyesters of chain-like or even spatially cross-linked structure. Plastic materials of the latter type are formed if, *e.g.*, ethylene glycol or glycerin is heated with boric acid at high enough temperatures to expel the water.[1]

In aqueous solution, polyhydric alcohols and boric acid combine in the formation of compounds of uncertain composition which are more acidic than free boric acid and permit quantitative titration of the latter. According to Magnanini,[2] Boesekeu,[3] Hermanns,[4] etc., these products form only if hydroxyl groups are available in the 1,2 position on adjacent carbon atoms and they presumably possess a cyclic structure. There is also evidence that in some cases boric acid enters into combination with two molecules of the polyhydroxy compound, forming ionized monobasic "borospirans."[5] It is generally conceded that these products are not very sharply defined and that their formation, as concluded from conductivity measurements, depends greatly on the steric disposition and probably on the electronic environment of the hydroxyl groups.

Of outstanding interest are macro-molecular substances carrying hydroxyl groups on their chain molecules. It has been observed that dextrines and starches which contain hydroxyl groups on adjacent carbon atoms, do not react with boric acid. Polyvinyl alcohol, in which hydroxyl groups occur on every other carbon atom (1-3) becomes soluble in alcohols if about one mol boric acid is present.[6] However, other high-molecular compounds on whose molecules isolated hydroxyl groups occur only in sparse numbers and distant spacings, (1-7 or more), such as polyvinyl acetals and cellulose esters or ethers, show a most remarkable effect even of minute additions of boric acid.* These substances are converted into insoluble and infusible masses, a clear indication that through the agency of boric acid, their macro-molecular chains have been inter-linked into continuous networks of rigid spatial structure.†

* It is of interest to note that borax which in part is constituted as a boric acid anhydride, shows a reverse effect: it gels polyvinyl alcohol, and has a similar effect on starches and dextrines; however, it is entirely without action on polyvinyl acetals and cellulose derivatives. The probable reason of this difference must again be sought in the steric disposition of the interacting groups.

† The formation of gel lattices by progressive chain cross-linking apparently depends on conditions or configurations which preclude ring-closure.

If boric acid is added to a solution of one of the above-mentioned hydroxyl-bearing resins, the whole solution is converted into an elastic gel. The solvent which formerly was the medium in which the macro-molecules were independently dispersed is now converted into a dispersed phase held between the meshwork of the inter-linked resin lattice which imposes its solid-elastic gel character upon the whole system. Addition of further quantities of solvent does not change this physical character beyond softening the gel: the solvent is merely drawn into the elastic body and is incapable of exerting its dispersing power.

The function of the solvent within the gel structure is the same as that of a plasticizer. The latter, as a rule, is not a solvent of the resin but it is compatible as a dispersed solute, the resin being the medium. This explains why plasticizers admixed with the resin undergoing the boric acid treatment are in no way affected by it (see below).

Since the gel structure is held together by easily hydrolyzable linkages, water immediately destroys the lattice and returns the system to the condition of a viscous liquid.

The conversion of thermoplastic substances of the most widely used types into insoluble and infusible bodies by means of boric acid is entirely comparable to the vulcanization of rubber by sulfur. In both cases the molecules of the agent interpose themselves between the macro-molecules of the soluble and fusible plastic substance and thus create the continuous quasi-solid lattice.

However, there is one important practical difference. While the vulcanization of rubber is permanent and irreversible, that of hydroxyl-containing plastics by means of boric acid can be reversed with the utmost ease by mere contact with water. It is thus possible to convert such materials temporarily into inert, insoluble and infusible masses merely for the convenience of some operation which otherwise may be impossible, and then to recover the original plastic without change in its physical properties by washing with water.

The extremely sensitive response of polyvinyl acetal resins and cellulose derivatives toward boric acid may be put to practical use in many ways. For example, traces of boric acid of the order of about 0.2 per cent, which need not be removed, raise the softening point of molding powders enough to be of practical consequence where desired.[6] In another application [7] larger proportions can be used to convert plastic substances of the specified type into brittle masses which can be crushed or ground to impalpable powders without regard to heat evolution. After this treatment the fine powders may be re-converted to the fusible state by leaching with water. The inherent plasticity of the substance in its normal state does not interfere with this process, and it is entirely immaterial whether plasticizers are present, even to the extent of imparting a rubber-like character to the compound. The plasticizers accompany the resin throughout the treatment and they are recovered with it, without change in distribution and function. The resulting finely powdered thermoplastic resins or compounds cannot be obtained by any other known method. They represent a novel product of great potential usefulness in many fields.

The gelation of solutions of polyvinyl acetal resins, plasticized cellulose acetate or ethyl cellulose, etc., by means of boric acid, can be made use of in the practice of film casting.[6] The speed at which a film can be cast depends on the rate of evaporation of the solvent, on the tendency of the film material to retain solvent, and on the physical effects of such residual solvent. By adding boric acid to the film dope in amounts small enough not to interfere with the mechanical properties of the finished film, gelation can be brought about during the last stage of the casting operation, and the film becomes self-supporting, irrespective of solvent retention. Without this enforced phase inversion, the last traces of solvent are often very troublesome and their adequate removal may occupy a major part of the casting cycle.

To prevent gelation during the casting operation, a small amount of water must

be added, which keeps the dope fluid as long as it is present. The composition of the volatile vehicle must be so formulated that the water evaporates first. For example,[6] films were cast from a solution of 100 parts polyvinyl acetal resin (Alvar 15-80) in 250 parts ethyl acetate containing 5 parts water and 2 parts boric acid. The films were cast on a glass plate, lifted after a given number of minutes, and immediately placed under load. Blank tests were carried out without boric acid.

Film	Drying time (minutes)	Load (psi)	Time under Load (seconds)	Elongation (%)
Blank	6	15	Too soft	
Borated	6	15	Too soft	
Blank	9	20	10	Broke
Borated	9	20	30	150
Blank	11	30	5	Broke
Borated	11	30	60	100
Blank	15	30	30	Broke
Borated	15	30	Permanent	50
Blank	18	30	60	200
Borated	18	30	Permanent	Nil

In the homogeneous gelation of resin solutions by the action of boric acid, the solvent can be replaced by a plasticizer. In either case, the resin forms the continuous phase holding the solvent or plasticizer in dispersion as a solute no matter what functional distinctions may be evident in the absence of boric acid. Thus, the usual close limit of compatibility of most plasticizers disappears, and permanent soft gels can be produced which contain 500 to 1000 per cent plasticizer per 100 per cent resin. These gels are firm, elastic, non-adhesive, and essentially solid bodies, resistant to anhydrous and non-alcoholic solvents which do not dissolve the plasticizer. However, they are at once liquefied by water or alcohols.

The spatial structure of the borated resins may be interpreted in terms of molecular weight or chain length of the latter. Assuming that in order to create a continuous elastic network of inter-linked macro-molecules it be necessary to fix each molecule of the resin in at least two positions, 62 parts of boric acid should account for $3/2\ M$ parts of resin, where M is the average molecular weight of the latter. Since M usually is very large, the extreme smallness of the effective amounts of boric acid is understandable. It also follows that the greater the molecular weight, the smaller the quantity of boric acid required, and the more sensitive the physical response.* For example, a moderately high polyvinyl acetal of molecular weight 60,000 would be gelled by about 0.2 per cent boric acid; one of 6,000, by 2 per cent. These estimates are well within the observed range.

If an insufficient amount of boric acid is added to a resin composed of polymers of greatly varying chain length, the longest molecules will be favored by the highest probability of simultaneously acquiring two or more bridges. In other words, competition would result in fractionation, depending on the available quantity of boric acid and independently of the usually employed fine differences in solvent composition and temperature which are very difficult to control and to duplicate. As an example, two polyvinyl acetal resins of different average molecular weights were repeatedly fractionated according to this method. The separation was found to be sharp and practically complete in each case; the nature of the solvent (toluene, toluene-xylene mixtures) did not affect the results. Since fractionation is of practical interest for the purpose of eliminating undesirable low-molecular polymers in various types of resins, a new working method based on the use of boric acid may suggest itself.

The above account emphasizes the unique effect of boric acid on high-molecular substances containing a plurality of hydroxyl groups per molecule. In short, boric

* These phenomena recall those shown by antigens and antibodies in immunological reactions. See paper on Immunology by Wm. C. Boyd in Vol. V of this series, p. 957. J. A.

acid reacts with these substances on mere admixture, in the absence of water or alcohols, forming spatially inter-linked bodies which possess all characteristics of vulcanized or "cured" resins—with the distinction, however, that this effect is immediately reversed by mere contact with water or alcohols. This cycle is of more than theoretical interest, as many practical applications can be visualized, the more so as the resins susceptible to the treatment include some of the most widely used plastics.

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Silicones *

EUGENE G. ROCHOW AND FRANCIS J. NORTON

Research Laboratory, the General Electric Co., Schenectady, N. Y.

PART I. GENERAL CONSIDERATIONS (E. G. ROCHOW)

Silica and the silicate minerals are everywhere about us in great abundance, for silicon and oxygen together make up 76 per cent of the earth's crust. In the form of rock, clays and sand, these durable substances have been used since the days of antiquity as materials for constructing shelters and for fashioning objects. Out of these ancient uses have grown the ceramic arts, and with them our relatively recent knowledge of the chemistry of the silicates.

There are many other aspects of silicon chemistry which are not as well known and which have not been put to everyday use. Silicon forms several series of volatile covalent compounds, such as the hydrides, the halides, the esters, and the alkyls, which do not occur in nature but may be prepared and investigated in the laboratory by well-defined techniques. The organosilicon oxides, hydroxides, halides, and nitrogen compounds constitute another vast field which has been only partially explored by Kipping and others.[1] In spite of the availability of silicon and its chemical versatility, up to 1940 it had not become a raw material for chemical industry.

Some organic compounds of silicon now show promise of leaving the laboratory and entering the process industries in the form of useful oils, resinous polymers, and surface-treating agents. It is the purpose of this article to review briefly the fundamental chemistry of these organosilicon compounds, and then to point out some of their current and potential uses, particularly with respect to the alteration of surface properties of many common materials.

General Considerations

The simplest classes of volatile covalent compounds of silicon are the hydrides or silanes, the halides, the esters, and the alkyls or aryls.[2] Representative compounds may be wholly within one class, as in the case of silicon tetrachloride or silicon tetramethyl, or they may be "mixed," as in the case of dichlorosilane, SiH_2Cl_2, and dimethylsilane, $(CH_3)_2SiH_2$. Given four classes of substituents, it is evident that a great variety of such mixed compounds is possible. If —R represents an organic group attached to silicon, —X represents a halogen atom, and —OR represents an alkoxy or aroxy (ester) group, then a general formula for the volatile covalent compounds of silicon of importance to this discussion may be represented by

$$SiH_aR_bX_c(OR)_d$$

where a, b, c, and d have values from 0 to 4 and $a + b + c + d$ is always equal to 4.

Turning to specific classes of substances, the silanes are hydrides which parallel the paraffin hydrocarbons in structure: SiH_4 is called monosilane or simply silane,

* This article is taken in part from a book on Organosilicon Compounds by E. G. Rochow, to be published by John Wiley & Sons, Inc., and abstracted by permission of the author and the publisher.

Si_2H_6 is disilane, Si_3H_8 is trisilane, and so on. Such hydrides are prepared by the action of mineral acids on the "magnesium silicide" which results from the reduction of silica with magnesium,[3] followed by fractionation in an evacuated closed system. The silanes oxidize so readily that they take fire in air, and are readily hydrolyzed by moisture. The partial substitution of organic groups or halogen for hydrogen greatly decreases the inflammability of the silanes, but any hydrogen attached directly to silicon continues to be readily and quantitatively removable with dilute aqueous alkalies:

$$Si - H + H_2O \rightarrow Si - OH + H_2.$$

The halides range from a gas (SiF_4, b.p. −65° at 1810 mm pressure) to a solid (SiI_4, m.p. 120.5°), the most important to the present purpose being the volatile colorless tetrachloride ($SiCl_4$, b.p. 57.6°). This compound is available commercially at a cost sufficiently low to allow its use as a starting material for the synthesis of many organosilicon compounds and esters. As is true of all the halides, the chloride hydrolyzes rapidly to silica and the corresponding hydrohalogen acid; in this respect the silicon tetrahalides differ markedly from the tetrahalides of carbon, and reflect the higher maximum covalency of silicon.[4]

The esters may be considered as organic ethers or esters of the hypothetical orthosilicic acid, $Si(OH)_4$. They are usually derived from the halides by reaction with an alcohol or phenol, thereby splitting out the hydrohalogen acid and attaching the alkoxy or aroxy group to silicon by a process analogous to that of hydrolysis. The ester groups themselves may be hydrolyzed off, regenerating the alcohol and depositing silica. For this reason some of the silicic esters (particularly ethyl silicate) are used as sources of very pure silica and in the formulation of protective paints.[5]

The alkyls and aryls are true organometallic compounds in that the organic groups are linked directly to silicon rather than through oxygen or nitrogen. They may be prepared by the action of sodium on a mixture of the appropriate organic halide and silicon tetrachloride,[6] by reaction of an alkyl of zinc or mercury with a silicon halide or ester,[7] or by the action of the Grignard reagent on a silicon halide [8] or ester.[9] The sodium condensation is best adapted to complete substitution to form a tetra-alkyl or -aryl; the Grignard and the organozinc syntheses are more capable of stepwise control when partial substitution of an ester or halide is desired. Partially substituted silanes may also be made from SiH_4 by a series of reactions.[10]

Alkyls and aryls of the type SiR_4 are characterized by surprising inertness. Silicon tetramethyl is unaffected by concentrated sulfuric acid and customarily is separated from ether by the use of this reagent; silicon tetraphenyl boils without decomposition near 500° at atmospheric pressure and may be sulfonated and nitrated without destroying the carbon-silicon bond. The chemical resistance to oxidation and reagents differs among the various tetra-alkyls, being greatest for the tetramethyl and least for alkyls having rather long aliphatic chains. This useful property of the lower alkyls is conveyed to the corresponding organic-substituted silicon oxides to a like degree, and is the basis for the successful utilization of these materials in applications where high temperatures are encountered.

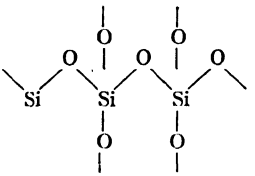
Since the energy of the carbon-silicon bond is almost the same as that of the carbon-carbon bond (57.5 kcal compared with 58.5 kcal), there would be no reason to expect from this fact alone that organosilicon compounds would necessarily be more stable than their purely organic counterparts. Yet there are certain structures involving C—Si bonds which exhibit this exceptional stability because of their special configuration: a CH_3—Si structure, for example, appears to be particularly resistant to oxidation, possibly because it contains no carbon-to-carbon bonds. The structure CH_3—CH_2—Si oxidizes more readily and C_4H_9—Si much more so; in general, the

larger the alkyl group on silicon the more readily it is removed by oxidation. The C_6H_5—Si configuration is remarkably stable, as has been shown,[11] yet benzyl groups are relatively easily removed from silicon by oxidation. Possibly the distinction between silicon carbide and carbon should be added to this list. At any rate, it must be emphasized that not all organosilicon compounds are more stable *per se* than organic compounds; the placement of a silicon atom somewhere in the structure does not convey this magical property. Only specific organosilicon structures have extraordinary stability, and these structures must be maintained if a material is expected to perform at elevated temperatures.

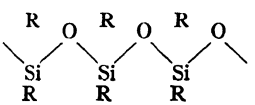
The Organosilicon Polymers

Attempts to prepare organosilicon polymers solely by condensing silicols with organic hydroxy compounds have not yet been well developed, and the copolymerization of Si=C structures with ethylenic compounds is not yet possible because no Si=C structure has been prepared.[12] The introduction of silicon into organic polymers by other means is undoubtedly possible, but there is always a possibility that the effect may be masked by dilution of the silicon with so much carbon.

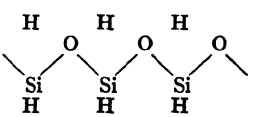
Greater success has attended the reverse procedure, that is, the introduction of suitable organic groups into a predominantly inorganic structure of silicon and oxygen. If we consider the structure of the silicon oxides, we find that they are composed of networks of alternate silicon and oxygen atoms arranged in such a fashion that each silicon is surrounded by four oxygen atoms and each oxygen is linked to two separate silicon atoms:



Fundamentally, the network is a series of spiral silicon-oxygen chains cross-linked with each other through oxygen bonds. If we were to attach two organic substituents to each silicon atom, there would then be room for only two oxygens on each silicon and a purely linear polymer should result:

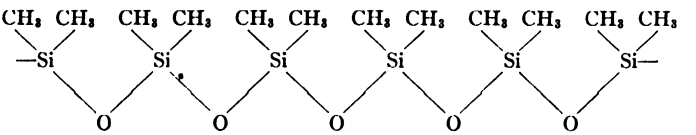


This result is more readily obtained in practice than might have been expected, for all oxygen-containing compounds of silicon polymerize readily in the same manner and for the same reason that silica does.[13] Thus prosiloxane, H_2SiO, forms a liquid hexamer and a long series of solid polymers [3] of the general structure which



are multiples of the unit $[H_2SiO]$. This is but an extension of the siloxane series, for disiloxane is $H_3Si—O—SiH_3$, trisiloxane is $H_3Si—O—SiH_2—O—SiH_3$, and so on. In fact, we may think of the —Si—O—Si—O—Si—O— chain as the siloxane chain, and consider it fundamental to all silicon oxides, whether substituted or not. The tendency to form such a chain is inherent in the silicon-oxygen configuration, and the

chief problem is one of controlling and directing this tendency in order to obtain a structure with the desired properties. It follows that an organosiloxane of the composition R_2SiO will assume a polymeric form such as is postulated above, and that a great many different cyclic and linear arrangements of the R_2SiO units will be possible. An example of such a linear polymer is shown in Fig. 1. This represents a scale model of a dimethylsiloxane polymer with six silicon atoms as the basis. The 12 methyl groups are arranged on the central silicon-oxygen chain, as in the formal representation



A compound of the type $[R_2SiO]_x$ is called a *silicone* by analogy to a ketone (R_2CO), but the resemblance is a purely formal one because a silicone is always polymeric, whereas a ketone is not. The silicon-oxygen bond bears no chemical or structural resemblance to the carbonyl group.

An organosiloxane or silicone of the type R_2SiO commonly is prepared by a process of condensation. Silicon tetrachloride may be partially methylated, for example, by one of the previously described methods to form dimethyldichlorosilane, $(CH_3)_2SiCl_2$. This hydrolyzes readily

$$(CH_3)_2SiCl_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl$$

but the hypothetical dimethylsilanediol has never been isolated because it condenses intermolecularly and spontaneously to dimethyl silicone:

$$x(CH_3)_2Si(OH)_2 \rightarrow [(CH_3)_2SiO]_x + xH_2O$$

If the hydrolysis is carried out at low temperature and with a large excess of water in a mutual solvent such as diethyl ether, the lower molecular weight species are formed in abundance. At higher temperatures and in the absence of a solvent, or under conditions that allow a high concentration of hydrochloric acid to build up, a larger proportion of high-molecular-weight polymers is formed. These are not predominantly cyclic, for ring structures containing more than four R_2SiO units appear to be less and less favorable, and nine units appear to be maximum. The larger polymeric forms therefore must be linear in structure (or a combination of chains and rings) with terminal hydroxy groups. Such molecules are capable of still further condensation by virtue of their OH groups; hence the average molecular weight can be caused to increase by heat alone or by treating the material with a dehydrating agent such as ethyl borate or even portland cement. As the molecular weight rises, further condensation becomes more and more difficult.

The rate of condensation of a silicol to a silicone is markedly influenced by the size of the organic group attached to silicon. Dimethylsilanediol, for example, condenses immediately upon formation, as shown above, but the corresponding phenyl silicol may be isolated from the hydrolysis reaction as a white crystalline substance which is quite stable at room temperature. Upon heating to its melting point (139°) this silicol slowly condenses, liberating bubbles of water vapor. Continued heating at 200° or more transforms the material to a viscous liquid which cools to a clear, brittle, resinous mass. This phenyl silicone resin remains fusible after long periods of heating at 200°, and requires a temperature in excess of 400° to "cure" further. In the fusible state it is soluble in benzene and toluene. Chlorination of the phenyl groups renders the resin non-flammable.[14] Both the chlorinated and unchlorinated phenyl silicones have very low electrical losses, the D. C. conductivity at 350° being less than that of borosilicate glass.

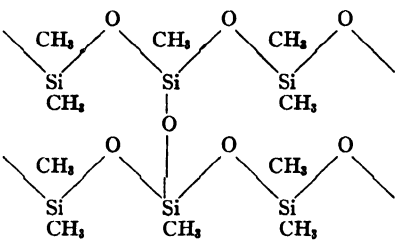
Dimethyl silicone, on the other hand, is obtained directly from the hydrolysis reaction as a colorless oil which contains many polymeric forms from the simplest structures to the non-volatile fornis of high molecular weight. This oil may be processed into a number of fractions which differ in viscosity but which all show remarkably little change of viscosity with temperature. The striking contrast between the temperature coefficients of viscosity of hydrocarbon oil and of methyl silicone oil can best be shown in Fig. 2. Here the viscosity of a high-grade paraffin oil (viscosity index = 100) is plotted against temperature, and the viscosity of a silicone oil is shown on the same scale.* It is seen that the silicone oil at −35° F has 7 times the viscosity it had at +100° F, while the paraffin oil of comparable viscosity shows an 1800-fold increase over the same range.

Silicone oils also are notable for their low pour points (−120° F to −130° F, depending on viscosity) and their chemical stability at high temperatures. At 300° F they are free from the acid formation, discoloration, and sludging which limit the usefulness of petroleum products, and they do not attack any of the common metals used for construction. In applications where boundary lubrication is not a factor, the silicone oils cause less wear than hydrocarbon oils because of this chemical inertness.

Since methyl silicone differs so much from phenyl silicone and does not thicken to a glossy resin at room temperature, other means must be found for preparing resinous polymers from it. One method accomplishes this by cross-linking methyl siloxane chains to produce an infusible, insoluble, three-dimensional polymeric structure.[15] Methyltrichlorosilane is added to dimethyldichlorosilane and the mixture is hydrolyzed:

$$(CH_3)_2SiCl_2 + 2H_2O \rightarrow (CH_3)_2Si(OH)_2 + 2HCl$$
$$CH_3SiCl_3 + 3H_2O \rightarrow CH_3Si(OH)_3 + 3HCl$$

The transitory silicols co-condense during the hydrolysis and subsequent heating, producing a cross-linked structure:



Since a trifunctional group results from the hydrolysis of each molecule of methyltrichlorosilane, the degree of cross-linking is conveniently governed by regulating the proportion of the trichlorosilane in the mixture. Silicon tetrachloride may similarly be used to provide the oxygen bridges for cross-linking. The three-dimensional network which results in either case contains fewer than two methyl groups per silicon atom, for each cross link replaces two methyl groups. The ratio CH_3/Si therefore provides an index of the degree of cross-linking, and in large part defines the character of the resulting polymer. At a CH_3/Si ratio of 1.0 to 1.3 the condensation proceeds at room temperature through a sticky stage to a hard, brittle resin. At a ratio of 1.5 the condensation requires several hours' heating at 150° or more, and the product is flexible and horny. Above a ratio of 1.5 the liquid products are increasingly volatile, and condense to soft gels rather than sticky resins. Further properties are given in reference 15.

* The authors are grateful to Dr. D. F. Wilcock for supplying Fig. 2. The silicone oil represented therein is General Electric No. 9981-LT-25.

Other organo-silanediols condense in a similar fashion, and the products may be cross-linked by the same method or by removing a desired proportion of R groups by oxidation.[16] Silicone resins of improved mechanical properties are made by hydrolyzing methylphenyldichlorosilane or a mixture of methyl and phenyl chlorosilanes and co-condensing the products to form a methyl phenyl silicone.[17] Ethyl silicone resins within a particular C_nH_n/Si range of composition have also been described.[18] By further variation of the type of organic group and the degree of cross-linking, it is possible to produce an endless array of silicone polymers based upon the same framework of alternate silicon and oxygen atoms.

Manufacture of Intermediates

The most straightforward procedure would be to adapt the Grignard synthesis to large-scale operation. In making the methyl chlorosilanes, for example, the use of methyl chloride[19] rather than methyl bromide (which is more convenient for laboratory use) results in a considerable saving of cost. By resorting to an autoclave, phenyl magnesium chloride for phenyl chlorosilanes can be made from chlorobenzene[20] rather than from the expensive bromobenzene required for laboratory synthesis, and excess chlorobenzene acts as the solvent for its magnesium derivative. The preparation of organosiloxanes on a large scale by the hydrolysis of organosilicon halides presents no particular problems.

If ethyl silicate is used instead of silicon tetrachloride as the source of silicon, an excess of the ester serves as a solvent for its reaction with the Grignard reagent.[21] The reagent likwise can be prepared in the absence of ether by the use of a little ethyl silicate added as catalyst to the mixture of halide and magnesium.[22] The combined procedures provide a means of making alkyl alkoxysilanes without the use of extra solvents, and these intermediates can then be hydrolyzed to obtain the alkyl silicones.[23]

Manufacture of organosilicon halides by sodium condensation of the appropriate halide with silicon tetrachloride does not seem promising because of the difficulty of controlling the reaction in order to stop at partial alkylation of the chloride. In those cases where an intermediate organosodium compound can first be made separately and then combined in the desired proportion with the $SiCl_4$, the process would obviously be more favorable.[24] The cost of the sodium is rather high at present, for two equivalents of sodium are required where one of magnesium would suffice.

A radically different method for preparing organosilicon chlorides has been described,[25] in which unsaturated hydrocarbons are absorbed directly by silicon tetrachloride under pressure:

$$CH_2{=}CH_2 + SiCl_4 \rightarrow ClCH_2 - CH_2 - SiCl_3$$
$$CH{\equiv}CH + SiCl_4 \rightarrow ClCH{=}CH - SiCl_3$$

Molar quantities of aluminum chloride and heavy-metal oxides or chlorides are used as catalysts. The reaction also proceeds with carbon monoxide and silicon tetrachloride to yield an interesting carbonyl chloride derivative:

$$CO + SiCl_4 \rightarrow O{=}\overset{\displaystyle Cl}{\overset{|}{C}} - SiCl_3$$

Part II. Application of Organosilicon Compounds to the Formation of Water-Repellent Films (F. J. Norton)

During an investigation of the preparation and properties of the methyl chlorosilanes, it was discovered that the vapors of certain combinations of these substances rendered the surfaces of paper, glass, cotton, and many other common materials water-repellent to a remarkable degree.[26] It has been found that such a layer greatly in-

creases the electrical surface-leakage resistance of steatite and other ceramic insulators under humid conditions and particularly when moisture is condensed on the surface.[27]

Surface Reaction

A mixture of methyl chlorosilanes was used to give the water-repellent surface treatment. This has a vapor pressure of about 200 mm at room temperature (25°).

The vapor of the chlorosilane reacts very rapidly with moisture adsorbed on the surface to be treated; hydrochloric acid is split off and a thin water-repellent film is deposited on surfaces where this reaction has occurred. The hydrochloric acid rapidly volatilizes from the ceramic surface, leaving the non-volatile layer which gives water repellency. One plausible picture of the nature of the layer is that the methyl groups (CH_3-) present a hydrophobic surface which water has little tendency to wet.

It will be observed from the reactions involved that water initially adsorbed on the surface causes the formation of the water-repellent film. Normally all surfaces have on them adsorbed water molecules, the number of which depends on the relative humidity and the nature of the surface.[28, 29]

Parks found that the water film on silica surfaces was about 13×10^{-6} cm thick, in equilibrium with saturated water vapor at 15°. Briggs found that at 80 per cent relative humidity the film on silica was 0.45×10^{-6} cm thick and at 99 per cent relative humidity the film was 2.7×10^{-6}. If $3\text{Å} = 3 \times 10^{-8}$ cm is taken as an approximation of the diameter of a water molecule, the water layer in very high humidities is about 100 molecules thick. Other more recent values for the absorption of vapors by crystalline solid surfaces have been measured.[30]

It has been found that to obtain best treatment on applying methylchlorosilane vapors, the steatite surfaces should be in equilibrium with 50 to 90 per cent relative humidity. The vapors should not be applied when the surface of the ceramic has on it visible condensed water. The latter condition would cause the formation of thick, isolated non-uniform patches of the hydrolysis product. Pre-conditioning at 50 to 90 per cent relative humidity is satisfactory.

The water-repellent film which deposits on steatite ceramics from the methylchlorosilane vapor is very thin. A ceramic coil form with a surface area of 400 cm^2 gained 0.0075 gram on treatment or 1.9×10^{-5} gram per $cm.^2$ If the density of the film is taken as 1, the film thickness is 1.9×10^{-5} cm, which is below the wave length of visible light.

A reasonable orientation of the film deposited from chlorosilane vapor is shown in Fig. 1. This yields a molecule with a closely packed surface consisting of methyl

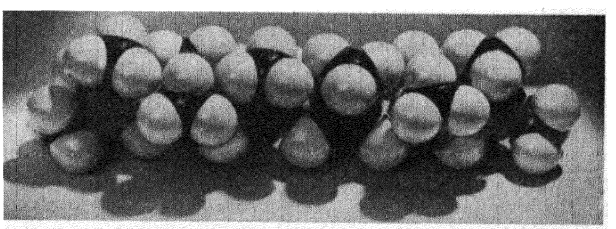


FIGURE 1. Model of organo-silicon molecule with six silicon atoms as the base.

groups, forming the water-repellent hydrophobic surface, characteristic of chlorosilane-treated ceramics. The silicon and oxygen atoms of the silicone are bonded to the underlying silicate by subsidiary valence forces.

This molecular arrangement offers one possible explanation of the thermal stability, tightness of bonding, and extremely water-repellent character of the outer surface.

A study of the molecular models also enables one to calculate theoretically the area which could be covered by one molecule of $(CH_3)_2SiCl_2$ reacting to form one $[(CH_3)_2SiO]$ unit in the surface layer. The methyl groups are the deciding factor in the spacing. They are about 3 Å apart from carbon atom to carbon atom, and the chains probably 4 Å apart; so the area is $3 \times (3 + 4) = 21$ sq Å per molecular unit of two methyl groups, one silicon atom, and one oxygen atom. One mole of $(CH_3)_2SiCl_2$ is 129 grams, and there are 6.023×10^{23} molecules per mole (Avogadro's number); so the area per mole is 21×10^{-16} cm^2 $\times$ $6.023 \times 10^{23} = 1.26 \times 10^9$ cm^2, or 1.26×10^5 m^2 per mole. That is about 1000 M^2 per gram of dichloride applied, for a monomolecular layer on the surface. Lack of detailed knowledge of structure of the surface layer may cause this calculated figure to be in error by a factor of two.

The thickness of a monomolecular layer of silicone on a surface, if in the orientation of Fig. 1, is about 6 Å units $= 6 \times 10^{-8}$ cm. This was obtained from measurements on the molecular-scale model.

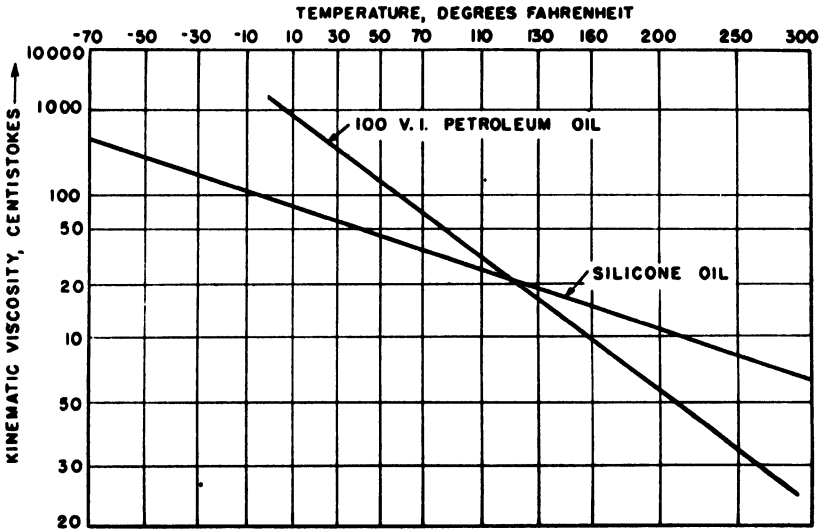


FIGURE 2. Viscosity of silicone oil and of petroleum oil as a function of temperature.

