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Volume VII

Phenoplasts: Their Structure, Properties, and Chemical Technology

By T. S. CARSWELL

INTERSCIENCE PUBLISHERS, INC., NEW YORK
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PHENOPLASTS

THEIR STRUCTURE, PROPERTIES, AND CHEMICAL TECHNOLOGY

T. S. CARSWELL

Commercial Solvents Corporation
Terre Haute, Indiana

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This book is respectfully inscribed to
Gaston F. Dubois
whose interest furnished the inspiration
for the work

PREFACE

The purpose in writing this book has been to describe, as accurately as the present information will permit, the physical and chemical structure of the phenoplasts, and to correlate their structure with their mechanical and chemical properties. The past five years have furnished much new information in these fields, and the record has not previously been collected in one volume. No attempt has been made to write a practical handbook on phenoplast manufacture. There is one chapter which covers the more practical aspects of phenoplast manufacture in a rather sketchy way, and one chapter on the elements of molding technique. These chapters were not included for the commercial resin chemist, but rather for the student or research worker who may not be familiar with the technical processes employed in the production of phenoplasts.

Every effort has been made to cover thoroughly the literature, particularly of the past ten years. References to patents, however, are given only when the patent is so basic that it has historical value, or when there is no other available literature. This policy was adopted because there is a tremendous volume of patent literature on the phenoplasts; the patent literature is important as far as the art of manufacture and application of the resins is concerned, but it has little theoretical value.

Despite the excellent work which has been done on phenoplast structure within the past few years, we must admit that our knowledge of the physical and chemical structure of the resins is far from perfect. It is hoped that the theoretical aspects of the field will attract more workers. It seems certain that further elucidation of phenoplast structure will require the development of new chemical techniques and new physical tools.

I am very grateful to the many friends who have helped in the preparation of this book. I particularly want to thank the Monsanto Chemical Company and its President, William M. Rand, for

permission to undertake the work. Mr. Archie J. Weith and his associates at the Bakelite Corporation have been kind enough to read and make helpful criticisms on the entire manuscript. The manuscript has also been read and criticized by members of the Plastics Division of the Monsanto Chemical Company, among whom I am happy to mention R. D. Dunlop, H. K. Nason, L. M. Debing, R. A. Barkhuff, R. S. Schatz, and David Telfair. They have been responsible for much of the work which is quoted in the text. Dr. Hermann P. Mark, with his deep insight into high-polymer chemistry, has been a constant inspiration. I am indebted to Dr. Donald S. Herr of the Resinous Products and Chemicals Company for the chapter on base-exchange resins, and to Mr. Carl H. Whitlock of the Monsanto Chemical Company for the chapter on molding technique. The photograph of Leo H. Baekeland is published through the courtesy of Bakelite Corporation.

T. S. CARSWELL

Terre Haute, Indiana
February 1947

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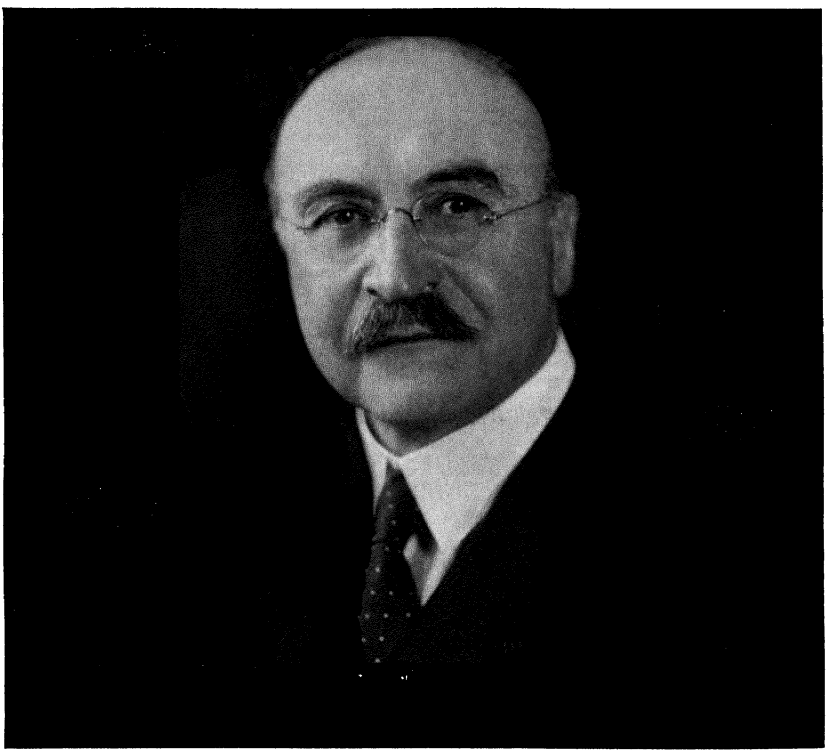
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Underwood & Underwood



I. HISTORY OF THE DEVELOPMENT OF PHENOPLASTS

The reaction between phenols and aldehydes was first described by Adolf Baeyer[1] in 1872. Basing his conclusion upon experiments with a number of phenols and aldehydes in the presence of acids, Baeyer stated that the reaction was a general one. In some cases, such as the reaction between pyrogallic acid and benzaldehyde, a crystalline compound was obtained. With phenol and formaldehyde, however, a clear resin was formed, but not a crystalline compound.

The early organic chemists were interested only in pure compounds which could be crystallized and identified. Consequently, little attention was paid to the resinous reaction produced between phenol and formaldehyde until the period 1890–1910. From the text of the numerous patents issued during this period to DeLaire, Smith, Lebach, and others, it seems that the principal effort of the investigators during that time was the production of an artificial shellac. None of the products produced by these investigators was a commercial success as a shellac substitute. Neither were they successful as molding compositions, because the resins were brittle, friable, and porous due to the evolution of water during curing. It is true that the porosity could be overcome by curing at temperatures below 100°F.; the curing time then became so long that commercial molding was not practical. However, this process was later revised to produce large cast-resin shapes which were subsequently machined to the desired shape and dimensions.

Leo H. Baekeland studied the phenol-formaldehyde condensation products from 1905 to 1909. He soon realized that these products could not be handled in the same manner as the conventional resins of that period, and he recognized that new techniques must be developed in order to bring out the full commercial value of these new products. Baekeland then made two proposals to overcome the difficulty previously experienced in molding the phenoplasts. These were: the use of a filler, such as wood flour, to over-

[1] A. Baeyer, *Ber*, **5**, 25–56, 280–282, 1094–1100 (1872).

come the brittleness; and the use of heat *and pressure* during molding. The application of pressure greater than the vapor pressure of water overcame the bubbling and porosity which the early investigators had observed, and the temperature could be raised so high that a short molding time was obtained.

Baekeland announced his discoveries at the February, 1909, meeting of the New York Section of the American Chemical Society.[2] He had previously applied for patents for his inventions and had given the product the trade name *Bakelite.* In 1910, the General Bakelite Company was organized, and the manufacture of Bakelite was begun at Perth Amboy, New Jersey. The announcement of Dr. Baekeland's work stimulated further investigation. J. W. Aylsworth, a chemical consultant in East Orange, New Jersey, for Thomas Edison, became interested in phenoplasts as a raw material for phonograph records. His work led to the formation of the Condensite Company in Bloomfield, New Jersey. At about the same time, Adolph Karpen of S. Karpen Brothers, furniture manufacturers located in Chicago, established a research fellowship at the University of Kansas under the direction of Robert Kennedy Duncan. The purpose of this fellowship was the development of superior furniture varnishes. Dr. L. V. Redman, of the University of Toronto, who received the fellowship, became impressed with the possibilities of the phenolic resins, and explored the field with his associates, A. J. Weith and F. P. Brock. Their work resulted in the formation of the Redmanol Company in Chicago.

The General Bakelite Company prosecuted a successful patent infringement suit against the Condensite Company, and, as a result, the latter was licensed under the Bakelite patent. Subsequently, the General Bakelite Company instituted a successful suit against a customer of the Redmanol Company; the suit was based upon U. S. Pat. 942,699 of December 7, 1909, commonly called the "heat and pressure patent." The result of this successful litigation was to give the General Bakelite Company such a strong patent position that, in 1922, the three companies were consolidated under the name of the Bakelite Corporation.[3] This company maintained its independence until 1939, when it became a part of Carbide and Carbon Chemicals Corporation.

The earliest Bakelite patents expired in 1926, after which the manufacture of phenoplasts was adopted by several companies. The firms in the United States which are now making phenoplast molding powders are:

---

[2] L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 149–161 (1909).

[3] L. V. Redman and A. V. H. Mory, *Ind. Eng. Chem.*, **23**, 595–597 (1931).

Company	Trade name
Bakelite Corporation	Bakelite
Durez Plastics & Chemicals, Inc.	Durez
Durite Plastics	Durite
General Electric Company	Textolite
Reilly Tar & Chemical Co.	Indur
Makalot Corporation (now a part of Interlake Chemical Corp.)	Makalot
Monsanto Chemical Co.	Resinox

There are also a number of manufacturers who produce adhesive, surface coating, and other specialty resins derived from the phenolformaldehyde condensation product.

During the first stages of their development, the phenoplasts were used principally in the manufacture of insulating parts for the electrical industry. For this purpose, the material has many natural advantages. It is a nonconductor, is relatively tough, can be machined, and the molding cost is low when large quantities of a single article are involved. The phenoplasts therefore found wide use in the manufacture of switch parts, connectors, insulators, radio tube sockets, and a great many similar articles. The rapid growth of the electrical and radio industries helped to accelerate the introduction of the electrical grades of molding powder and laminates. Wood flour, mica, and asbestos were employed principally as fillers in these early molding powders. It was later found that the impact resistance of molded phenoplasts could be greatly improved by the addition of more fibrous fillers, such as cotton floc or macerated canvas. The introduction of these types of molding powders led to their use in the manufacture of mechanical parts where strength was an important factor. The second World War focused attention on the need for plastic parts with high mechanical strength over a wide range of temperature, and the use of phenoplasts for such parts has been accelerated during the last few years.

Early research disclosed that fabrics and paper could be impregnated with phenolic resins, and subsequently laminated to produce tough sheets which were resistant to moisture and to many chemicals. The laminating industry has grown up side-by-side with the molding industry, and, at present, a large percentage of the phenoplasts are being used in the preparation of laminates.

In 1920 the firm of Kurt Albert in Wiesbaden, Germany, was making synthetic fossil resins for oil varnishes by combining phenol–aldehyde resins with ester gum. The process was brought to the United States by the Resinous Products Company of Philadelphia, an affiliate of the Röhm and Haas Company, and manufacture was begun about 1924. When these resins were experimented with by the paint and varnish industry it was

II. CHEMICAL STRUCTURE OF THE PHENOPLASTS

Despite the rapid commercial growth of the phenoplasts, our knowledge of their chemical structure and of the chemical reactions which take place during curing had been meager until recently. The reaction of phenol with formaldehyde leads to the formation of a number of products, which are difficult to separate and are readily susceptible to resinification by heat or reagents. Consequently, their study tended to be unattractive to organic chemists. The difficulty of the problem was recognized by Baekeland[1] who wrote in 1911:

"It should be pointed out that we have to deal here with substances which are amorphous, noncrystalline, nonvolatile, and cannot be purified in the usual ways. Furthermore, in any of these reactions, several substances are liable to be produced at the same time. These substances can form solid solutions one with another, or with any excess of the reacting materials employed."

Within the last five years, however, very significant work has been done in the study of the chemistry of the phenoplasts. For a more intimate knowledge of the reactions leading to resinification, we are indebted to Zinke and his co-workers[2-11] at the University of Graz in Germany; to Hultzsch and his associates with the firm of Kurt Albert[12-20] in Wiesbaden;

---

[1] L. H. Baekeland, *J. Ind. Eng. Chem.*, **3**, 518–520 (1911).
[2] A. Zinke, F. Hanus, and E. Ziegler, *J. prakt. Chem* , **152**, 126–144 (1939).
[3] F. Hanus and E. Fuchs, *ibid.*, **152**, 327–336 (1939).
[4] F. Hanus, *ibid.*, **158**, 245–253 (1941).
[5] A. Zinke and F. Hanus, *Ber.*, **74**, 205–214 (1941).
[6] A. Zinke and E. Ziegler, *ibid.*, **74**, 541–545 (1941).
[7] E. Ziegler, *ibid.*, **74**, 841–844 (1941).
[8] A. Zinke and E. Ziegler, *ibid.*, **74**, 1729–1736 (1941).
[9] A. Zinke, M. Tomis, and K. Lercher, *ibid.*, **75**, 151–155 (1942).
[10] E. Schauenstein and S. Bontempo, *ibid.*, **76**, 75–80 (1943).
[11] A. Zinke and E. Ziegler, *ibid.*, **77**, 264–272 (1944).
[12] K. Hultzsch, *J. prakt. Chem.*, **158**, 275–294 (1941).
[13] K. Hultzsch, *Ber.*, **74**, 898–904 (1941).
[14] K. Hultzsch, *J. prakt. Chem.*, **159**, 155–179 (1941).

and to von Euler and his co-workers[21-37] at the University of Stockholm in Sweden; as well as to a number of others who have published less extensively.

A. GENERAL REACTION OF PHENOLS WITH ALDEHYDES

In general, phenols react with aldehydes to form condensation products if there are free positions on the benzene nucleus ortho or para to the phenolic hydroxy group, and if the length of any of the substituents on the nucleus is not so great as to cause steric hindrance. Because of its greater reactivity, formaldehyde is by far the most widely used aldehyde. For this reason, the discussion in this chapter will be confined to reactions with formaldehyde; the use of other aldehydes will be discussed in Chapter III. The discussion in this chapter will also be limited to the monohydric phenols—that is, phenols with only one hydroxy group for each benzene nucleus. The polyhydric phenols will be discussed in Chapter IV.

The reaction of phenol with formaldehyde in the absence of any other

[15] K. Hultzsch, *J. prakt. Chem.*, **159**, 180–188 (1941).

[16] K. Hultzsch, *Ber.*, **74**, 1533–1538 (1941).

[17] K. Hultzsch, *ibid.*, **74**, 1539–1543 (1941).

[18] K. Hultzsch, *ibid.*, **75**, 106–114 (1942).

[19] K. Hultzsch and G. Schiemann, *ibid.*, **75**, 363–368 (1942).

[20] K. Hultzsch, *Kunststoffe*, **32**, 69–76 (1942).

[21] H. v. Euler, E. Adler, and D. Friedmann, *Arkiv Kemi Mineral. Geol.*, **B13**, No. 12, 1–7 (1939).

[22] H. v. Euler, E. Adler, and G. J. Gie, *ibid.*, **B14**, No. 9, 1–7 (1940).

[23] H. v. Euler, E. Adler, S. de Kispeczy, and A. Fagerlund, *ibid.*, **A14**, No. 10, 1–20 (1940).

[24] E. Adler, *ibid.*, **B14**, No. 23, 1–7 (1940).

[25] E. Adler, H. v. Euler, and H. G. Hasselquist, *ibid.*, **B14**, No. 24, 1–8 (1940).

[26] H. v. Euler, E. Adler, and B. Bergström, *ibid.*, **B14**, No. 25, 1–6 (1941).

[27] H. v. Euler, E. Adler, and B. Bergström, *ibid.*, **B14**, No. 30, 1–6 (1941).

[28] H. v. Euler, E. Adler, and J. O. Cedwall, *ibid.*, **A14**, No. 14A, 1–20 (1941).

[29] S. Kyrning, *ibid.*, **A15**, No. 2, 1–9 (1941).

[30] E. Adler, H. v. Euler, and J. O. Cedwall, *ibid.*, **A15**, No. 7, 1–17 (1941).

[31] H. v. Euler, E. Adler, G. Eklund, and O. Törngren, *ibid.*, **B15**, No. 9, 1–7 (1942).

[32] E. Adler, S. Tingstam, and A. O. Caspersson, *ibid.*, **B15**, No. 10, 1–8 (1942).

[33] H. v. Euler, E. Adler, and S. Tingstam, *ibid.*, **A15**, No. 10, 1–11 (1941).

[34] S. Kyrning, *ibid.*, **B15**, No. 11, 1–8 (1942).

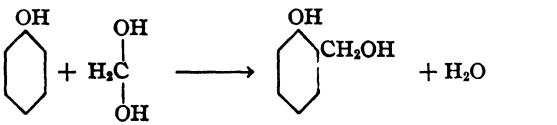
[35] H. v. Euler, E. Adler, J. O. Cedwall, and O. Törngren, *ibid.*, **A15**, No. 11, 1–19 (1942).

[36] E. Adler and S. Kyrning, *Svensk Kem. Tid.*, **53**, No. 1, 5–11 (1940).

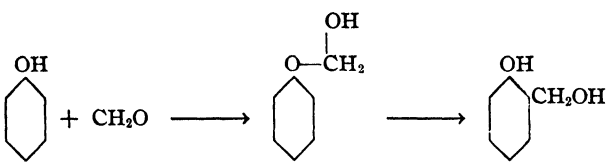
[37] H. v. Euler, E. Adler, and A. O. Caspersson, *Arkiv Kemi Mineral. Geol.*, **A16**, No. 11, 1–14 (1943).

reagents is very slow, and catalysts are always added to accelerate the reaction. These catalysts may be either acids or bases, and the nature of the reaction product depends considerably upon the type of catalyst which is used.

The mechanism of the addition of formaldehyde to phenol is not entirely understood. Manasse[38] suggested in 1894 that the formaldehyde may react in alkaline solution as methylene glycol, as indicated in Equation (1), or it may undergo an acetal addition, with subsequent rearrangement of the hemiformal, as shown in Equation (2). The latter suggestion was also made by von Tollens, and later by Baekeland and Bender.[39]

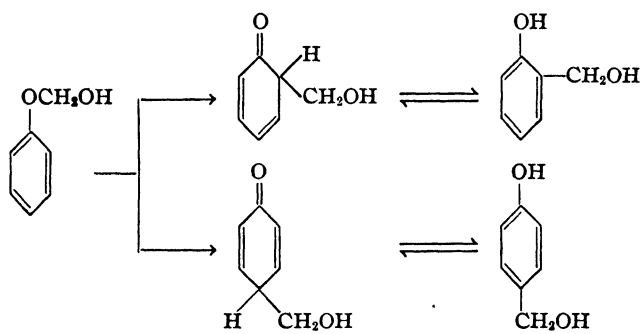


(1)



(2)

Walker[40] favors the idea of the formation of a primary phenolic hemiformal, and suggests that the formation of the phenol alcohols may involve tautomeric rearrangements of the type indicated below:



(3)

The hemiformal is very unstable, and rearranges rapidly to the phenol alcohol; because of this instability, the hemiformal from a phenol has never been isolated.

[38] O. Manasse, *Ber.*, **27**, 2409–2413 (1894).

[39] L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225–237 (1925).

[40] J. F. Walker, *Formaldehyde*. Reinhold, New York, 1944.

Whatever the exact mechanism of formaldehyde addition may be, the phenolic hydroxy group activates the benzene ring so that the methylol groups always enter the nucleus in ortho and para positions to the phenolic hydroxy group. When some of the ortho and para positions are occupied, the reaction of the phenol becomes much slower; when all of the ortho and para positions are unavailable, no reaction takes place. The presence of substituents in the meta position also has a pronounced effect upon the rate of reaction with formaldehyde. Alkyl groups in the meta position tend to accelerate both the initial condensation and the subsequent resinification. The presence of a hydroxy group in the meta position, as in resorcinol, greatly increases the reactivity.

The nature of the reaction products depends upon the type of catalyst used. When alkaline catalysts are used, the primary reaction products are phenol alcohols, and are called *resoles*. When acid catalysts are used, the primary reaction products are apparently also phenol alcohols, but these rearrange quickly under the influence of the catalyst to give diphenylmethane derivatives to which the name, *novolacs*, was given by Baekeland[41] in 1909. Because of this important difference the chemical structure of these two classes of phenoplasts will be discussed separately.

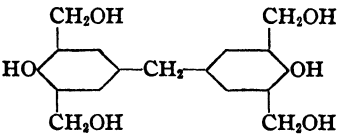
B. THE RESOLES

The resoles are formed when formaldehyde acts upon a phenol in alkaline solution. Almost any alkali may be employed: alkali metal hydroxides; hydroxides of the earth metals, such as barium or calcium; ammonia, or quaternary ammonium bases. There is some evidence to indicate that the products formed are not identical when different bases are used, especially in those cases where the phenol has several reactive positions. It is almost definite that ammonia and amines, when employed as catalysts, enter into the condensation reaction. The nature of the catalyst may affect to some degree the position in the ring which is occupied by the methylol group. For example, Auwers[42] states that strong alkalis favor the production of para methylol derivatives. However, not enough work has been done to present any definite data on this point.

Walker[43] has shown that, from the condensation of phenol with formaldehyde under alkaline conditions, it is possible to isolate a tetramethylol derivative of 4,4′-dihydroxydiphenylmethane, having the probable con-

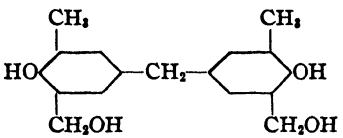
[41] L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 545–549 (1909).
[42] K. Auwers, *Ber.*, **40**, 2524–2537 (1907).
[43] E. E. Walker, *Trans. Faraday Soc.* (Sept., 1935).

stitution of Formula I. Seebach[44,45] isolated the same product, melting



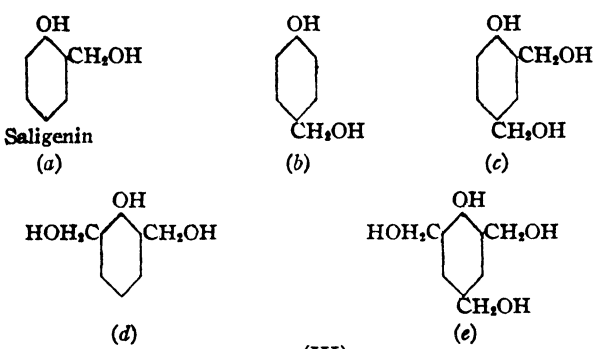
(I)

at 145°C., by the action of more than three moles of formaldehyde on one mole of phenol, using a little magnesium oxide as a catalyst. From *o*-cresol, the product which is obtained has the constitution shown in Formula II. From these observations, it is concluded that the first condensation takes place in the para position. The existence of the tetramethylol derivative implies branching of the chains at an early stage.



(II)

Reference has already been made to the fact that the methylol group enters the ring ortho or para to the phenolic hydroxy group. When more than one such position is available, polymethylol compounds are formed. Thus, from phenols with three reactive positions, the series of methylol derivatives shown in Formulas III may be formed. In the case of the



Saligenin

(*a*) (*b*) (*c*) (*d*) (*e*)

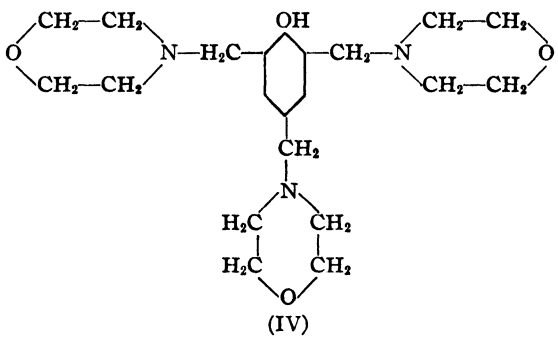
(III)

reaction of formaldehyde with phenol, the presence of all of these alcohols has been confirmed either through isolation of the alcohol itself or of a

[44] F. Seebach, *Ber.*, **72**, 1635–1638 (1939).

[45] F. Seebach, *ibid.*, **73**, 1338–1346 (1940).

derivative. The monophenol alcohols, saligenin (*o*-hydroxybenzyl alcohol) and homosaligenin (*p*-hydroxybenzyl alcohol) were separated and identified by Manasse.[38] Kurt Meyer[46] was able to prove the presence of the two dialcohols by methylation of the phenolic hydroxy group, followed by oxidation of the methylol groups to carboxyl. The formation of the trimethylol compound was definitely established by Bruson and McMullen.[47] They condensed three moles of formaldehyde with phenol in the presence of a strongly basic, nonaromatic secondary amine. With morpholine, for example, a definite crystalline compound, melting at 106–107°C., was formed, which had the structure shown in Formula IV. The quantity of



(IV)

dialcohols formed depends upon the ratio of formaldehyde to phenol, but even with equimolar ratios, some quantities of polyalcohols are formed, because of the great velocity of the addition reaction.

It is difficult to obtain the trialcohol, but derivatives may be formed such as the addition compound described by Bruson. Stäger and Biert[48] attempted to isolate the trialcohol in pure form, but failed. As Granger[49] states, the addition of the third molecule of formaldehyde becomes very slow as the reaction progresses, although it is comparatively rapid in the earlier stages.

Curing Stages of Resoles

The mechanism by which the phenol alcohols condense to resins is very complex. Our present knowledge of the curing reactions will be discussed in detail later in this chapter. For convenience, the curing mechanism has

[46] K. H. Meyer, *Trans. Faraday Soc.* (Sept., 1935).