Method of Applying Methylchlorosilanes

A convenient laboratory method is to place the specimens to be treated (after prehumidification, if necessary) in an enclosed glass vessel, such as a desiccator with inlet and outlet tubes. Dry air is bubbled through two or three bottles of chlorosilane at room temperature, and this gas stream led into the vessel holding the specimens. This gives more nearly equilibrium and unchanged vapor compositions out of the last bottle when mixtures are used. The reaction with surface moisture is very rapid, and only a few minutes exposure is needed. This should give time for diffusion of the vapor to all parts of the specimen. The treated specimens are then aired to allow the hydrochloric acid to volatilize. It has been found that most of the acid is gone within ten minutes and two hours airing time is ample. Some further improvement of the electrical characteristics of the deposited film has been noted on aging over 24 hours.

Caution should be used in handling the methylchlorosilanes as these are volatile materials, and breathing the vapors or spilling on the skin results in the production of hydrochloric acid, with uncomfortable results. They should be handled under a hood, with good ventilation and flames kept away, as they will burn. No cumulative

toxic results have been encountered by the research group handling these materials over several years.

Method of Test

In order to subject the steatite surfaces to the most severe test, the electrical surface-leakage resistance was measured during actual condensation of liquid water droplets on the ceramic surface. The specimens were cooled to about −10° by placing them in the freezing compartment of an electric refrigerator; then they were placed in a chamber at 25°, 100 per cent relative humidity. Electrical measurements were made with a megohm bridge. The leads from the bridge went through long glass tubes into the humidity chamber to provide long leakage paths, and this glass was protected against moisture effects by treatment with methylchlorosilanes. The megohm bridge read to one million megohms, but 200,000 megohms was adopted as the highest practical reading. The bridge measures resistance with 500 volts D.C. applied to the specimen.

The resistance dropped, generally within a minute, when the sample was placed in the 100 per cent relative humidity, and went down for 5 or 10 minutes. This lowest reading was taken as that of the surface under dewpoint conditions. After several hours in 100 per cent relative humidity, 25°, the surface resistance would gradually rise somewhat until the liquid droplets had disappeared and the surface assumed its resistance value for approximately 100 per cent relative humidity without condensation. The lowest resistance reading always accompanied the actual presence of visible condensed moisture.

The general appearance of the moisture film paralleled the electrical resistance of the surface under dewpoint conditions. On materials having the water-repellent surface given by the methylchlorosilane treatment, the water condensed in very tiny isolated droplets, velvety in appearance, and standing up on the surface with a high contact angle. These were not in contact with each other, and the electrical resistance of such a surface was high. Untreated ceramic surfaces, glazed or unglazed, gave large droplets or whole wetted areas, with relatively poor electrical-surface resistance.

Waxed surfaces had an intermediate appearance with medium-sized droplets, and the resistance of these surfaces was intermediate in value.

Previous Measurements on Surface Resistance

The most comprehensive work in this field is reported by Curtis.[31, 32] His data for glazed and unglazed porcelain at different humidities, and for lavite—a material somewhat similar to unglazed steatite—are given in Fig. 3. On the 100 per cent relative-humidity line, represented by dewpoint conditions, are put the values found in the research reported here for unglazed steatite untreated and treated by methylchlorosilanes. It will be observed that the value for untreated steatite fits into the extension of Curtis' curves. The treated steatite, under the very severe condition of 100 per cent relative humidity, dewpoint condensation, has about the same value as lavite at 50 per cent relative humidity, or glazed porcelain at 60 per cent relative humidity.

Smail, Brooksbank and Thornton [33] measured the electrical resistance of moisture films on glazed surfaces, arriving at somewhat higher values than did Curtis, but showing the same strong dependence on relative humidity.

Other data are given by Hausner [34] and by Yager and Morgan.[35]

Tests on Various Types of Surfaces

As a preliminary study of surface types, steatite ceramic end plates for tuning coils were used. These end plates were 3 in square and ¼ in thick. A bolt in the central hole formed one electrode; the other was formed by two bolts on each side connected

together and each at one-inch distance from the central electrode. This gave 4 parallel paths over the surface.

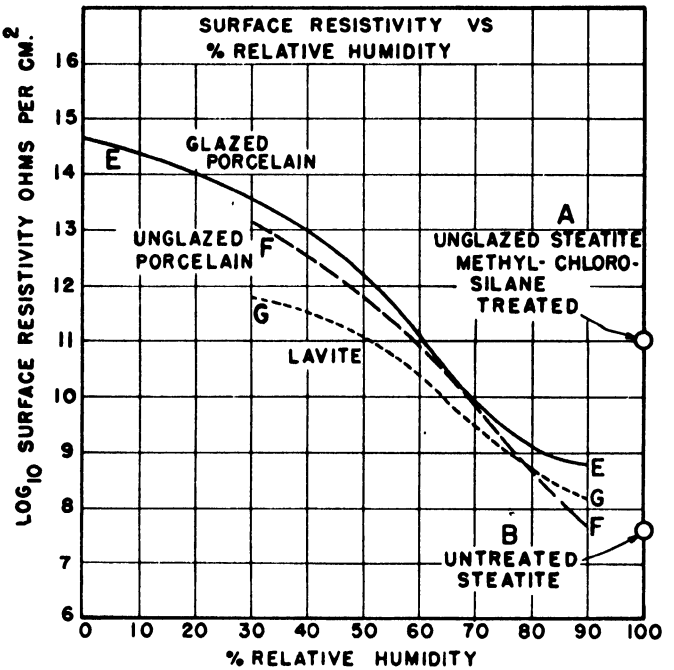


FIGURE 3. Data of H. L. Curtis, Bull. Bur. Stds. **11**, 359 (1915). With present measurements under dewpoint conditions.

These offered four types of surface:

(1) Unglazed steatite, no treatment at all.
(2) Unglazed steatite treated with ceresin wax by the manufacturer.
(3) Unglazed steatite treated with the vapor of methylchlorosilanes.
(4) Glazed steatite, glazed specially by the manufacturer.

These surfaces were tested under the following conditions:

(a) Pre-cooled to −10°, then put into 100 per cent relative humidity 25° and measured in that humidity as the water droplets actually condensed on the surface.
(b) No pre-cooling, but put directly into 100 per cent relative humidity and measured. This is not nearly so reproducible a condition as (a), since fractions of a degree variations in the specimen may change the surface condition of the moisture.

Table 1 shows the results obtained.

Various other types of glazed surfaces were tested under dewpoint conditions, and the surface resistance in megohms is given in Table 2.

For other details of electrical tests on chlorosilane-treated ceramics, and factory methods of treatment, see reference.[27]

Rapid Evaporation of Condensed Moisture

The fine, velvety appearance of moisture condensed on surfaces treated by methylchlorosilanes has been mentioned. This is due to the very small droplets, visible under 20-power magnification, which condense on such a surface contrasted to the

much larger droplets which deposit under comparable conditions on an untreated surface.

Table 1. Tests on Ceramic End Plates

a. Pre-cooling + 100% Relative Humidity 25° C (Dewpoint conditions with droplet condensation)

Resistance (megohms)	Resistance (megohms)
1. Unglazed, untreated	3. Unglazed, methylchlorosilane-treated
1.8	>200,000
1.5	>200,000
1.0	>200,000
Ave. 1.4	Ave. >200,000
2. Unglazed, waxed	
400	4. Glazed, no other treatment
120	15
170	70
Ave. 230	

b. No Pre-cooling + Approx. 100% Relative Humidity 25°

1. Unglazed, untreated	3. Unglazed, methylchlorosilane-treated
130	>200,000
650	>200,000
10,000	
2. Unglazed, waxed	4. Glazed, no other treatment
13,000	700
5,500	2,400
70,000	

Table 2. Glazed Surfaces—Megohms Resistance

Condition of Surface	Chocolate Glaze	White Glaze A	White Glaze B
Dirty	0.5	0.75	0.4
Cleaned	48	2.8	4.6
CCl_4 + alcohol			
Treated by methylchlorosilanes	30,000	100,000	>200,000

It was observed that moisture evaporated much more rapidly when it was present in this finely divided form. To measure this, a ceramic-coil form was given a partial treatment with Dri-Film * methylchlorosilanes so it would not be too high in resistance under dewpoint condensation. Under identical conditions, the electrical surface-leakage resistance of two coil forms, treated and untreated, was measured with water condensed on the surface at 100 per cent relative humidity. The untreated specimen had 2 megohms surface resistance, the treated specimen 400 megohms. Each was then moved into open air, 50 per cent relative humidity, and the surface resistance measured as evaporation proceeded. Within two minutes, the treated specimen reached 100,000 megohms resistance due to rapid water evaporation, whereas the untreated coil form was 740 megohms after 20 minutes. The recovery curves are shown in Fig. 4.

Lower Inflammability Limits of Methylchlorosilanes and Air †

The methylchlorosilanes can burn, and the following is the probable reaction for a type compound:

$$(CH_3)_2SiCl_2 + 4O_2 \rightarrow SiO_2 + 2CO_2 + 2HCl + 2H_2O$$

* "Dri-Film" is the trade mark of the General Electric Company's water-repellent compounds.

† The data in this section are taken from work done by E. W. Balis and H. A. Liebhafsky of the General Electric Research Laboratory.

Hence, when mixed with air there are certain limits of concentration of air and chlorosilane vapor below which ignition cannot occur, and above which self-propagation of a flame can occur when the mixture is ignited with a spark or flame. There are similar flame-propagation limits, of varying values, for mixtures of air with all combustible vapors.

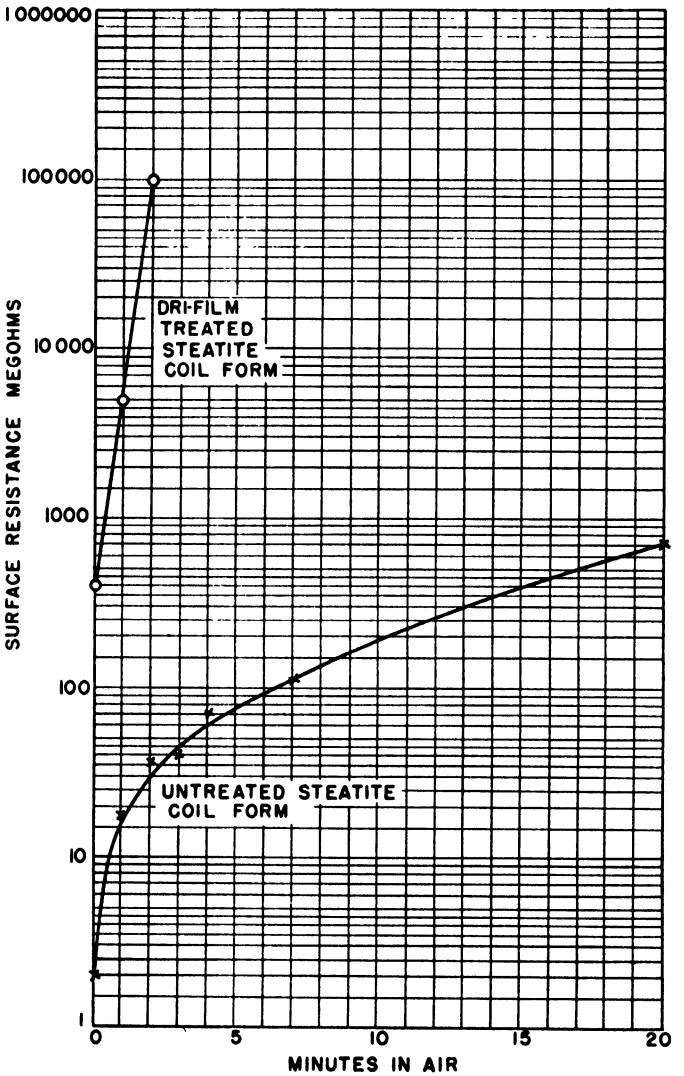


FIGURE 4

Various mixtures of air and methylchlorosilanes were made and a spark passed through them. It was found that below the values given in Table 3, of vapor concentration in per cent by volume, no ignition of the mixture occurred. Above the value, a flame formed and was propagated through the mixture.

Table 3. Lower Inflammability Limits

Material (in Vapor Form)	Per Cent by Volume in Air
$(CH_3)_2SiCl_2$	3.4 ± 0.1
$(CH_3)SiCl_3$	7.6 ± 0.3

Because of the nature of the material being used, it is advisable to use these precautions during the water-repellent treatment:

(1) Hydrochloric acid is given off during the treatment. It rapidly leaves the ceramic surface, but ceramics with metal inserts or connections should not be treated because of this acid.

(2) Care must be taken to adjust the size of the cabinet and amount of treating material so the inflammability limits are not exceeded.

(3) Very good ventilating conditions must be maintained to carry off excess chlorosilane vapors and acid.

The advantages of the methylchlorosilane treatment for ceramics may be summed up very briefly as follows:

(1) By a simple vapor treatment, thousands of ceramic pieces at a time may readily be treated at low unit cost so as to give a water-repellent surface. The factory process is simple compared to a waxing process.

(2) This treated surface gives very high surface electrical leakage resistance, especially under dewpoint condensation conditions. These surface-resistance values are higher than those for waxed, glazed, or unglazed surfaces.

(3) The surface film is so thin that dimensions of the ceramic and of holes in it are unchanged.

This application of methylchlorosilanes to the alteration of the surface properties of ceramic materials has been discussed in detail because it represents one phase of research in the field of organosilicon chemistry which is of particular interest to the readers of this work. Many other new developments have arisen from related investigations, but their detailed description would be inappropriate here. Some specific information may be gained from the references which have been cited, and it is to be hoped that there will be many more publications in the near future so that the unique properties of the new organosilicon compositions will become known to all industry.

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Ion Exchange Resins

FREDERICK J. MYERS

Resinous Products and Chemical Co.

Introduction

The principles of base exchange, and the satisfactory adaptation of materials capable of such reactions to commercial processes is by no means new, since Way,[17] in 1852, noted the adsorption of cations by soils, and Eichorn,[6] in 1858, demonstrated that the cations were mutually exchangeable, or that the process was reversible. Gans,[9] in 1906, is reported to have made commercial application of naturally occurring zeolites to water-softening processes, thus establishing the use of ion exchange materials in industrial applications.

Later developments in the field of ion exchange materials have been covered in detail elsewhere,[14] but the work in the early years following Gans' application dealt mainly with the production of high-capacity siliceous type cation exchangers by the so-called "activation" of naturally occurring greensands, or with the production of synthetic siliceous zeolites by the reaction of alkalies with alumina minerals. High temperature reactions produced the 'fused" type, while aqueous reactions produced the so-called "gel" zeolites.

Although synthetic zeolites are superior to greensands from the standpoint of exchange capacity, they are susceptible to attack by aggressive waters, and will function satisfactorily only in a narrow pH range. One natural result of these limitations is that the products can be used only in the sodium cycle (sodium chloride as regenerant) and the commercially valuable applications of hydrogen cycle operation cannot be realized.

The work of Fischer and Fuchs,[7] Borrowman,[5] and Hepburn,[11] focused attention on the possible use of materials of humic origin (peat, lignite, coal, wood, etc.) in the conditioning of water by exchange processes. Since that time the commercial development of sulfonated humic products has been realized, and the carbonaceous zeolites find use in various water-treating processes.

The discovery by Adams and Holmes [1] in 1935 that certain synthetic resins exhibited exchange reactions has brought about the development of an entirely new field of resin technology, and has markedly enlarged the scope of application of exchange materials in industry. Although prior to this date synthetic resins had always been evaluated on the basis of physical properties, and although one of the prime requisites of synthetic resins had been their chemical non-reactivity in the finished product, it occurred to these workers that a phenol-formaldehyde resin in the completely polymerized, or "C" stage, should possess phenolic hydroxyl groups capable of functioning as acids, since the hydroxyl group does not take part in the condensation reaction. Their preliminary work showed that resins prepared from monohydric phenols exhibited no exchange capacity, although this point has been disputed by later workers.[2, 4] Adams and Holmes [1] finally accepted polyhydric phenols as their most suitable raw materials, using the polyhydric nucleus of naturally occurring tannins as a convenient source of supply. Later work showed that improved exchange properties were obtained by the introduction of sulfonic acid groups into the resin lattice. Many methods of accomplishing this are proposed.

Early work on the preparation of materials capable of anion removal dealt mainly with the formation of insoluble double salts with heavy metal ions or with the use of basic inorganic or organic substances. Later work [7, 14] led to the production of insoluble dyes of the aniline black type by the oxidation of aniline or similar aromatic amines. By means of suitable binders, these compounds can be manufactured in the required screen grading, but, although of interest, they have generally failed in use because of discoloration of the effluent and physical deterioration.

Synthetic resins exhibiting acid adsorbent properties were prepared by Holmes by the condensation of aromatic amines such as *m*-phenylenediamine with formaldehyde. These resins made possible for the first time the application of acid-adsorbent materials to commercial processes since they exhibited most of the required physical and chemical properties.

As sole licensees in the United States, the Resinous Products and Chemical Company have conducted further research on the original ideas of Adams and Holmes [1] and commercial production of synthetic ion exchange resins has been established. The well-defined chemical constitution of these products, their high exchange capacity and high exchange velocity, coupled with the excellent resistance to physical or chemical disintegration have stimulated a revival of interest in exchange processes. Furthermore, because of the variety of possible reactants, the types of exchange resins possible are very numerous. There is evidence to prove that "tailor-made" resins can be prepared, and although previous studies [1] have shown no exchange properties exhibited by alkyd, hydrocarbon-formaldehyde, urea-formaldehyde or vinyl types, it should be remembered that these resins were not specifically prepared for ion exchange study, and reassessment of their virtues in the light of the new ion exchange resin techniques would appear to be warranted.

Theory of Use of Resinous Exchangers

The following equations represent the reactions involved in the use of the resinous exchangers:

(a) Cation

$$2NaR + CaX_2 \rightleftharpoons CaR_2 + 2NaX$$
$$HR + NaX \rightleftharpoons NaR + HX$$

(b) Anion

$$RNH_2 + HCl \longrightarrow RNH_2 \cdot HCl$$
$$RNH_2 + HCl + Na_2CO_3 \longrightarrow RNH_2 + NaCl + CO_2 + H_2O$$

Where NaR = sodium salt of cation exchange resin
HR = hydrogen form of cation exchange resin
RNH_2 = acid-adsorbent resin

Thus it appears from the equation that the reaction of the cation is a true metathesis, and that the reaction should be reversible. This reaction has been proven to be stoichiometric in character, and the calcium ion (or other heavy metal ion) removed in the sodium cycle is replaced by an equivalent amount of sodium ion. When operating in the hydrogen cycle, the titratable acidity of the effluent is exactly equivalent to the salt concentration of the influent. Regeneration of the resins is effected by the use of relatively concentrated (approx. 5 per cent) solutions of salt or mineral acids, this causing reversal of the reactions, as shown in the above equations.

Although the acid adsorbents have been referred to as "hydroxyl exchangers" or "anion exchangers," these terms are technically incorrect, and may have arisen originally from the observation that solutions of salts, especially those which were easily hydrolyzed, would become alkaline after treatment with these acid adsorbents. This is not difficult to explain in the light of later work, and is apparently due to the

adsorption by the resin of the acid formed by hydrolysis, which in turn results in an alkaline solution. All data at present point to the formation of insoluble amine hydrochlorides, hydrosulfates, etc., by the reaction of the activated amino groups in the resin lattice with the free acids of the solution. Thus the mechanism of reaction is a salt formation and not an exchange of ions.

This fundamental difference between the type of reaction of the two materials is further shown by a consideration of the regeneration efficiencies of the cation type exchange resins and the acid-adsorbent type. Whereas the first portions of the regenerant solution from a cation exchanger may contain only 20 per cent of unused regenerant, the concentration of unused regenerant increases very rapidly and, in general, the regeneration reaction is only 30-40 per cent efficient; that is to say, a two to three-fold excess of regenerant must be used for satisfactory operation. Contrasted with this, the first portions of regenerant from an acid-adsorbent column may contain only 2 to 5 per cent of unused regenerant, and this does not increase appreciably until the regeneration is complete. Consideration of the data shows conclusively that whereas the cation resin functions by an exchange reaction which is therefore reversible, the acid adsorbent removes acid by an addition reaction, and the regeneration of the depleted resin is actually a neutralization reaction, and not a reversal of a metathetical reaction. Careful consideration of these facts has led to marked economies in commercial operation.

The physical chemical aspects of the mechanism of exchange reactions have not received the attention which they warrant, but much work is being conducted on this subject at the present time, especially insofar as the resinous materials are concerned. Griessbach [10] has presented studies of the exchange equilibria of hydrogen exchange resins, and a recent paper by Beaton and Furnas [3] represents another theoretical approach to the general problem. A paper by Myers, Eastes, and Urquhart [18] presents a preliminary theoretical study of the mechanism of reaction of the acid-adsorbent resins. Whereas the only technique previously accepted for the determination of "break-through" capacity of an exchange material was column testing, these workers realized that a more scientific approach to the problem would not only throw more light on the mechanism of reaction, but might also provide a rapid means of evaluating the numerous new products which were being developed.

The exchange reactions occurring in a column of resin were considered to be a species of chromatographic adsorption [16, 18] in which a band of the exchanged cation (or adsorbed acid) would move progressively downward through the column.* The break-through capacity, the point at which the incoming ion (or acid) first appeared in the effluent, was considered to be the adsorption or exchange volume of the resin in contact with a solution with a concentration equal to that of the influent. While the black color of the cation exchange resins prevents visual observation of any banding effects, certain newly developed acid-adsorbent resins are light orange in color in the regenerated form, while the hydrochloride is brown, and the hydrosulfate reddish orange. It was noted that definite color bands were formed when a mixture of hydrochloric and sulfuric acids was passed through a column of the regenerated resin, the top band being reddish orange, the band below this being brown. As depletion progressed, the bands moved downward, and, when the brown band reached the bottom of the column, break-through of hydrochloric acid only occurred. If the flow were continued, only hydrochloric acid could be detected in the effluent, but the concentration was equivalent to the total acid concentration of the influent. This also proved that sulfuric acid was more strongly adsorbed, and would "flush off" the hydrochloric acid from the resin bed. In order to determine the degree of completeness of this preferential adsorption, a column was run to break-through, sectioned, and analyzed. The results were as follows:

* Re chromatography, see paper by Beverly L. Clarke in Vol. V of this series. J. A.

Table 1

Section	Sulfur (%)	Chlorine (%)	Color
1	11.64	0.00	Orange
2	11.59	0.00	"
3	11.59	0.00	"
4	11.36	0.00	"
5	. . .	1.17	"
6	3.20	12.32	Bands overlap
7	0.00	18.31	Brown
8	0.00	13.00	"

Thus the assumption that the acid-adsorbent resins exhibit typical chromatographic adsorption appears to be valid; and similar but less striking effects have been noted for the cation exchange resins.

Wilson's theory [18] of chromatography has been extended by Myers *et al.*[13] so that the probable break-through capacity of an exchange resin can be calculated from the data on its adsorption isotherm. The experimental technique is described in detail,[13] and the results have shown that it is possible to predict the capacity of an exchange resin from a knowledge of its adsorption isotherm. Agreement with the data obtained by column studies is good.

Applications of Resinous Exchangers

When considering the possible uses of exchange materials it is found that they may be divided into two general classifications: (a) water conditioning and (b) special applications.

Water Conditioning. The best known application of zeolites is for softening water, *i.e.*, removing the hardness-producing ions (calcium and magnesium) and the substitution of the harmless sodium ion. The resinous cation exchangers have been successfully used for this purpose and show the following points of superiority:

(1) *Higher capacity*, as shown by the following table:

Table 2

Type of Exchanger	Capacity [a]	Salt Value [b]
Greensand	2,800	0.45
Synthetic gel zeolite	10,000	0.50
Carbonaceous zeolite	7,000	0.50
Resinous exchanger	12,700	0.50

[a] Capacity in terms of grains (as $CaCO_3$) per cu ft exchanger in place.
[b] Salt value is pounds NaCl per kilograin hardness removed (as $CaCO_3$).

Furthermore, higher salt values will appreciably increase the capacity of the resinous exchangers, and it has been proved definitely that this high capacity is maintained for at least 500 complete cycles and does not drop off as in the case with many gel zeolites.[19]

A comparison of the capacity of the resinous "anion exchangers" with previously existing products is practically impossible, since no acid adsorbents have proved successful commercially. However, the capacities of resinous acid adsorbents are extremely high, as illustrated by the following data:

Table 3. Capacity of Resinous Acid Adsorbent [a]

Acid [b]	Capacity [c]
HCl	25,000
H_2SO_4	50,000
$HCl + H_2SO_4$ (1:4)	45,000

[a] Resin used was commercially available product (Amberlite IR-4).
[b] Acid as 500 ppm influent (as $CaCO_3$).
[c] Capacity as grains ($CaCO_3$) per cu ft resin in place.
[d] Regenerant was Na_2CO_3 (2 per cent solution) 0 5 lb Na_2CO_3 (as NaCl) per kilograin acid removed (as $CaCO_3$).

(2) *High exchange velocity,* which permits high flow rates without possibility of leakage of ions.

(3) *The capacity of the resinous cation exchangers* does not vary with the influent concentration and comparatively high concentrations of sodium ion do not cause leakage of calcium ion (when operating in the sodium cycle). Furthermore, the ratio of calcium ions to magnesium ions in the influent does not affect the softening capacity of the resin. All the above factors affect, more or less, the other exchangers, and necessitate the use of "compensated hardness" factors for waters high in sodium or "hardness" ions.

(4) Being "C" stage resins, the exchangers are characterized by *excellent physical and chemical resistance.* They are free from iron and silica, and thus can impart neither to the effluent. Furthermore, because there is no silica in the structure, low silica content waters are without effect, and cause no deterioration such as is noted with gel zeolites. The products function satisfactorily over a wide pH range.

The use of the hydrogen form of the exchanger, alone, or in conjunction with the sodium cycle, results in a reduction of the bicarbonate alkalinity and in the total solids. If the hydrogen exchanger is used alone, sufficient raw water is by-passed to bring about neutralization of the mineral acids formed by the conversion by the hydrogen exchanger of the chlorides and sulfates in the original water. The hydrochloric and sulfuric acids are neutralized by the bicarbonates of the raw water, and the carbon dioxide so formed is removed by aeration. This process finds wide use in the production of water for boiler feed, artificial ice plants, beverage manufacturers, etc.

The most important application which has become economically feasible since the advent of resinous exchangers is the production of very pure water, comparable to distilled water in degree of purity. The process is very simple and easily operated, and consists of treatment of the water by a hydrogen cation exchange resin, followed by treatment with a resinous acid adsorbent. The soluble salts are converted by the hydrogen exchanger to their corresponding acids, and the acids are removed by the acid adsorbent. Admittedly silica is not removed, but there are many effective pretreatments for the removal of this impurity. Carbon dioxide, unadsorbed by the acid adsorbent, is removed by aeration. The recent trend to extremely high boiler pressures makes the need for pure water imperative, and this process provides a convenient and economical source. The many industries wherein distilled water is used in quantity have been quick to realize the potentialities of this process, and the results obtained to date have been excellent.

Special Applications

It is in this field that the superior properties of the ion exchange resins have been most quickly recognized, and although a comparatively new development, the synthetic resin exchangers have found many applications, and have opened the way to new processes which were formerly impractical because of the limitations of the previously existing exchange materials.

In many manufacturing processes the removal of salts from aqueous solutions of non-electrolytes is desirable; and in some cases this is effected by the use of dialytic procedures. However, as these are in general slow, expensive, and incapable of high throughput, they are used only when absolutely necessary. In many other cases, due to lack of suitable economical methods of treating, the salts are not removed without subsequent harm to the product or lowering of yield. An excellent example is the purification of sugar, both cane and beet, as described in an interesting paper on this topic by Rawlings and Shafor.[15] Naturally dialysis could not be considered, but if the salts could be removed from the juice prior to evaporation, appreciably increased yields of sugar could be obtained. Although variations of this idea have been tested periodically for many years, the process has proved economically practical only since

ion exchange resins have become available. The high exchange capacity and high rate of reaction of the resinous materials has permitted high flow rates, thus holding to a minimum the inversion of the sucrose, and the completeness of ion removal has resulted in extremely pure treated juice.

By using the resinous acid adsorbents it is possible to "neutralize" acid solutions without the addition of undesirable metal ions. Thus aqueous solutions containing free acid impurities can be treated to decrease or completely remove the free acids by passage through a bed of the resin. This procedure has been applied on a commercial scale to the removal of formic acid from formaldehyde, and other modifications are under study in the experimental stages. Due to the high activity of these resinous acid adsorbents, an interesting additional purification is noted. Traces of iron, copper, and other heavy metal ions, apparently present as weakly hydrolyzed salts and very difficult to remove, are removed by the anion exchanger. That is to say, the acid formed by hydrolysis is fixed by the free base, and the hydroxide or oxide of the metal precipitates on the bed. Periodic treatments with acid remove these deposits, and the bed is again ready for use.

The applications of these new materials are too numerous to list individually, and when the newness of the development is considered it is impossible to predict the scope of their ultimate use. Beaton and Furnas [3] discuss one aspect, and many other ideas are disclosed in the literature.[10] It does appear, however, that the ion exchange resins have made available an entirely new unit process for the chemical industries.

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A New Method of Preparation and Purification of Some Hydrous Oxide Sols

JOHN W. RYZNAR

National Aluminate Corp., Chicago, Ill.

In general sols can be formed by either condensation or dispersion methods. In the former the small particles of molecules condense or agglomerate to give particles of colloidal size; in the latter, large particles are reduced to small ones of colloidal size.

The sols made by the new method described here are formed by condensation. This method is an improvement in the ease of formation of relatively pure sols over the older methods which depend on double decomposition or hydrolysis followed by dialysis for their formation and purification.

None of the older dialytic methods for the preparation of sols substantially free of electrolytes are well adapted to large scale production inasmuch as the methods of purification are slow and the processes rather expensive. On the other hand, this method is simple, inexpensive, and adaptable to producing large quantities of sols in a short time. It makes use of various ion exchangers which may be classified as follows:

I. Cation exchangers
   1. Inorganic: natural and synthetic
   2. Organic: sulfuric-acid-treated coal, wood, waste petroleum sludge or lignite; resins of the polyhydric phenol-formaldehyde and tannin formaldehyde types.

II. Anion exchangers
   1. Inorganic: metallic oxides
   2. Organic: synthetic resins of the meta-phenylenediamine formaldehyde type, as well as other resins of amine-aldehyde condensation type.

Ion exchangers have been the subject of much study and development in recent years. Cation exchangers can be regenerated with acids, so that metallic cations can be replaced in solution by a hydrogen ion, leaving only the corresponding acids in the effluent. Similarly, the anion exchangers can be regenerated with sodium carbonate or sodium hydroxide; on passing the effluent from an acid-regenerated cation exchanger through the anion exchanger, all anions such as $SO_4^=$, Cl^-, etc., are removed, resulting in a deionized water as the final product. This method for deionizing various waters has been adopted by industry and is practiced on a large scale. The following list gives several plants using this method for getting a water equivalent to distilled water.