[47] H. A. Bruson and C. W. McMullen, *J. Am. Chem. Soc.*, **63**, 270–272 (1941).

[48] H. Stäger and J. Biert, *Helv. Chim. Acta.*, **21**, 641–650 (1938).

[49] F. S. Granger, *Ind. Eng. Chem.*, **24**, 442–448 (1932).

been divided into three phases. This classification was first made by Baekeland[50] and later amplified by Lebach.[51] The three phases are:

A-stage resin (resole).—This represents the initial condensation product of phenol and formaldehyde. The resin consists mainly of phenol alcohols, although it is probable that some condensation has taken place to give methylene ethers, methylol derivatives of diphenylmethane, and perhaps methylenequinone or its polymers. Lebach[52] termed this stage *resole* from the Latin "resina" (a resinous body) and "ol" which referred to the solubility in alkalis and pointed to the probable presence of hydroxy groups.

B-stage resin (resitol).—This represents the second stage of condensation. The resin is no longer soluble in alkalis because the molecular weight has advanced to such a size that the alkaline salts are no longer soluble. It is partly or even completely soluble in organic solvents, such as acetone or alcohol. Cross linkage, however, has not proceeded very far and the resin is still softened by heat and is plastic while hot, although hard and brittle when cold. Lebach[51] called this stage the *resitol.*

C-stage resin (resite).—This represents the final stage of polymerization, with a large amount of cross linkage. The resin is completely insoluble and infusible. Lebach called this the *resite.*

It is important to note that these stages of resin formation are not clearly defined, but pass gradually one into the other. As has been indicated above, even the A-stage resin does not consist entirely of phenol alcohols, but contains appreciable amounts of higher condensation products. In the B stage, phenol alcohols are still present, together with much more highly condensed resins, and appreciable amounts of partly cross-linked resins. As will be explained later, it is probable that methylene ethers are present in this stage. There are usually present, even in the C-stage resin, from 3 to 6% of products which can be removed by vigorous extraction with acetone.

Kinetics of A-Stage Reaction

Although a great deal is known qualitatively about the nature of the initial reaction of phenol and formaldehyde, there have been few quantitative measurements on the kinetics of the reaction. Novak and Cech[53] attempted to follow the progress of resinification by a study of the refrac-

[50] L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 149–161 (1909).
[51] H. Lebach, *J. Soc. Chem. Ind.*, **32**, 559–564 (1913).
[52] H. Lebach, *Z. angew. Chem.*, **22**, 1598 (1909).
[53] J. Novak and V. Cech, *Ind. Eng. Chem.*, **20**, 796–801 (1928).

tive index, viscosity, and bromine value. Another empirical approach is represented by the work of Holmes and Megson[54] who studied the behavior of various phenols with a series of catalysts. In their work, 0.4 gram mole of the phenol was mixed with 0.6 gram mole of 40% formalin and the catalyst, and immersed in boiling water. An arbitrary time, the resinification time, was measured from initial heating to the appearance of a permanent turbidity. Table I shows the resinification time in minutes for various

TABLE I

RESINIFICATION TIME FOR VARIOUS PHENOLS

Phenol used	Resinification time, min.
m-5-Xylenol	6
m-Cresol or *p*-xylenol	27
o-4-Xylenol	43
m-4-Xylenol	58
o-Cresol	108
Phenol	139
p-Cresol	144

phenols, when 0.5 g. of trimethylamine was used as a catalyst. More detailed experiments were then carried out with phenol, the three cresols, and *m*-5-xylenol; the catalysts employed were trimethylamine, triethylamine, pyridine, and ammonia. The reaction curves were roughly hyperbolas of the form:

$$w(t - a) = b$$

where t is resinification time, w is weight of catalyst, and a and b are constants. The relative reactivities of some of the phenols depended upon the catalyst used; for example, *o*-cresol was slower than phenol only when pyridine was used as the catalyst.

For the purpose of comparing the catalytic activities of the more common bases, *m*-cresol was condensed in the presence of 0.75 g. of each base (except ethylenediamine, where 0.375 g. was used). Table II shows the resinification times obtained. The values for sodium hydroxide, potassium hydroxide, and lithium hydroxide, when reduced to molecular proportions, lie on the same curve.

The effect of higher temperatures on the condensation of *m*-cresol was examined by condensing one mole fraction (27 g.) with one mole fraction of paraformaldehyde (7.5 g.) and 2 g. of pyridine in cyclohexanol as a solvent.

[54] E. L. Holmes and N. J. L. Megson, *J. Soc. Chem. Ind.*, 52, 415–418T (1933).

TABLE II

RELATIVE ACTIVITY OF BASIC CATALYSTS

Catalyst used	Resinification time, min.	Catalyst used	Resinification time, min.
Ammonia	34	Diethylamine	53
Methylamine	26	Di-*n*-propylamine	83
Ethylamine	49	Dibenzylamine	270
n-Propylamine	101	Trimethylamine	86
iso-Propylamine	100	Triethylamine	43.5
Benzylamine	300	Pyridine	250
Ethylenediamine	22	Sodium hydroxide	27.5
Hexamethylenetetramine	32	Lithium hydroxide	24.5
Dimethylamine	16.5	Potassium hydroxide	29

Condensations were carried out until the first signs of resin separation appeared. The following reaction times were obtained for the temperatures given:

110°C. 5.5 hrs.	140°C. 1.3 hrs.
120°C. 2.3 hrs.	150°C. 1.0 hrs.
130°C. 1.8 hrs.	160°C. 1.0 hrs.

Dostal and Raff[55] studied the condensation of one mole of *p*-cresol with one mole of formaldehyde at temperatures of from 100–130°C. No catalyst was employed, and the formic acid present in the formaldehyde was neutralized by shaking with calcium carbonate. They derived an equation which may be simplified to the following form to express the kinetics of the reaction (for *p*-cresol only):

$$R = 2aT/(0.3 + 2aT)$$

where R is the total condensation product, a is a constant, and T is the time in hours. For *p*-cresol under the conditions studied, $a = 0.05$. Excellent agreement was found between the values of R calculated from the above equation and those found by experiment.

Nordlander[56] studied the ammonia catalyzed condensation of phenol with formaldehyde. He classified the two general types of reaction as (*a*) the primary reaction, in which phenol and formaldehyde react to form water-soluble intermediates of the oxymethylene–phenol type (A stage), and (*b*) the secondary reaction, in which these intermediates react further by condensation to give water-insoluble resinous products. The reaction was studied by measuring the rate of disappearance of formaldehyde and the

[55] H. Dostal and R. Raff, *Z. physik. Chem.*, **B36**, 117–129 (1936).

[56] B. W. Nordlander, *Oil Paint Drug Reptr.*, **130**, 3, 27 (1936).

manner in which the bromine value of the water-soluble portion of the reaction mixture varied as the reaction proceeded.

The results disclosed that the primary reaction is confined to the interaction of one mole of formaldehyde with one mole of phenol; no formaldehyde reacts with any of the intermediates formed. This reaction is apparently of monomolecular order, with the rate proportional to the concentration of free phenol. The influence of the catalyst is complex; apparently both hydrogen ions and hydroxyl ions, and probably other ions, derived from the catalyst, promote the reactions. At very low ammonia concentrations the reaction order changes to one of apparently bimolecular type, which is characterized by a reaction rate proportional to the square of the formaldehyde concentration.

The secondary reaction seemed to be of monomolecular order; the catalyst action was complex and similar, but not identical, to that governing the primary reaction. Weakly alkaline catalysts which are sufficiently active to bring about a primary reaction of the same type as that induced by ammonia are unable to initiate the secondary reaction to any extent. When the catalyst was a weak alkali, such as ammonia, phenol did not take any part in the secondary reaction which was then limited to the phenol alcohols. Nordlander reported that the temperature coefficient varied for the two reactions; the secondary reaction rate increased much more rapidly with the temperature than the primary reaction rate.

Nordlander developed the following expression for ammonia catalyzed reactions which were initially equimolar with respect to phenol and formaldehyde:

$$K = \frac{1}{C^{1.38}t} \log \frac{a}{a - x}$$

where C is catalyst concentration, a is the initial formaldehyde concentration, and $a - x$ is the formaldehyde concentration at time t.

Sprung[57] made a very thorough study of the kinetics of the reaction of paraformaldehyde in the presence of a number of phenols, using triethanolamine as a catalyst. He determined that the addition phase of the reaction apparently followed a first-order rate law. Figure 1 compares the reactivities of the various phenols at 98°C. The apparent first-order rate constants, as taken from the slopes of the straight lines, are listed in Table III. The introduction of a methyl group in the meta position increased the reaction rate by a factor of 2.8. The introduction of a methylol group, as

[57] M. M. Sprung, *J. Am. Chem. Soc.*, **63**, 334–343 (1941).

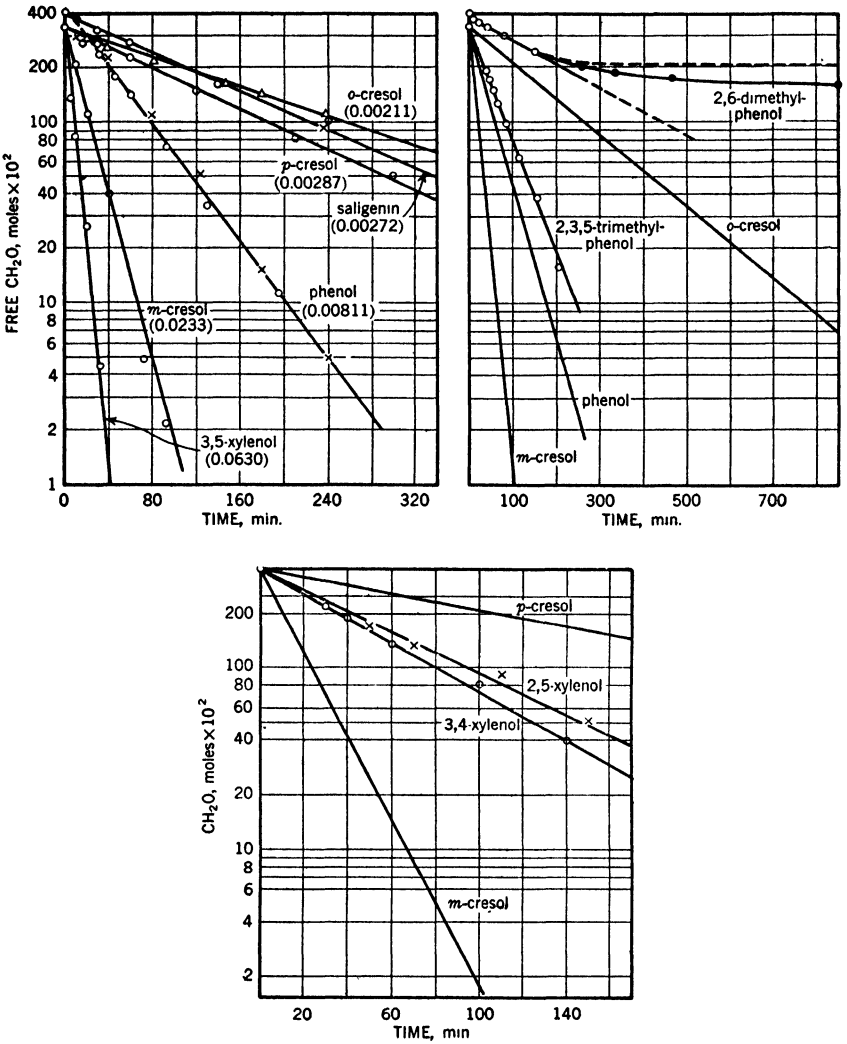


Fig. 1. Comparison of reactivities of various phenols at 98°C.[57]

in the case of saligenin, depressed the reactivity of phenol to about the same extent as a methyl group similarly placed. This indicates that the rate law as experimentally determined for a di- or trifunctional phenol apparently expresses a summation of the rates at which the first, second, and presumably also the third molecule of formaldehyde react.

TABLE III

EFFECT OF SUBSTITUTION ON REACTIVITY OF PHENOLS

Phenol used	Apparent first-order rate constant	Comparative rate, phenol taken as unity
3,5-Xylenol	0.0630	7.75
m-Cresol	0.0233	2.88
2,3,5-Trimethylphenol	0.0121	1.49
Phenol	0.00811	1.00
3,4-Xylenol	0.00673	0.83
2,5-Xylenol	0.00570	0.71
p-Cresol	0.00287	0.35
Saligenin	0.00272	0.34
o-Cresol	0.00211	0.26
2,6-Xylenol	0.00130	0.16

When the *ratio of paraformaldehyde to phenol* is increased, the speed of the reaction is decreased. The relation between the rate of reaction and the molar ratio of phenol to formaldehyde was found to be linear, and is given by the expression:

$$K = 0.0069\ C_F$$

where K is the rate of disappearance of formaldehyde, and C_F is the molar ratio of phenol to formaldehyde.

The effect of the *catalyst concentration*, using triethanolamine, was determined with *m*-cresol at 98°C. The catalyst function was shown to be defined by the equation:

$$\log K = -1.20 + \log C_c^{0.708}$$

where C_c is the catalyst concentration in moles per mole of *m*-cresol.

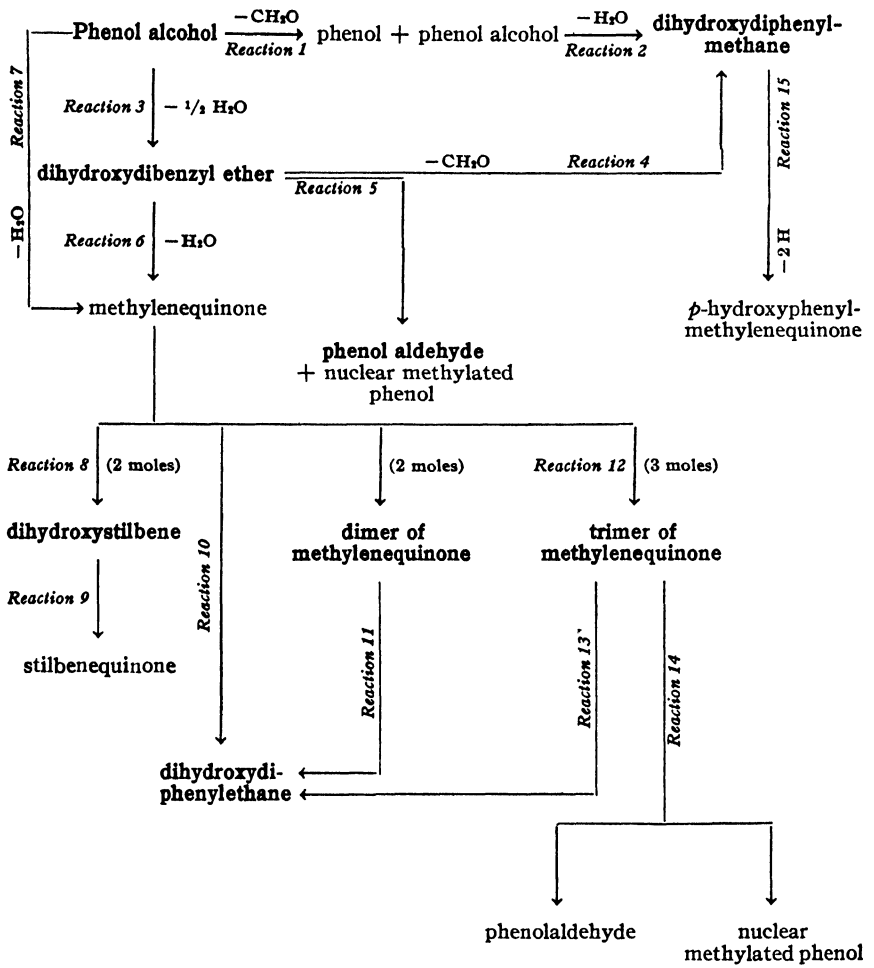
The effect of temperature upon the reaction velocity was determined over the range 68–98°C., using *m*-cresol, with 0.0241 mole of triethanolamine per mole of cresol. The heat of activation was calculated to be 13,800 cal. per mole for the initial addition reaction. Dostal and Raff[55] had earlier given the heat of activation in the neighborhood of 20,000 cal. per mole. The average temperature coefficient over the range studied was 1.71 per 10°C.

Chemistry of Curing Reactions

As has been previously stated, very little definite information on the mechanism of curing has been available until within the last few years. It was generally accepted that the phenol alcohols condensed, with the elimination of water, to yield three-dimensional macromolecules, which were cross linked by methylene bridges. However, in the case of phenols with

three reactive positions, the curing reactions were so rapid and so complex that little progress had been made in isolating and identifying compounds from the later stages of the condensation.

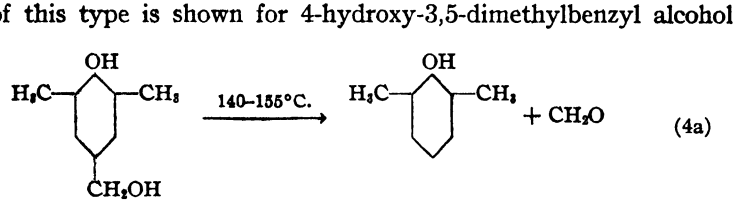
In order to overcome these difficulties, recent workers have studied the curing reactions of phenols in which one or two of the reactive ortho or para positions are blocked. In this way, only mono- or di-phenol alcohols can be formed, and insoluble cross-linked products in general cannot be obtained. In most cases, considerable yields of crystalline products are obtained,



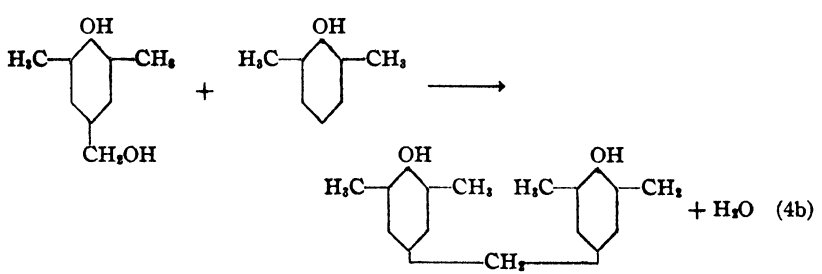
Scheme 1

and these products can be identified and their further reactions studied. It was through this line of attack that Zinke, Hultzsch, von Euler, and their respective associates have built up our present knowledge of the curing mechanism. As a result of their studies, it has been shown that the phenol alcohol, which results from the primary condensation of a phenol and formaldehyde in alkaline solution, undergoes a complex series of reactions. The extent to which these various reactions take place depends upon the structure of the initial phenol, the temperature at which the phenol alcohol is heated, and the time of heating. Scheme 1, taken from von Euler, Adler, Cedwall, and Törngren,[35] gives in diagrammatic form the various reactions which a phenol alcohol may undergo on curing. Those compounds which have been isolated in pure form are in heavy type. These various reactions will now be discussed in more detail.

Reactions 1 and 2: When a phenol alcohol is heated, some formaldehyde is split off, with a regeneration of the original phenol. The phenol then combines with the unchanged phenol alcohol, with the splitting out of water, and a dihydroxydiphenylmethane derivative is formed. A typical reaction of this type is shown for 4-hydroxy-3,5-dimethylbenzyl alcohol

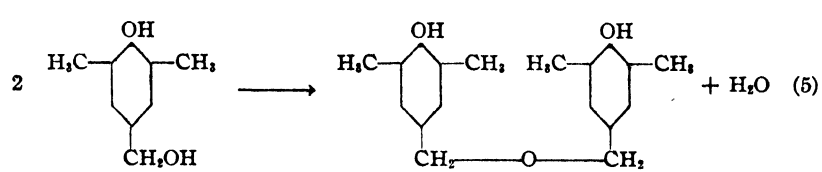


(4a)



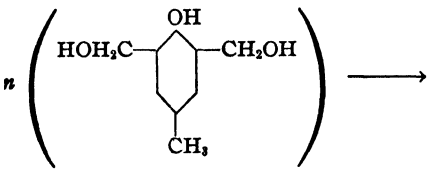
(4b)

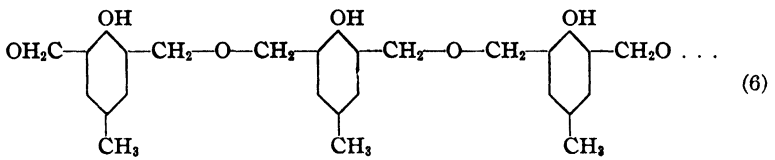
(Eqs. 4a and 4b). The extent to which this reaction takes place depends very much upon the structure of the initial phenol.



(5)

Reaction 3: Reaction *3*, as shown in Equation (5), indicates the formation of a dihydroxydibenzyl ether. When a dialcohol is used, as for example the dialcohol from *p*-cresol, long-chain ethers are formed, as shown in Equation (6). It is apparent that this reaction is, in general, the most

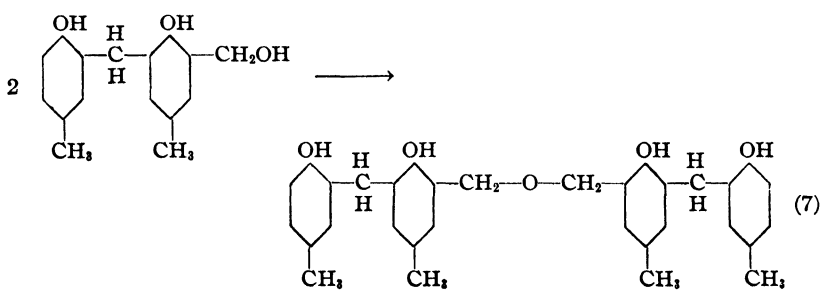




(6)

important primary reaction in the curing of highly substituted phenol alcohols. In many cases, the dibenzyl ethers form the largest single product which can be isolated from the cured reaction mass.

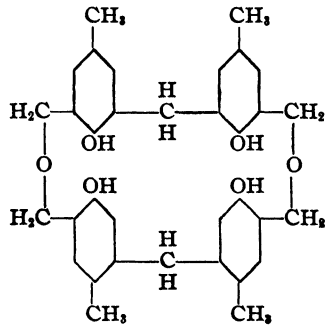
In the case of 3-(2-hydroxy 5-methylbenzyl)-2-hydroxy 5-methylbenzyl alcohol, Adler, von Euler, and Hasselquist[25] showed that only the reaction indicated in Equation (7) took place. An analogous reaction took place



(7)

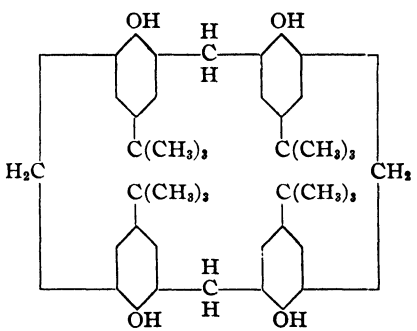
when the dialcohol was used, but in this case, in addition to a resinous linear ether, about 6–10% of a cyclic ether was formed with the structure shown in Formula V.[27] The ether formation appears to take place more slowly in the case of *p*-methylol derivatives than in the case of the ortho derivatives.

Ether formation is retarded by an increase in the curing temperature, or by the presence of alkali.[11] When alkalis are present, the formation of methylene bridges is favored. Thus, when a resole from *p-tert*-butylphenol contains alkali, it yields on heating a fairly large quantity of a crystalline



(V)

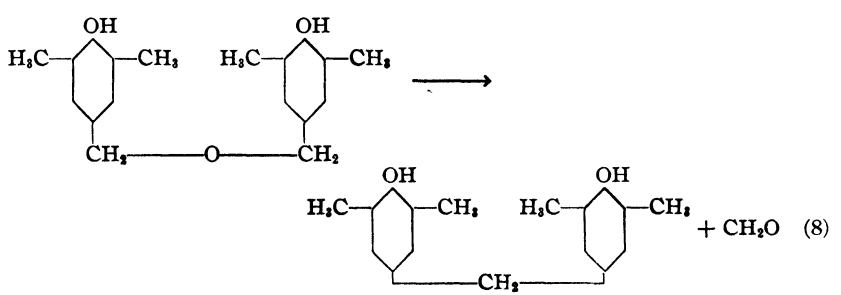
product which was identified by Zinke and Ziegler as the cyclic compound VI. It is interesting to note that this compound is similar in structure to



(VI)

the cyclic ether shown in Formula V. Apparently the action of the alkali is to split off formaldehyde from the ether, producing the cyclic methylene compound.

Reaction 4: On further heating, particularly at temperatures higher than are needed to form the ether, the latter may split off formaldehyde and give



(8)

a dihydroxydiphenylmethane which is identical with that obtained through reactions *1* and *2*. Reaction *4* may be written as in Equation (8).