	Capacity of Exchangers in Gallons per Minute
Aluminum Co., Phoenix, Arizona	500
Pratt Whitney, Kansas City, Missouri	100
Abbott Laboratories, No. Chicago, Ill.	100
Diakel Corp., Cincinnati, Ohio	500

More detailed discussion of these ion exchangers can be found in the literature.[8, 9, 10, 12]

In the small scale laboratory tests used for preparing the sols described later, the exchanger beds were set up in Pyrex tubes. The depth of the exchanger beds was approximately 12 inches, and the surface area was 0.018 square foot. This gave a bed of exchange material with a volume of approximately 0.02 cubic foot. The flow rate, unless otherwise noted, was maintained at approximately 0.2 gallon per square foot of cross-sectional area per minute. One liter of solution was generally used in forming the corresponding sols. In laboratory tests the sols were passed through the exchange beds twice in order to remove the maximum amount of electrolyte.

In all laboratory tests ordinary distilled water was used in washing out regenerants. Washing was stopped on the acid cycles when the effluent was alkaline to methyl orange indicator and stopped on the alkaline cycles when the effluent was colorless to phenolphthalein indicator. In large scale plant production of silica sols, Lake Michigan water is used in the washing process.

Cation Exchangers

In this process Na^+, Ca^{++}, Mg^{++}, Al^{+++}, and other metal ions are removed and replaced with an H^+ ion. The use of an acid regenerated cation exchanger will be illustrated by its adaptation to the formation of relatively pure silica sols. These sols have been made by a number of different methods in the past.

Graham [6] is generally credited with the discovery of silica sol in 1861 when he prepared it by dialyzing a mixture of water glass and 10 per cent hydrochloric acid. Jordis [8] formed sols by peptization of silica gels. The formation of silica sols by action of water on silicon sulfide, chloride, and fluoride has been reported; [5] electrodialysis of the sol formed by hydrolysis of methyl silicate [7] or ethyl silicate tetrachloride [11] has given very pure sols.

Bird was the first to apply the cation exchangers to the formation of silicic acid sols as well as sols of other acidic oxides.[2] In this process relatively pure silica sols are obtained by passage of a dilute solution of sodium silicate through an acid regenerated cation exchange bed. The sodium ion in the sodium silicate is replaced by a hydrogen ion to give a silicic acid sol in the effluent.

$$ExH_2 + Na_2SiO_3 = ExNa_2 + H_2SiO_3$$

In plant operation, solutions of sodium silicate having as high as 3.5 per cent silica have been passed through the cation exchanger without difficulty. A flowrate through the exchange bed of about one gallon per square foot of cross-sectional area is used. A typical analysis of the composite effluent obtained is 2.5 per cent silica and 0.05 per cent sodium oxide.

It is possible to obtain sols of lower sodium oxide content, but unless certain precautions are taken these sols easily form stiff gels which are irreversible and, for many applications, undesirable. A sample of such a sol taken during a regular plant run had the following analysis: SiO_2, 2.5 per cent; Na_2O, 0.005 per cent; SO_4, 0.0027 per cent. This sets to a stiff gel in a few hours.

The pH of these pure sols is generally around 6.0 to 6.3, which is near the 6.8 pH of the very pure sols formed by hydrolysis of silicon tetrachloride and subsequent electrodialysis.[13] Bradfield [4] reported a pH of 6.5 obtained after repeated washing and centrifuging of silica.

By allowing some sodium silicate to pass into the effluent after the bed capacity is exhausted, the sol can be stabilized by the alkalinity from the sodium silicate; it can then be concentrated by evaporation to a silica content as high as 30 per cent with no danger of gel formation. Analysis of a concentrated sol made in large quantities and used for various industrial applications is: SiO_2, 20 per cent; Na_2O, 0.37

per cent. These concentrated silica sols are unusual inasmuch as they remain liquids with a low viscosity.

The silica sols of maximum purity can be stabilized by other methods. For example, ammonium hydroxide, which does not increase the mineral content, can be used. Likewise, low concentrations of aluminum ions will stabilize these sols.

After the exchanger has become exhausted, it is back-washed and regenerated with acid in the usual way.[2] Any highly ionized acid may be used, but sulfuric acid is preferred in most cases because of low cost. The excess acid is washed out of the bed and the exchange material is then in condition for the next run.

During the first part of the process, the effluent from the exchange bed is practically neutral or else slightly acid depending on: (a) how thoroughly the excess acid used in the regeneration was removed, (b) purity of the water used in washing out the excess acid, (c) purity of the water used in diluting the sodium silicate, and (d) purity of the sodium silicate itself. Any sodium or other salts present other than sodium silicate and sodium hydroxide will give a corresponding amount of free acid in the effluent.

The silica sol obtained by the above described method behaves in much the same manner as a sol purified by dialysis. At first it is clear, and does not give a luminous beam with a Tyndall optical test, an indication that the silicic acid particles are not large enough to scatter light. On ageing there is an increase in the intensity of opalescence, indicating a continuous condensation into larger units. The point at which condensation ceases is dependent upon the alkalinity or the presence of other stabilizers.

The ageing of the sol to give larger particles of silicic acid can be accelerated by heating. It may be of interest to mention that in clarification of water, silicic acid sols have been used along with alum, sodium aluminate, and other coagulants in giving larger and tougher floc particles.[1] In this process the pure sol having the small particle size is ineffective. It is only the larger particle size of the silicic acid formed on ageing or heating, or that which is obtained prior to incipient gelation, which gives the highly hydrated, effective floc in clarification. It would appear from this behavior that the silicic acid undergoes hydration as well as condensation in the ageing process.

Silica sols produced by this process have already found numerous applications in such widely divergent fields as ceramics, textiles, detergents, and insecticides. Important uses for it are in the molding of foundry sands and in making precision castings. It has been used as a thickening agent in printing inks. In the ceramic industry silica sol is used along with such materials as magnesium sulfate, lime, and sodium aluminate to form plasticizing and bonding gels. In refractories it is used to provide a dry bond, to accelerate the fluxing reaction, and to prevent the migration of auxiliary flux constituents. No doubt there are many other applications in which the silica sol would be useful.

Other sols can be made in the same manner as the above discussed silica sol. Dilute tungstic oxide sols with a mineral content of 99 per cent tungstic acid and 0.5 per cent sodium oxide have been prepared. The soluble salt of many insoluble acidic oxides can be used to prepare the corresponding oxide sol. In some cases the sols as they are prepared are unstable and may largely precipitate on the bed. This is true when sodium aluminate or sodium stannate are used in preparing the corresponding sols.

An interesting example showing the effect of the exchange bed itself on the final composition of a sol was encountered in the passage of a solution of sodium molybdate through acid-regenerated cation exchange beds of two different types. When a clear colorless solution of sodium molybdate was passed through a sulfonated phenol-formaldehyde resin, the effluent contained colloidal yellow molybdic acid; but when a solution of sodium molybdate was passed through an exchanger of the sul-

furic-acid-treated coal type, the effluent contained the colloidal molybdenum blue complex. When a reducing agent such as hydroquinone was added to the sodium molybdate solution and this solution then passed through the sulfonated phenol-formaldehyde cation exchanger, a dark blue molybdenum complex was obtained in the effluent. This indicated that the sulfuric-acid-treated coal type of exchange material has a reducing action when first made. This reducing capacity no doubt would disappear on continued use.

Anion Exchangers

$SO_4^=$, Cl^-, NO_3^-, and other anions are removed in this type of process. Sols of hydrous aluminum oxides, ferric oxides, and other metal oxides have been prepared by use of an alkali regenerated anion exchanger. Typical reactions may be expressed as follows:

$$Ex(OH)_3 + AlCl_3 = ExCl_3 + Al(OH)_3$$
$$Ex(OH)_6 + Fe_2(SO_4)_3 = Ex(SO_4)_3 + 2Fe(OH)_3$$
$$Ex(OH)_3 + 3HCl + Fe_2O_3 = ExCl_3 + Fe_2O_3 + 3H_2O$$

Alumina sols prepared in this way are not, on the whole, so free of electrolyte or so stable as the silica sols and the other sols already discussed. With aluminum salt solutions of about 1 per cent or higher, there is a strong tendency for gelation or precipitation of the sols in the anion exchange bed with a resulting hardening or caking of the bed. On the other hand, 82.2 per cent conversion of a 1 per cent solution of aluminum sulfate to the hydrous oxide has been obtained. This conversion is based on the ratio of sulfate to alumina in the effluent. Likewise, with a 0.45 per cent solution of aluminum chloride, 99.2 per cent conversion to the hydrous aluminum oxide has been obtained, based on the chloride and alumina in the effluent. In both of the above examples a fairly high proportion of the Al_2O_3 was lost in the bed.

Trivalent salts of iron behave in much the same fashion as the aluminum salts. A 0.12 per cent solution of ferric sulfate passed through an anion exchanger showed 95.1 per cent conversion of the ferric sulfate to the hydrous ferric oxide sol. Sols from ferric salts in concentrations of 1 per cent or greater had a pronounced tendency to precipitate out in the exchange bed. A better method for the preparation of an iron sol substantially free of electrolyte was the following. A concentrated solution of ferric chloride was added slowly to a larger volume of boiling water. A dark red sol of hydrous ferric oxide was formed which was very stable. The reaction may be expressed as

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl$$

On passing this sol through an alkali regenerated anion exchanger, the hydrous ferric oxide sol was obtained in the effluent unchanged but the chloride ion was removed. A sol obtained in this manner analyzed as follows: pH, 5.9; Fe_2O_3, 0.236 per cent; Cl as $FeCl_3$, 0.018 per cent. This shows that 97.1 per cent conversion of the ferric chloride to hydrous ferric oxide sol was obtained with the corresponding removal of the chloride ion. The pH of the influent was 1.3.

Combination of Cation and Anion Exchangers

Cations and anions are removed and replaced with hydrogen and hydroxyl ions in this process. A combination of cation and anion exchangers can be used as a medium for the purification of colloids that are formed by other methods. Colloidal sols formed by double decomposition or hydrolysis can be passed through the two exchange beds in series with a resultant removal of most of the electrolytes. This is, in effect, the equivalent of dialysis but is a much simpler and quicker method of purifying the sols.

The following example illustrates the use of both cation and anion exchangers in removing the electrolytes from a previously formed sol. A silica sol was formed by neutralizing a dilute solution of sodium silicate with sulfuric acid to a pH of 8.2. Fifty-three grams of the neutralized JM brand 42° Bé sodium silicate were diluted to 1000 ml.; the resulting solution had a silica content of 1.5 per cent. The electrolyte to be removed was sodium sulfate. The cation and anion exchangers were of the synthetic resin type.

Passage of this sol through the cation exchange bed resulted in the replacement of sodium ions with hydrogen ions. The effluent from this bed then contained silica sol and sulfuric acid. Passage of this effluent through the anion exchanger resulted in the replacement of the sulfate ions with hydroxyl ions. The final effluent contained the silica sol. The following analysis, based on the mineral content, indicates the purity of the sol obtained: SiO_2, 99.3 per cent; Na_2O, 0.51; SO_4, 0.022; Cl, 0.118; Fe_2O_3, 0.04.

It may be possible to produce sols of greater purity by considering the following points.

1. Wash the cation and anion exchangers with distilled water for a longer period of time to remove the maximum amount of excess regenerant present in the bed.
2. Increase the length of contact time in passing the sol through the exchangers.
3. Improve the exchanger characteristics toward prevention of what is ordinarily termed "slippage" of ions, such as sodium ions through the cation exchanger and chloride ions through the anion exchanger.

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Chlorinated Rubber

JOHN S. TINSLEY

Hercules Experiment Station, Hercules Powder Company, Wilmington 99, Delaware

Chlorinated rubber is a raw material in its own right. Its position in modern American industry is affirmed by the fact that at the end of October, 1941, the material was placed under rigid priority control by the Office of Production Management. It is used primarily in coating compositions. Since, only as recently as 1930, the chemical technology of this product had advanced to the stage of the introduction on the market of the first stable chlorinated rubber in dry form, the reasons for the rapid and wide adoption of this raw material must be closely allied with the chemical transformations produced within the rubber molecule during chlorination.

The effects of chlorination are most easily demonstrated by contrasting the physical and chemical properties of rubber and chlorinated rubber.

Property	Rubber	Chlorinated Rubber
Physical form	Slabs or sheets	White granules
Film clarity	Opaque or opalescent	Clear
Film color	Brown to black	Water-white
Odor	Slight	None
Flammability	Burns readily	Nonflammable
Chemical resistance:		
Sulfuric acid	Chars	Good
Sodium hydroxide	Good	Good
Oxidizing agents	Poor	Good

It is quite obvious from this brief comparison that the introduction of chlorine into the molecule has resulted in a product entirely different from the parent rubber. This is not surprising, however, since the new molecule formed consists of two-thirds chlorine by weight. The marked influence of chlorine on the space relationship in the molecule is shown in Figs. 2-5.

Early History

That reaction takes place between chlorine and rubber is not a twentieth-century discovery. According to Eck,[10] the earliest attempts at reacting these two substances indicated that rubber was quite resistant to chlorine. Fourcroy,[14] towards the end of the eighteenth century, in his studies on acid coagulation of latex, used chlorine water and observed no change in the rubber. During the 1830's Lüdersdorff [25] and Berzelius [6] even recommended the use of rubber flasks and hose for use with chlorine. In 1835, however, Himly [18] reported that distillates from rubber showed strong reactivity with chlorine and other halogens.

More purposeful research on chlorinated rubber is evident in the work of investigators during the last half of the nineteenth century. Traun [36] in 1859 obtained a white substance, neither elastic nor flexible, by reacting chlorine with rubber dissolved in carbon disulfide and subsequently adding water. Engelhard and collaborators [13] in 1859 patented a practical process (improved by Marquard [27] in 1865) for preparing a white, ivory-like product by the action of chlorine on solid lumps of

rubber or on rubber dissolved in chloroform. Helm[16] in 1871 described a process for preparing a brittle mass by immersing small pieces or sheets of rubber in chlorine water or liquid chlorine and in the absence of swelling agents.

Goodyear's discovery in 1839 of the vulcanization of rubber revolutionized the rubber industry and had a decided influence on the trend of future investigations on chemical treatment of rubber. The hope of achieving an improved vulcanization with chlorine and the natural disappointment over results undoubtedly retarded an intensive investigation of the chlorinated product, which did not possess rubber-like properties. The structure of the rubber molecule was the other problem uppermost in the minds of rubber investigators. In this connection, it was natural that the addition of chlorine to double bonds was studied. The instability and complex nature of the products made accurate analysis impossible; consequently, other types of reaction were studied to explain the constitution of rubber. A detailed history of the various attempts at halogenation of rubber, including both patent and technical publications, may be found in Marchionna's book.[26]

Commercial Production

The first commercial process for chlorinated rubber was developed by Peachey in 1915,[32] and the product produced was introduced to the trade as "Duroprene" or "caoutchouc glass."[34, 37] A solvent inert to chlorine was specified and the rubber was dissolved in carbon tetrachloride before treatment with chlorine gas. The material was recommended as a celluloid substitute and for acid-resistant varnishes. This product and those of Edison,[11] Ellis,[12] and other early inventors[26] were prepared either by chlorinating rubber in swelling agents or solvents with cooling or without allowing the temperature to exceed 40 to 50°, or by treating rubber in a solid or plastic condition with free chlorine. They contained usually from 60 to 65 per cent chlorine and, in the dry condition, they decomposed readily with loss of hydrochloric acid at temperatures below 150°.

During the early introduction of the newer, more stable chlorinated rubber, considerable adverse criticism was made, notably by Krumbhaar,[22] regarding its utilization in protective coatings. This was based largely on the disheartening results obtained with the earlier unstable chlorinated rubbers. More recent experience has demonstrated that the poor stability of the earlier products was the result of the method and temperature of preparation and incomplete chlorination. The significance of the reaction temperature for the stability of the product was first successfully demonstrated by Deseniss and Nielsen,[8] who about 1930 prepared a stable, chlorinated rubber by carrying out the chlorination reaction at temperatures above 80°. To the trade, a stable, chlorinated rubber has been introduced under such trade names as Tornesit,*[30] Detel,†[2] Alloprene,‡ Pergut,§ and Parlon.¶

The commercial process now used in the United States is essentially as follows. Rubber is dissolved in carbon tetrachloride, or other solvent which does not react with chlorine. Chlorine is added until a product of maximum chlorine content (about 68 per cent) is obtained. The solution containing this product is then discharged into water to precipitate the granular, stable, completely chlorinated product. Traces of hydrochloric acid are removed by washing, and the material is dried. Temperatures and pressures are carefully controlled during the entire process, which requires several hours. To obtain a white, uncontaminated, and uniform product and because of the corrosiveness of the materials used, the design and selection of construction materials of the equipment are important problems.[23]

* Manufactured by Deutsche Tornesit-Ges.m.b.H., New York Hamburger Gummiwaaren Cie., and Hercules Powder Company.
† Manufactured by Detel Products, Inc.
‡ Manufactured by Imperial Chemical Industries, Ltd., London.
§ Manufactured by I. G. Farbenindustrie.
¶ Manufactured by Hercules Powder Company.

Theory of Chlorination of Rubber

It was less than fifty years ago that the first fundamental scientific investigation of the chlorination of rubber was carried out. Gladstone and Hibbert [15] studied the reaction between chlorine and a 1 per cent solution of rubber in chloroform. The authors concluded, from the evolution of hydrogen chloride during the reaction and the chlorine analysis of the product (65.18 per cent for the best specimen), that both substitution and addition occurred. Although at this time the structure of rubber was not clearly understood, they assigned to chlorinated rubber the formula $C_{10}H_{14}Cl_8$. Ditmar,[9] on the basis of his experiments on the chlorination of balata, suggested the formula $C_{10}H_{12}Cl_6$. Caspari [7] proposed $C_{30}H_{46}Cl_{14}$. Hinrichsen, Quensell, and Kindscher [19] in 1913 studied the effect of temperature on the product obtained by the method of Gladstone and Hibbert. When ice-cooled rubber solutions were used, they obtained a white, amorphous product to which they assigned the formula $C_{10}H_{14}Cl_6$. Peachey [32, 33] specifically characterized his product as the "heptachlor caoutchouc" possessing the formula $C_{10}H_{13}Cl_7$.

McGavack [28] in 1925 published the results of an uncontrolled-temperature gas-analytical study of the chlorination of rubber in carbon tetrachloride solution. He demonstrated that the rapid evolution of hydrogen chloride during the first period of the reaction indicated that substitution was taking place almost to the exclusion of addition. Temperature decreased as the reaction proceeded, with resulting decrease in the evolution of hydrogen chloride. Finally a point was reached at which substitution was practically complete and addition began. Analysis of the end product gave a chlorine content of 65 per cent. The calculated chlorine content of a product containing three atoms of substituted and four atoms of added chlorine would be 65.1 per cent. McGavack therefore accepted the formula $C_{10}H_{13}Cl_7$ proposed by Peachey.

If the chlorination reaction were one involving addition only, the saturated chlorinated compound of rubber $(C_{10}H_{16}Cl_2)_x$, on the basis of the rubber formula $(C_{10}H_{16})_x$, would contain only 51 per cent chlorine.

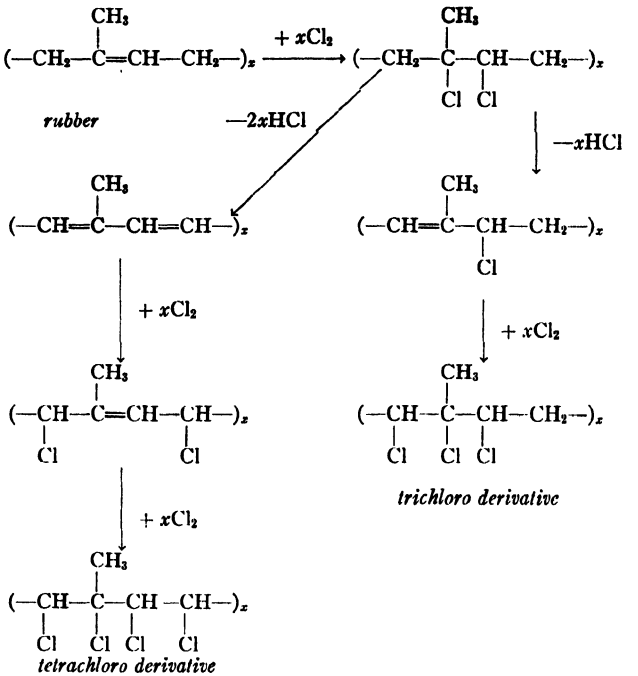
$$(-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-)_x + xCl_2 \longrightarrow (-CH_2-\overset{CH_3}{\overset{|}{C}}(Cl)-CH(Cl)-CH_2-)_x$$

Since the end product always contains more chlorine than this equation indicates, and since hydrogen chloride is always evolved during its preparation, substitution as well as addition must occur during the reaction.

Kirchhof could not harmonize the taking up of only seven atoms of chlorine by two isoprene $(C_{10}H_{16})$ units with the accepted conception of the regular continuous-chain isoprene-unit rubber molecule. He therefore assigned the formula $(C_{10}H_{12}Cl_8)_x$ to the final product of chlorination of rubber and proposed the theoretical explanation for its formation [21] appearing on page 1121.

The trichloro derivative of an isoprene unit contains 61.3 per cent of chlorine and the tetracholoro 68.2 per cent. A mixture of equal parts of these two would give a product containing approximately 65 per cent, the amount found by McGavack in his experiments. Other combinations of these two products would give different chlorine contents. In general, the current commercial product contains 66 to 68 per cent chlorine, which corresponds approximately to $(C_{10}H_{13}Cl_7)_x$, a combination of the tri- and tetra-chloro derivatives. Kirchhof's explanation of the course of the reaction accounts for the immediate evolution of hydrogen chloride when chlorine is added. Chlorine saturates the newly formed double bonds so, as the reaction proceeds, addition should replace substitution.

Nielsen [30] has proposed a different reaction scheme involving a shifting of double bonds, so that the chlorine atom split off in hydrogen chloride is not the one bound



to the tertiary carbon atom. This mechanism is based upon the assumption that the atom bound to the tertiary carbon atom is much more firmly held, and therefore much more difficultly split off, than the atom bound to the secondary carbon atom. Studies of Harries * and Baxter [4] support this theory.

Experimental work to date is insufficient for a decision as to which explanation, if either, actually corresponds to the true course of the reaction. In the final product, which contains a maximum of 68 per cent chlorine, there is no evidence of double bonds. Attempts at further chlorination result in degradation of the molecule. The total hydrogen chloride evolved during the reaction may be expressed by the following equation:

$$C_{10}H_{16} + 6Cl_2 \longrightarrow C_{10}H_{12}Cl_8 + 4HCl$$

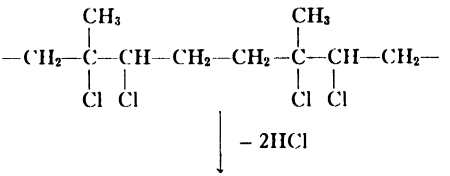
This equation, however, gives no information as to the structure or properties of chlorinated rubber.

An approximate idea of the comparative structures of rubber and chlorinated rubber may be obtained by examining photographs of molecules built up from Fisher-Hirschfelder atom models of the various elements concerned. Rubber is shown in both *cis* and *trans* positions but the molecule was found to rotate freely around any carbon atom except where double bonds made the structure rigid. When the model of a molecule of chlorinated rubber equivalent to $C_{10}H_{12}Cl_8$ was examined, it was found that movement is highly restricted and complete rotation is impossible without disruption of the chain. It was also found that there was insufficient space for additional chlorine to be added without severing the chain. The comparatively rigid molecule of chlorinated rubber may well account for certain of its physical properties, notably loss of elasticity.

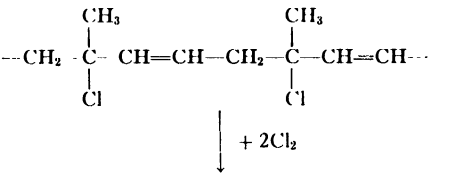
* Harries, in his researches beginning in 1904, investigated the ozonides and other derivatives of rubber, and his results are the most convincing evidence we have for the basic structural unit of the rubber hydrocarbon.

Thus:

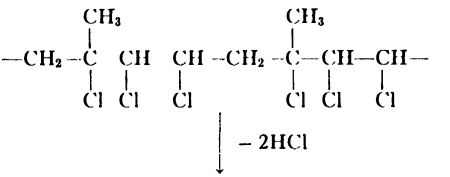
Primary addition:



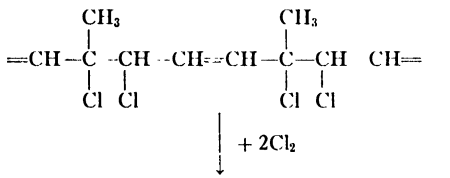
Cleavage product:



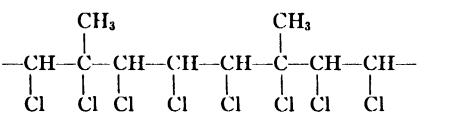
Secondary addition:



Cleavage product:



End product:



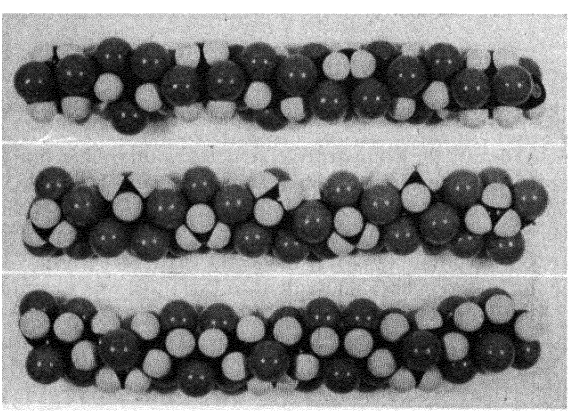


FIGURE 1. These photographs show three different views of the same fragment of a chlorinated rubber molecule, made from Fisher-Hirschfelder atom models, illustrating clearly the space limitations and surprising symmetry of the molecule.

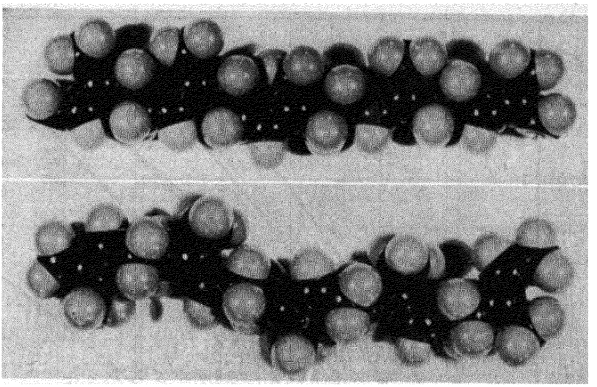


FIGURE 2. The above photographs show the *cis* and *trans* configuration of the same fragment of the rubber molecule, made from Fisher-Hirschfelder atom models, illustrating the freedom of movement around adjacent carbon atoms.

Properties

As indicated earlier in this section the appearance and physical properties of rubber are altered so profoundly by chlorination that the product must be considered entirely apart from rubber. Several comprehensive discussions of the properties of chlorinated rubber have appeared in the literature.[3, 5, 17, 29, 30, 31, 35, 37]

Chlorinated rubber resembles the cellulose derivatives in properties more nearly than it does its parent substance. Granules and films of chlorinated rubber do not have the elasticity and tendency to tackiness of latex or digested rubber. Vulcanization of rubber removes some of the elasticity by cross linkage, making the molecule more rigid. Other types of treatment produce rigidity by cyclization. Neither of these processes appears logical in the case of chlorination. It is more probable that the preponderance of large chlorine atoms in the molecule prevent the folding and free rotation within the chains to produce elasticity.

Solubility. Introduction of chlorine into the rubber molecule has considerably altered the solubility characteristics, resulting in a much wider selection of solvents with a greater tendency toward solubility in compounds of intermediate polarity. Solvent types include aromatic hydrocarbons, ketones, higher-molecular-weight aliphatic esters, drying oils, and pyridine. Nonsolvents include paraffin hydrocarbons, mineral oils, and low-molecular-weight alcohols.

Solutions of chlorinated rubber exhibit an increase in viscosity with concentration as usually found with colloidal dispersions of high-molecular-weight compounds. The rate of increase in viscosity is much lower than that exhibited by rubber dispersions. It is possible to prepare dispersions of chlorinated rubber at concentrations above 50 per cent without obtaining gels. In Fig. 5 the increase in viscosity with concentration is shown for nitrocellulose, ethyl cellulose, and chlorinated rubber dispersions. Dispersions of chlorinated rubber are only slightly colored and exhibit a high degree of clarity.

Stability. Early experience with chlorinated rubber revealed that these products were handicapped by a gradual breakdown and the evolution of acid gases. This development of acidity was very rapid at even moderately elevated temperatures. Present-day material still exhibits this property at elevated temperatures, but to a much less extent. Hoekstra [20] investigated the rate of breakdown with wet and dry heat at 100° and found that the total amount of HCl split off was greater when water was present. The maximum quantity under these adverse conditions was of the order of 1.5 per cent for 500 hours' heating.

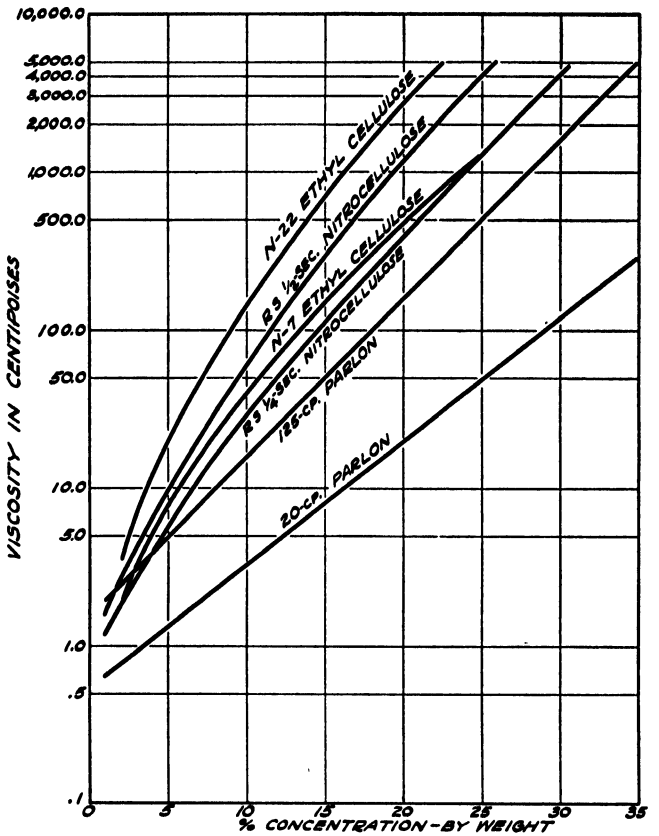


FIGURE 3. Viscosity-concentration relationship between Parlon,* ethyl cellulose, and nitrocellulose.

Material	Solvent	Conversion Factor 5/16-in steel ball 10-in drop
Parlon	Toluene	410 cps = 1 sec
RS Nitrocellulose	Butyl acetate 3 Ethyl alcohol 1	377 cps = 1 sec
Ethyl cellulose	Toluene 4 Ethyl alcohol 1	420 cps = 1 sec

Chlorinated rubber is quite stable to acids and alkalies, at normal temperatures, over a wide range of concentration of the reagents. When heated with sodium hydroxide or other alkaline solutions, chlorinated rubber darkens and loses its smooth solution characteristics. Lichtenberger and Naftali [24] found that chlorinated rubber heated in solution with pyridine underwent deep-seated changes with the loss of chlorine. Gelation products formed were thought to be quaternary pyridinium salts.

A further description of chlorinated rubber † is summarized on the next page.

* Chlorinated rubber manufactured by Hercules Powder Company.

† The properties given were determined on chlorinated rubber as produced by Hercules Powder Company under the trade name Parlon.