Hanus and Fuchs[3] have been able to show that when phenol alcohols are heated to a certain temperature, only water is split off; when the temperature is then raised to another definite point, formaldehyde is split off, indicating the beginning of reaction *4*. The temperature increase required to initiate reaction *4*, over that required for reaction *3*, is definite and depends upon the size and nature of the substituent group. Table IV summarizes

TABLE IV

SPLITTING OFF OF WATER AND FORMALDEHYDE FROM SUBSTITUTED PHENOL ALCOHOLS

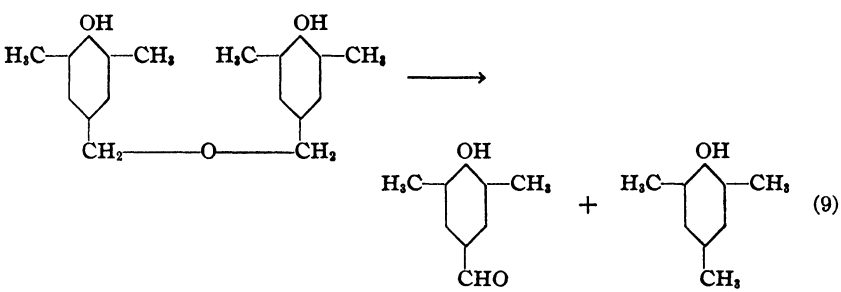
Substituent group	Temperature at which water is split off, °C.	Temperature at which CH_2O is split off, °C.	Difference, °C.
Methyl, CH_3	135	145	10
Ethyl, C_2H_5	130	150	20
Propyl, C_3H_7	130	155	25
n-Butyl, C_4H_9	130	150	20
tert-Butyl, $C(CH_3)_3$	110	140	30
Phenyl, C_6H_5	125	170	45
Cyclohexyl, C_6H_{11}	130	180	50
Benzyl, $CH_2C_6H_5$	125	170	45

the effect for dialcohols of various para-substituted phenols. The amount of water which is split off is very nearly one mole for every two moles of phenol alcohol (or one mole for every mole of phenol dialcohol) which reacts. Even under the most favorable conditions, however, much less than one mole of formaldehyde is split off for one mole of the ether. In their best experiment, Zinke and Hanus[5] were not able to get more than 0.6 mole of formaldehyde split off. This is attributed either to side reactions, or to the tendency of formaldehyde to combine further with the dihydroxydiphenylmethane derivative.

It is interesting to note that the presence of a free phenolic hydroxy group is required for reaction *4* to take place, although a free phenolic hydroxy group is not needed for the ether formation (reaction *3*). This was shown by Zinke, Hanus, and Ziegler,[2] who treated the dialcohol from *p*-cresol with *p*-toluenesulfonyl chloride to form the tosyl derivative. The latter split off water readily to form a chain ether, but this ether was stable and on further heating did not split off formaldehyde. Von Euler, Adler, Eklund, and Törngren[31] state that neither reaction *3* nor *4* takes place when the phenolic hydroxy group is etherified. Thus, the monomethyl

ether of *p*-cresol dialcohol was almost unchanged after heating one hour at 160°C., although the free *p*-cresol dialcohol resinified quickly at 130°C.

Reaction 5: Small quantities of phenol aldehydes are usually found in the cured products. Zinke has suggested that these may be formed by the thermal cracking of the dihydroxydibenzyl ethers, as shown in Equation (9). The equation also shows that a nuclear methylated body is formed simultaneously. The quantities of aldehydes formed are usually quite small (4%) even from the highly substituted phenols employed in these experiments, and the yield depends upon the nature of the substituent groups on the original phenol. Zinke and Ziegler[8] have shown that very considerable amounts of aldehyde are formed upon heating the dibenzyl ether of 3,5-dichloro-2-hydroxybenzyl alcohol (obtained by the action of formaldehyde on 2,4-dichlorophenol).



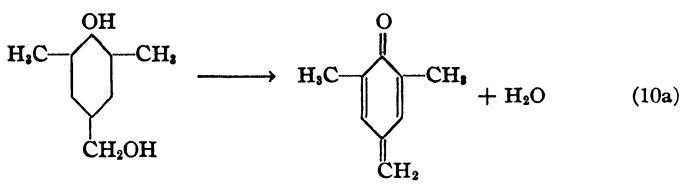
(9)

Hultzsch[18] does not favor the theory that phenol aldehydes are formed as indicated above. He points out that the reaction as written would require equimolar quantities of phenol aldehyde and nuclear methylated phenol to be formed; experiment shows that this is not always the case. Hultzsch, therefore, prefers to consider the phenol aldehyde formation as an oxidation-reduction action of methylenequinone. The presence of both dialdehydes and monoaldehydes in the curing products of cyclohexylphenol dialcohol was confirmed by Mayer-Pitsch and Troger[58] through ultraviolet light absorption studies. In any case, it is important to note that aldehyde formation plays only a minor part in the curing reaction; this is particularly true in the case of commercial phenoplasts, where phenols with two or three reactive positions are used.

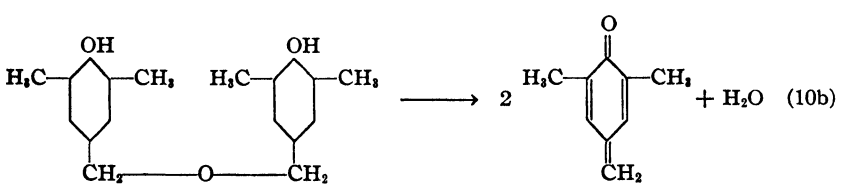
Reactions 6 and 7: The formation of methylenequinone, or quinonemethide, is particularly interesting because it indicates a mechanism by which phenoplasts, or at least a part of the resin, may be formed by *polymerization* rather than *condensation.* Baekeland had suggested that

[58] E. Mayer-Pitsch and H. Troger, *Z. Elektrochem.*, **47**, 60–65 (1941).

polymerization played a part in the formation of phenoplasts, although he offered no definite mechanism. Wohl and Mylo[59] suggested in 1912 that the polymerization might proceed through the methylene derivative of the tautomeric form of phenol, although definite proof was lacking. Novak and Cech[58] also felt that polymerization played a part in the curing reaction; it is interesting to note that these investigators showed[60] that the curing reaction was catalyzed by treatment of the formaldehyde with ozone, whereby peroxides are presumably formed. The latter would evidently be catalysts for a polymerization reaction, and would be expected to have no effect upon a condensation. Later investigators have definitely identified dimers and trimers of methylenequinone in the reaction products from the curing of highly substituted phenols. The monomer, itself, has never been identified, as it is very unstable and polymerizes rapidly. The methylenequinone may be formed directly from the phenol alcohol, as shown in Equation (10a), or it may be formed by loss of water from the dihydroxybenzyl ether, as shown in Equation (10b).

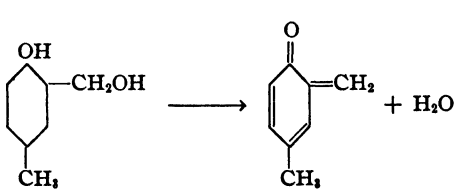


(10a)



(10b)

The equations above indicate only the formation of *para* methylenequinone, but the *ortho* compound is also formed when the methylol group is in the ortho position, as is shown in Equation (11). Generally speaking,



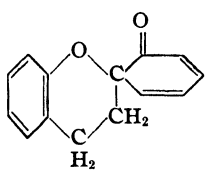
(11)

[59] A. Wohl and B. Mylo, *Ber.*, **45**, 2046–2054 (1912).

[60] J. Novak and V. Cech, *Ind. Eng. Chem.*, **24**, 1275 (1932).

the course of the reaction is the same whether the methylol group is in the ortho or para position relative to the phenolic hydroxy group.

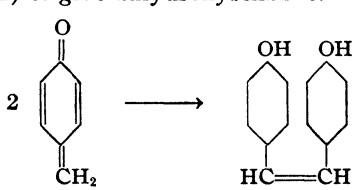
In the curing of phenol alcohols, it is probable that both reactions shown in Equation (10) take place simultaneously. However, the formation of the dihydroxydibenzyl ether is usually the predominating reaction, and this compound is usually formed at low temperatures (below 150°C.); it is rather stable at these temperatures and only breaks up into methylenequinone at higher temperatures (about 200°C.). The monomeric form of methylenequinone is unstable and polymerizes rapidly to form dimers or trimers. The dimer is colored yellow, and Pummerer and Cherbuliz have attributed to this compound the general formula of a cyclic quinone ether, as shown in Formula VII. The presence of the quinone nucleus accounts for the yellow color.



(VII)

The trimers are colorless, and apparently do not contain a quinone nucleus. Their constitution, however, is not yet known. Hultzsch[15] considers that much substitution in the phenol nucleus leads mainly to dimer formation.

Reaction 8: Methylenequinone, as has been indicated, is a very reactive and unstable substance. It may polymerize in the regular manner, as will be pointed out later under reactions *10* and *12*, but it may also dimerize as shown in Equation (12) to give dihydroxystilbene.

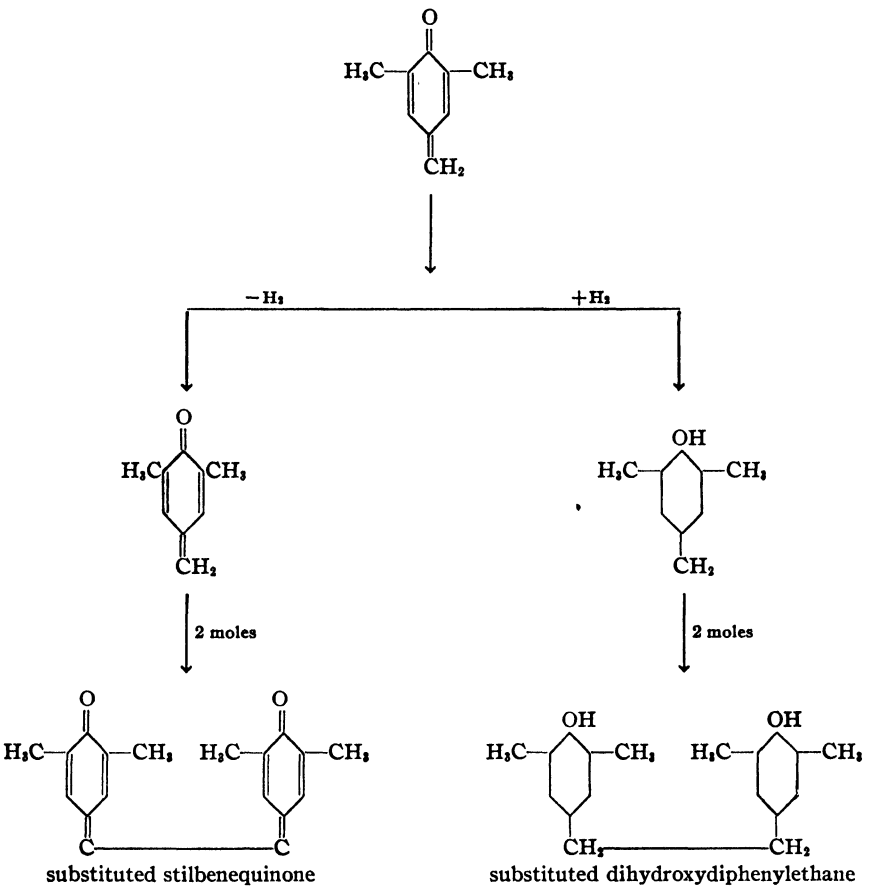


(12)

According to von Euler, Adler, and Caspersson[37] this is the only reaction which is observed in the case of the *p*-methylenequinones. The *o*-methylenequinones may go through reaction *8*, or they may dimerize and trimerize as shown in reactions *10* and *12*.

Reaction 9: It is also possible that methylenequinone may undergo a direct disproportionation while in an unstable state, and yield radicals which become stabilized by the formation, on the one hand, of a stilbene-

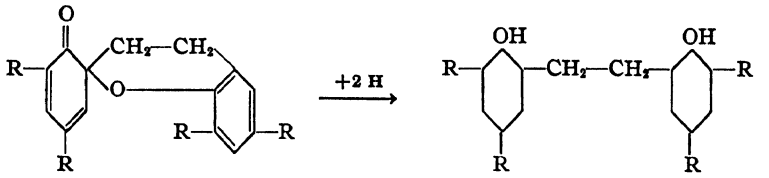
quinone, and on the other to a diphenylethane as shown in Scheme 2. Obviously, the stilbenequinone may then undergo still more reactions, resulting in more complex substances.



Scheme 2

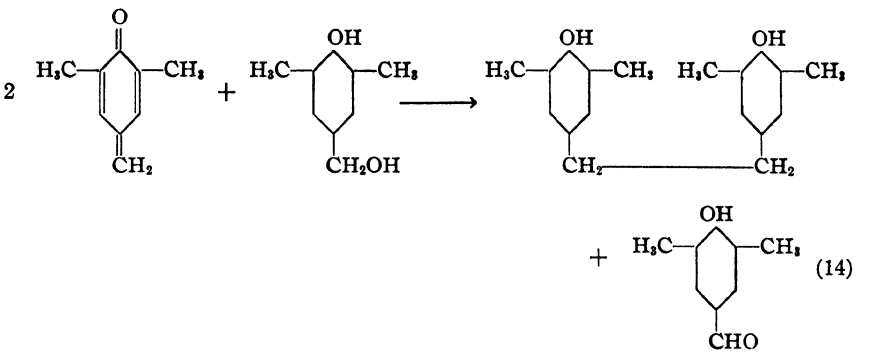
Reactions 10 and 12: These reactions, as indicated in Scheme 1, are simple polymerization reactions of methylenequinone.

Reactions 11 and 13: One possible mechanism for the formation of a dihydroxydiphenylethane derivative has been suggested under reaction *9*. Another possibility lies in the rearrangement of the dimer of methylenequinone to form a cyclic quinone ether, which may then serve as a hydrogen acceptor and produce a diphenylethane derivative:



(13)

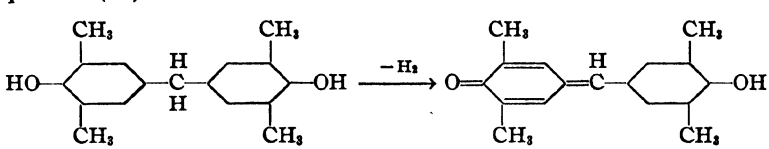
Reaction 14: The formation of phenol aldehydes by cracking of the dihydroxybenzyl ether has already been discussed under reaction *5*. In addition to this mechanism, phenol aldehydes may be formed by the reaction of two moles of methylenequinone with one mole of unchanged phenol alcohol, as shown in Equation (14). At the same time, one mole of a dihydroxydiphenylethane derivative is formed.



(14)

From the dialcohols, dialdehydes may be formed by an analogous reaction.

Reaction 15: Von Euler and his associates identified small quantities of a compound which was apparently a *p*-hydroxyphenylmethylenequinone. This seems to be formed during the curing reaction by dehydrogenation of the corresponding dihydroxydiphenylmethane derivative, as shown in Equation (15).



(15)

This concludes the discussion of the curing reactions of the resoles as explained by the results of the recent work of Hultzsch, Zinke, von Euler, and their respective co-workers. It is important to understand that many of the above reactions may take place only to a very limited extent in the case of phenols with three reactive positions, such as are used commercially

at present. This point will be covered in greater detail in the subsequent discussion on the curing of technical resins. To prove the existence of many of the above reactions, it is necessary to use highly substituted phenols. However, regardless of the constitution of the phenol, it is certain that the curing of a resole represents a complicated series of reactions.

Kinetics of the Curing Reaction

It is understandable that no exact mathematical study of reaction kinetics has been made since so many complicated reactions may take place at one time. However, a few authors have made an attempt at a qualitative, and even a semiquantitative, study of the reaction. Megson[54] determined what he called the heat-hardening time. This was the time required to form a permanent cloudiness when 0.25 gram mole of the phenol was heated at 100°C. with paraformaldehyde equivalent to 0.25 gram mole of formaldehyde. Pyridine was employed as a catalyst. Table V contains the heat-hardening time for various phenols with varying quantities of catalyst.

TABLE V

EFFECT OF CATALYST ON HEAT-HARDENING TIME (IN HOURS)

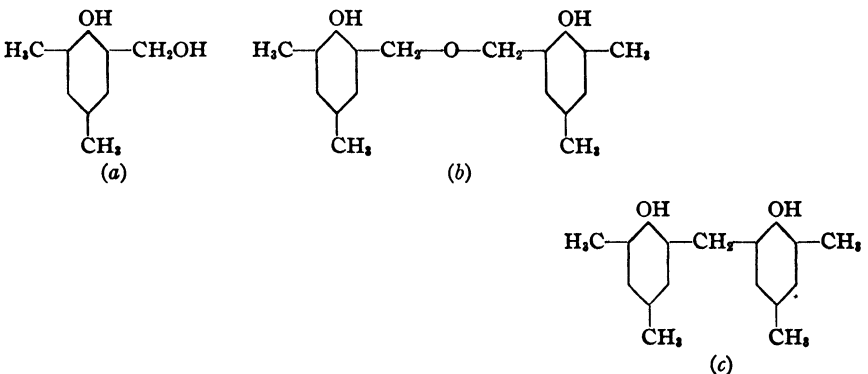
Catalyst	Amount of pyridine, g.						
	0.05	0.1	0.25	0.5	1.0	2.0	3.0
Phenol	...	...	16.0	12.5	9.0	6.1	10.0
m-Cresol	5.2	4.3	3.3	2.5	2.1	1.9	1.7
p-Cresol	...	...	...	...	14.5	12.5	16.0
m-5-Xylenol	1.8	1.4	1.0	0.85	0.80	0.75	0.75

o-Cresol gave no cloudiness after 120 hours. The reaction in the case of the other phenols appears to have stopped at the B stage, since Megson states that the resins were swollen in acetone.

Sprung[57] studied the kinetics of the curing reaction and estimated the heat of activation for *m*-cresol resins at 15,800 calories per mole in the range 68–98°C. This is about the same value found by Sprung for the addition reaction.

The presence of catalysts, and their concentration and type, certainly must have a profound influence on the curing reaction. However, very little is known, even qualitatively, on this point. It appears that the presence of alkali accelerates the formation of diphenylmethane compounds from the long chain ethers, although the effect seems to be influenced by the substituents on the nucleus. For example, Zinke and Ziegler[8] report

that either 3-5-dimethyl-2-hydroxybenzyl alcohol (Formula VIII*a*) or its ether (Formula VIII*b*) changes rapidly to the diphenylmethane derivative (Formula VIII*c*) on boiling with alkali. However, when 3,5-dichloro-2-hydroxybenzyl alcohol is similarly treated, no diphenylmethane derivative is formed.



(VIII)

C. THE NOVOLACS

When phenol is condensed with formaldehyde in *acid* solution, the product which is obtained is entirely different from that which is obtained in *alkaline* solution. When less than six moles of formaldehyde are used per seven moles of phenol, the products are permanently fusible and soluble, and are called *novolacs*.

It has been quite well established by a number of authors[51,61–74] that the

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[61] M. Koebner, *Chem.-Ztg.*, **54**, 619 (1930).

[62] F. Pollack and F. Riesenfeld, *Z. angew. Chem.*, **43**, 1129–1132 (1930).

[63] N. J. L. Megson and A. A. Drummond, *J. Soc. Chem. Ind.*, **49**, 251–257T (1930).

[64] M. Koebner, *Z. angew. Chem.*, **46**, 251–256 (1933).

[65] N. J. L. Megson, *Phenomena of Polymerization and Condensation.* Faraday Society, London, 1935.

[66] A. Vanscheidt, A. Itenberg, and T. Andreeva, *Ber.*, **69**, 1900–1907 (1936).

[67] F. Seebach, *Chem. Weekblad*, **27**, 55–56 (1987).

[68] F. Seebach, *Kunststoffe*, **27**, 287–290 (1937).

[69] A. Vanscheidt, *Org. Chem. Ind.* (*U.S.S.R.*), **3**, 385–393 (1937).

[70] F. Seebach, *Chem.-Ztg.*, **62**, 369–371 (1938).

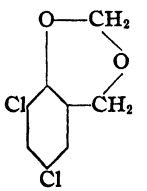
[71] M. Koebner, *Brit. Plastics*, **14**, 95–101 (1942).

[72] G. T. Morgan and N. J. L. Megson, *J. Soc. Chem. Ind.*, **52**, 418–420T (1933).

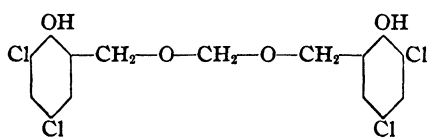
[73] N. J. L. Megson, *ibid.*, **52**, 420–424T (1933).

[74] J. Scheiber and R. Barthel, *J. prakt. Chem.*, **147**, 99–109 (1936).

novolacs are long-chain polymers, in which the phenolic nuclei are connected by methylene bridges. It appears probable that the initial compound formed even in acid solution is a phenol alcohol, and that this condenses instantly under the influence of the acid catalyst to give a diphenylmethane derivative.[74] In support of this view, Baekeland[75] claimed to have isolated crystals of phenol alcohol from the condensation product of phenol and formaldehyde in the presence of hydrochloric acid. Ziegler and Simmler[76] showed that when 2,4-dichlorophenol is condensed with trioxymethylene at 0°C. in a mixture of acetic and sulfuric acids, the primary product of reaction is the phenol alcohol. With an excess of formaldehyde, either ring or chain acetals (Formula IX*a* or *b*, respectively) are formed; with an excess of phenol, the usual diphenylmethane derivative is produced. There is an equilibrium between the formation of *a* or *b*, depending upon the concentration of acid; concentrated acid favors formation of the chain acetal.



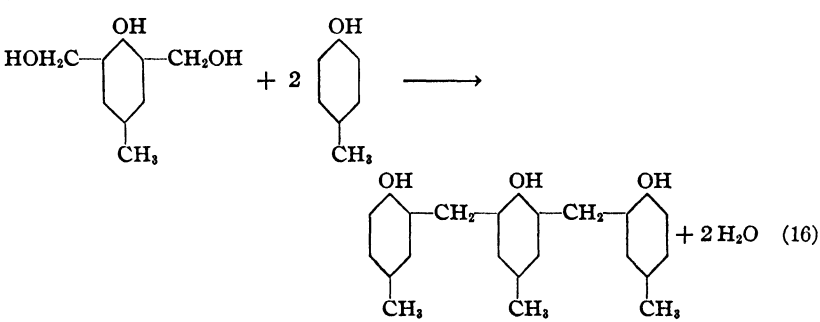
(*a*)



(*b*)

(IX)

As Koebner[77] and others have shown, novolac chains may also be obtained by the condensation of phenol dialcohols with phenols in acid solution. For example, with *p*-cresol dialcohol the following reaction takes place:



(16)

[75] L. H. Baekeland, *J. Ind. Eng. Chem.*, **4**, 737–743 (1912).

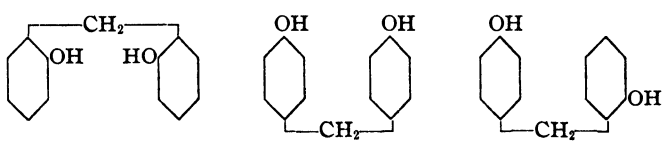
[76] E. Ziegler and I. Simmler, *Ber.*, **74**, 1871–1879 (1941).

[77] M. Koebner, *Chem.-Ztg.*, **54**, 619 (1930).

Niederl and Ruderman[78] have shown that when a phenol dialcohol reacts with a phenol in which the para position *only* is blocked, polynuclear compounds of a resinous nature are formed (i.e., long chain novolacs). When both one ortho and the para position of the phenol are blocked, trinuclear compounds *only* are formed. Thus, by condensing *p*-cresol with the appropriate methylol derivatives of dicresylmethane, Koebner[79] was able to isolate pure compounds with two, three, four, and five cresyl rings; the melting points were 126°, 215°, 170°, and 202–206°C., respectively.

The general method for the preparation of novolacs is the condensation of formaldehyde with a phenol in acid medium; however, under certain special conditions, a novolac may be obtained by the action of phenol on a resole. Koebner[71] showed that a novolac could be obtained when ten moles of phenol were condensed with five moles of formalin in the presence of ammonia as a catalyst; the water and excess phenol were then removed by distillation without vacuum up to a temperature of 160°C., after which the remainder of the excess phenol was removed by distillation under vacuum up to a temperature of 170°C. Apparently, the phenol alcohols condensed with the excess phenol at the high temperature to give diphenylmethane chains. When vacuum was applied immediately after condensation, and the excess phenol removed at a low temperature, only a resite was formed.

The simplest type of novolac is dihydroxydiphenylmethane. Substitution may occur in either the ortho or para position. In the case of phenol itself, three isomers are possible, as shown in Formula X.



(*a*) (*b*) (*c*)

(X)

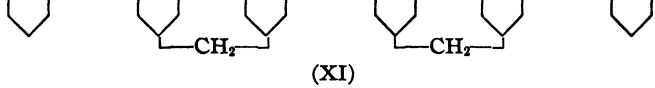
Of these three, only *b* and *c* have been isolated. According to Megson[65] there appears to be a connection between the time of condensation and the yield of *c*, and the latter appears to be of more importance than *b* as an intermediate in resin formation.[80] The compound *a* has not been identified as such, but exists in a dehydrated form as xanthene.