Physical Properties

Specific gravity	1.64
Specific volume (cu in per lb)	16.9
Bulking value (gal per lb in solution)	0.0735
Index of refraction	1.554
Water absorption (80% R.H. in 24 hrs) (per cent)	0.27

Electrical Properties (Unmodified Clear Film)

Specific surface resistivity (ohms $\times 10^{-10}$)	2000
Dielectric strength (volts per mil)	2300
Dielectric constant 25° (1000 cycles)	3.1
Power factor 25° (1000 cycles)	0.0015 to 0.0030

Mechanical Properties (Unmodified Clear Film)

Tensile strength (dry) (lbs per sq in)	4000-4500
(wet) (lbs per sq in)	4000-4300
Elongation at break (dry) (per cent)	3.5
(wet) (per cent)	3.5

Flexibility increases with increase in viscosity.

Uses

The rapid growth of chlorinated rubber into an important material for protective coatings in this country has been largely based upon the product sold under the trade name of Parlon. More recently another chlorinated rubber has been offered under the name of Raolin.*

The properties of chlorinated rubber as set forth in earlier sections of this chapter recommend it for a wide variety of uses. To recapitulate, these properties include chemical resistance, wide solubility and miscibility with modifiers, and nonflammability. The selection of the proper type of chlorinated rubber and the use of properly selected modifiers for a particular application is important to achieve the most satisfactory results.

Chlorinated rubber is manufactured in a variety of viscosities. The five most common ones are 5, 10, 20, 125, and 1000 centipoises. All viscosities are determined on a 20 per cent solution in toluene at 25° in a capillary-tube viscometer. As the viscosity of the material increases, the flexibility increases, but the miscibility with resins and modifiers decreases. The 5-cp material is chiefly used in printing inks for paper which must come in contact with alkali; it may also be used in small quantities to reinforce house paints and finishes such as bulletin colors. The 10-cp material is chiefly used as a fortifying agent for alkyd resin and oleoresinous varnishes. The 20-cp type is used in general protective coatings and for fortifying alkyd resin and oleoresinous varnishes. When the amount of chlorinated rubber in the composition is 50 per cent or more of the vehicle solids, it is advisable to use the 20-cp rather than the 10-cp type for fortification because of the increase in flexibility obtained thereby.

The 5-, 10-, and 20-cp types may all be sprayed in useful solids concentration, but the higher-viscosity types are better fitted for brush, roll, or knife application. The 125-cp type is used in paper coatings, adhesives, textile coatings, and other special finishes. The 1000-cp type is chiefly used in adhesives and textile finishes because of its flexibility. In addition to conventional lacquer-type formulations, chlorinated rubber emulsions have been found useful in application to surfaces such as paper, textiles, and porous construction materials.

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Casein Plastics

H. V. DUNHAM

Casein Co. of America, Bainbridge, N. Y.

The casein plastics industry, insofar as successful commercial operations are concerned, was developed in Germany in about 1900. While many patents more or less relating to the art appeared prior to 1899, it is believed that they were never of any commercial value. Some time prior to 1899, Dr. A. Spitteler was carrying on research in connection with casein plastics in Austria, and in 1899 he obtained a German patent relating to this art. His process in brief consisted in dissolving acid-precipitated casein with caustic soda by various methods, and after adding coloring matter precipitating with an acid or acid salt, or in some cases precipitating the casein solution with acid salts which in themselves gave a color to the resulting precipitated casein. The precipitated casein was washed, ground to a medium mesh, and in the wet condition placed in forms, such as wooden boxes with cloth or screened bottoms, and slowly dried. As the material dried, the casein particles joined or felted together, something after the manner of paper fibers, so that there was finally obtained a hard continuous board-like sheet. At some point during the drying process, the material was immersed in a formaldehyde bath for a sufficient length of time to formalize the casein thoroughly. After the material was thoroughly dried, it was ready to be cut into objects such as combs, buttons, buckles, beads and the like. This process was not only expensive, but had many other defects, the most serious being that while the material was felting together and drying, cracks would develop in a most unexpected way, with the result that a large portion of the finished material was useless and large or medium large sheets could not be produced.

At about this same period, William A. Hall was developing the industrial uses of casein at Bellows Falls, Vermont, and his laboratories were working along similar lines to those of Spitteler. Hall eventually obtained a U. S. patent on his process, but it had the same general defects as the Spitteler process. It is believed that only after Vereinigten Gummiwarenfabriken of Hamburg became interested that the industry advanced commercially. The German company were experts in hard rubber manufacture, and they applied their knowledge and technique of rubber to casein with successful results. This Spitteler wet process was discarded and extruding machines with rennet casein as the raw material were substituted. From this period on, the industry grew and spread to several other countries in Europe and finally to the United States. The basic process today is fundamentally the same as that first used in Germany. Various patents of limited scope have appeared from time to time in the way of improvements, but the process still involves the use of somewhat modified hard-rubber extruding machines and a high grade of rennet casein.

It is not my purpose to go into great detail regarding the manufacture of casein plastics. In general, the process involves the following procedure:

A high-grade rennet casein is ground and mixed with a small amount of water, 20 to 30 per cent or thereabouts, plus coloring matter if desired. The coloring matter may be various pigments, dyes, or both. The use of a small amount of water is for the purpose of temporarily plasticizing the casein during the extruding process. After proper mixing, the casein goes into the extruding machines where it is ex-

truded as rods, tubes or ribbons. The machine may be run hot or cold, depending upon the final type of product desired. If sheet material is to be produced, the extruded rods or ribbons are cut to desired lengths, placed in sheet forms and pressed in hydraulic presses for a short time. The rods join and felt together into a continuous uniform sheet. After extrusion or sheeting the product is placed in a formaldehyde bath until complete formalization takes place. It is then washed and carefully dried.

While from this general description the process seems very simple, yet in reality, the successful commercial manufacture of casein plastics is quite complicated, and there are many carefully guarded secrets relating to production and processing. A few of the difficulties which may be encountered are: a tendency for the development of excessive strains in the material during some stage of the manufacture, resulting in cracks and checks; development of tiny pin holes in the finished material; lack of uniformity of color from batch to batch; lack of uniformity of proper quality of the rennet casein used for the manufacturing operations. Difficulties are encountered in making a uniform design or pattern, such as horn substitute and the like.

Casein plastics are of particular interest and value in the manufacture of buttons, buckles, beads, etc. Remarkable color effects can be produced and the great beauty and brilliance of design is outstanding. For many purposes, casein plastics are not at all suitable for industrial uses because of their lack of resistance to water or excessive moisture. Various new patents appear from time to time relating to this industry, but I am aware of no outstanding recent developments.

Casein Fiber

D. G. CARMICHAEL

Director of Research, Aralac, Inc.

Contrary to general conception, the manufacture of synthetic textile fiber from casein is nothing new. One of the first patents in this field (U.S.P. 625,345) was issued in 1898 to Adam Millar,[7, 4] who disclosed the extrusion, through orifices, of casein dispersed in an alkaline medium; coagulation in an acid bath; and hardening the bands of thread in formaldehyde, chrome alum or bichromate of potash.

Dr. Frederick Todtenhaupt,[8, 9] a German, took out a series of patents about 1905-1907. In U.S.P. 836,788, he described the production of artificial silk or hair from casein, by forcing an alkaline solution of casein, in the form of fine threads, into an acid bath. According to the patent, the casein was then converted into a very elastic compound of great hardness, insoluble in water. This compound could be further hardened by formaldehyde or other means. In spite of many years of investigation by research workers and inventors, all the fibers produced lacked flexibility and resistance to textile processing.

Research on casein fibers appeared to have been abandoned until 1935, when Antonio Ferretti,[5, 6] an Italian chemist, announced a fiber made from casein, that had excellent textile properties. Ferretti found, after numerous experiments and years of study, that different caseins required different spinning conditions. He patented a process for manufacturing a textile casein which gave the best results for the manufacture of his fiber. In the United States, considerable interest has been shown in the commercial production of casein fiber. This product was studied by E. O. Whittier and S. P. Gould[11] of the U. S. Bureau of Dairy Industry, whose patents (1939) were assigned to the public.

In 1936 Francis Clark Atwood[2] was retained by National Dairy Products Corporation to study casein fiber, and on December 13, 1939, he applied for a patent for making proteinaceous fiber. In 1940, Aralac, Inc., a subsidiary of National Dairy Products Corporation, the only American producer of casein fiber, started production in a pilot plant in Bristol, Rhode Island, with a daily output of 4,000 pounds. The next year the plant was moved to Taftville, Connecticut, and the production increased to a daily output of 30,000 pounds (1944).

During 1941, approximately 115,000,000,000 pounds of whole milk were produced in the United States, about half of which was separated to secure cream and butterfat for creamery use, leaving 60,000,000,000 pounds. About 48,000,000,000 pounds of this never left the farms, because farmers producing for centralized creamery operations take only butterfat to the creamery. The skim milk, because of its high nutritive value, is used to feed stock. As only three pounds of casein are obtained from 100 pounds of skimmed milk, its transportation to the casein manufacturer offers an economic problem.

Casein is the main protein in milk, and varies in content, depending on breed, individual cow and herd, season of year, and other factors. It exists in fresh milk in colloidal form and is precipitated when milk is allowed to sour, or when a dilute mineral acid is added. The casein in fresh milk is in combination with calcium

oxide, as calcium caseinate, which is decomposed by the acid. When rennet or rennet-like substances are added to milk, calcium paracasein is obtained as in insoluble curd. Rennet casein is not used by casein fiber manufacturers, who prefer casein precipitated with sulfuric or lactic acid, although the hydrochloric-acid type may be used.

Casein fiber is made by a wet-spinning process in a manner similar to viscose rayon; but these two processes are similar only in one respect, the extrusion of the spinning solution through a spinnerette into a coagulating bath. Casein spinning solutions are simpler to prepare than viscose solutions, but later the process becomes much more complicated.

The casein may be dispersed or dissolved by a variety of solvents or dispersing agents. Some that have found practical use are sodium hydroxide, potassium hydroxide, ammonium hydroxide, (barium hydroxide and calcium hydroxide with other substances), borax, trisodium phosphate, sodium tetraphyrophosphate, triethanolamine, urea, sodium sulfite, sodium pentasulfide, and combinations of alkali hydroxides, sulfonated naphthenates and fatty alcohols.

Ferretti used acidities greater than those ordinarily used in commercial casein manufacture. The high-acid casein gave softer fibers than those manufactured from ordinary commercial casein. Sulfuric- and lactic-acid caseins gave stronger fibers than those manufactured from hydrochloric acid. Temperature, pH, and other factors in the manufacture of casein affect the spinning, viscosity, strength, and softness of the resulting fibers.

In the Ferretti process, the prepared textile casein is processed with an alkali, usually a hydroxide of an alkali metal, and matured with controlled heat and dilution to yield a viscous solution. Sodium hydroxide is the usual alkaline agent, but potassium hydroxide may be employed. The temperature of maturation or "ripening" is about 75° F, and should be kept well within the range of 58 to 95° F. If higher temperatures than 75° F are used, less sodium hydroxide is required. Temperature and pH affect the viscosity and time of maturation. Example: 100 kilos of casein (10 per cent moisture) are poured into 200 liters of water at a temperature of 24° C, and the mixture stirred for two or three hours. A solution containing 23 liters of 64 TW. (44 per cent sodium hydroxide) and 77 liters of water, temperature 24° C, is then added with constant stirring.

When the mixture has become uniform, the stirring is continued only at intervals during maturation. A few hours after the casein solution has become viscous it is gradually diluted, so that at the end of 48 hours there is a final volume of 550-600 liters for each 100 kilos of casein. When a greater or lesser volume is desired, the maturing time is increased or diminished respectively. Maturation exceeding 96 hours may be detrimental to the final quality of the fiber. The final spinning viscosity depends on the casein, pH, dilution and time of maturation.

When the desired volume and viscosity have been obtained, the temperature may be lowered to stabilize the viscosity before spinning. Sulfides and xanthogenates which accelerate subsequent coagulation may be added to the alkaline casein solution. Aqueous solutions with a small percentage of sulfates to increase viscosity and final volume may be added, as well as soap solutions to introduce fat.

The casein solution is filtered and extruded through nozzles, at the rate of 80-120 meters per minute, into an acid bath where it is coagulated. The coagulation bath contains per liter: 144 cc H_2SO_4 at 60° Bé; 400 grams Na_2SO_4; and 140-200 grams $Al_2(SO_4)_3$. Small quantities of $MgSO_4$, $(NH_4)_2SO_4$, or $ZnSO_4$ may be added to increase efficiency of coagulation. Aluminum sulfate accelerates hardening.

The continuous casein filaments emerging from the coagulating bath are led to the top of the machine, thus forming a continuous band of filaments. The band is passed, always under tension, through a sodium chloride solution to remove acid from the coagulating bath, and then through a solution containing sodium chloride

and aluminum salts, with or without formaldehyde. The band passes through the baths at the same speed at which it is spun, and may be immersed continuously or intermittently, by leading it upward and downward so that it remains in the baths over distances of 10 to 15 centimeters, with one-meter distances between successive immersions.

The moist bands are cut to the desired staple length by an automatic cutter, and the cut staple fiber is collected for final hardening in a bath made by adding 10 parts by weight of 40 per cent formaldehyde to 90 parts of 12 per cent sodium chloride solution. The fiber is then washed and dried and various softeners used in the textile may be applied.

Whittier and Gould [12] give the following example in their public U. S. Patents:

Formula 1

Spinning Solution in Water		Coagulating Bath	
Casein	10.0 %	Sulfuric acid	2.0 %
Oleic acid	1.0	Formaldehyde	5.0
Sodium hydroxide	0.27	Glucose *	20.0
Sodium aluminate	0.80		

The casein is allowed to swell for half an hour in half the calculated amount of water, and the necessary amount of sodium hydroxide is then added as an 8 per cent solution. The mixture is stirred until uniform and the oleic acid is added; the stirring is continued; then the sodium aluminate is added, in solution in the balance of the water. The completed solution is stirred thoroughly, deaerated under vacuum for several hours, and is then ready for spinning, after which it is coagulated and hardened by immersion in a formaldehyde solution.

Formula 2

Spinning Solution in Water		Coagulating Bath in Water	
Casein	8.0 %	Phosphoric acid	5.0 %
Sodium lauryl sulfate	1.6	Monocalcium phosphate	10.0
Calcium hydroxide	0.8	Glucose	20.0

The casein is soaked in half the calculated amount of water and the sodium lauryl sulfate is stirred in. The calcium hydroxide, previously mixed with the remainder of the water, is added slowly to the casein mixture and stirred until the dispersion is uniform. It is then deaerated and handled as in the previous example. Oleic acid is added to increase flexibility and sodium aluminate and calcium hydroxide to increase strength.

Astbury, Barley and Chibnall, in British Patent 467,812, used urea as a solvent for casein in their process of making casein filaments.

Example: A solution of:

2 parts 40 per cent formaldehyde
1 part gelatin
1 part salicylic acid
30 parts urea
78 parts water

is stirred with 40 parts of casein containing 10 per cent moisture. The casein disperses rapidly, the solution becomes viscous and is ripe for spinning after standing two hours. The solution is extruded into a coagulating bath composed of the following:

10 parts ammonium sulfate
2 parts zinc chloride
4.5 parts glacial acetic acid
75 parts water (35-40°).

* Commercial glucose approximates 15 per cent water, the dry content being about half dextrin and half dextrose. J. A.

The filament may be strengthened by immersion in aqueous solution of formaldehyde.

Casein fibers were being produced commercially before 1939 in Italy (*Lanital*), Germany (*Tiolan*), Holland (*Lactofil* and *Casolane*), Belgium (*Cargan*) and England (*Courtald's Casein Fiber*).

Da Schio [8] made an ultimate analysis of casein fiber, which is listed below in comparison with that of wool:

Elements	Casein Fiber	Wool
Carbon	53	49.31
Hydrogen	7.5	7.57
Oxygen	23	23.66
Nitrogen	15	15.86
Sulfur	0.7	3.6
Phosphorus	0.8	0.0

Its amino acids are distributed as follows: [10]

Alanine	1.5	Tryptophane	1.7
Valine	7.2	Proline	8.0
Leucine	9.4	Methionine	1.4
Aspartic Acid	4.1	Lysine	6.0
Glutamic Acid	21.6	Arginine	3.8
Serine	0.5	Histidine	2.5
Hydroxygutamic Acid	10.5	Hydroxyproline	0.3
Phenylalanine	3.2	Ammonia	1.6
Tyrosine	4.5		87.8

Since the sulfur present in casein is in the form of methionine, no disulfide linkages exist.

Casein particles in milk are spherical in shape; but after denaturation and spinning they tend to become more rod-like and orient into the chains. Formaldehyde may establish methylene bonds, and aluminum bridges may be formed by aluminum sulfate. The methylene bridge recalls the cystine linkage in wool.

An x-ray examination of casein fiber shows the usual pair of rings similar to the skeletal structure of the molecular chains in natural keratin fibers. Optical examination will confirm that the orientation of these chains is not as regular as those found in natural wool, where the reversible elastic properties are due to the coiling and uncoiling of its regularly arranged polypeptide chains. The randomly oriented chains of casein fiber give a partial coiling and uncoiling effect, with a lesser degree of elasticity.

Casein fiber has an opaque silk-like luster similar to that of natural protein fibers. On microscopic examination, viewed lengthwise, casein fibers resemble certain types of rayon, with fine dots and striations. They are nearly circular in cross-section.

Compared with natural protein fiber, casein fibers are more sensitive to alkalies, particularly at elevated temperatures; but when treated with strong alkaline solution, they gelatinize and dissolve more slowly. Mild alkalies, such as disodium phosphate, sodium bicarbonate, borax, and sodium tetrapyrophosphate cause little if any damage at moderate temperatures. Treatment with dilute acids produces no visible effect, although the acids are held tenaciously. Strong mineral acids decompose casein fibers, but cold sulfuric acid does not do so appreciably. Casein fibers assume a yellow color when treated with nitric acid, and are diazotized by the action of nitrous acid.

In general, reducing agents have no apparent action on casein fibers, and in some instances are used as bleaching agents. Sodium and zinc formaldehyde sulfoxylate are satisfactory for the purpose. Casein fibers become yellow and harsh when immersed in hypochlorite solutions and their tensile strength is diminished.

Tensile Strength: Dry: Approximately 75 per cent of natural protein fiber; Wet: Approximately 30 per cent of natural protein fiber.

Moisture Regain: 13 per cent at 70° F, and 65 per cent relative humidity.

Resistance to Heat: Continued exposure to elevated temperatures causes harshness, brittleness and loss of tensile strength, comparable to that of natural protein fibers.

Total Water Absorption: The same as for natural protein fibers. The plastic flow of casein fibers is greater wet than dry, and immersion in water weakens them considerably, as is the case with rayon. Casein fibers swell in water to the same degree as natural protein fibers; but in 10 per cent caustic soda, they swell more.

Casein fibers are attacked by molds and mildew and bacteria. Although poor conductors of electricity, they easily acquire a static charge. Their elongation and elasticity are affected by moisture and temperature. At 70° F, and 65 per cent relative humidity, the elongation is 12-15 per cent. A relationship in variation will be found in fineness, strength and elongation.

Diameter of Fiber: At present in the United States there are three grades of casein fibers: 20-micron, equivalent to 70's; 25-micron, equivalent to 60's, and 30-micron, equivalent to 50's.

Aralac

Aralac, the first American-produced casein fiber, differs from all others in that it is acetylated.[1] This chemical treatment makes it more resistant to boiling water, acids, and particularly to alkaline solutions. Its chemical reactivity, *e.g.*, to dyes, is altered.

Upon heating or boiling un-acetylated fiber in aqueous solutions, it becomes soft, slippery and slimy. If then dried it becomes somewhat brittle and decreases in tensile strength. Mixed with natural protein fibers and dyed, it has a tendency to absorb all the dyestuff, and leave the natural protein fibers undyed and merely stained. By acetylation, however, the chemical properties are so altered, that they closely approximate the dyeing properties of wool; thus both kinds of fibers, by selection of dyestuffs, can be dyed the same shade in the same bath.

Uses of Casein Fibers

In the United States, casein fiber has been used in all types of textile spinning systems, such as those used for wool, rayon, cotton and silk. It may, therefore, be combined with any or all of these other fibers. It has been largely used in dress goods, but also in suitings, coatings, sports wear, men's and women's hats, sweaters, snow-suits, ankle socks, housecoats, robes, blankets, comforters, pocketbooks, interlinings, felts and in beauty shops instead of mohair for making "permanent waves." Interlinings containing 100 per cent casein fiber are being used.

Considering the progress already made and the research being done, many improvements may be expected in the future.

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Soybean Plastics

A. A. Horvath

The average composition of soybeans is: protein, 40 per cent; oil, 18 per cent; phosphatides, 2.5 per cent; nitrogen-free extractives, 21.5 per cent; fiber, 3 per cent; ash, 5 per cent; moisture, 10 per cent. Nearly all the protein matter of soybean consists of a globulin, glycinin, which is believed to be present in the seed in the form of glycinates of alkaline earths as well as adsorption products with alkaline-earth phosphates. In the seed glycinin probably also forms complex coacervates with some of the phosphatides.[1]

Solutions containing more than 2 per cent NaCl dissolve glycinin freely; glycinin can also be extracted from ground soybeans by leaching with water, owing to the dissolving action of acid potassium phosphate present in the seed.[2] It has been established on the basis of osmotic pressure measurement of colloidal solutions of glycinin that its micellar weight is 52.000, and that glycinin consists of fractions having various solubilities; measurement of the energy of surface tension of glycinin hydrosol places glycinin among the surface-active molecular compounds.[3] The isoelectric point of glycinin is a pH of 5.0.[4]

Using consecutive extractions with water, 10 per cent NaCl, and 0.2 per cent NaOH, it is possible to extract from whole ground soybeans about 80, 10, and 5 per cent respectively of the total nitrogen; from commercial benzine-extracted soybean meal, 25, 10, and 50 per cent respectively can be obtained.[5] Evidently, nearly one-half the total protein of the soybean meal has become insoluble in water, but soluble in dilute NaOH solution. The denatured protein contains less total nitrogen and more hydrogen and oxygen than the original glycinin. The isoelectric range of normal soybean protein is wider than that of soybean protein denatured during defatting by benzine, and the quantity of HCl required to bring about the maximum turbidity in an alkaline solution of denatured protein is larger for normal soybean protein than for denatured protein. It was also found that the denatured glycinin had a higher viscosity, a lower isoelectric point, and was richer in free amino and carboxyl groups, richer in enol groups, and simultaneously poorer in amide nitrogen than normal glycinin. Deamination and hydration are suggested as a partial explanation of these changes.[5]

Solvent extraction of dry beans denatures the protein less than when moist beans are subjected to this procedure. Azeotropic mixtures of benzine and methyl alcohol were found to give a better industrial protein than benzine alone, and much better than the expeller meal protein. The duration of oil extraction by organic solvents should be as short as possible, the temperature of extraction low, and the meal freed from the solvent at not over 40°.

In order to remove from the solvent-extracted meal the soluble carbohydrates, such as cane sugar and stachiose, "which may affect the resistance of the plastic materials manufactured therefrom against moisture and its mechanical strength," as well as "to separate mucilaginous substances, such as galactan and araban, which choke off the filter press, as well as give great difficulties in the clarification of proteins," it was suggested over two decades ago [6] to leach the meal with water, acidu-

lated with acetic acid, in order to prevent solubilization of the glycinin without affecting extraction of the carbohydrates.

An extensive study of the extraction of protein from the defatted soybean meal by the same author [6] showed that the yield depends on the fineness of the meal, as well as on the nature and concentration of the chemical used. Thus, for Na_2SO_3 the maximum yield in per cent was 0.3, for Na_3PO_4 0.3, for Na_2CO_3 1, for $Na_2B_4O_7$ 5, for CH_3COONa 5, for NH_4OH 0.5, for NaOH 0.2, for Na_2SiO_3 5, for Na_2S 10, for NaCl 10, for Na_2SO_4 1, for $(NH_4)_2SO_4$ 5, etc. The best plasticity was exhibited by the protein extracted by Na_2SO_3, the next by Na_3PO_4, the next by sodium carbonate, borate, and acetate, this being followed by ammonium and sodium hydroxides; the extractions by neutral salts occupied the last place, and were considered less suitable for plastics. The extracted protein, when precipitated from its solution by H_2SO_3, was found to give a material most suitable for plastics; phosphoric, sulfuric, and acetic acids give a protein of medium quality, while hydrochloric and nitric acids give an inferior quality.[6] *

A few years ago, the investigation of peptization of soybean protein from oil-free meal was extended to include also a study of the effect of pH of the extracting solution; [8] some of the results can be seen from Fig. 1.

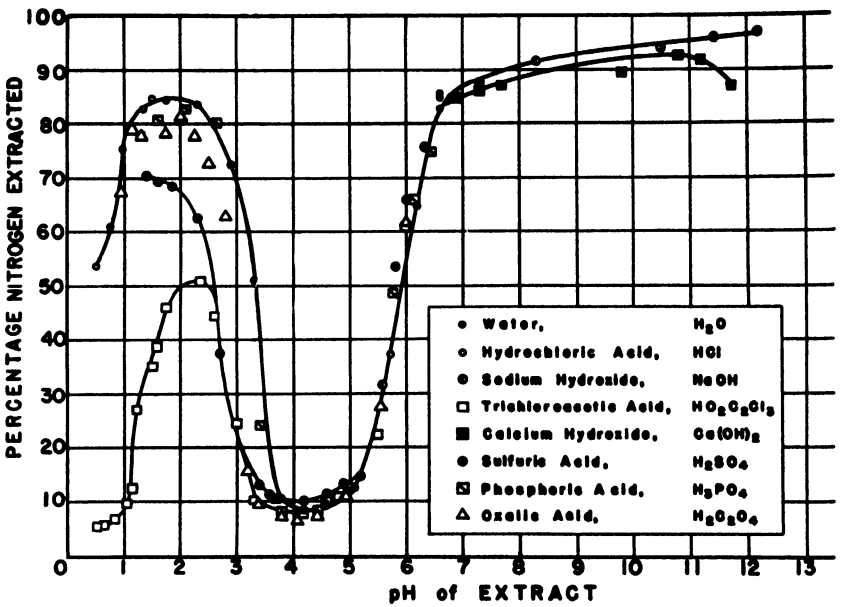

FIGURE 1

Since the protein is here denatured, its isoelectric point is at a pH of 4.1.

Soybean meal (defatted), with the normal moisture content of about 9 per cent, plasticized quite satisfactorily when subjected to a temperature of 100° and a pressure of 5000 pounds per square inch for 5 minutes. As the moisture content was lowered below about 5 per cent, the resulting plastic became lighter in color, its transparency increased, and the product assumed a hard, vitreous, and somewhat resin-like appearance. Commercial soybean protein plasticized excessively with heat and pressure.[9]

Since proteins are amphoteric, they react with many compounds of basic as well as of acid nature. Soybean protein thus glutinized will have different properties depending on the glutinizing agent employed. An extensive study of various glutinizers

* A detailed presentation of these investigations is to be found in Ref. 7.

conducted two decades ago [10] showed that glutinizers of amphoteric properties give the best quality protein material for plastics. This study included also a thorough investigation of the soybean protein-formaldehyde reaction as applied to plastics.* It was found that the speed of "coagulation" of protein by formaldehyde is inversely proportional to the degree of its hydrolysis, and the condensing action of formaldehyde may thus easily be controlled.† By subjecting soybean protein to the action of superheated steam, which causes some hydrolysis, it was possible to produce from it a transparent plastic material by direct treatment with formaldehyde, omitting the glutinizing process. Formaldehyde was found to be a less effective coagulant for soy protein than acids, especially in weak solutions.[6] The latter produce on standing a jelly-like mass, which, when coated on paper, forms a hard, glossy, transparent film. A recent study [11] showed that the isoelectric point of formaldehyde-treated soybean proteins obtained by various methods is lowered by from 0.1 to 0.7 point, whereas that of defatted soybean oil meal remains unchanged.

In 1914 and 1915 a British and U. S. Patent were granted [12] on the preparation of semiplastic material from the soybean, which embodied the main principles of today's procedure, such as removal of the oil, leaching with either water or a solution of an alkali or salt capable of dissolving the protein, and separation of the insoluble residue, followed by precipitation of the protein from its solution (or "emulsion") by a coagulant. "The coagulation may be effected in the presence of formalin, and the coagulant employed may be any salt, acid or substance having the property of coagulating proteins. In some cases it is preferred to use as the coagulant aluminum sulfate or a mixture of aluminum sulfate and an acid, such as HCl. The maceration may, in some instances, be effected with a solution of calcium or sodium hydroxide and the emulsion, solution, or suspension treated with aluminum sulfate."

The product may be colored by the addition of dye. For certain purposes glutinous, filling, hardening mordants or other materials may be introduced at a convenient stage. The coagulate is strained off, placed in suitable molds and subjected to moderate pressure. A formula is given when the molded material is subsequently hardened in formaldehyde solution. The effect of temperature on the reactions taking place is also mentioned. This seems to be a typical "wet process," which requires a long time for hardening, a long time for drying, and which results in a material with high water absorption and deformation on drying.

In 1923 a "dry powder process" was developed,[10] wherein the glutinized soya protein, after being kneaded with formaldehyde or other condensing agents, is immediately subjected to drying, the dried mass being then reduced to a fine powder. "The powder has a thermo-plastic property, and is easily molded into any desired shape under heat and pressure at a temperature of 90° to 95° and about 2000 to 3000 pounds per square inch." It is claimed that this product does not deform or crack, and that it absorbs only from 1 to 2 per cent of water in 48 hours. The nature of the glutinizing agent used is not disclosed, although the physicochemical properties of the molded product are discussed at length.‡

In 1938 it was found [13] that commercial soybean protein hardened by an aldehyde at or near its isoelectric point is thermoplastic, and that the best plastic with the lowest water absorption is produced by treating the protein with an aldehyde in its isoelectric range. Water absorption was found to increase sharply on either side of

* Other active methylene compounds were also studied, such as hexamethylenetetramine, trioxymethylene, acetaldehyde, oxymethansulfonic acid, etc. The latter has a glutinizing, as well as a condensing effect on soybean protein. When this reagent comprises 20 per cent of the weight of the dry protein, the first phenomenon taking place is glutinization, and the condensation follows. The condensing speed can be controlled by the quantity of water added, and the product can be molded in a hot press, and hardens.

† Special glutinizers which react with formaldehyde simultaneously with the protein were found to retard the condensing speed remarkably.[10]

‡ Details of this process, as well as of a semi-dry and a wet process by the same author are reviewed in Ref. 7.

this range. But even the best product, treated with formaldehyde at a pH of 4.2, did absorb 10 per cent water in 24 hours, and 17.9 per cent water in 48 hours. When the same soybean protein was hardened by other common aldehydes and ketones, by chromium or aluminum salts, or by tannin, materials were obtained with still higher water absorbtion. In all these experiments one part of the commercial soybean protein (containing about 8 per cent of moisture) was added to two parts by weight of a 20 per cent hardening solution and allowed to stand 24 hours at room temperature. The excess hardening solution was then washed out with water and the hardened protein air-dried to a moisture content of about 10 per cent. The hardened powder was pressed into discs. The 10 per cent moisture left in the hardened protein evidently acts like a plasticizer on molding, and does not prevent the absorbtion by the molded material of additional 17.9 per cent water in 48 hours. The plastic flow of the material obtained was evidently also unsatisfactory, and further experimentation [14] centered around plasticization and waterproofing, neither of which was successful. Ethylene glycol was found to be the best of the plasticizers tested, but it increased the water absorption from 10 to 21 per cent (in 24 hours). The incorporation of oleanolic acid and aluminum stearates reduced the water absorption only to 17 and 19 per cent respectively. These results do not justify the claims of the authors that "recent developments have made it possible to approach from new angles the problem of developing a protein plastic molding material." One should also acknowledge the fact that a "dry powder" soy protein molding material had been developed fifteen years earlier,[10] when, in addition, a study was initiated which laid the foundation for the mixed type soya plastics, which so far are the only commercially successful ones.