Edell[81] prepared the various dihydroxydiphenylmethanes by the reaction

[78] J. B. Niederl and I. W. Ruderman, *J. Am. Chem. Soc.*, **67**, 1176–1178 (1945).
[79] M. Koebner, *Z. angew. Chem.*, **46**, 251–256 (1936).
[80] G. T. Morgan, *J. Soc. Chem. Ind.*, **49**, 245–251T (1930).
[81] G. M. Edell, *Dissertation*, Columbia University, May, 1932.

of eight moles of phenol with one mole of formaldehyde in the presence of hydrochloric acid, and separated a series of crystalline isomers. From these he identified the 2,4′- and the 4,4′-dihydroxydiphenylmethanes. He also claims to have isolated the 2,3′-dihydroxydiphenylmethane. If a rigid proof of the identity of this compound had been supplied it would have been interesting, since it would have been the first case of meta substitution definitely reported in the phenol formaldehyde condensation. However, a study of the original paper shows that there is considerable doubt as to the correct identity of the third compound isolated by Edell.

Appreciable yields of dihydroxydiphenylmethane are obtained only when a large excess of phenol is used—in the neighborhood of ten moles of phenol to one mole of formaldehyde. When lower ratios of phenol are employed, as is usual in commercial manufacture, a series of long-chain compounds are formed, with varying chain lengths. The resin formed thus has a distribution curve which is very similar to that of a thermoplastic polymer, such as polystyrene. However, the average chain length is much shorter; a novolac will usually consist of only eight to twelve units, while a commercial thermoplastic such as polystyrene may contain 1000 or more units. A typical formula for a commercial novolac is given in Formula XI below.



(XI)

It must be understood that this formula is highly idealized. The phenolic nuclei are actually connected by methylene bridges in ortho and para positions in an entirely random manner. The number of possible isomers is very large, depending upon the number of reactive positions in the phenol nucleus and the length of the novolac chain. Table VI, which is taken from Megson,[73] indicates the number of straight-chain isomers which theoretically can be obtained from various phenols, up to a length of only five units in the polymer chains. This table does not exhaust the possibilities of isomerism, because phenols which can form trialcohols may produce branched-chain isomers. On the other hand, the number might be somewhat less as steric hindrance might prevent the formation of some of the theoretically possible isomers.

Phenols which have only one reactive position, such as 1,2,4-xylenol, 1,2,6-xylenol, and pseudocumenol give only dihydroxydiphenylmethanes, and not resins, as they have no active positions free for further condensation.

TABLE VI

ISOMERIC NOVOLACS WHICH CAN BE OBTAINED FROM SUBSTITUTED PHENOLS

Phenolic compound	2-ring compounds	3-ring compounds	4-ring compounds	5-ring compounds
Mesitol	...	...	...	...
m-2-Xylenol *m*-4-Xylenol	1	...	...	...
p-Cresol	1	1	1	1
Phloroglucinol	1	1	1	1
o-Cresol *o*-3-Xylenol *o*-4-Xylenol *p*-2-Xylenol	3	4	10	16
Phenol *m*-5-Xylenol Resorcinol	3	7	21	57
m-Cresol	6	27	135	?

Koebner[71] has shown that the mean molecular weight of the novolac increases as the molar ratio of formaldehyde to phenol increases. Table VII, taken from Koebner, shows the manner in which this increase takes place; hydrochloric acid was used as the catalyst.

TABLE VII

EFFECT OF FORMALDEHYDE–PHENOL RATIO ON MOLECULAR WEIGHT OF NOVOLAC

Moles formaldehyde per 10 moles phenol	Mean molecular weight of resin	Type of resin
1	229	Dihydroxydiphenylmethane
2	256	Novolacs
3	291	
4	334	
5	371	
6	437	
7	638	
8	850	
9	1000	
12	?	Insoluble resite

Vanscheidt[69] has developed from Koebner[64] the formula shown below to compute the average molecular weight of the novolac when the quantity of aldehyde reacted and the yield of anhydrous resin are known:

$$M = 94\,A/(A - 106)$$

where M is the average molecular weight of the resin and A is the yield of anhydrous resin in grams per gram mole of reacted aldehyde. Vanscheidt,

Itenberg, and Andreeva[66] have shown that a novolac may be fractionated either by partial extraction with alkali or by partial precipitation from alcohol solution. In the first case, the compounds with lower molecular weight are extracted first; in the second case, the compounds with higher molecular weight are precipitated first. In Vanscheidt's experiments, the novolac was prepared by condensing 7.8 moles of phenol with 6.0 moles of formaldehyde, using a little hydrochloric acid as a catalyst. After the condensation was complete, the mixture was steam distilled to remove the excess phenol, and the resin was dehydrated. Table VIII shows the results obtained by alkali extraction, while Table IX shows the results of fractional precipitation from alcohol.

TABLE VIII

FRACTIONATION OF NOVOLAC BY ALKALI EXTRACTION

Physical characteristics	Fraction				Original resin
	I	II	III	IV	
Molecular weight	203	468	763	980	642
Degree of polymerization	1.03	3.5	6.3	8.4	5.2
Average melting point, °C.	61	95	119	130	108
Relative viscosity, 30% alcoholic solutions	2.15	5.64	7.9	9.8	6.7

TABLE IX

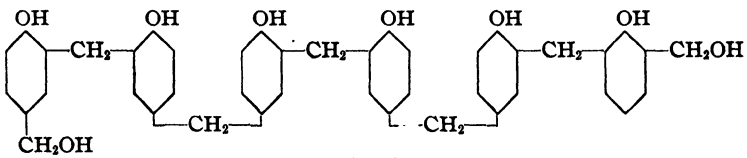
FRACTIONATION OF NOVOLAC BY PRECIPITATION

Physical characteristics	Fraction					Original resin
	I	II	III	IV	V	
Per cent of original resin	10.7	37.4	16.4	19.5	16.0	...
Molecular weight	210	414	648	870	1270	642
Degree of polymerization	1.1	3.0	5.25	7.3	11.1	5.2
Phenolic hydroxy group, %	...	16.6	...	...	16.15	16.05
Average melting point, °C.	64	89	111	125	134	108
Relative viscosity in 30% alcoholic solutions	2.57	5.12	6.83	8.88	12.5	6.7

Because the phenolic hydroxy group is still present, the novolacs are soluble in sodium hydroxide; however, the solubility of the phenates decreases as the length of the novolac chain increases; compounds which have as many as seven nuclei give salts which are almost insoluble in water.[82]

[82] M. Koebner, *Brit. Plastics*, 11, 7–9, 43 (1939).

The novolacs are permanently fusible and soluble, and do not of themselves pass into a cross-linked state. Consequently, for commercial use they must be further reacted with formaldehyde. This is usually done in two ways: (*1*) The novolac may be further condensed with formaldehyde in *alkaline solution*, when a type of resole is formed which then goes through the curing reactions previously described. (*2*) The novolac may be intimately mixed with hexamethylenetetramine, which on heating becomes a source of methylol groups. In either case, the course of curing is probably the same: one or more methylol groups are added to the novolac chain to give a complex phenol alcohol of the type shown in Formula XII (compare



(XII)

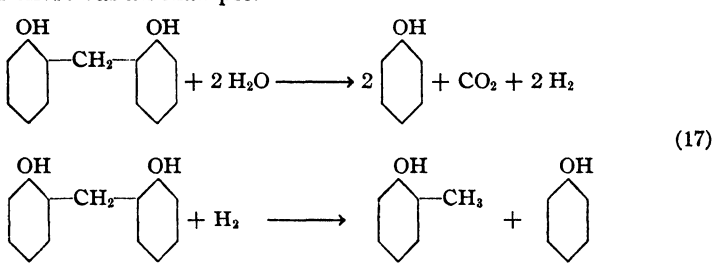
with the idealized formula previously given for a typical novolac). It must be stressed that this formula is only an idealization; in fact, a series of isomers is formed, and the methylene bridges and methylol groups may be present in any of the statistically possible ortho and para positions. However, these compounds are typical resoles, with free methylol groups, and so can undergo any or all of the curing reactions which have already been detailed for the resoles.

The fundamental difference between a resole and a novolac is the presence of one or more methylol groups on the former; it is through the reactions of these methylol groups that cross linking is accomplished. Scheiber and Barthel[74] have shown the importance of free *o*- and *p*-reactive positions in the curing reaction. They point out that when a phenol with three reactive positions is used in the condensation, every chain composed of n phenol nuclei has no less than $n + 2 = N$ reactive points. Thus the combination of such a chain to a structure with twice as many nuclei gives at once $N(N + 1)/2$ possibilities for orientation. This means, for example, that when a 5-chain combines to form a 10-chain there are 28 possibilities. Then to form a 20-chain from the 10-chain there are 78 possibilities, and for the conversion of this to a 40-chain there are 253 possibilities. Thus, it may be seen that size of the molecule offers no statistical obstacle to orientation, and such difficulties become less as the chain length increases. This explains not only the cause of the surprisingly strong tendency toward resite formation but also the reason for the abrupt, direct transition to the resitol and then to the resite stage.

Decomposition Products of Resites

In all the work to which references have so far been made, the structure of the resins has been determined by the isolation of definite compounds from the condensation reaction. The problem has also been approached by a study of the thermal decomposition products of the cured resin, or by a study of the products obtained by prolonged digestion with sodium hydroxide.

In 1921, Herzog[83] digested various phenolic resins with sodium hydroxide, and found that part of the phenol could be recovered. Allen, Meharg, and Schmidt[84] heated the cured resin in an autoclave, at 300°C. for several hours with 10–15% sodium hydroxide. The hydrolysis product always contained a greater proportion of higher boiling phenols than did the material from which the resin was made. This shift toward the higher phenols was more noticeable the further advanced the resin and the higher the ratio of formaldehyde to phenol. Often phenols were formed which did not occur in the original raw material. A considerable amount of hydrogen was also formed. While the mechanism of the reaction was not completely explained, it is evidently connected with the rupture of methylene bridges. The net effects may be illustrated by Equations (17), in which the simplest methylene bridged compound, dihydroxydiphenylmethane, is chosen as an example.

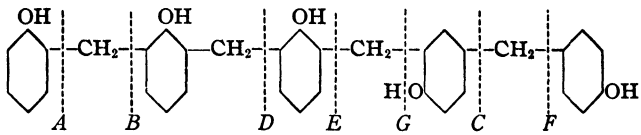


(17)

Megson[65] made a thorough study of the thermal decomposition of novolacs. The resin, after washing with hot water to remove catalyst, excess formaldehyde, and water-soluble phenols, was decomposed in a distillation flask by heating up to 450°C.; the distillate was collected and the various fractions identified. Megson points out that a typical novolac from phenol, in which the methylene bridges are distributed at random in *o*- or *p*-positions to the phenolic hydroxy group, might be expected to rupture at the dotted lines of Formula XIII.

[83] W. Herzog, *Z. angew. Chem.*, **34**, 97 (1921).

[84] I. Allen, V. E. Meharg, and J. H. Schmidt, *Ind. Eng. Chem.*, **26**, 663–669 (1934).



(XIII)

If rupture takes place at *A*, phenol will be broken off from the end of the molecule. If rupture occurs at *B* or *C*, *o*- or *p*-cresol should result. If breaking should take place at *A* and *D* simultaneously, *m*-2-xylenol should be produced, and similarly splitting between *E* and *F* would yield *m*-4-xylenol. If decomposition should occur simultaneously at *B* and *E*, a dihydroxydiphenylmethane would be formed. If cross linking of the long chains were present, mesitol could theoretically be produced.