It was found in 1923 [10] that phenol, salicylic acid, resorcinol, pyrogallol and naphthols react strongly in their fused state with dry powdered soya protein, forming a homogeneous liquid, which solidifies on cooling to a hard, brittle mass. Among aromatic compounds, cresols have the strongest dissolving power on protein. Dry soy protein swells up in half its weight of cresol to a soft elastic body, while in twice its weight of cresol it forms a fluid colloidal solution. Wet soy protein (55 per cent moisture) reacts with phenol or cresol with the formation of a white, elastic, rubber-like substance, which is stretchable like raw rubber, having a silky luster due to the presence of emulsified water. This water cannot be easily expelled by heat or otherwise, unless dried in an air bath at 100°. "On treating the protein, glutinized by phenols, with formaldehyde, it coagulates immediately to an agar-like mass, which changes on the application of heat into a glue-like viscid fluid, which can be diluted with organic solvents, such as methyl, ethyl, and amyl alcohol, or acetone." These solutions in organic solvents give on glass, metal or wood a hard, lustrous, transparent film. When a smaller proportion of phenol was used (from 10 to 30 per cent) a solid product was obtained, suitable for treatment with formaldehyde.

It was also found [10] that when dry soybean protein was kneaded with the oily condensation product of phenol with formaldehyde in the presence of ammonia, the protein liquefies into a heavy viscid semi-fluid, which on heating is converted into a hard, strong, insoluble and infusible (thermosetting) body. The condensation reaction can be controlled so as to give an intermediate product of thermoplastic nature, which, when reduced to a fine powder, can be used as a substitute for Bakelite.

About ten years ago the Ford Motor Company developed a commercially successful mixed plastic, containing defatted soybean oil meal * instead of the protein.[15] A representative batch consists of 330 pounds soybean meal, 250 pounds phenol, 250 pounds formaldehyde, 300 pounds wood flour, 30 pounds ammonia, and 25 pounds lime. The batch is worked for two hours at 200° F in a jacketed Baker-Perkins

* Although the protein gives a higher-grade plastic, the added expense for its isolation has not been justified in view of the satisfactory results obtained by using the whole defatted meal.

mixer, followed by additional working for two to three hours at a lower temperature. Coloring pigment is added near the end of the mix, as is also a small amount of zinc stearate and stearic acid which serve as mold lubricants. Whereas during the mixing process the material lumps and becomes tough, the final contents of the mixer must be put through a Banbury internal mixing machine, such as is used in rubber compounding. From the Banbury the material goes to a Raymond kiln mill where the temperature is kept below 150° F to avoid premature curing. The powder goes to a tumbler to obtain a uniform blend, and from there it is fed to the molding machines, where it is subjected to a pressure of 2,000 lbs per sq in and a temperature of 360° F. The last stage of curing, which requires about three minutes, takes place in the presses. The plastic obtained is both waterproof and durable. The cost per pound of these plastics is greater than steel, but the finishing of steel brings the final cost of many steel parts in excess of that for the finished product fabricated from the soybean material. The River Rouge plant of the Ford Motor Company was capable of turning out over 100 tons of plastic per day in the form of distributor parts, gear-shift lever knobs, light switches, horn buttons, coil parts and window frames. In recent years, before our entry into the war, the Ford Motor Company has also experimented with soybean plastics in molding automobile bodies.

In a recent study,[16] flow properties of a woodflour-filled phenolic molding powder were compared with those of a phenolic plastic modified with formaldehyde-hardened soybean meal. The properties were determined by running preheat tests and distance-pressure characteristics on the Rossi-Peakes flow tester. A 60-40 mixture of soybean meal and resin had more flow than a 60-40 mixture of wood flour and resin. It was also noted that the soybean meal mixture was slightly slower in setting up at all temperatures used except at 140°. The soybean meal-resin mixture exhibited a higher heat conductivity than the woodflour mixture.

A 1942 paper [17] states that the use of 20 per cent soybean meal with 40 per cent of phenol-formaldehyde resin and 40 per cent of wood flour does not decrease the quality of the plastic, as compared with a 50:50 mixture of resin and wood flour, thus making it possible to save 10 per cent of the phenol-formaldehyde resin.* The author recommends a pretreatment of the defatted meal by leaching it with dilute acid, and by hydrolyzing it in a moist state under pressure by heat, when superheated steam is being generated.† Formulas and discussions are presented in McKinney's paper, as well as in a 1941 U. S. Patent,[18] assigned to the Secretary of Agriculture; the use of alpha ‡ protein is required in both claims.

Recently, an extensive laboratory study of soybean meal-furfural plastics was published,[19] revealing that good plastics can be produced. Impact test showed that soybean meal plastics were stronger than samples from standard phenolic molding powders. Tensile strength was not far below that of the phenolic, urea, and acetate plastics on the market. Water absorption was as low as, or lower than, that of commercial phenolic, acetate, and urea plastics. While they are apparently thermosetting, some cooling was necessary before removal from the press. The following procedure gave a high-grade plastic: 30 parts by weight of furfural, 24 parts phenol, and 4 parts ammonium hydroxide were refluxed for 1 hour. To this mixture were added 32 parts soybean meal and 3 parts lime, and the whole was heated at 110° to 120° for 4½ hours with constant mixing. The material was dried and ground to pass a 60-mesh screen. Equal parts of the powdered resin and woodflour filler were mixed with 4 parts hexamethylenetetramine, molded at 200° and 1,800 lbs per sq in for 3½ minutes, cooled under pressure for 2 minutes and removed from the mold. Asbestos filler may be used instead of the wood flour, using 120 parts. The raw

* When the resin polymerizes to the insoluble, infusible state, it no longer plasticizes the protein, and the whole mixture gives a thermosetting plastic.

† Thus, the recommendations of an early investigator [6, 10] have been accepted.

‡ A commercial product.

material cost for the plastic containing 50 per cent filler is calculated at 6 cents a pound.

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Zein

L. C. Swallen and J. P. Danehy

Research Department, Corn Products Refining Company, Argo, Ill.

Zein is the prolamine from corn. It was isolated and named by Gorham [1] in 1821. Other early investigators were Bizio,[2] Stepf,[3] Ritthausen,[4, 5, 6, 7] and Osborne and his co-workers.[8, 9] Recently zein has been investigated in considerable detail because it is a readily available protein having properties which are rather unusual; has shown considerable promise in commercial applications.

Zein occurs primarily in the endosperm of the corn kernel.[10] It is present in varying amounts depending on the variety of the corn and the conditions under which the corn was grown. Showalter and Carr [11] have shown zein contents varying between 2.21 and 10.44 per cent of the dry substance in various corn samples. This and other investigations show that, if desired, the potential yield of zein may be increased to a very considerable extent by proper selection of the type of corn submitted to the process.

The raw material available for the preparation of zein is the gluten fraction obtained in the process of producing starch from corn. In this process a mixture of starch and gluten is obtained by steeping the corn, disintegrating it, and separating the germ and fiber by mechanical means. The remaining suspension of starch and the gluten of the endosperm are separated by settling procedures. The gluten finally obtained from this process contains 50 per cent or more of protein. Approximately 70 per cent of the protein is zein. This available zein content amounts to about 1.4 pounds per bushel of corn of which, as indicated below, about 1 pound is considered available by present means of recovery.

Aqueous alcohols have been used as the extraction solvents in almost all the methods of isolation. Typical of the earlier work is that of Osborne,[12] who used 80 per cent alcohol and various procedures for isolating the zein from the extract. Other solvents proposed in the earlier work have been amyl alcohol [13] and alkali.[14] The latter method may under proper conditions extract the major part of the zein. It is, however, not selective and is likely to change the chemical nature of the protein. Later work has emphasized the use of more concentrated alcohols.[15, 16, 17] Ethyl and isopropyl alcohols are preferred, since methyl alcohol has less solvent power and a greater tendency to denature the zein. While a considerable number of other solvents or solvent mixtures described under the heading of "Zein Solvents" may be satisfactory for the extraction, none is considered practical, except possibly some combinations of alcohols and aromatic hydrocarbons [18] or of chlorinated hydrocarbons.

The fundamental characteristics of extraction with either ethyl or isopropyl alcohol of varying water content are illustrated in Figure 1. The difference in yields obtainable under the conditions illustrated is due partly to varying ability of the zein to diffuse into the solvent and partly to a fractionating effect. The main fraction dissolves readily in strong alcohols, whereas another fraction, extracted primarily with intermediate alcohol concentrations, is relatively insoluble in the strong alcohols but soluble in the presence of larger amounts of water.

Crude zein extracts are subject to spontaneous denaturation leading to the formation of insoluble protein. A degree of stabilization is effected by the removal of catalytic materials by clarification.[19] The oil and xanthophyll color may be removed from zein either by pre-extraction of the raw material [20] or by treating the extract with a hydrocarbon [21, 22, 23, 24] or a chlorinated hydrocarbon.[25] The oil-free extract may be precipitated by a variety of methods. Under alkaline conditions precipitation with water yields a finely divided precipitate rather than a dough.[26] The same results may be attained by spraying the alcoholic zein solution into a rapidly moving body of water.[27]

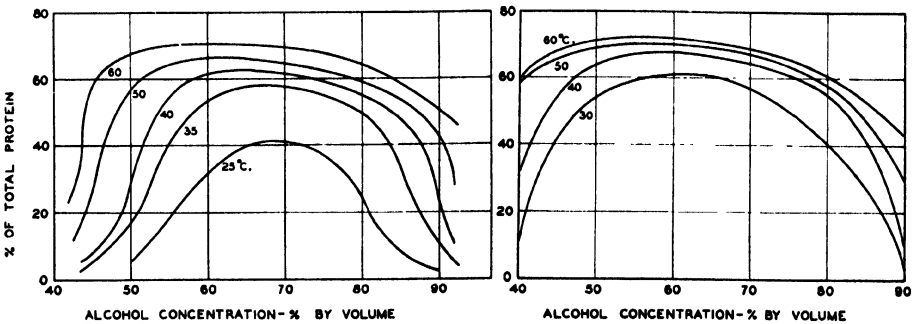

FIGURE 1. Zein extraction yields with ethyl alcohol (left) and isopropyl alcohol (right).

The precipitated zein may be either spray-dried or flash-dried.[28] Direct spray-drying of the zein solution, preferably in concentrated form, is also satisfactory.

The commercial process for producing zein involves extraction of gluten meal with 85 per cent (by volume) isopropyl alcohol at 55 to 60°, using a contact time of 1.5 to 2.5 hours. The equipment may be a countercurrent extractor,[29] or if a finely divided meal is used, filtration or centrifugal separation is also adaptable. The residual meal is treated for solvent recovery. The extract, containing about 6 grams of protein per 100 cc, is stabilized by cooling and filtration. The oil and xanthophyll color are removed and the solution is concentrated to 20% protein concentration by addition of an equal volume of hexane followed by centrifugal separation. The phase relations in this step are very sensitive to variations in the water content of the extract. The zein is precipitated by spraying into water and the precipitate is flash-dried.

Hydrolysis Products. The products of the ultimate hydrolysis of zein—the amino acids—have been the object of numerous quantitative investigations. The earliest attempt to obtain a comprehensive assay of the amino acids in zein was made by Osborne and Clapp.[9] These investigators were able to account for only 57.9 per cent of the amino acids * but they made the important observation, later substantiated, that glycine, lysine and tryptophane are entirely absent from the hydrolyzate. In 1923 Dakin [30] applied his butanol extraction method to zein hydrolyzates and brought the total value up to 77.2 per cent; the values which he established for leucine (and isoleucine) and glutamic acid, quantitatively the two most important amino acids, correspond to the values accepted today. In 1938 the latest and most definitive analysis was presented by Vickery,[31] who succeeded in bringing the total value up to 105.95 per cent (see Table 1). If to this value is added a tentative value of 5 per

* It is customary to express the percentage of amino acids as the ratio of the weight of amino acids found to the weight of the original protein sample. Since one mole of water is taken up at each peptide linkage on hydrolysis, the weight of the hydrolyzate would be greater than 100 per cent of the weight of the protein; in the case of zein this would be between 110 and 120 per cent.

Table 1. Amino Acids in Zein

Amino Acid	Molecular Weight of Amino-acid Residue	Weight Per cent of Amino-acid Residue	Nitrogen in % of Protein Nitrogen (16.13)	Moles × 10^5 Amino Acid per Gram Protein	Assumed No. of Amino Acid Residues per Mole Zein	Calculated Molecular Wt. from 5 and 6
Glycine	57.03					
Alanine	71.04	7.81	9.55	110.0	44	40,000
Serine	67.08	0.85	0.85	9.8	4	40,816
Threonine	101.10					
Valine	99.08	1.59	1.39	16.0	6 or 7	43,750 37,500
Leucine and Isoleucine	113.08	21.56	16.56	190.7	76	39,854
Proline	97.08	7.63	6.83	78.6	31 or 32	40,704 39,432
Oxyproline	113.06	0.69	0.53	6.1	2 or 3	49,179 32,786
Phenylalanine	147.08	6.77	4.00	46.0	18 or 19	41,306 39,132
Methionine	131.18	2.07	1.37	15.8	6	37,974
Cystine	222.18	0.84	0.66	7.6 *	3 *	39,471
Tryptophane	186.08					
Tyrosine	163.08	5.31	2.83	32.6	13	39,871
Histidine	137.08	0.72	1.37	5.3	2	37,736
Arginine	156.08	1.43	3.18	9.2	4	43,480
Lysine	128.08					
Aspartic Acid	115.08	1.56	1.18	13.6	5 or 6	44,118 36,765
Glutamine	128.06	27.69	37.56	216.2	86	39,798
Hydroxyglutamic Acid	145.08	2.22	1.33	15.3	6	39,216
Total		88.74	89.19			

* Calculated as Cysteine.

cent for threonine [31a] (discovered in 1935) we have a total value of about 111 per cent for the amino acids from zein.

Though tryptophane has occasionally been reported as a component of zein hydrolyzates, recent work [32] indicates that it arises from other proteins present as impurities in the zein preparations.

Since the side chains extending from the peptide chain of a protein are the determining factors in such properties as solubility and chemical reactivity, examination of a sufficiently complete amino-acid analysis of a protein affords an explanation of some of its properties. The first attempt to correlate the composition of zein with some of its properties was made by Cohn, *et al.*[33] These investigators concluded that the very low concentration of diamino acids explained the absence of any basic properties (practically insoluble in any mineral acid at any concentration) and that its acidic properties are such as might be expected from the dicarboxylic acids present that are not found as amides. They emphasized the chemical inertness of zein.

In addition to the low acid- and base-binding capacity of zein, two other facts of the greatest interest are apparent on examining the amino-acid composition of zein: the very high proportion of non-polar (hydrocarbon) side chains and of acid amide side chains. If the composition of zein is expressed as moles (10^5) of amino acid per gram of zein, we find a total of 362 moles of amino acids furnishing non-polar side chains (110 methyl groups from alanine, 16 isopropyl groups from valine, 191 branched butyl groups from leucine and isoleucine and 46 benzyl groups from phenylalanine); a total of 245.1 moles of dicarboxylic acids (13.6 from aspartic acid, 216.2 from glutamic acid and 15.3 from hydroxy glutamic acid; and a total of only 165

Table 2. Nature and Number of Side Chain Groups of Proteins of Molecular Weight 34,000-44,000

	Zein (40,000)	Gliadin (42,000)	Insulin (35,000)	Egg Albumin (43,000)	β-Lactoglobulin (42,000)
Cationic Groups, Polar$^+$					
Guanidine	4	9	6	14	7
ε-Amino	0	2	3	15	28
Imidazole	2	9	24	4	4
Anionic Groups, Polar$^-$					
Carboxyl	11	18	36	44	61
Phenolic Hydroxyl	13	8	24	10	9
Non-Ionic Polar Groups					
Amide	85 or 86	128	34	31	32
Hydroxyl	6 or 7	1	20		
Methionyl	6	6		15	9
Indole	0	2		3	4
Sulfhydryl	3	8	36	6	12
Non-Polar Groups					
Paraffin	126 or 127	43	80	55	
Benzene	18 or 19	6		13	
Pyrrolidine	31 or 32	48		16	
Summation					
Dipolar Ionic Pairs	6	18	33	33	39
Polar Groups	131	191	183	142	166
Non-polar Benzene Rings	18	6		13	
Non-polar Pyrrolidine Rings	31	48		16	
Non-polar CH_2 Groups	368	129	>328	178	

moles for all other amino acids. The 245.1 moles of dicarboxylic acids furnish only 27.5 carboxyl groups; the remaining 217.6 moles furnish acid amide side chains. This high proportion of non-polar and amide groups, found only in the prolamines, accounts for their solubility in many organic solvents and in binary aqueous-organic solvents.

Molecular Characteristics. Many physical-chemical techniques have been applied to the examination of the proteins during the last twenty years in an effort to solve the problem of the size and shape of these giant molecular species. Numerous recent reviews and symposia indicate the wide scope of these varied methods and the striking success of the application of physical chemistry to protein systems.[34] Reference to these papers will furnish the theoretical explanations and the experimental procedures for these methods.

The first attempt to apply these experimental methods to zein was made by Williams,[35] who presented his data on the molecular kinetic behavior (sedimentation velocity in an ultracentrifugal field, diffusion) and dielectric behavior of zein in 1938, though a preliminary communication had been made in 1936. Williams has offered evidence, obtained by fractional precipitation from alcoholic solution with water, that zein consists of two or more fractions. The sedimentation and diffusion data give a molecular weight of approximately 40,000 for the principal constituent. The extremely low sedimentation constant for zein, taken in conjunction with the molecular weight calculated from diffusion data, indicate a highly asymmetric molecule. Assuming that the molecule is an elongated ellipsoid of revolution (cigar-shaped), a

Table 3. The Amino Acid Composition of the Proteins

	Egg albumin %	Insulin %	Zein %	Gliadin %	Casein %	Edestin %	Coconut globulin %	Gelatin %	Hemoglobin (horse) %	Serum albumin %	Silk fibroin %	Spider silk fibroin %	Wool keratin %	Salmin %	Fibrin (cattle) %
Glycine			0.0	0.0	0.45	3.80	Trace	25.5			43.8	35.13	0.6		
Alanine	2.22		9.79	2.0	1.85	3.60	4.11	8.70		2.68	26.4	23.40	4.4		
Serine		3.57	1.02	0.13	5.0	0.33	1.76	3.3		0.60	13.57		2.9	7.80	
Threonine		2.66			3.5			1.4			1.36				
Valine	2.50		1.88	3.34	7.93	5.6	3.57	0.0					2.8	4.30	
Leucine and Isoleucine	10.71	30.00	25.00	6.62	9.70	20.90	5.96	7.10		20.0	2.50	0.76	11.5		
Proline	4.15		9.04	13.22	8.70	4.10	5.54	19.7		1.04	1.00	3.68	4.4	11.00	5.1
Oxyproline			0.8		0.23	2.00	2.05	14.4							
Phenylalanine	5.07		7.6	2.35	3.88	3.09		1.40		3.08	1.50				
Methionine	5.23		2.35	2.03	3.25	2.39					2.59		0.67		2.59
Cystine	1.78	12.50	0.91	2.40	0.42	1.36	1.46	0.17	1.02	5.71					1.51
Tryptophane	1.18			1.10	1.54	1.46	1.25	0.0	1.28	0.53			1.8		3.0
Tyrosine	3.97	12.52	5.90	3.04	5.36	4.54	3.18	0.0	3.15	4.79	13.2	8.20	4.8		6.5
Histidine	1.48	10.7	0.82	3.30	2.50	2.41	2.42	2.94	7.64	3.40	0.07		0.66		2.50
Arginine	5.66	3.05	1.60	2.57	3.72	16.76	15.92	8.68	3.59	4.90	0.76	5.24	10.2	87.40	7.70
Lysine	4.97	1.26	0.0	0.69	6.25	2.37	5.80	5.92	8.10	13.20	0.25		2.8		10.14
Aspartic acid	8.1		1.8	0.77	5.95	12.0	5.12	3.40	8.9	3.12			7.27		5.9
Glutamic acid	16.1	30.00	31.30	43.66	21.6	20.7	19.07	5.80	6.3	1.52		11.70	15.27		14.1
Hydroxyglutamic acid	1.36		2.50	7.70	10.5		0.0	0.0							
Ammonia	1.23	1.65	3.64	5.22	1.61	2.15	1.57	0.40	1.22	1.29		1.16	1.37		
Total	75.71	107.89	105.95	100.14	103.94	109.56	78.78	108.81	41.20	65.86	107.00	89.27	71.44	110.50	59.04

Reproduced from E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," New York, Reinhold Publishing Corp., 1943.

ratio of major to minor axis of 14 to 1 is calculated. The molecular weight calculated from the dielectric constant data (38,000) was found to be in substantial agreement with that obtained from ultracentrifugal data. The dissymmetry ratio, however, was found to be 8 to 1—a discrepancy as yet unresolved.

It is interesting to note that the average value for the molecular weight, established by independent methods, is twice the value (19,400) calculated by Cohn [33] as the minimum molecular weight from composition.

The dipole moment of zein has a value of 380 debye units; this value, for a protein known to have relatively few ionic pairs, indicates a symmetrical spacing of those present.

Some study has been made of monolayers (monomolecular films) of zein at liquid-air interfaces.[36, 37, 38] It is not as yet possible to interpret this type of work in terms of molecular structure.

Solubility. The solubility behavior of zein is similar to that of other high molecular weight materials. The same types of relations hold true with respect to viscosity and the behavior toward primary and secondary solvents and diluents which tend to cause precipitation if used in excess. A convenient measure of solvent power of a given solvent mixture for zein is the temperature (cloud point or critical peptization temperature) at which the solution separates into two phases. Early work of this nature was done by Galeotti and Giampalmo [39] and Dill.[40] The earlier work however, is not particularly significant, because the type of zein used was not sufficiently well defined and did not correspond in properties to that now available. This method may be used for the investigation of a wide variety of binary and ternary mixtures as well as for pure solvents. In these systems the tolerance for secondary solvents or diluents can be determined directly from these curves by noting the solvent composition at which the curve crosses the desired temperature line. Manley and Evans [41a] have made a very detailed, quantitative study of the solubility of zein in primary, binary and ternary solvent systems. In the latter two cases their data are presented graphically and cover the whole range of solvent composition.

Active solvents for zein require the presence of a highly polar group: carboxyl, hydroxyl, amino, amide or aldehyde. In addition, a proper balance between polar group and hydrocarbon residue is necessary. Unsaturation, particularly of the type present in the benzene or furan rings, tends to increase the solvent power, or conversely to decrease the precipitating tendency of the hydrocarbon residue. In many cases such as the ordinary monohydric alcohols, a certain proportion of water is required to produce solubility at ordinary temperatures. The relationships in the case of a denatured ethyl alcohol (Shellacol), isopropyl alcohol and *n*-butyl alcohol are given in Figure 2. The addition of water to other primary solvents or mixtures of

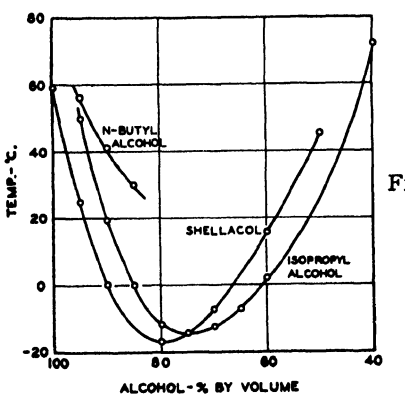

FIGURE 2. Zein solubility in aqueous alcohols.

primary and secondary solvents tends, in general, to lower the cloud point (critical peptization temperature). Solvents may be classified as follows with respect to their effect on zein. It should be noted that all the primary solvents are good secondary solvents as well. That is, the addition of moderate amounts of them to alcohol will produce a zein solvent of lower cloud point. The following tables list the more important solvents but are by no means exhaustive. Manley and Evans [41] have studied the solubility of zein in all concentrations of ethyl alcohol and have determined the critical peptization temperature for absolute alcohol to be 122°.

Acetone-water mixtures are zein solvents within the limits of 53 to 78 per cent by weight of acetone at 20°.

Zein is soluble in aqueous alkalies, but requires a pH of at least 11.5 for solution. It is therefore not dispersed by weak alkalies commonly used for casein and similar proteins. Zein is readily soluble in dilute, aqueous sodium hydroxide (0.02 N-0.2 N); at higher electrolyte concentrations solution is prevented, and protein already in solution is "salted out." The alkaline solutions are subject to rapid deterioration due to chemical reaction: denaturation, peptide and amide hydrolysis.

Table 4. Solvents for Zein

Primary	Strong Secondary	Weak Secondary	Diluents
Methanol	Methylene chloride	Benzene	Petroleum hydrocarbons
Ethanol (aqueous)	Chloroform	Toluene	Turpentine
Isopropanol (aqueous)	Ethylene dichloride	Xylene	Saturated cyclic hydrocarbons
Butanol (aqueous)	Tetrachloroethane	Carbon tetrachloride	*n*-Butyl chloride
tert.-Butyl alcohol	Propylene dichloride	Trichloroethylene	*n*-Amyl chloride
Furfuryl alcohol	Dichloroethyl ether	Tetrachloroethylene	Dibutyl ether
Tetrahydro-furfuryl alcohol	Chlorobenzene	Pentachloroethane	Ethyl acetate
Diacetone alcohol	Glycerol	Butyraldehyde	Butyl acetate
Benzyl alcohol	Dioxane	Acetone	
Cyclohexanol	Dioxolane	Methyl ethyl ketone	
Ethylene glycol	Propylene oxide	Ethyl formate	
Propylene glycol	Formaldehyde	Ethyl acetoacetate	
Diethylene glycol	Acetaldehyde	Dimethyl aniline	
Triethylene glycol	Furfural	Nitromethane	
Methyl "Cellosolve"	Nitropropane		
"Cellosolve"	Nitrobenzene		
Butyl "Cellosolve" (aqueous)			
Methyl carbitol			
Carbitol			
Cresol			
Aldol			
Methyl lactate			
Ethyl lactate			
Butyl lactate			
Acetic acid			
Propionic acid			
Lactic acid			
Formamide			
Butyl amine			
Aniline			

Zein is dispersed in aqueous solutions of a wide variety of surface-active agents, including the alkali, ammonia, or amine soaps of the fatty acids, rosin, sulfonated oils or fatty acids, sulfated fatty alcohols, tall oil and sulfonated tall oil. These solutions are quite sensitive to salting out by means of electrolytes and in most cases are stable only in the pH range where the dispersing agent is in the salt form. Exceptions to this are found in the case of certain sulfated fatty alcohol type dispersing agents.

Plasticizers. Plasticizers for zein must fulfill the same requirements as those described above for zein solvents; that is, they must contain a polar group and a proper balance between polar groups and hydrocarbon residue. While plasticizers

which are satisfactory in all respects have not yet been developed, the following types are suitable for many purposes.

Fatty acids, although of restricted compatibility, may be used either alone or with other substances such as rosin, which are more powerful zein solvents. The compatibility is improved by unsaturation. The saturated series of acids, up to and including caprylic acid, show very good compatibility and plasticizing power.

Glycols and glycol derivatives are excellent plasticizers, but their use is usually limited by their water solubility or volatility. The polyglycols are particularly important and are good plasticizers even where the actual group (hydroxyl) is present in relatively small amounts.

Glycerol and the carbohydrates, while rich in hydroxyl groups, are only moderately good plasticizers. Glycerol alone is completely incompatible with zein. The plasticizing power is enhanced by etherification, the mono ethers and mono esters of glycerol being very satisfactory.

The N-substituted aromatic sulfonamides are among the better plasticizers.

The hydroxy acids and hydroxy esters have excellent plasticizing power. Lactic acid is particularly useful with formaldehyde cured zein, although its practical value is somewhat decreased by its volatility and water solubility. The tartrates, particularly dibutyl tartrate, are applicable to a wide variety of uses.

Other substances which are useful primary or secondary plasticizers are as follows: glycol phthalate, chlorinated hydrocarbons, phenols, amides, amino alcohols, and nitro alcohols as primary plasticizers; chlorinated aromatic hydrocarbons as secondary plasticizers.

Zein is compatible with resins and film-forming substances of the following types:

Highly acidic resins such as rosin, Manila or shellac
Phenolic resins which may also act as curing agents
Nitrocellulose
Glyptal type resins of highly acidic types

These materials in zein solutions tend to extend the material giving gloss and body in coatings and flowing characteristics and decreased cost in plastic compositions.

Zein reacts slowly with formaldehyde unless suitable catalysts are present. The reaction differs greatly from that of proteins containing primary amino groups, in which it is very rapid even in the absence of catalyst. The reaction with zein, which has few or no free amino groups, probably takes place at the amide groups, yielding N-hydroxymethyl derivatives at first, which later condense to some extent to form methylene cross-linkages. The reaction is catalyzed by acids and further promoted under acid conditions, by ammonia or primary amines. The maximum amount of formaldehyde combining with zein has not yet been established. The curing action of formaldehyde increases the tensile strength and elongation of zein, a maximum tensile strength of about 14,000 pounds per square inch being obtainable in the case of films in the absence of plasticizers. The curing reaction improves the water resistance but not beyond that obtainable with other proteins. With films, the minimum water absorption at equilibrium is about 18 per cent.

Zein can be cured by formamide, but at least 30 per cent by weight is required. These cured products, however, tend to become brittle on aging.

While zein is much more stable toward denaturation than most proteins, it does tend to become insoluble when stored in solution. It has been claimed that the gelation of zein solutions is autocatalytic, but the experimental evidence on this point is in conflict. Other accelerating factors are agitation, presence of water, high temperature, and high zein concentration. The reaction may be delayed by avoiding the factors mentioned above, by using acidic substances such as rosin or acetic acid, by using certain chlorinated hydrocarbons as secondary solvents, and by using aldehydes.

In the last case a heat treatment is particularly advantageous.[41b] The instability of zein solutions due to denaturation is to be distinguished definitely from separation into phases or gelation due to the use of insufficiently powerful solvent mixtures.

Zein has been proposed for a number of practical uses. It may be used in lacquers,[42, 43, 44] printing inks,[45] stencil coatings,[46] grease-proof coatings,[47] adhesives,[48] flexible films [49] and plastics.[50, 51, 25]

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Synthetic Resin Adhesives

CHARLES B. HEMMING

Chief Chemist, United States Plywood Corporation

Introduction

The term "plastic plywood" has recently come into being as a result of the fact that modern forms of plywood are bonded with adhesives made from synthetic resins, often called plastic resins. The term, in the true sense, is a misnomer, but is understandable because of the marvelous growth of the plastics industry and because of the way that plastics have caught public fancy. Nevertheless, in order to understand the true function of the adhesive and of the plywood commonly called plastic plywood, we must understand clearly just what properties each component contributes.

Untreated wood is not a plastic material in the true sense, and when properly used, is never permitted to withstand loads anywhere near its elastic limit, so that plastic effects are avoided. Furthermore, it is very rarely, even for special work, bonded with a plastic, or more specifically, a thermoplastic adhesive. Instead, thermosetting adhesives are used, and these are even less plastic than wood.

The best example that can be given to illustrate this is to point out that in a 4′ × 8′ × ¼″ 3-ply panel, there are 29 pounds of wood and only 0.8 pound of synthetic resin adhesive. Plywood is therefore obviously a very distinct material in its own right, and its physical properties are very largely those of the wood of which it is composed and not of the synthetic resin.

This in no way belittles the extreme importance of the synthetic resin, because it can also be safely said that the customer buys a glue line when he buys plywood. Individual veneers are obviously worthless as a material of construction. The plywood exhibits its inherent physical properties only so long as the adhesive used holds it together with a bond stronger than the wood itself. A corollary to this statement is that the durability for conditions of extreme use is largely the durability of the glue bond under those conditions.

Summarizing, the synthetic resin permits the outstanding physical properties which nature built into wood to be used to best advantage. Thus, the two components are perfect complements of each other.

Classification of Adhesives

Plywoods are classified broadly as materials to be used for (1) construction, (2) decoration, (3) combination construction and decoration, (4) packaging, and (5) temporary construction aids. Obviously, these divisions are arbitrary and are based on the ultimate uses. All forms could be bonded with an adhesive sufficiently durable for the most stringent use, but this would penalize economically the lower cost forms which need not have maximum quality.

The adhesives can be classed in a somewhat similar manner, but a more useful classification recognizes the inherent chemical material. There is the broad use classification of primary bond adhesives, and the secondary or assembly adhesives. Primary bond adhesives are those used to form the plywood itself. Secondary adhesives are used in the assembly of finished or semi-finished articles from the plywood. The

more valuable classification dealing with the chemical nature lists the adhesives as phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, interpolymers of any or all of these groups, animal protein, vegetable protein, vegetable, and occasionally combinations of two or more of any of these groups. The animal and vegetable substances naturally are not synthetic in their derivation and are mentioned only for the sake of completeness.

There are other less used and newer adhesives so far not broadly used or economically important. These are vinyl derivatives, styrene derivatives, and vinyl acetates. This last group is thermoplastic, with consequent limited usefulness, although very recently, they have been compounded so that they can be "cross-linked," or made to form copolymers with thermosetting substances to give, in effect, thermosetting properties.

There is still another method of classification, which is important to the plywood manufacturer only. Many of these adhesives can be subdivided as hot-setting, warm-setting or cold-setting. The ranges are broadly 190° to 300° F for the hot-setting material, 120° to 190° F for the warm-setting, and 70° to 120° F for the cold-setting types. This subdivision is particularly applicable to phenol-formaldehyde and urea-formaldehyde resins, examples of which can be had in each range. In the thermoplastic groups, low-temperature products are worthless because of the ease with which they are remelted. In the case of the cross-linked compounds, the more successful ones only fit into the hot-setting range.

The form in which the several adhesives are supplied *varies*. Some of the resins are liquid in themselves. Some are in the form of dispersions in water or organic solvents, or mixtures of water and organic solvents. Some are furnished as dry powders or lumps. Many adhesives contain their own catalyst or require none. Still other forms have a separate catalyst which may be a chemical in solution, a liquid, or a dry powder.

The form in which the adhesives are generally used is a solution of a consistency suitable for spreading on a roller coating machine. A notable exception to this is film glue in the form of a phenol-formaldehyde resin impregnated in a very thin sheet of paper and dried without advancing the cure of the resin. There has been some work done with spray application, and the process is successful, but it entails spray losses and the necessity of filtered mixtures, neither of which is an insurmountable problem, but must be considered. There have been a number of attempts to spread synthetic resin adhesives by dusting or sifting the powder onto the surface. This too has been made to work satisfactorily, but it entails a number of operating difficulties, not the least of which is caking during seasons of high humidity.

The keeping qualities of most of these adhesives are limited for the obvious reason that they are actually resins in an intermittent or arrested stage of formation. Often, the catalyst is not added until just before use as a simple expedient of increasing the storage life of the resin. Notable exceptions to this are the thermoplastic adhesives, which may be said to have indefinite keeping qualities.

The Nature of Adhesion

There is considerable controversy over the exact nature of the adhesive action.* One school of thought views the mechanism as being largely mechanical, wherein small surface irregularities allow the synthetic resin adhesive to grip or be locked securely to the surface adhered. Another group believes that except in the case of very open or porous surfaces, the action is specific; that is, there is a natural affinity between certain substances brought into close contact, possibly explained by the theory of residual valencies. This writer believes that the preponderance of evidence indicates that the effect is almost always a combination of the two phenomena,

* For a detailed discussion see paper on "Cohesion and Adhesion" by J. W. McBain and J. Alexander in Vol. III of this series. J. A.

but that the specific adhesion theory is an extremely important part of the explanation.

There is an additional effect which must be understood in adhering relatively porous materials such as wood. Repeated experiment has indicated that a wide variation in bond strength can be obtained by controlling the degree of penetration of the adhesive into the surface layers. If the adhesive is so disposed that it makes only surface contact, an adequate bond is generally obtained, but one which is near the minimum permissible value. If, on the other hand, the same adhesive is encouraged to penetrate for a short way into the surface layers of the wood without at the same time causing a "starved" glue line, a sharp increase in the bond strength is obtained. This is obviously due to the reinforcing effect of the adhesive that has penetrated. Synthetic resins vary widely in their ability to penetrate to the proper degree to give maximum strength, and the variation appears to be tied in with specific adhesion and the molecular size of the polymer used.

While on the general subject of the mechanism of adhesion, it might be well to comment briefly on some of the very new adhesives that have been successful in adhering widely dissimilar substances such as wood and plastic, and wood and metal. These adhesives almost invariably are two-component materials, compatible with each other, but in which one component adheres preferentially to one surface and the other component to the other. If, in addition, there are wide differences in expansion and contraction coefficients with either temperature or humidity changes, these adhesives must have a sufficiently low modulus of elasticity to avoid development of excessive shear forces within the glue line which may disrupt the glue line, at the same time being high in resistance to plastic flow, at all service temperatures.

Having disposed of adhesives broadly and some of the methods of classification, as well as the mechanism of adhesion, it is now in order to give specific comments on the several types.

Phenol-Formaldehyde Resins

The most widely used and the most important adhesives are based on resins known broadly as phenol-formaldehyde resins. This family obviously includes a considerable array of resins other than those made out of the simple chemical substance phenol; for example, substituted phenols, xylenol, cresol, resorcinol, furfural, and other less common phenolic type compounds capable of reacting with formaldehyde. The family is broadly characterized as producing bonds of extreme resistance to water, weathering, temperature variations, and chemical agents. The glue line is of itself extremely resistant to the attack of micro-organisms and insects. However, strange as it may seem, thoroughly polymerized phenol-formaldehyde resins are so inert that they have no germicidal action; they are incapable of supporting life that might destroy them, because they are either indigestible or do not furnish enough moisture to support the life processes of the organisms.

Phenol-formaldehyde resin adhesives can be obtained which will polymerize over the complete range of temperatures between 70° and 300° F and in the alkaline, neutral, or acid state. Temperatures above 300° F are harmful to wood and are not generally used.

For details of the production of synthetic resins of the phenolic type the reader is referred to appropriate texts on the subject of which there are a few excellent ones. A brief description of the procedure follows.

Approximately equal molecular ratios of phenol and formaldehyde are allowed to condense in a corrosion-resistant reaction kettle under non-refluxing conditions. Either acid or alkaline catalysts may be used, but the reaction is more easily controlled in the presence of alkali. The reaction is exothermic so that, once started, cooling is likely to be necessary for control.

After a few hours' heating, two layers form. The upper layer is water and may be removed by decantation. The lower layer is the resinous result of the condensation, containing some water which may be removed by heating under a vacuum or by spray drying. If vacuum-dried, the resin is cooled in pans and pulverized. The powder is in either case dissolved in alcohol for early type phenolic adhesives. More commonly by adjustment of the condensation reaction, syrups can be made that are miscible with water, although often some sodium hydroxide or alcohol is necessary to insure a stable dispersion. These syrups are sold ready for immediate use or after thinning to the proper consistency. If spray dried with the proper amount of caustic admixed, the newer type powders can also be dissolved in water or in water and alcohol.

Urea-Formaldehyde Resins

This class of resins produces adhesives which are lower in cost than the phenol-formaldehyde types, and for many uses, when properly applied, they give results every bit as satisfactory. As a class, they are less resistant to chemical agents, elevated temperatures, and weather. Nevertheless, bonds made with simple urea-formaldehyde resin adhesives have surprising dry heat resistance up to 170° F and good moist heat resistance up to 150° F. As far as is known, low temperatures are no more harmful to urea-formaldehyde resins than to phenol-formaldehyde resins.

There has been considerable criticism of urea-formaldehyde resins due to their extreme brittleness and the tendency of free films to craze. However, it was pointed out long ago that this undesirable effect was either prevented or greatly retarded by the presence of cellulose. As a result, properly compounded adhesives often have a small amount of cellulose fiber in them. A little deduction indicates that the best guarantee of performance of the urea-formaldehyde glue line is to have an intimate fit between the wood parts so that, in effect, the urea-formaldehyde is intimately mixed with cellulose. It is only when carelessly prepared, thick glue lines are permitted that urea-formaldehyde resins give trouble, or when they are used for purposes to which they are not suited.

This family of adhesives has the surprising ability to withstand relatively enormous degrees of admixture with cellulose and starch of various forms and still produce excellent bonds. Unfortunately, after a certain limit has been exceeded, the deterioration in durability is so great as to make such adjuvants desirable only for lowest cost and lowest quality services. Urea-formaldehyde resins can be obtained that will set anywhere between 70° and 250° F, but catalysis is almost always in a slightly acid medium, preferably in the presence of a buffer. Keeping properties of dry urea-formaldehyde resin powder, even with catalyst added, are surprisingly good, with the result that it has been possible to merchandise an excellent household and shop adhesive for the woodworking industry.

Urea-formaldehyde resin adhesives are produced in much the same manner as phenol-formaldehyde types, with the exception that a two-stage process is used in which dimethylol urea is generally first formed. Urea resins useful as adhesives are furnished as syrupy solutions in water or as spray-dried powders soluble in lukewarm water.

Phenol Urea-Formaldehyde Resins

There is a growing group of interpolymers which have produced very useful adhesives, combining some of the good properties of each class of resins. They have particularly good flow during the early stages of heating, which has been extremely advantageous in low-pressure molding work. These adhesives have the additional advantages of being rather easy to cure and sufficiently durable for all but the most severe uses.

Cross-Linked Resins

Certain vinyl polymers and styrene polymers which are normally thermoplastic can be given the general properties of thermosetting resins by combining them with condensation plastics, or with chemical agents, or both. This family make excellent adhesives for special purposes, their big drawbacks being their relatively high cost and the fact that they are generally sufficiently high in intrinsic viscosity to make the normal spreading solution rather low in solids content, necessitating more than one coat unless special equipment for coating and drying is used. This group of resins has been descriptively called "thermosetting thermoplastics," because they have rather long flow periods, after heat is applied and before infusibility sets in, which allows for any necessary slip of parts during laminating or molding. Furthermore, they produce glue lines of greater toughness than commonly obtained from the more brittle condensation resins such as the urea and phenol-formaldehydes. This has been thought by some to be of advantage in wood parts which must have great resistance to severe vibration or alternating stresses. Unfortunately, fatigue measurements to date have not been conclusive in proving this theoretical advantage.

The so-called cross-linked and copolymer adhesives are for the most part proprietary secrets at the present time or have been classed as "restricted" because of their value to the war effort. Therefore it is not possible to describe their exact nature or their method of manufacture at this time.

Thermoplastic Resins

Thermoplastic resins are little used in the production of plywood, but in the early days of low-pressure molding they were the only ones sufficiently tolerant of the then imperfect techniques to produce sound parts. The most notable of these are polyvinyl acetate and polyvinyl butyral. They have a great affinity for wood, and there is no curing period involved. However, cooling under pressure is a necessary operation. Because these are true thermoplastics, parts so adhered must never be exposed to temperatures approaching the melting point of the glue line. However, yield values have been found to be higher for properly thermoplastic resin-bonded plywood than might be predicted from the melting points of the free resin. This appears to be due to a large component of friction resulting from the normal roughness of wood. As a result, some of the early molded plywood so bonded has shown excellent durability in service.

These resins, like the cross-linked types and some of the copolymers, have a high intrinsic viscosity. Therefore, solutions at spreadable consistency are low in solids, often requiring double and triple coating. This, coupled with their relatively high cost, further serves to decrease their popularity.

General Discussion

It is important and interesting to understand the mechanical effect produced by the glue line in forming plywood. Ordinary dimension stock, or lumber, has the very well known property of expanding and contracting with increase and decrease of moisture content, initially induced by changes in relative humidity. Furthermore, this dimensional change is three-fold in nature and is not uniform. Thus, there is tangential, radial, and longitudinal dimensional change. The end results are generally warping, and the well known tightening and loosening of joints. In extreme cases, cracking and checking are experienced.

Wood is anisotropic; that is, there is a large difference in strength along the grain and across the grain. This variation in strength is remedied in the production of plywood by the simple expedient of crossing alternate plies. Care is exercised in seeing to it that there is just about as much wood running the long way as there is across the panel so that the final panel has about equal strength in both directions.

This equalization could not come into being unless the alternate layers were intimately connected mechanically. This is the function of the adhesive. Modern synthetic resin adhesives with their great strength and resistance to plastic flow have another action. They force the veneers mutually to restrain each other from expanding and contracting with moisture changes. Thus, all but about 10 per cent of the normal dimensional instability of lumber is absorbed in the best grades of multi-ply plywood. Furthermore, this restraining or balancing action retards warping and twisting. Splitting, and for the most part checking, is also reduced, except under very extreme conditions not normally experienced by plywood.

The modern synthetic resin glue line has other interesting properties. Both urea and phenol-formaldehyde adhesives are unsoftened by and are impermeable to greases and oils. Thus, a good glue line has a surprising barrier effect. This barrier action is sometimes a disadvantage. There have been many processes proposed for the impregnation of plywood to achieve various purposes such as resistance to fire, fungus, rot, or to increase hardness. However, even with vacuum and pressure impregnation, the synthetic resin glue lines prevent any worthwhile degree of absorption except in the outer plies and around the edges. The answer, of course, is to impregnate the veneers and then make the plywood from these. A gluing problem may result, but with the wide array of resins currently available, it should not be insurmountable.

There is one barrier action unjustifiably accredited to these synthetic resins based on a mistaken understanding of their nature. The synthetic resins are for the most part so completely water insoluble and unsoftened that they are truly waterproof. The bond that results from their use has the same character. This has led many people to believe that they are also moisture-vapor proof. While there is a slight retarding action, it is so inappreciable that it is better to neglect it and assume that water vapor will pass freely through a synthetic resin-bonded plywood panel.

Improved Wood

Current interest stemming from special war projects is running high in synthetic resin impregnations of wood and veneers. These resins are closely allied to the resins used in producing adhesives, and often, they perform as adhesives in addition to impregnants. However, their principal purpose is to produce changes in the physical properties of the wood.

A number of years ago, the Forest Products Laboratory of the United States Department of Agriculture was casting about for a means of destroying wood's habit of changing dimensions with changes in moisture content. After trying many different chemicals, they found that certain water-soluble forms of phenol-formaldehyde and urea-formaldehyde resins not only gave the best and most reliable results, but produced interesting new properties. The Forest Products Laboratory concentrated their efforts on the phenol-formaldehyde type, calling it "Impreg," whereas the du Pont Company has been successful with the urea-formaldehyde type. Which of the two is to be favored for a given purpose can only be decided by a complete understanding of the needs of the individual problem. The urea-formaldehyde impregnation is odorless, colorless, lower in cost, and somewhat easier to use. However, the phenol-formaldehyde type produces the maximum dimensional stability, and as would be expected, maximum durability and general chemical inertness.

It is pretty generally thought that the dimension stabilizing action results from diffusion of these synthetic resins into the cell walls of the wood where the actual chemical reaction which takes place at the time of polymerization, involves the cellulose molecules.* The end result is that the formerly hydrophilic cellulose molecule becomes hydrophobic like the cured synthetic resin. Having thus destroyed the

* It seems quite likely that structural units above the molecular range may be involved. See paper on "Cellulose" by Wanda K. Farr in Vol. V of this series. J. A.

desire for moisture, and even though the intercellular space may be filled with water, swelling is prevented because the cells will not take up water. Generally, a thorough phenolic resin impregnation will remedy about three-quarters of wood's tendency to take up moisture and thus change dimension. It is interesting to learn that during the impregnation process, the wood is actually swollen beyond its original green state. The polymerization of the impregnating resin in the cells prevents subsequent shrinkage, so that there is also what might be called a mechanical fixation of dimensions.

Naturally, the presence of this hard resin in the cells and in the intercellular spaces changes other characteristics. An increase in surface hardness and a considerable increase in brittleness are noted. While impregnated wood will pick up water by capillary action, the water has none of the effects that are normally expected. Improved weathering, particularly with regard to the prevention of grain raising and checking, is noted, and it is possible to apply good synthetic resin finishes over the impregnation, although one must be sure to see that the type chosen has adequate adhesion. The chemical inertness of the impregnating resins is imparted correspondingly to the impregnated wood, but above all, is the gain in dimensional stability. This is very well illustrated if one will metal-spray a piece of ordinary plywood and a piece of otherwise identical but impregnated plywood by one of the well known metal-spray processes. If these panels are either exposed to the weather or alternately soaked and dried out, it will not be long before the metal film is either all cracked or peeled off or the panel badly warped in the case of the regular plywood, while in the case of the impregnated plywood, the metal film is unaffected.

During the work on wood impregnation, it was noted that the impregnating resin produced a profound softening or plasticizing effect. As a matter of fact, to avoid compression, normal plywood bonding pressures had to be reduced. This phenomenon was the cause of the investigation of the use of high pressures on impregnated, uncured veneers. There results a densified wood designated "Compreg," by the Forest Products Laboratory, having a specific gravity in the vicinity of 1.43, and increased hardness and strength figures practically directly proportional to the increase in density. Furthermore, mechanical hysteresis was found to be amazingly low compared to older phenol-fiber and phenol-fabric, high-pressure laminates. Impact strength was initially unfortunately low, but has since been substantially increased without more than nominal loss in dimensional stability. Lack of dimensional stability in compressed impregnated wood shows up in the form of "springback" or loss of density with time. "Compreg," whether made with phenolic or urea resins, is still rather costly, but with the aid of radio frequency heat for curing and improvements in technique now under study, a new and important structural material for very severe services appears to be on the way.

Radio-Frequency Curing of Adhesives

It might perhaps be in order to add a few comments on the use of radio frequency heat to cure adhesives. As was indicated above, synthetic-resin adhesives can be had which will cure over a wide range of temperatures. Those which cure at room temperature and slightly above have a very short assembly time, which poses several production problems. On the other hand, resins requiring higher curing temperatures are chosen to obtain the advantages of long assembly times, ease of control, low cost and reliability; and there are many structures that are not easily made because of the difficulties attending introduction of heat and maintenance of temperature during cure. Examples are aircraft wing assemblies and thick plywood or laminated constructions. It is in these fields that high radio-frequency electrostatic heating has given the best results and been most worthwhile. This is because the application of heat can be readily localized and controlled and because in the case of thick assemblies, heat is generated simultaneously throughout the structure so that there is no heat transmission problem.

At the present state of the art there are three problems to be faced. First, the adhesive or at least the assembly must be readily susceptible to heating by a radio frequency electrostatic field. Second, the assembly must permit of electrode arrangements with adequate spacing to avoid arc-over with the power required for reasonably fast heating. Third, the assembly must be capable of being properly coupled to the oscillator or generator. This last requirement includes a number of considerations that must be left to the radio engineer, although once the circuit is properly established a trained operator is all that is needed for production.

Choice of adhesive, though not fundamental to success beyond the limits posed by point one above, can make the difference between an erratic and a smooth operation or between an economic and a costly one. For example in the case of wood, an adhesive curing above the boiling point of water may take twice as much energy to set, as would be required if the adhesive cured below the boiling point. This is because water requires relatively large amounts of energy to heat and to evaporate. If boiling can be avoided and required temperature rises can be kept moderate, the time of cure can be shortened or the size of the required equipment can be substantially reduced. However, it is not enough to choose the adhesive that is easiest to cure. The adhesive must have a practical assembly time and yield a bond of adequate durability for the intended service. This field is a study in itself and so far there has been very little published, particularly with regard to how to choose an adhesive or what specific adhesives have been utilized successfully. However, there are now a number of urea- and phenol-formaldehyde adhesives available that give very excellent results.

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Potential Nuclear Energy and Some Consequences of Its Release

Including "The Atomic Bomb"

JEROME ALEXANDER

The separation of the uranium isotopes by gaseous diffusion at the huge plant in Tennessee, was based on the pioneer work of Thomas Graham, father of colloid chemistry. In the course of his work on diffusion, Graham introduced the word "colloid" and the basic nomenclature of colloid chemistry.

". . . it is not in the nature of things for any one man to make a sudden violent discovery; science goes step by step, and every man depends on the work of his predecessors. When you hear of a sudden unexpected discovery—a bolt from the blue as it were—you can always be sure that it has grown up by the influence of one man on another, and it is this influence which makes the enormous possibility of scientific advance. Scientists are not dependent upon the ideas of a single man, but on the combined wisdom of thousands of men, all thinking of the same problem, and each doing his little bit to add to the great structure of knowledge which is gradually being erected." Lord Rutherford.[1]

The general public, and even many scientists, are unimpressed by the announcement of newly found scientific facts or principles, unless obvious consequences directly affect or threaten to affect their personal welfare or localized interests. It is not surprising, therefore, that in the last half century, there was quietly formed by the labors of many scientists in many fields, a nidus of facts and theoretical understanding from which developed with apparent suddenness the awe-inspiring atomic bomb. The object of this brief paper is to trace, in epitome, the main and some collateral developments which led to this striking climax; naturally the last section is limited to parts of such information as has been officially released.

This historical survey considers work in many branches of science and in many countries; but it is not all-inclusive, nor does it attempt to assess the relative importance of individual contributions. That many of the scientists mentioned received, or deserve Nobel Prize awards, speaks for itself; and many prognosticated the "atomic bomb."

Factors involving colloid chemistry emerge here and there, and we may yet find industrial uses for the kind of nucleation developed by subatomic particles in the Wilson "cloud chamber" (C. T. R. Wilson, Nobel Prize, 1927), leading to formation of the strings of colloidal water droplets which appear to the eye as streaks of light. But the changes resulting in the release of nuclear energy occur at a level of material structure listed as being of the first order of complexity in the Table on page 9, of Vol. V of this series; the Appendix of Vol. 5 lists 670 elemental and isotopic nuclei, with their properties (atomic numbers, atomic weights, half life, radiation emitted with nature, and charge and energies, also nuclear moments), prepared by Robley D. Evans as of Jan. 1st, 1943. The Table ends with the transuranic element of atomic number (Z) 93, atomic weight or mass number (A) 239; but for reasons of national security no mention could be then made of neptunium or of plutonium.

The Discovery of Radioactivity

The discovery of x-rays by Wilhelm Conrad Röntgen (Nobel Prize, 1901) in 1895 had tremendous scientific repercussions. I recall how, at that time, one of my professors in chemistry, Dr. L. H. Friedburg, showed us a photograph of his hand, taken with the aid of one of the Crookes' tubes in the laboratory of Prof. R. Ogden Doremus. It was quickly observed that the cathode rays could cause brilliant phosphorescence in many substances; and Henri Antoine Becquerel (Nobel Prize, 1903) began (1896) experiments in this field, an interest inherited from his father, also a professor at Paris, for whom in 1880 he had prepared some crystals of the double sulfate of uranium and potassium, which show a beautiful glow when exposed to light. Seeking a connection between phosphorescence and x-rays, Becquerel placed a number of phosphorescent substances carefully wrapped in black paper, over photographic plates; but on development nothing appeared. Recalling his uranium salt, he exposed some of it to light, and then placed the phosphorescent material, wrapped in black paper, on a photographic plate. Development, following several hours exposure, showed a noticeable photographic effect, which also appeared even when the packet of uranium salt rested on a thin glass plate, designed to prevent possible vapors from reaching the sensitive surface. While Becquerel at first thought that the photographic effect was due to the phosphorescence, he later found that it was just as marked when the uranium salt had been kept in the dark for weeks. Furthermore, he found that all uranium salts as well as uranium metal itself, emit radiations capable of penetrating black paper. He thus revealed the phenomenon we now term "radioactivity," which has since been working as a leaven in many interrelated fields of science.

New Powerfully Radioactive Elements

Marie Skladovska Curie (Nobel Prize, 1903 and 1911), working for her doctor's degree at Paris, began a study of the ability of uranium rays to discharge an electroscope. Trying available salts of uranium, she found that the quantity of radiation is always dependent upon the weight of uranium present, irrespective of the nature of its chemical combination, or external conditions. This led to the notion that *the radiation is an atomic property;* so Mme. Curie examined great numbers of other chemical substances for radioactivity. Thorium was also found to be radioactive. But fortunately Mme. Curie went further—she examined the original minerals (pitchblende, carnotite) from which uranium is derived, and made the epoch-making discovery that they show much *higher* radioactivity than the purer uranium compounds derived from them. This pointed to the fact that the minerals must contain some "impurity" responsible for this excess radioactivity; and with her husband, Prof. Pierre Curie (Nobel Prize, 1903), she began the arduous task of trying to separate and study this potent impurity. A joint paper in Comptes Rendues, July, 1898, "On a New Radioactive Substance Contained in Pitchblende" stated: "We believe the substance we have extracted from pitchblende contains a metal not yet observed, related to bismuth in its analytical properties. If the existence of this new metal is confirmed we propose to call it *polonium,* from the name of the original country of one of us." And on December 26th of the same year there appeared the paper announcing the new element *radium.* "The new radioactive substance contains a very strong proportion of barium; in spite of this its radioactivity is considerable. The radioactivity of radium therefore must be enormous." (Actually, it is about two million times as great as that of uranium.)

As an indication of the speed with which the import of these discoveries spread, consider what Sir Ernest Rutherford (Nobel Prize, 1908) said in his article on "Radioactivity" in Encyclopedia Britannica, Vol. 22, p. 802 (11th ed., 1910):

"Experiments on the evolution of heat from radium and its emanation have brought to light the enormous amount of energy accompanying the transformation of radioactive matter where particles are emitted. For example, the emanation from one gram of radium in equilibrium with its products emits heat initially at the rate of about 90 gram calories per hour. The total heat emitted during its transformation is about 12,000 gram calories. Now the initial volume of the emanation from one gram of radium is 0.6 cubic millimetres. Consequently one cubic centimetre of emanation during its life emits 2×10^7 gram calories. Taking the atomic weight of emanation as *222*, one gram of emanation emits during its life 2×10^9 gram calories of heat. This evolution of heat is enormous compared with that emitted in any known chemical reaction. There is every reason to believe that the total emission of energy from any type of radioactive matter during its transformation is of the same order of magnitude as for the emanation. The atoms of matter must consequently be regarded as containing enormous stores of energy which are only released by the disintegration of the atom."

In order to understand the difficulties faced by the Curies in making their important discoveries, the following paragraph is quoted from "Madame Curie—A Biography," by Eve Curie, her daughter (Eng. trans. by Vincent Sheean—Doubleday, Doran & Co., Inc., 1937):

"It was necessary, of course, to buy this crude material and pay for its transportation to Paris. Pierre and Marie appropriated the required sum from their very slight savings. They were not foolish enough to ask for official credits. . . . If two physicists on the scent of an immense discovery had asked the University of Paris or the French government for a grant to buy pitchblende residues they would have been laughed at. In any case their letter would have been lost in the files of some office, and they would have had to wait months for a reply, probably unfavorable in the end. Out of the traditions and principles of the French Revolution, which created the metric system, founded the Normal School, and encouraged science in many circumstances, the State seemed to have retained, after more than a century, only the deplorable words pronounced by Fouquier-Tinville at the trial in which Lavoisier was condemned to the guillotine: "The Republic has no need for scientists." (pp. 166-7)

Development of the Nuclear Theory of Atomic Structure

When Ernest Rutherford entered the Cavendish Laboratory at Cambridge (Eng.) in 1895, he began work on the ionization of gases by x-rays, and on reading Becquerel's paper made a systematic examination of uranium radiations. He found two types of radiation: one (α-rays) produced intense ionization but was absorbed in a few centimeters of air; the other (β-rays) produced less ionization but was more penetrating. In 1898, Villard discovered the still more penetrating γ-radiation, a hard type of x-ray. In that same year at McGill University (Montreal) Rutherford found that thorium gives off an "emanation," which could pass through paper but was stopped by a thin sheet of mica. The emanation could be absorbed on substances and made them radioactive. About this time, (1903) Sir William Ramsay (the Nobel Prize, 1904, went to Lord Rayleigh, with whom Ramsay was associated in the discovery of argon) showed that helium is continuously formed in radioactive minerals in quantities sufficient to be recognized spectroscopically, and that it represents another gaseous product of the radioactive transformations—the α-particles are helium nuclei carrying two positive charges.

Frederick Soddy investigated the chemical properties of the successive products of radioactive transformations and noticed that there is often a simple relation between the positions in the periodic table of the original and final elements involved in a radioactive disintegration series; and about the same time Dr. A. S. Russell, Prof. K. Fajans, and Dr. Soddy announced the "displacement law"—when a substance emits an α-particle (helium nucleus) it *moves two places down* in the atomic table, and when it emits a β-particle (electron) it *moves up one place,* in the table. In 1906 Boltwood observed that his newly discovered radioactive element ionium is chemically so similar to radium that no known chemical process would separate their salts, if mixed. This and other similar facts led Soddy to state (1910): "These

regularities may prove to be the beginning of some embracing generalization, which will throw light, not only on radioactive processes, but on elements in general and the Periodic Law . . . Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several different atomic weights, or that any atomic weight is not merely a mean number." Later it was shown that U^{235} loses 8 α-particles to become Pb^{206}, while Th^{232} loses six α-particles to become Pb^{208}. (Theodore W. Richards of Harvard received the Nobel Prize, 1914, in recognition of his accurate determinations of the atomic weights of many elements, in the course of which he found marked differences in the atomic weight of lead from different sources.) Soddy further wrote: "The same algebraic sum of the positive and negative charges in the nucleus when the arithmetical sum is different, gives what I call 'isotopes' or 'isotopic elements' because they occupy the same place in the periodic table. They are chemically identical, and save only as regards the relatively few physical properties which depend upon atomic mass directly, physically identical also." * Soddy received the Nobel Prize in 1921.

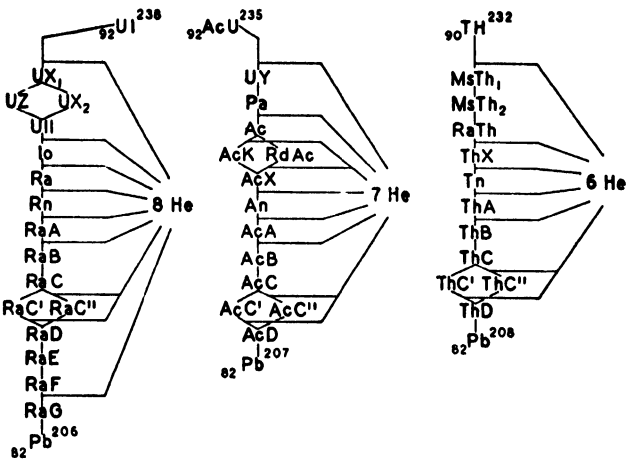

FIGURE 1. The radioactive series.†

Jean Servais Stas, a great Belgian chemist noted for his painstaking determinations of atomic weights, had written (about 1865): "I have arrived at the absolute conviction, the complete certainty, so far as is possible for a human being to attain to certainty in such matters, that the law of Prout is nothing but an illusion, a mere speculation definitely contradicted by experience." (It must be noted, however, that shortly before his death in 1891, he was led, by noting the close approximation to integers shown by a number of atomic weights when hydrogen is taken as unity, to remark: "Il faut croire qu'il y a quelque chose la-dessous.") In 1932 Soddy wrote: "After many vicissitudes and the most convincing apparent disproofs, the hypothesis thrown out so lightly by Prout, an Edinburgh physician, in 1815, has, a century later, become the corner-stone of modern theories of the structure of atoms. There is something surely akin to if not transcending tragedy in the fate that has overtaken the life work of that distinguished galaxy of nineteenth century chemists, rightly revered by their contemporaries as representing the crown and perfection of accurate scientific measurement. Their hard won results, for the moment at least, appear as

* Heavy water and deuterium were then unknown.

† From Goodman and Evans, *loc. cit. infra.* A. V. Grosse, E. T. Booth and J. R. Dunning describe the fourth ($4n + 1$) radioactive series in a paper in *Physical Review* (1941), *59*, 322-3.

of little interest and significance as the determination of the average weight of a collection of bottles, some of them full and some of them more or less empty."

Atomic Structure and Empty Space

In 1905 Philipp Lenard received the Nobel Prize because, in connection with cathode ray experiments with Heinrich Hertz, he had found that the rays could pass through a window of thin aluminum foil, and still retain sufficient power to cause fluorescence and phosphorescence. He concluded that the atoms in the foil must have quite an open structure * with large spaces between them, and also that in atoms might have spheres of positive and negative electric charges. Shortly thereafter, Sir J. J. Thomson (Nobel Prize, 1906) developed this notion and calculated how negative electrons would be distributed in a sphere of positive charge; and this threw interesting light on the fundamental nature of the periodic table.

The Nuclear Atom

Rutherford had observed the scattering of α-particles, and his assistant, Dr. E. Geiger had found that in thin pieces of heavy metal the scattering is generally small, of the order of one degree. Rutherford set Drs. Geiger and E. Marsden to work to see whether, by striking atoms, any α-particles could be scattered through a large angle; and a few days later they excitedly reported that they had found some α-particles *coming backwards*. "It was almost as incredible," said Rutherford later, "as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration I realized that this scattering backwards must be the result of a single collision, and when I made calculations I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus. It was then that I had the idea of an atom with a minute massive centre carrying a charge. I worked out mathematically what laws the scattering should obey, and I found that the number of particles scattered through a given angle should be proportional to the thickness of the scattering foil, the square of the nuclear charge, and inversely proportional to the fourth power of the velocity. These deductions were later verified by Geiger and Marsden in a series of beautiful experiments." [1]

Since α-particles could go very close to the nucleus and still be scattered normally, the nucleus must be very tiny, and the magnitude of the nuclear charge in this case was about 100 times the charge of the electron, *e*. "Geiger and Marsden examined the scattering in different elements and found that the amount of scattering varied as the square of the atomic weight. This result was rough but quite sufficient: it indicated that the charge on a nucleus was roughly proportional to the atomic weight." [1]

Thus was born the theory of the nuclear atom.

The relation between nuclear charge and atomic number was taken up by Henry G. Mosley, whose death at Gallipoli in 1915, at the early age of 28, was consequent upon the unwise drafting of highly trained men, and was thus both a calamity and a disgrace. Using a Bragg crystal spectrometer (Sir William H. Bragg, and his son and collaborator, Sir William Lawrence Bragg; Nobel Prize, 1915), Mosley discovered a direct correlation between the wave lengths of x-rays emitted from tubes where different metals were used as targets, and the atomic number of the metal. The x-ray spectra varied uniformly and regularly, being all similar but shifted in frequency in passing from one element to the next; for they are dependent upon electrons circulating about the nucleus, whose net positive charge he supposed to be identical with the atomic number. This was later proven by Sir James Chadwick.

* If the proton nucleus of a hydrogen atom be represented by a mustardseed shot in New York, the circulating electron would, on the same scale, be represented by a pea in

Then Dr. Niels Bohr (Nobel Prize, 1922) developed his quantum theory of spectra and the arrangement of electrons in the outer atom, referred to by Rutherford as one of the greatest triumphs of the human mind. Within 10 years all the main features of optical spectra were understood, largely helped by applications of wave mechanics by Werner Heisenberg (Nobel Prize, 1932), Edwin Schrödinger (Nobel Prize, 1933), and P. A. M. Dirac (Nobel Prize, 1933).

Atomic Transmutation, the Alchemists' Dream, Experimentally Demonstrated

"The discovery of the disintegration and transmutation of stable elements by controlled experiments is attributed to the great experimental genius, Sir Ernest Rutherford. Outsiders might say the discovery was an accident, but to those who knew him well it was the result of a long series of well-planned experiments. True, he did not predict the phenomenon and then discover it, but his long experience with radioactivity and his keen insight enabled him to recognize the meaning and importance of the phenomenon when it was first observed. Due credit must also be given to the admirable work of his collaborators and to experimenters in other laboratories who have since carried the work much further." (Dr. Harvey E. White, in "Classical and Modern Physics" p. 564, D. Van Nostrand Co., 1940.)

In 1919 Rutherford made the astounding discovery that when light atoms are bombarded by α-particles shot out from radioactive material at very high speeds, scintillations could be observed which, when nitrogen gas was bombarded, struck out 40 centimeters or more in the Wilson cloud chamber. By passing these new rays through a magnetic field and observing their deflection, Rutherford found that they had the mass and charge of protons, that is, they were hydrogen nuclei. His explanation was that the helium nucleus (α-particle) enters the nucleus of a nitrogen atom and remains there, but forces the nitrogen nucleus to eject a proton; so that the net result is a nucleus with a charge of +8 and a mass of 17, that is, the nucleus of one of the isotopes of oxygen. In present day notation this is written thus:

$$_2He^4 + {}_7N^{14} \rightarrow {}_8O^{17} + {}_1H^1$$

It is believed that prior to the ejection of the proton there exists temporarily the highly unstable nucleus of $_9F^{18}$, an isotope of fluorine not found in nature. Atomic transmutation, the alchemist's dream, had thus become an experimentally demonstrated reality.*

Discovery of the Neutron

The discovery of the neutron, a subatomic particle with the mass of a proton but without external charge, by Sir James Chadwick (Nobel Prize, 1935), opened the way to an understanding as to how the heavy proton and the agile electron can be associated in atomic nuclei. The fact that, under sufficient excitation or impact, electrons (β-rays) and also positrons may emerge from atomic nuclei, is as yet without complete explanation; but Rutherford suggested that, within the confines of the nucleus, where the forces between particles are enormous and where the particles are at relatively close grips, protons may change to neutrons and *vice versa*. The positron had been discovered (1932) by Carl David Anderson (Nobel Prize, 1936); and P. A. M. Dirac predicted that if a high frequency γ-ray (a high energy photon) were to pass near enough to an atomic nucleus, the powerful nuclear field would "annihilate" the γ-ray, and "create" a pair of particles, an electron and a positron. This phenomenon, known to physicists as ***pair production,*** was soon observed by

* Of Rutherford some scientific wag wrote:
He made plain the invisible;
He broke up the indivisible;
He changed the immutable;
And he unscrewed the inscrutable.

P. M. S. Blackett and others, using γ-rays emitted by Thorium C″. There is no room here for further discussion of these interesting and important matters, and others like the function of the mesotron. The reader must consult recent special books covering these questions; no doubt the end of the war will release much new information for publication.

Demonstration of Isotopes

Just prior to World War I (1912), Sir J. J. Thomson, while studying the relative masses of various elements by noting to what extent their positive ions were deflected in the electric and magnetic fields of his recently developed mass spectrograph, observed that neon gave two parabolas, one corresponding to particles with mass 20, the other, a much fainter one, to particles with mass 22, indicating the presence of two kinds of neon atoms. In 1919, following the end of that war, Francis William Aston (Nobel Prize, 1922), using improved apparatus, not only confirmed Thomson's views as to neon, but also reported the discovery of isotopes of elements in a steady stream. K. T. Bainbridge and A. J. Dempster are also well known workers in this field. Speaking of the high accuracy of recent work, Aston stated (1936) that it is important in the nuclear chemistry of the future, dealing with artificial transmutations. "Armed with such knowledge the nuclear chemists, I am convinced, will be able to synthesize elements just as ordinary chemists synthesize compounds, and it may be taken as certain that in some reactions subatomic energy will be liberated." [1]

Discovery of Induced Radioactivity

In 1934, Jean Frederic Joliot and his wife Irene Curie-Joliot (Nobel Prize, 1935), while bombarding aluminum with α-particles from polonium, found that even after the polonium emitter has been removed, the aluminum still continued to emit radiation—it had become radioactive. What happened may be understood from the following:

$$ {}_2He^4 + {}_{13}Al^{27} \rightarrow {}_{15}P^{30} + {}_0n^1 $$
$$ \searrow {}_{14}Si^{30} + {}_1e^0 $$

The entering α-particle had changed the aluminum into an unstable isotope of phosphorus with the ejection of a high speed neutron; the phosphorus nucleus gradually changed into a stable isotope of silicon, with the emission of a positron. By dissolving the radiated aluminum in HCl, adding some ordinary inactive phosphorus salt, and then carrying out an ordinary group separation, the radioactivity followed the phosphorus.

In 1932 Ernest O. Lawrence (Nobel Prize, 1940) had announced the cyclotron, described in Vol. V of this series, pp. 373-380; one instrument, in use a few years ago, produced deuterons with an energy of 16 Mev and α-particles of 34 Mev, and a 100 million electron-volt machine was in course of construction. Following announcement of the Curie-Joliot's discovery, Lawrence bombarded sodium with 2 Mev deuterons from his cyclotron, and found that it became radioactive. The radiosodium formed has a half-life of only 15 hours; it transforms into a stable isotope of magnesium, giving off an electron and a γ-ray. The table of Robley D. Evans, published in Vol. V of this series, lists the hundreds of synthetic isotopes that have been recognized up to 1943. Two of those omitted from this table, namely neptunium and plutonium, will be referred to later on.

The cyclotron paper in Vol. V indicates how, when a high speed deuteron from the cyclotron smashes into a beryllium nucleus, an unstable, radioactive isotope of boron is formed, which transforms into a stable isotope of boron by ejecting a neutron of 21 Mev. Unstable nuclei are capable of undergoing *multiple* and also *branch disintegrations.* Thus boron when bombarded by protons, forms an unstable

carbon nucleus, ${}_6C^{12}$, which breaks down in steps to give three α-particles (helium nuclei). And when lithium is bombarded by deuterons, the unstable ${}_3Li^6$ formed may break down either into ${}_3Li^7 + {}_1H^1$, or into ${}_2He^4 + {}_2He^4$.

Nuclear Fission

Soon after Chadwick had discovered the neutron, Enrico Fermi (Nobel Prize, 1938) made a number of new radioactive isotopes by exposing various elements to this uncharged missile. Usually the nucleus would capture the neutron, and often the atom would return to a stable state by emitting a β-ray, thereby yielding an element having an atomic number one unit higher in the periodic table than the parent atom. Fermi wanted to see what would happen in the case of uranium, last element in the atomic table, with an atomic number of 92. After prolonged exposure to neutron bombardment, the activity showed the existence of particles with *four* half-lives, with indications of others, while uranium has only *three* isotopes. This led to the notion that one of the supernumerary activities might be due to a newly formed *transuranic* element 93, which ought to appear in the periodic table in the same column as Mn. So the irradiated uranium was dissolved with a manganese salt, and the Mn was precipitated as MnO_2, which carried with it part of the 13-minute and 90-minute activity. Many scientists took up the quest for transuranic elements. Otto Hahn, and F. Strassman made careful chemical separations of the dissolved irradiated uranium, and were astonished to find radioactive atoms belonging to a number of different elements, mostly those about the center of the periodic table. The results were passed to Prof. Niels Bohr (then at Princeton University), reaching him at a meeting of the American Philosophical Society, and many nuclear physicists attending the meeting confirmed the results (see *Physical Review*, Jan. 15th and Feb. 15th, 1939). H. D. Smyth states:[2] "Just before Bohr left Denmark two of his colleagues, O. R. Frisch and L. Meitner (both refugees from Germany), had told him their guess that the absorption of a neutron by a uranium nucleus sometimes caused that nucleus to split with the release of enormous quantities of energy, a process that soon began to be called nuclear 'fission.'" (1.53) Smyth states that by June, 1940, it was definitely and generally known that the fission of uranium could be produced by fast or by slow (so-called thermal) neutrons; specifically, that thermal neutrons caused fission of one isotope, U^{235}, but not the other, U^{238}, and that fast neutrons had a lower probability of causing fission in U^{235} than thermal neutrons. ". . . The principle of operation of an atomic bomb or power plant utilizing uranium fission is simple enough. If one neutron causes a fission that produces more than one new neutron, the number of fissions may increase tremendously with the release of enormous amounts of energy."[2]

Before considering further details regarding the atomic bomb, as made public by the Smyth Report, let us consider whence come the huge amounts of energy released by nuclear fission.

The Relation Between Mass and Energy

About the end of the last century Hendrik Antoon Lorentz (Nobel Prize, 1902) in developing an electron theory of matter, assumed that the mass of an electron increases with increase of its velocity according to the following equation:

$$m = \frac{m_0}{1 - \left(\frac{v}{c}\right)^2}$$

where m is its mass when moving, m_0 its mass when at rest, v its velocity, and c the velocity of light. In this equation if $v = c$, the denominator becomes 0, and the value of m becomes infinity. This leads to the view that no material body can travel with

the speed of light.* Measurements on electrons emitted at high speeds from radioactive elements indicate that those with velocities of 1% the velocity of light (*i.e.*, 1,860 miles per second) showed no appreciable increase in mass. At 50% the velocity of light the mass increased 15%, while at 99% the velocity of light it increased more than seven times its mass when at rest. Albert Einstein (Nobel Prize, 1921) also derived the same equation from his restricted theory of relativity. Einstein also derived what is known as the *mass-energy equation,*

$$E = mc^2$$

E being the energy equivalent of mass, c the velocity of light, and m the mass. This means that one pound of matter, *if* it could be *entirely* converted into energy, would yield $1 \times (186{,}000 \times 5{,}280)^2$ foot-pounds of energy, or nearly 11½ billion kilowatt hours of energy, an amount nearly equal to the total monthly output of the electric power industry in U. S. A., as of 1939. In the fission of the U^{235} nucleus only about one tenth of one per cent of the total mass-energy is released, *i.e.*, 11½ million kilowatt hours.

Under the heading *"Experimental Proof of the Equivalence of Mass and Energy,"* H. D. Smyth states (1.38): "Gradual improvements in high voltage technique made it possible to substitute artificially produced high-speed ions of hydrogen or helium for natural alpha particles. J. D. Cockcroft and E. T. S. Walton in Rutherford's laboratory were the first to succeed in producing nuclear changes by such methods. In 1932 they bombarded a target of lithium with protons of 700 kilovolts energy and found that alpha particles were ejected from the target as a result of the bombardment. The nuclear reaction which occurred can be written symbolically as

$$_3Li^7 + {}_1H^1 \rightarrow {}_2He^4 + {}_2He^4$$

where the subscript represents the positive charge on the nucleus (atomic number) and the superscript is the number of massive particles in the nucleus (mass number). As in a chemical equation, quantities on the left must add up to those on the right; thus the subscripts total four and the superscripts eight on each side.

"1.39. Neither mass nor energy has been included in this equation. In general, the incident proton and the resultant alpha particles will each have kinetic energy. Also, the mass of two alpha particles will not be precisely the same as the sum of the masses of a proton and a lithium atom. According to our theory, the totals of mass and energy taken together should be the same before and after the reaction. The masses were known from the mass spectra. On the left ($Li^7 + H^1$) they totalled 8.0241, on the right (2 He^4) 8.0056, so that 0.0185 units of mass had disappeared in the reaction. The experimentally determined energies of the alpha particles were approximately 8.5 million electron volts each, a figure compared with which the kinetic energy of the incident proton could be neglected. Thus 0.0185 units of mass had disappeared and 17 Mev of kinetic energy had appeared. Now 0.0185 units of mass is 3.07×10^{-26} gram, 17 Mev is 27.2×10^{-6} ergs and c is 3×10^{10} cm/sec. If we substitute these figures into Einstein's equation, $E = mc^2$, on the left side we

* In "Nature," November, 1913, F. Soddy suggested that while the principle of relativity indicates that relative velocities greater than that of light are physically impossible, yet there is an actual possibility of observing in nature a relative velocity considerably greater. Thus if two β-particles are shot out by a radioactive body in opposite directions each having a velocity of nine-tenths that of light, their actual relative velocities would be 1.8 c. Regarding this, E. Cunningham ("Relativity and The Electron Theory," Longmans, Green & Co., London, 1915) states: (p. 40) "This is quite true, and the principle of relativity has nothing to say against it. The principle maintains that a velocity greater than c *relative to the observer* cannot be observed. . . . The position is not that velocities greater than c are not conceivable, but that real bodies become illusory in observation if they are conceived to be moving faster than light. We shall also see later that the electrical constitution of matter seems to indicate that a body would suffer dissolution if it were accelerated so that its velocity were made greater than c."

have 27.2×10^{-6} ergs and on the right side we have 27.6×10^{-6} ergs, so that the equation is found to be satisfied to a good approximation. In other words, these experimental results prove that the equivalence of mass and energy was correctly stated by Einstein." [2]

Source of the Sun's Radiant Energy

The energy received by the earth from the sun, according to C. G. Abbott, is about 1.7 H.P. per sq. yd. (1.47 kw per sq.m.). This indicates an emission by the sun's surface 7.88×10^4 H.P. per sq. yd. (6.79×10^4 kw per sq.m.), enough to melt 39.6 ft. of ice or to vaporize 5.92 ft. of water per minute. Together, the planets receive less than $\frac{1}{120}$ of one millionth part of this tremendous energy, which the sun has been pouring out for billions of years. Apart from the fact that solar temperatures enormously exceed those of any known chemical reaction, a sphere of coal the size of the sun, burning in pure oxygen, would last only about 6,000 years. The notion that meteoric matter, falling into the sun, is a material factor in maintaining its heat, has long been dismissed, as has also the notion of Helmholtz that solar contraction can account for maintenence of solar heat. The discovery of radioactivity, however, opened the door to a new vista, and R. A. Sampson, writing in Enc. Brit., 11th ed., 1910, Vol. 26, p. 88, remarked: ". . . if the sources of energy within the atom can be drawn upon, there is here an incalculable source of heat which takes the cogency out of any calculation respecting the sources of maintaining the sun's radiation. An equivalent statement of the same conclusion may be put thus: supposing a gaseous nebula is destined to condense into a sun, the elementary matter of which it is composed will develop in the process into our known terrestrial and solar elements, parting with energy as it does so."

In the A.A.A.S. Bulletin for September, 1945, there is reprinted part of a criticism, by Professor T. C. Chamberlin (Univ. of Chicago), of views as to the age of the earth advanced (1897) by Lord Kelvin on the assumption that the Helmholtz contraction theory is valid. See *SCIENCE*, Vol. 9, (1899) pp. 666-74, 704-11 for Kelvin's address, and Vol. 9, 889-901; Vol. 10, 11-18, for Chamberlin's reply, in the course of which he wrote:

"What the internal constitution of the atoms may be is yet an open question. It is not improbable that they are complex organizations and the seats of enormous energies. Certainly, no careful chemist would affirm either that the atoms are really elementary or that there may not be locked up in them energies of the first order of magnitude. No cautious chemist would probably venture to assert that the component atomecules, to use a convenient phrase, may not have energies of rotation, revolution, position and be otherwise comparable in kind and proportion to those of a planetary system. Nor would he probably feel prepared to affirm or deny that the extraordinary conditions which reside in the center of the sun may not set free a portion of this energy. The Helmholtzian theory takes no cognizance of latent and occluded energies of an atomic or ultra-atomic nature."

H. A. Bethe has advanced a theory (Astrophysical Jour., 1940, *92*, 118), now generally accepted as reasonable, that the heat radiation of the sun is mainly due to a series of nuclear transformations which may be indicated thus:

(1) $_6C^{12} + {}_1H^1 \longrightarrow {}_7N^{13}$
(2) $_7N^{13} \longrightarrow {}_6C^{13} + {}_1e^0$
(3) $_6C^{13} + {}_1H^1 \longrightarrow {}_7N^{14}$
(4) $_7N^{14} + {}_1H^1 \longrightarrow {}_8O^{15}$
(5) $_8O^{15} \longrightarrow {}_7N^{15} + {}_1e^0$
(6) $_7N^{15} + {}_1H^1 \longrightarrow {}_6C^{12} + {}_2He^4$

The final result of these changes is the transformation of hydrogen into helium and positrons ($_1e^0$), with the release of about thirty million electron volts. We know nothing of what is happening within the body of the sun, but to maintain its high radiation, the sun must be losing mass at the rate of about 4,000,000 tons per second.

ince the total mass of the sun is estimated to be 2.2×10^{27} tons, it would require bout a million years for the sun to lose one ten millionth of its mass, provided that othing fell into it.

So terrific is the development of solar energy, that huge bursts of brilliantly eated matter are being continually projected from the sun's surface, some of these prominences" jumping hundreds of thousands of miles outward. During the clipse of 1919 there was seen a gigantic prominence resembling an ant-eater, 350,000 iles from snout to tail. While still under observation it rose about 475,000 miles bove the sun's surface. We may give here a comparison between nuclear and hemical heat:

4 grams H + 32 grams O = 36 grams H_2O + 136,000 calories
1 gram H + 7 grams $_3Li^7$ = 8 grams $_2He^4$ + 5 billion calories

The annihilation energy of one electron is 0.5 Mev, while that of one mass unit is 931 Mev.

Origin of the Solar System and Age of the earth

In Vol. I of this series (1926) W. D. MacMillan outlined the Planetesimal Hypothesis of T. C. Chamberlin and F. R. Moulton, which in epitome is that some ten or twenty billion years ago the sun passed sufficiently close to another star to raise vast tides and to stimulate greatly the sun's internal activities, so that streams of matter were ejected, both towards and away from the visiting star. While most of this matter fell back into the sun, about ½th of one per cent of the sun's mass remained swirling about the sun, all in one direction. The larger masses served as nuclei upon which the smaller masses collected into the planets and their satellites. This accounts well for the fact that the planets and most all satellites move in the same direction and approximately in the plane of the ecliptic. The few retrograde bodies may represent "captures."

This hypothesis has been attacked by Lyman Spitzer, Jr. (Astrophys. Jour., 1939, **90**, 675-688), who holds that material ejected from the sun or a star by tidal action or by collision, would be too hot to condense to form separate bodies, but would dissipate into space. In the same journal (March, 1945), C. S. von Weizsaker advanced another hypothesis, and still others are discussed in "The Observatory," August, 1945; but there is no agreement as to the origin of the solar system. Astrophysicists face conditions not found on our earth; thus in some stars, *e.g.*, the faint companion of Sirius, atomic fragments are so closely packed, compared with matter as we know it, that a single quart has an estimated mass of, say, 40 tons. The density of atomic nuclei is much greater; according to one estimate, it is billions of grams per cubic centimeter.

There is more agreement, however, as to the probable age of the earth. According to Prof. Louis B. Slichter, (Bull. Geological Soc. of Am., Apr. 1, 1941 pp. 562-599), geophysicists recognize three major divisions in the earth: (1) a heavy *core* with a mean density of 10.7, apparently fluid and possibly consisting of nickel-iron; (2) a thick but much lighter *mantle* (density, 3.4 to 5.7) overlying the core and composed of ultrabasic rocks, the iron content increasing inwards; (3) above the mantle lies the thin *crust* (total thickness ca. 20 to 60 kilometers), consisting of several layers of lighter rocks. "It has long been recognized that the radioactive heat being generated in rocks is large enough to be a major influence in the earth's thermal history. . . . Radioactive determinations of old crustal rocks indicate that the time which has elapsed since the solidification of the oldest rocks is about 1½ to 2 billion years." (p. 567.)

Since $_{92}UI^{238}$, $_{92}AcU^{235}$, and $_{90}Th^{232}$ are continuously degenerating at constant speed into $_{82}Pb^{206}$, $_{82}Pb^{207}$, and $_{82}Pb^{208}$, respectively, with the respective liberation of 8, 7, and 6 helium nuclei, geophysicists use an "age equation" of the following form:

$$\text{Age} = \frac{\text{Amount of disintegration product}}{\text{Rate of production of disintegration product}}$$

"Age" means the time elapsed since the final solidification of the rock or mineral containing the radioactive element. Some helium is apt to be lost, but the helium method, with rocks preceding the Cambrian, indicates an age of 1,830 million years, which about checks with a lead age ratio as determined on a uraninite found in Russia. (For further information, see the paper by Clark Goodman and Robley D. Evans on "Age Measurements By Radioactivity," in Bull. Geological Soc. of Am., April 1st, 1941, pp. 492-541.)

For several years past, automatic recording of the radioactivity of geological strata by measurement of gamma ray activity, which passes readily through well-casings, has been used to give a "log" of relative intensities useful in oil-field engineering. In general, shales have a higher emission than sandstones or limestones. A neutron curve may also be obtained by bombarding the formation surrounding the well bore, and recording the effect produced by measurement with an ionization chamber. See Tech. Pub. No. 1923, by Warren J. Jackson and John L. P. Campbell, Am. Inst. Min. and Met. Engrs., (February, 1945), which gives some practical aspects, and also a bibliography of thirty papers.

Volcanism and Nuclear Energy

At Paricutin, in Mexico, we have now been witnessing the birth and formation of a sizable volcanic cone on what had previously been flat farming country. This manifestation, however, is mild compared with what happened at Krakatoa; and Prof. Wilbur A. Nelson estimated that during the Cretaceous period a volcano in Tennessee spat up over fifty cubic miles of material, part of which settled down to form bentonite beds extending nearly 500 miles north and south and nearly 400 miles east and west of the crater.

At Krakatoa, a small volcanic island in Sunda Strait between Java and Sumatra, a prehistoric explosion had blown the volcano away, leaving an outer ring of islands outlining the huge crater. Later, the main cone, built up by subsequent eruptions, rose over 2,600 feet above sea level. About 1877 earthquakes began, and on Aug. 26th, 1883 there started a series of gigantic explosions, lasting three days, which blew away the entire north and lower portion of the island, leaving a bare vertical cliff which revealed the interior of the volcanic cone Rakata, and replacing heights of from 300 to 1,400 feet with submarine cavities 1,000 feet deep in some places. The huge amount of matter cast out to an estimated height of 17 miles, gave off a colloidally dispersed dust cloud which travelled to Europe, Asia, Africa, North and South America, and throughout Australasia, reaching northern Scandanavia and the Cape of Good Hope, and causing brilliant sunsets for several years. Pumice floated hundreds of miles, and ocean waves, some 50 feet high, reached Cape Horn (nearly 8,000 miles) and perhaps the English Channel (11,000 miles). Upwards of 36,000 people were killed, and the sound of the explosions carried nearly 3,000 miles, being heard in the Philippines, Ceylon, and in South and West Australia—by far the greatest distance sound has been known to travel. On the morning of Aug. 27th, a most powerful explosion originated an atmospheric wave which, being reflected or reproduced at the antipodes to Krakatoa, "was observed not fewer than seven times at many of the stations, four passages having been those of the wave travelling from Krakatoa and three those of the wave travelling from its antipodes, subsequently to which its traces were lost." (Sir R. Strachy).

The comparatively recent explosive eruption of Mont Pelé (Martinique) was much milder and more akin to the atomic bomb. On April 25th, 1902 there was a discharge of ashes, and a heavy flow of lava on May 2nd and 3rd. On May 8th a sudden explosion tore away the whole side of the mountain (the gash was clearly

evident in 1939), and released a *nuée ardente* (R. Zsigmondy) supposed to have been a cloud of superheated steam, gases, and colloidally dispersed rock. About 40,000 persons perished, and all ships in the harbor, except the "Roddam," were destroyed. Metal work on the "Roddam" was melted by the blast, but a prisoner confined in a dungeon cell in the town was later found alive, though spoons nearby his cell had melted. This bespeaks the intense but short-lived heat. It is known that under heat and pressure water "dissolves" in silicates, and the effects may have been due to the explosive release of such a superheated mass, with atomization of the rock.

Dr. Leason H. Adams, Director of the Geophysical Laboratory, Carnegie Institution of Washington, has kindly prepared for me the following note on a theory of volcanism based on radioactivity, which is here printed by his courtesy:

"The central problem of volcanism is to devise a mechanism which will explain the existence of local hot spots in the Earth's crust, whereby at present, as during past geological epochs, eruptions of molten lava and hot gases may take place in localized areas. Volcanism is still a highly controversial subject among geologists and geophysicists, though many attempts have been made to explain it. A theory which has appealed to some of those who have given much attention to the subject, attributes the local heating to slight variations in the average radioactive content of the rocks forming the crust in the active area. The theory is based on the following considerations:

"(1) The rocks of the Earth's crust contain a minute but very important amount of uranium and its disintegration products, including radium. In terms of radium, the amount of radioactive material in the usual igneous rocks is of the order of magnitude of one part in a million million; but the heat generated in volume of rock measured in cubic miles, by even this minute amount of radium, is very considerable.

"(2) The temperature gradient in the crust of the Earth (now judged to be more than 2,000 million years old) is profoundly affected by radioactive heat generated in the crust. Something like three-fourths of the present thermal gradient may be attributed to radioactive heat, and the balance to the residual heat of the originally molten globe.

"(3) Any reasonable interpretation of the laws of heat conduction leads to the conclusion that at moderate depths within the Earth's crust, say a few tens of miles, the temperatures are still very close to the melting points of the rocks at the particular depths.

"(4) From the foregoing it may be concluded that a relatively small increase in the radioactive content of the Earth's crust at a particular locality, will raise significantly the temperatures of the rocks at depths miles below the surface, and may easily bring the temperatures above the melting point, thus maintaining a lava reservoir in that region. In other words, a somewhat greater amount of radium averaged through the vertical extent of the crust (but still very small in absolute magnitude), could account for the existence of a volcanic region.

"Against this theory, it has been urged that examinations of volcanic lavas and emanations have failed to reveal any striking increase in radioactive elements. It must be noted, however, that since the excess of radium required to produce a volcanic region is proportionately so small in amount, it would be difficult to establish experimentally, without careful sampling; and particularly that the examination of a few samples of rocks would not be conclusive as to the local average radioactive content in a particular region.

"It must be admitted that the explanation of volcanism on radioactive grounds has not been generally accepted, although some thoughtful geologists and geophysicists have been impressed with the idea. An alternative theory explains volcanism, in part at least, by chemical reactions taking place in the rising lava column. Perhaps the radioactive theory should best be regarded as a subject for further observation and analysis." *

* See "Temperatures at Moderate Depths Within the Earth," by L. H. Adams *J. Wash. Acad. Sci.*, 1924, **14**, 459-472; and "The General Character of Deep-seated Materials to

Hot springs and geysers are also readily understandable on the basis of the regular development of heat from localized deposits of radioactive material.

The "Atomic Bomb"

It is fortunate for the world and for civilization that we were able to win the feverish race to produce the atomic bomb; for our enemies had been making desperate efforts to accomplish this difficult task and to use against us and our allies this most potent of all weapons. We can read the Smyth Report[2] with mingled feelings—pride in the splendid scientific achievements revealed; joy for the speedy and enforced surrender of those who had set out to enslave the world, and for the saving of millions of lives on both sides, soldiers and civilians, who would otherwise have perished in continuance of the war; sorrow for the much lesser number who died in the nuclear explosions, and for the fact that these epoch-making scientific discoveries were prostituted to military uses, instead of being used for the direct benefit of humanity.

Within the limited space available, we can give merely an outline of some of the facts as have been officially released. For further details the Smyth Report must be consulted. Parts of it are here quoted, for the fly leaf states: "Reproduction in whole or in part is authorized and permitted."

Uranium, as found in nature, contains only about 0.71 per cent of isotope AcU ^{235}, 0.006 per cent of isotope $_{92}$UII ^{234}, and 99.28 per cent of isotope $_{92}$UI ^{238}. Since it was already known that U ^{235} would undergo nuclear fission by slow speed (thermal) neutrons, successful attempts were made to separate out this isotope by various methods (mass spectrograph, referred to in a paper in this volume; centrifuge; thermal diffusion; fractional distillation; chemical exchange; electrolysis). It is interesting to note that Thomas Graham's paper "Liquid Diffusion Applied to Analysis" (Phil. Trans. Roy. Soc. London, (1861), *115,* 129-166), in which he coined the term "colloid," begins with the following words: "The property of volatility, possessed in various degrees by so many substances, affords an invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it." Graham also developed the mathematical expression or "law" regarding gaseous diffusion, namely that the rates of diffusion of gases under like conditions, through chemically indifferent septa is inversely proportional to the square roots of their molecular weights. Uranium hexafluoride, which has a vapor pressure of one atmosphere at a temperature of 56°C, has the two important isotopes U $^{235}F_6$ and U $^{238}F_6$ whose molecular weights are 349 and 352, respectively (fortunately, fluorine has only one natural isotope $_9F^{19}$, the three synthetic isotopes having but a short life). Immense technological difficulties had to be overcome in order to make this process successful, especially with such a highly corrosive substance. (See Smyth Report[2], 9.14, and Chapter X.)

Meanwhile, it was found that by radiating $_{92}$U ^{238} with neutrons, it could be transformed into $_{92}$U ^{239} by taking the neutron into its nucleus and emitting γ-rays. The new nucleus promptly emits a negative electron, and becomes an entirely new element, Neptunium (Np), which somewhat more slowly emits another negative electron and becomes another new element, Plutonium (Pu). The Smyth Report (8.5) represents what happens when the bombarding neutron is absorbed, as follows:

Volcanic Activity," by L. H. Adams, *Trans. Am. Geophysical Union, 10th and 11th Annual Meetings,* 1930, pp. 309-41.

See also section on "Origin of the Heat" (pp. 298-9) in chapter on "Volcanoes and Volcanism" by Adolf Knopf, in "A Textbook of Geology," Longwell, Knopf, and Flint, Part I, 2nd ed. J. Wiley & Sons, Inc., New York, 1939.

$$_{92}U^{238} + {}_{0}n^{1} \longrightarrow {}_{92}U^{239} + \text{gamma rays}$$

$$_{92}U^{239} \xrightarrow[23\ \text{min.}]{} {}_{93}Np^{239} + {}_{-1}e^{0}$$

$$_{93}Np^{239} \xrightarrow[2.3\ \text{days}]{} {}_{94}Pu^{239} + {}_{-1}e^{0} + \text{gamma rays}$$

"Plutonium 239 is the nucleus rightly guessed to be fissionable by thermal neutrons." (Smyth, 1.58).

Plutonium was "manufactured" in a "pile," consisting of a graphite matrix with cylindrical passages into which rods of uranium material could be inserted. The graphite matrix * slowed down high speed neutrons sufficiently to obtain the desired thermal neutron effect; but the intense radiation fields in the pile changed the electric resistance, the heat conductivity, and the elasticity of the graphite. The intense heat generated in the pile was carried off by streams of water, for "the production of one gram of plutonium per day corresponds to a generation of energy at the rate of 500 to 1,500 kilowatts." [2] (7.3).

In order that the pile should continue to function, conditions had to be chosen to maintain a "chain reaction" by continuous formation of sufficient neutrons, allowing for such wastes as occur by non-effective neutron collisions. ". . . most important in a pile are the collisions between neutrons and U^{235}, but the high energy fission of U^{238} and the thermal fission of Pu^{239} also take place. Collisions . . . between neutrons and U^{238} . . . occur for neutrons of all energies, but they are most likely to occur for neutrons whose energies lie in the 'resonance' region located somewhat above thermal energies." [2] (8.5). "Since the object of the chain reaction is to generate plutonium, we would like to absorb all excess neutrons in U^{238}, leaving just enough neutrons to produce fission and thus maintain the chain reaction. Actually the tendency for the neutrons to be absorbed by the dominant isotope U^{238} is so great compared to their tendency to produce fission in the 140-times rarer U^{235} that the principal design effort had to be directed toward favoring fission (as by using a moderator, a suitable lattice, materials of high purity, etc.), in order to maintain the chain reaction." [2] (8.7).

When sufficient plutonium had been formed in the pile, the uranium slugs were dissolved, and the plutonium was separated by co-precipitation with some other element, a process commonly used in radioactive chemistry. Previously, the chemistry of plutonium had been worked out with the exceedingly small quantities of this new element made experimentally, on what Smyth [2] (6.34) terms an "ultra-microchemical scale."

Practically all operations in the several processes had to be conducted by remote control, with the personnel shielded and protected by suitable walls and barriers from the dangerous radiations emitted throughout the several processes. Plutonium is "one of the most dangerous substances known if it once gets into the body. However, the really troublesome materials are the fission products, *i.e.*, the major fragments into which uranium is split by fission. The fission products are extremely active and include some thirty elements. Among them are radioactive xenon and radioactive iodine. These are released in considerable quantity when the slugs are dissolved and must be disposed of with special care. High stacks must be built which will carry off these gases along with the acid fumes from the first dissolving unit, and it must be established that the mixing of the radioactive gases with the atmosphere will not endanger the surrounding country." [2] (7.35).

* A process was also developed wherein "heavy water" (D_2O), discovered by Harold C. Urey (Nobel Prize, 1934), was used as a "moderator" of high-speed neutrons. The German heavy water plant in Norway was repeatedly bombed by the R.A.F. and by Norwegian patriots.

Even the cooling water became highly radioactive, as well as the air surrounding the pile.

It is impossible to give here any of the alternative methods worked out—it is estimated that a complete report of the results of only one of the scientific divisions will require thirty volumes. The magnitude of the project may be gauged from the statement[2] (8.50): "On the 6th of April, 1943, ground was broken for the Hanford construction camp. At the peak of activity in 1944, this camp was a city of 60,000 inhabitants, the fourth largest city in the state." (Washington). For work done with the "Calutron" (a name representing a contraction of "California University cyclotron"), and with the "isotron," (an electro magnetic mass separator using an extended source of ions, instead of usual slit sources), the Smyth Report[2] must be consulted.

To be effective, an explosion must release suddenly in a small region a large amount of energy. ". . . the efficiency of the atomic bomb will depend upon the ratio of (a) the speed with which the neutrons generated by the first fissions will get into other nuclei and produce further fission, and (b) the speed with which the bomb flies apart. Using known principles of energy generation, temperature and pressure rise, and expansion of solids and vapors, it was possible to estimate the order of magnitude of the time interval between the beginning and end of the nuclear chain reaction. *Almost all the technical difficulties of the project came from the extraordinary brevity of this time interval.*"[2] (12.9)

". . . it is impossible to prevent a chain reaction from occurring when the size [of a bomb] exceeds the critical size. For there are always enough neutrons (from cosmic rays, from spontaneous fission reaction, or from alpha-particle induced reactions in impurities) to initiate the chain. Thus until detonation is desired, the bomb must consist of a number of separate pieces each one of which is below the critical size (either by small size or unfavorable shape). To produce detonation, the parts of the bomb must be brought together rapidly. In the course of this assembly process the chain reaction is likely to start—because of the presence of stray neutrons—*before* the bomb has reached its most compact (most reactive) form. Thereupon the explosion tends to prevent the bomb from reaching that most compact form. Thus it may turn out that the explosion is so inefficient as to be relatively useless. The problem, therefore, is twofold: (1) to reduce the time of assembly to a minimum; and (2) to reduce the number of stray (pre-detonation) neutrons to a minimum."[2] (12.16) The successful explosion of a pilot bomb at Alamogordo, near Albuquerque, New Mexico,* on July 16th, 1945, was followed on August 6th, when surrender was refused, by the bombing of Hiroshima, Japan, with an atomic bomb equivalent in explosive force to about 20,000 tons of trinitrotoluol. Such a comparison leaves out the fact that the temperatures developed by nuclear explosions greatly exceed those developed by the atomic and molecular changes which dominate ordinary explosives. Surrender still being refused, another atomic bomb was dropped on the naval base of Nagasaki, Japan, on Aug. 9th, and soon thereafter the war came to an end.

Under the heading "Prognostication" the Smyth Report[2] states (13.4): As to the future, one may guess that technical developments will take place along two lines. From the military point of view it is reasonably certain that there will be improve-

* Makers of photographic plates, film, etc., conduct routine tests on the paper and cardboard used in wrapping these sensitive surfaces, so that nothing will be used that exhibits radiation or the like. Tests on strawboard cut in Illinois on Aug. 6th, showed radioactivity, and the lot was rejected. It seems likely that minute amounts of radioactive dust thrown up on July 16th by the trial bomb at Alamogordo, N. M., had fallen on the straw or entered the water servicing the paper mill. It is well known that dust sucked up by storms, *e.g.*, from the Sahara Desert, may be carried in huge quantities for thousands of miles; the same is the case with colloidal dusts flung up by volcanoes. A main source of iodine, so essential to many animals, is colloidal sea-salt, formed by drying of ocean spray. This is carried great distances, and goitre is more common in places like Switzerland and Montana where little of such dust falls. (*See* Time Magazine, Nov. 12, 1945.)

ments both in the processes of producing fissionable material and in its uses. It is conceivable that totally different methods may be discovered for converting matter into energy since it is to be remembered that the energy released in uranium fission corresponds to the utilization of only about one-tenth of one per cent of its mass. Should a scheme be devised for converting to energy even as much as a few per cent of the matter of some common material, civilization would have the means to commit suicide at will." As Prof. Smyth states in the Preface: "The ultimate responsibility for our nation's policy rests on its citizens and they can discharge such responsibilities wisely only if they are informed."

The writer hesitates to select names for mention, since reference to much of the work reported is not even referred to here. In the Foreword of the Smyth Report, Major General L. R. Groves, USA, states: "The success of the development is due to the many thousands of scientists, engineers, workmen and administrators—both civilian and military—whose prolonged labor, silent perseverence, and wholehearted cooperation have made possible the unprecedented technical accomplishments described." Many of our great corporations and foundations also gave important and unselfish service.

In conclusion, it is imperative that leaders of all nations and peoples compose or arbitrate differences, and learn to live peaceably together, despite variations in manners, habits, and religious, social or political beliefs. The health, happiness and contentment of humanity demand all we can give of our labor, energy and courage.

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See also article on "Chemical Warfare" in Vol. III of this series; and a communication of Dr. Niels Bohr in *Science, 102,* 363-4 (Oct 12th 1945) entitled: "A Challenge to Civilization," and footnote on p. 855 of this volume.

In *Mining and Metallurgy* for November, 1945, there is a letter by Cyril Stanley Smith on the importance of metallurgy in the production of the bomb, also a warning as to the extreme importance of international agreement and control. The same issue has an article by Frank T. Sisco along similar lines.

In *Science* of Nov. 30th, 1945 (102, 556), Glenn T. Seaborg and Joseph G. Hamilton announce that by bombardment with forty million electron volt helium ions from the 60 inch cyclotron at Berkeley, Cal., element 95 was produced from Uranium 238 and element 96 was produced from Plutonium 239. The new elements were identified by their chemical and radioactive properties.

APPENDIX I

Synthetic Rubber

E. A. HAUSER AND D. S. LE BEAU

Massachusetts Institute of Technology

Since the manuscript was submitted, a great amount of work on the chemistry and production of synthetic rubber has been carried out. Due to secrecy regulations, publications are only now appearing in various scientific periodicals. Since these publications are too numerous to discuss here in detail, the reader interested in compounding, vulcanization and properties of synthetic rubbers is referred to articles on these subjects which appeared in 1944 and 1945 in Industrial and Engineering Chemistry, India Rubber World, Rubber Age, and India Rubber Journal (London).

In the field of X-ray diffraction, R. E. Morris and C. B. Jordan published a paper on Buna S vulcanizates in Rubber Age **55**, 161 (1944).

The structural features of Buna S in relation to its physical properties are discussed by A. R. Kemp and W. G. Straitiff in Ind. Eng. Chem. **36**, 707 (1944).

A paper by H. A. Braendle and W. B. Wiegand discusses GR-S, an elastically inverted polymer, in India Rubber World **110**, 178 (1944).

Reclaiming of GR-S is discussed by R. L. Randall in Rubber Age **56**, 65, (1944).

The use of GR-S latices is discussed by L. H. Howland, C. R. Peaker and A. W. Holmberg in India Rubber World **109**, 577 (1944).

E. A. Hauser and D. S. le Beau have published a paper in Ind. Eng. Chem. **37**, 786 (1945) on microscopic studies of lyogels in which a new microscopic technique * is discussed which permits the study of lyogels, particularly natural and synthetic rubber, comparable to the results obtained with the electron microscope. The two microphotographs (Figs. 2 and 3) demonstrate this technique.

In the form of books, reference should now be made to "Synthetic Rubber from Alcohol, a Survey Based on the Russian Literature" by A. Talalay and M. Magat, Interscience Publishers, Inc., New York, N. Y. (1945).

* This is the Ultropak of H. Heine (Z. wiss. Mikroskop., **48**, 450 (1931); U. S. Pats. 1,840,448 (1932) and 1,935,444 (1933)). "The Ultropak differs from the standard type of dark-field optics by making use of ultra-illumination with indirect light. This means circular illumination of the preparation from above; it causes a dark-field effect, but the light does not pass through the magnifying lens system before it is reflected by the specimen through it into the observer's eye or onto the photographic film. The path the light takes is shown schematically in Fig. 1."

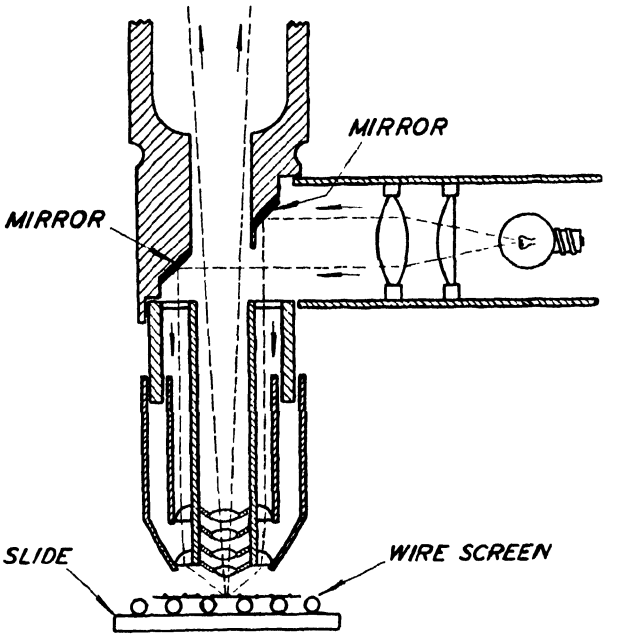

FIGURE 1. Path of light through lens system of ultropak misroscope for ultra-illumination with incident light.

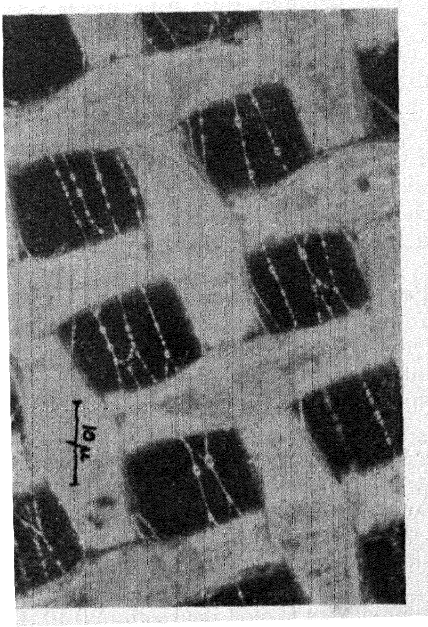

FIGURE 2. Crepe sol recovered from benzene. Magnification approximately 1000.

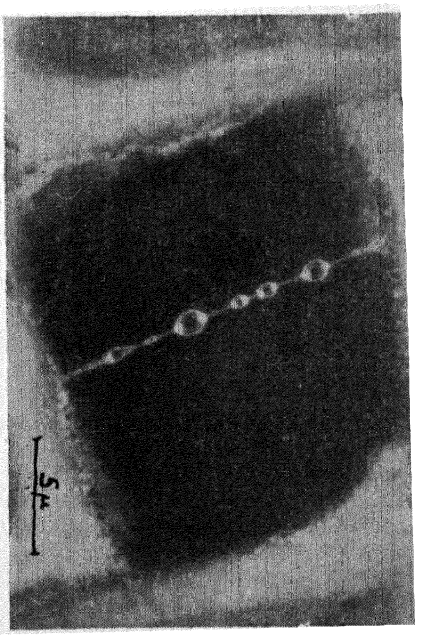

FIGURE 3. Crepe sol recovered from benzene. Magnification approximately 3000.

APPENDIX II

Adsorption and Elution as a Concentrating Process

W. A. HELBIG

Chemical Engineer, Darco Corporation

Instead of absorbing impurities from a solution of a product, it may at times be desirable to adsorb the product itself from dilute solution and recover it from the carbon at higher concentration by means of a suitable eluting solvent.

This procedure has been brought to large-scale commercial application in the production of penicillin. As a metabolic product of the Penicillium Notatum mold, penicillin is found in very low concentration in the nutrient medium upon completion of the organism's life cycle. After removal of the mold, the nutrient solution is treated with activated carbon, which adsorbs the penicillin, together with proteins, colloids, and complex organic compounds that have been introduced with the nutrient ingredients, or developed by the mold.

The adsorption step follows the conventional procedure of stirring the carbon with the solution for an adequate period, which is usually twenty to thirty minutes, followed by filtration. A carbon of high purity is required, since penicillin is very sensitive to acidity, alkalinity, and metals; it should also be a carbon of highest adsorptive capacity, since the effectiveness of the concentrating procedure requires a minimum bulk of solids to be eluted with the smallest possible volume of solvent. Toward this same end, a carbon of high bulk density is most desirable.

Under average conditions, with a suitable carbon, an adsorption of approximately 3,000 Oxford units of penicillin per gram of carbon may be expected. This figure applies to adsorption from a substrate containing corn steep liquor as a nutrient ingredient; from pure penicillin solutions, much higher adsorption is obtainable. The lower figure for nutrient solution adsorption results from the co-adsorption of the proteins and colloids present.

The adsorption of penicillin follows the Freundlich adsorption equation. Excellent isotherms can be obtained from which an investigator may determine optimum adsorption conditions, carbon dosage and efficiency, and such information as completeness of subsequent elution. The slope of the isotherm is of the order of 0.2, which is too low to offer any advantages in counter-current or split feed application of carbon.

The pH range used for adsorption is 6.5-7.0. This is dictated by the stability of penicillin in the broth, and is probably not the optimum range for greatest adsorption efficiency. At pH 6.5-7.0, the penicillin is in the form of a salt; in its acidic form penicillin is much less soluble, and should therefore be more strongly adsorbed. However, at low pH values (e.g. 2.0-3.0) penicillin is rapidly destroyed while still in broth solution.

Stability considerations have also led many producers to chill the broth to 0-10° C immediately after harvesting, and to maintain this temperature during the carbon adsorption.

From studies of filtration behavior of carbon in penicillin broth, it appears reasonable to conclude that proteins and colloids are not only adsorbed by the carbon, but precipitated by it. The mechanism of this precipitation is probably the adsorption by the carbon of a colloid-protecting substance. This co-precipitation may greatly impede filtration of the carbon from the broth, because of its probably slimy and compressible nature. Such difficulty is frequently encountered with surface culture broth, or with the percolate from the bran-culture method; it is much less marked with submerged culture broth.

The elution (desorption) of penicillin from the carbon is dependent upon subjecting the adsorbate to liquid-solid inter-facial energy conditions of opposite character to those prevailing during adsorption. This is effected through water-organic solvent mixtures. Two such mixtures are in general use: One, a saturated solution of amyl acetate in water, the other, an 80% solution of acetone in water.

The first of these is a two-phase system, consisting of the saturated solution of amyl acetate in water, and excess amyl acetate to maintain saturation during elution. (The carbon adsorbs amyl acetate from the solution; it should not be assumed, however, that the desorption of penicillin is an exchange adsorption. Amyl acetate alone will not desorb penicillin; neither will an unsaturated solution of the ester in water; the elution requirements are a *saturated* solution: i.e., the liquid-solid interfacial energy conditions presented by such a solution.)

Other two-phase systems such as water and ethyl acetate, iso-propyl acetate, and ethyl methyl ketone, have been used, but most of them have the disadvantage of too great a mutual solubility. Two-phase systems in general have the weakness that troublesome emulsions and foams are developed even in careful operation during the carbon elution. The great advantage of the single phase 80% acetone solution is that such difficulties are avoided; in addition, the acetone solution can be filtered from the carbon very readily, whereas filtration difficulties are frequently encountered with two-phase systems.

There are two general procedures for elution. The first involves the removal of the penicillin-bearing carbon filter cake from the filter used in separating it from the spent broth; the carbon is then slurried with the eluting solvent, and filtered off. This method is necessary with two-phase eluting solvents. Stirring should be carefully controlled to avoid incorporating the excess solvent into the suspension of carbon in the saturated water solution; the excess solvent has no other function than to maintain saturation in the water phase. Beating of excess solvent into this phase results in foams and emulsions, which are stabilized by the carbon and also the colloids and proteins associated with it.

"Static" elution consists in circulating the eluting solvent through the carbon cake without removing it from the filter after separation from the spent broth. At least two passes of the eluent through the cake are necessary; three or four are desirable: The objective, of course, is to reach desorption equilibrium. The effectiveness of static elution depends upon a number of factors. The first of these is dimensional: The filter used must have sufficient area and solids capacity to handle the broth filtration effectively, and must be small enough to require a minimum volume of solvent to fill the free space around the carbon cake, as well as the pump, pipe lines, etc., and leave a sufficient "heel" in the solvent container so that the pump will not suck air. Secondly, the filter should be of such design that the carbon cake will be distributed evenly over the entire filtering surface, and will not slough off that surface readily with slight pressure changes. Thirdly, the design must be such that the solvent is uniformly distributed over the carbon cake, and will flow through the cake uniformly, instead of seeking paths of least resistance, such as cracks in cake, etc.

It is helpful to bear in mind that adsorption and elution with solid adsorbents are closely analogous to the distribution of a solute between two immiscible solvents, and that the equilibria governing these phenomena are very similar. With a solid

adsorbent, distribution occurs at a liquid-solid interface, instead of across a liquid-liquid interface; under adsorption conditions, the solid becomes "enriched" with the adsorbate, while under elution conditions, the solvent becomes "enriched." As in the case of distribution between two solvents, a given decrease in concentration in the liquid phase can be effected with less solid adsorbent when the latter is applied in two increments, than if the adsorption is to be effected in one step. It is, of course, necessary to separate the first increment, after this has reached adsorption equilibrium, before adding the second. Conversely, a given degree of elution can be effected with less solvent in two steps than if the solvent were applied in a single step.

It is, therefore, better practice, in the elution of penicillin from carbon, to use two successive portions of solvent. This holds whether the eluting agent is a two-phase system such as amyl acetate-water, or a single-phase system such as 80% acetone in water.

The volume of eluent to be used is in linear proportion to the amount of carbon to be eluted. This direct proportionality arises as follows: In the adsorption step the carbon dose should be set to leave a residual of 3-5 units of penicillin per milliliter at adsorption equilibrium. Since the Freundlich equation $\frac{X}{M} = KC^{1/n}$ governs the adsorption, the $\frac{X}{M}$ value for C = 3-5 units/ml, i.e., the units of penicillin adsorbed per gram of carbon, will always be substantially the same, (approximately 3,000 units per gram) regardless of the initial concentration of penicillin in the broth. Thus with an initial concentration of 100 units, the carbon dose to reach C = 3-5 units/ml will be about 3.2%; with an initial concentration of 85 units, the dose will be about 2.7%; in *both* cases $\frac{X}{M}$, the concentration of penicillin on the carbon will be approximately 3,000 units per gram, since in both cases the same equilibrium concentration C = 3-5 units was reached.

With broth potencies on the order of 100 units per milliliter, it is the practice to use two volumes of amyl acetate-water eluent, each equal to about 10% of the original broth volume. With 80% acetone under similar conditions, the eluent volume consists of two successive portions each approximately 35% of the broth volume. (Much larger eluting volumes can be employed than with amyl acetate; after elution the acetone is distilled off, so that the final aqueous volume containing the penicillin is only about 14% of the original broth volume.)

In designing an elution procedure, close attention should be given to the amount of liquid mechanically retained by the carbon filter cake. Directly after the adsorption step, the retained liquid will be spent broth which is customarily washed out with water: No appreciable loss of penicillin is thereby incurred. The cake should then be blown with clean air to reduce the retained water to a minimum to avoid excessive dilution of the eluting solvent. After the second elution step, the cake should again be blown, to recover as much as possible of the retained penicillin-bearing solvent.

Even after thorough blowing, the carbon will still contain an irreducible minimum of retained liquid, the amount of which is a definite function of the bulk density of the carbon. It can be calculated with reasonable accuracy from the equation $R = \frac{11}{D^{1.4}}$, in which R is retention in gallons per dry weight pound of carbon, and D is bulk density in pounds per cubic foot.* The reliability of this equation is, of course, dependent upon the effectiveness with which the carbon cake has been blown; it must be considered as giving the minimum retention attainable. Since the retention is inversely proportional to bulk density, and the rate of change is governed by an

*For determination of bulk density, see "Adsorption from Solution by Activated Carbon," by W. A. Helbig, in this volume.

exponent of 1.4, the advisability of using a carbon of maximum bulk density to secure minimum filter cake retention is evident.

The successful application of activated carbon in concentrating penicillin by adsorption and elution has suggested its use on other products such as hormones and vitamins. Previous work on vitamins had been discouraging, because of the difficulties in elution which were encountered, but it is expected that this work will now be re-examined and possibly revived, in the light of experience with two-component eluting agents.*

* See paper by Richard Willstatter in Volume I of this series (1926) for pioneer work on adsorption and elution. J. A.

APPENDIX III

Styrene and Polystyrene

J. LAWRENCE AMOS

Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan

* Kern and Kämmerer [121] have developed a method of determining the chemical molecular weight of polystyrene. Their method is based upon the determination of bromine in polymers prepared with para bromo benzoyl peroxide in toluene at 50° C. The brom tracer catalyst reacts with the styrene and initiates a polymerization chain in which one mole of catalyst is utilized for each chain. This catalyst is present in the end groups of the macromolecule in a combined state (Bartlett and Cohen [92] as well as Price, Kell and Krebs [125] have described how para bromo benzoyl peroxide reacts with styrene during polymerization). Polymers with the same degree of polymerization (osmotic and viscosimetric methods used—very little difference in results) were prepared by using the same concentration of benzoyl peroxide and para bromo benzoyl peroxide with styrene. These polymers, which contained bromine, were subjected to as many as twenty precipitations from toluene with methanol so as to remove uncombined bromo benzoyl peroxide and other impurities.

Chemical analysis of these purified fractions for bromine revealed that the bromine content increased with decreasing molecular weight, furthermore the average number of combined bromine atoms per average molecule is four. This was found to be true for polymer fractions of average molecular weights ranging from 6,800 to 109,900. The significance of the number four is that it is a measure which shows that the different polymer fractions of different average molecular weight are homogenous and that two brom atoms are present in each end group in the polymer.

On the basis of this data obtained from the homogenous polymers a relationship between the number of determinable end groups, bromine content of the polymer was expressed in an equation, which allows calculation of the chemical molecular weight of the polymer. The chemical molecular weights as calculated are in good agreement with those determined by the specific viscosity method. For heterogenous polymers this chemical method would give a number average molecular weight.

These authors believe that this method will be useful in investigating the chemical structure of polystyrene especially the amount of branching in polymers.

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† Molecular Weights from Light Scattering

This method was first reported by Debye [26] who pointed out that the measurement of light scattering in solutions may be used to determine the molecular weights of high polymers.

Doty, Zimm and Mark [106, 107] have published data and some of the limitations and pitfalls of this method. Low molecular weight, coarse and color impurities of the

* The next four paragraphs are to be read as following paragraph three on page 998. Editor

† See page 1004.

solvent or the polymer present some difficulties, which effect the accuracy of this method and shows that considerable improvements will have to be made in the technique of this measurement before it will be widely used. Table 4 give the results obtained by these authors, of comparisons of the molecular weights of high polymers as determined by the osmotic pressure and light scattering methods.

Table 5. Comparison of Molecular Weight Measurement

Material	Molecular Weight	
	Osmotic Pressure	Light Scattering
Polystyrene No. 1	172,000	178,000 *
Polystyrene No. 2	198,000	182,000
Polystyrene No. 3	91,000	107,000
Polystyrene No. 4	———	190,000
Polystyrene No. 5	———	445,000
Cellulose Acetate No. 1	(125,000)	123,000
Cellulose Acetate No. 3	75,000	76,000

* This value was checked independently by two other laboratories.

* Foote [110] has made a study of the plastic flow of polystyrene by utilizing the parallel plate compression and capillary flow test methods. On the basis of this work nomographs for both methods have been presented for calculating the viscosity of the polystyrene at the temperature and conditions of the flow test.

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* See p. 1006.

Table Showing Orders of Dimensions in Meters, Grams, and Seconds.*

SPACE		MASS		TIME	
Meters		Grams		Seconds	
1.9×10^{28}	Einsteinian Universe	8×10^{78}	Einsteinian Universe (est.)	1.5×10^{18}	Sun to radiate ½ its mass
4.7×10^{20}	Milky Way (diameter)	3×10^{55}	Milky Way		
3.1×10^{18}	Parsec (distance of star whose parallax = 1 sec. of arc)				
9.5×10^{15}	Light-year (ca. 9½ million million km)				
				6×10^{16}	Age of Earth
1×10^{13}	Solar System (dia. 10 billion km)			2.6×10^{16}	Proterozoic Era (850 million years)
					Mesozoic Era (420 million years)
					Cenozoic Era (150 million years)
1.5×10^{11}	Earth to Sun (149 million km)			6×10^{15}	Quaternary Period (man appears)
6.9×10^{8}	Sun (radius = 692,000 km)	2×10^{33}	Sun	2.2×10^{11}	Recorded History (say, 7,000 years)
6.4×10^{8}	Earth (radius = 6,377 km)	5.99×10^{27}	Earth		
				2.3×10^{6}	Moon, rotation about Earth, 27.8 days
				8.6×10^{4}	Earth, revolution on axis (1 mean solar day)
1.7×10^{0}	**Man** (av. height = 1.7 m)	7.5×10^{1}	**Man** (av. wt. = 166 lbs)	ca 9×10^{0}	100 yard dash, by good runner
				1×10^{-2}	Single motor nerve impulse (10σ)
				6.4×10^{-2}	Motion picture frame on screen (64σ
				$2\text{-}4 \times 10^{-3}$	Sound Vibrations
				1×10^{-3}	Oscillograph
ca. 5×10^{-5}	Cells, *Drosophila* {nucleus = 5-15μ chromosomes = 0.2-3μ}				
2×10^{-5}	Coccus (ca. 2μ)				
8×10^{-7}	Red Blood Corpuscle (850 mμ)	4×10^{-10}	Sensitivity of Microbalance (0 4γ)		
2.5×10^{-7}	Limit of Microscopic Resolution	2×10^{-12}	Mercaptan (detect. by odor = 0.002γ)		
1×10^{-7}	Large Colloid Particles	ca. 2×10^{-18}	Colloid Particles		
1.3×10^{-8}	Shortest Ultraviolet (13 mμ)	3×10^{-22}	Water Molecule		
5×10^{-9}	Small Colloid Particles; Oil Films	1.66×10^{-24}	H Atom		
$0.2\text{-}5 \times 10^{-9}$	Molecules (0.2-5 mμ)				
$1\text{-}6 \times 10^{-10}$	Atoms (100-600 $\mu\mu$)				
5.3×10^{-11}	Electron Orbit in H Atom (53 $\mu\mu$)				
1.9×10^{-11}	Hard X-rays (19 $\mu\mu$)				
5×10^{-14}	Cosmic Ray (50 R.U.)				
1×10^{-15}	Rutherford Unit * (R.U. = 0.00001 Å)				
$3\,8 \times 10^{-15}$	Electron (dia. = 3.8×10^{-5} Å)	9×10^{-28}	Electron	5×10^{-14}	Yellow Light Oscillation
2×10^{-13}	Proton (H nucleus = 2×10^{-8} Å)	1.66×10^{-24}	Proton (H nucleus)	1×10^{-22}	Cosmic Ray Oscillation

1 km = 1,000m; 1 m = 1,000mm; 1 mm = 1,000μ
1 μ = 1,000 mμ, 1 mμ = 1,000 $\mu\mu$; 1 mμ = 10 Å

* The Rutherford Unit (R.U.) is first mentioned and defined in Vol. I of this series, page 15.

1 kilo = 1,000 grams; 1 gram = 1,000 mg; 1 mg = 1,000μg; 1μg = 1,000γ; 1γ = 0.000,000,001 gram
1 second = 1,000σ, 1σ = 1,000 mσ; 1mσ = 1,000$\mu\sigma$.

* Based mainly on data in "Hackh's Chemical Dictionary," Third Edition.

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