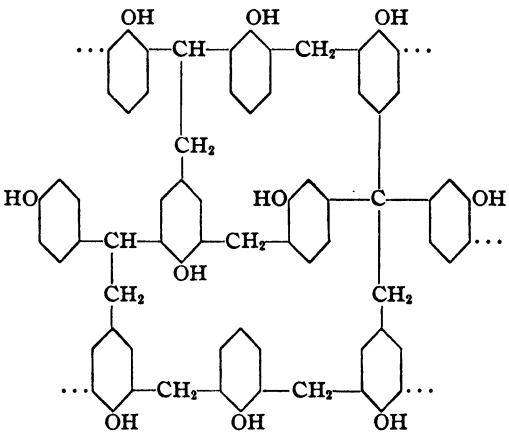
Experiment actually showed that only phenol and *o*- and *p*-cresols were present in the acidic portion of the distillate when phenol was the starting material. The yield of *p*-cresol was small compared to the ortho isomer; this was interpreted as meaning either: (*1*) that *p*-substitution was of less frequent occurrence than *o*-substitution; (*2*) that decomposition takes place more readily at *o*-linkages; or (*3*) that the resin contains a high proportion of *o*-linkages, brought about by preferred condensation in the *o*-position. In addition to phenol bodies, xanthene and its methyl homologues were present in the neutral portion of the distillate. The production of these homologues was explained by splitting of the novolac chain at *A* and *G* simultaneously with the elimination of water between hydroxy groups. Analogous results were obtained by the decomposition of resins from *m*-cresol, *p*-cresol, and *m*-5-xylenol. Megson's work, in general, fully supported the hypothesis that the novolac resins consist of complex mixtures of long-chain molecules connected by methylene bridges. These conclusions have been more recently confirmed[85] by studies of the thermal decomposition of 3,5-*bis*-hydroxymethyl-*p*-cresol.

Waterman and Veldman[86] criticized the results of straight thermal decomposition, largely on the ground that, when a decomposition product like phenol has been formed, two hydrogen atoms are wanted on the spot where the rupture has taken place. If these hydrogen atoms are not available, noncontrollable reactions may occur. To overcome these objections, Waterman and Veldman decomposed the resin under hydrogen pressure, in the presence of molybdenum as catalyst. The principal products from a novolac were phenol, benzene, cresols, and toluene. From resoles, the

[85] M. G. Barclay, A. Buraway, and C. H. Thomson, *J. Chem. Soc.*, **1944**, 400–404.

[86] H. I. Waterman and A. R. Veldman, *Brit. Plastics*, **8**, 125–128, 182–184 (1936).

yields of these products were much less, and the ratio of cresols to phenol was much greater. The authors concluded that in the fully cured resin, methylene bridges may exist between methylene bridges which have already been formed, as shown in Formula XIV.



(XIV)

D. ACID-CURED RESITES

Resites—that is, insoluble and infusible cross-linked resins, may be obtained when resoles are treated with acids or with metal chlorides.[87] They may also be obtained when a phenol with three reactive positions is condensed with a large quantity of formaldehyde in acid solution. Soluble and fusible novolacs are formed only when less than six moles of formaldehyde are condensed in acid medium with seven moles of phenol. When a higher ratio of formaldehyde is used, the resins formed become insoluble. The formation of the insoluble resin is apparently very sensitive to the quantity of formaldehyde employed. Thus, Pollack[62] has shown that when the formaldehyde ratio is increased from 6.04 moles to 6.075 moles, insoluble gel lumps begin to form in the reaction mass. The cause of insoluble resin formation is not clear, and nothing is known as to the structure of these resins. It is difficult to understand why such a slight additional amount of formaldehyde would cause the straight-chain type of novolac to cross link. The structure and formation of the acid-cured resins appear to be a fruitful subject for future resin research.

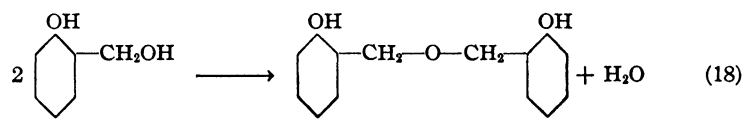
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[87] L. E. Stout and C. R. McAlister, Jr., *Modern Plastics*, **18**, 59–61, 98 (Nov., 1940).

E. COMPOSITION OF TECHNICAL RESITES

Recent investigators of the curing mechanism have, of necessity, used highly substituted phenols, with one or more of the ortho or para positions blocked. This procedure was necessary in order to reduce the complexity of the reaction, and to obtain crystalline products which could be identified. In contrast, the commercial resin manufacturer uses pure phenol or meta substituted phenols, with three reactive positions, in order that the resin may cure as rapidly and as completely as possible. The question then becomes: Do these technical resins go through the same curing scheme as shown in Scheme 1 on page 18?

It seems clear that they do, although the extent and proportionality of the various reactions of Scheme 1 cannot be predicted. Due to the greater reactivity conferred by the large number of reactive positions, it seems probable that the various reactions of Scheme 1 take place more nearly simultaneously than in the case of the more highly substituted phenols. As Hultzsch[14] has mentioned, the reactions in technical phenoplasts take place at lower temperatures than in the case of pure substances. Ziegler[7] has studied the behavior of *o*-hydroxybenzyl alcohol (saligenin), one of the primary reaction products from the alkaline condensation of phenol and formaldehyde. When this compound was heated at 140°C., a 16% yield was obtained of the dibenzyl ether, as shown by Equation (18).



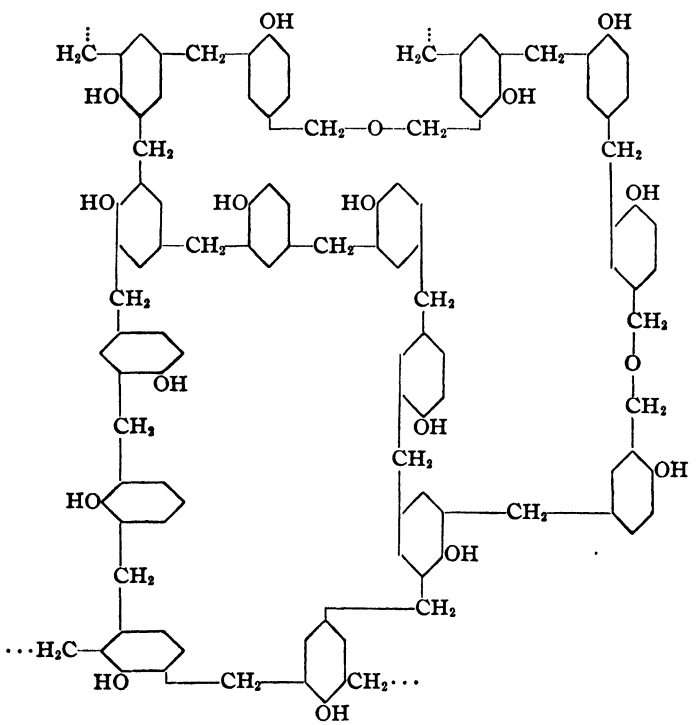
(18)

This ether had been known for a long time under the name of saliretin, although its identity had not been established. Proof that it is formed from saligenin indicates that phenols with several reactive positions also go through the stage of dibenzyl ether formation. Barthel[88] has recently shown that the phenol alcohols and their ethers can be acetylated without resinification. It is possible that the application of this technique may permit a more exact study of the curing products from commercial resins based on phenols having three reactive positions.

A word must now be said regarding the probable structure of the *cured* technical phenoplasts. In order to obtain rapidity of cure and maximum resistance to solvents, the technical products are made from phenols having three reactive nuclear positions, such as phenol itself. The reaction conditions differ from the purely scientific studies, in that high concentra-

[88] R. Barthel, *J. prakt. Chem.*, **161**, 77–80 (1942).

tions of phenol and formaldehyde are used.[89] Slightly more than one mole of formaldehyde is employed when the resoles are formed. Consequently, the finally cured product has a maximum of cross linking with branching in three dimensions, and is largely insoluble in all solvents. Usually, there is present about 4% of material which can be extracted with acetone. The bridges among the phenol nuclei appear to be methylene groups, although some ether groups may still be present, depending upon the degree of cure. Some of the macromolecules are probably formed by a methylenequinone polymerization; this is not necessarily the polymerization of methylenequinone itself, but may be the polymerization of a methylenequinone grouping at the end of a diphenylmethane or dibenzyl ether chain. It is obviously impossible to give any definite formula for a cross-linked pheno-



(XV)

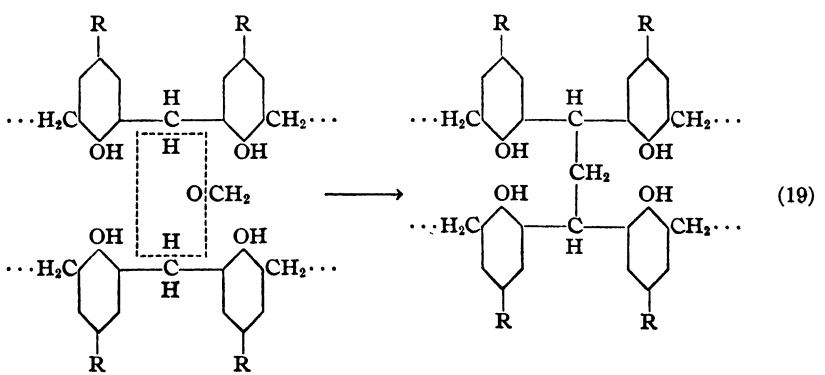
[89] J. H. de Boer, R. Houwink, and J. F. H. Custers, *Rec. trav. chim.*, **52**, 709–718 (1933).

plast, but Formula XV, analogous to that of Dreher,[90] indicates the type of structure which is probably present. Dreher's original formulation showed only methylene bridges; in Formula XV a few ether bridges have been added to indicate the possibility that these may be present. It is also probable that more complex linkages are present, such as those resulting from the methylenequinone condensations. In an effort to avoid too great a complexity in the figure, such linkages have not been shown.

In place of the cross-linked chains shown in Formula XV, some authors, such as Blumfeldt,[91] have attempted to ascribe a condensed ring structure to the cured resite; such speculations have often been made with little or no experimental evidence. The falsity of these assumptions has been shown by the fact that fusion of the resin with caustic gives good yields of phenol and cresols, and by the fact that oxidation of the resin with nitric acid gives large quantities of picric acid.[2]

Further evidence of the presence of methylene bonds was provided by de Boer, Houwink, and Custers[89] who studied the changes in light absorption and refraction during the formation of synthetic resins. The spectra of cured and uncured phenoplasts gave curves which were almost identical from 2300 to 3750 Å.; the curve of the cured resin was displaced about 50 Å. to the lower end of the spectrum, which is characteristic of the presence of methylene groups. The spectrum resembled that of alkyl phenols, but not phenol ethers, showing that the methylene group was on the nucleus, and not on the phenolic hydroxy group. The magnitude of the displacement suggested both ortho and para substitution.

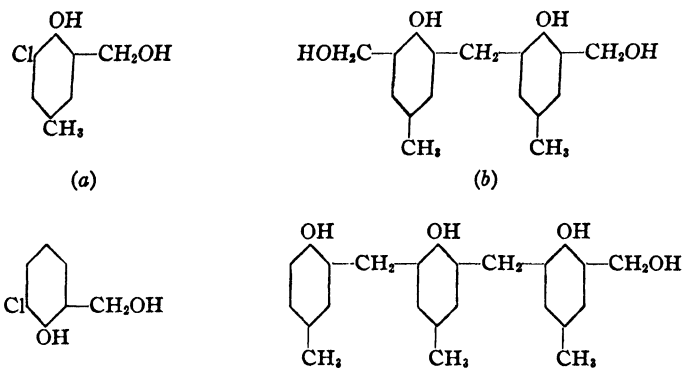
There is a possibility that some cross linking may take place through formaldehyde addition to the methylene bridge. One type of such cross



(19)

[90] E. Dreher, *Zur Chemie der Kunststoffe*. Lehmanns Verlag, Munich, 1939, pp. 69–91.
[91] A. E. Blumfeldt, *Chem.-Ztg.*, **53**, 493–494 (1929).

linking has already been referred to in Formula XIV. Zinke and Hanus[5] have discussed the possibility that formaldehyde may add to methylene bridges as shown in Equation (19). This possibility is suggested by the fact that polynuclear phenol alcohols (for example, those shown in Formula XVI), on heating, split out less formaldehyde per mole, but far more water, than in the case of the mononuclear alcohols. Since the polynuclear alcohols illustrated have no further reactive positions on the nucleus, Zinke and Hanus conclude that the greater elimination of water can only be due to condensation of methylene groups with the formaldehyde which is split off during resinification.



(XVI)

The possibility of a type of linkage other than methylene bridges between phenolic nuclei has been suggested by Redfarn,[92,93] who claims to have obtained thermosetting resins from hemimellitenol (Formula XVII*a*), and 4-chloro-1,3,5-xylenol (Formula XVII*b*). These phenols have only two reactive positions, and consequently could not give cross-linked resins through methylene or methylene ether bridges alone.



(XVII)

[92] C. A. Redfarn, *Brit. Plastics*, **13**, 481–482 (1942).
[93] C. A. Redfarn, *ibid.*, **14**, 136 (1942).

SUMMARY

From the above discussion it is evident that the chemical structure of a cured phenoplast is complex, and that a variety of reactions take place during the curing process. There are still many gaps in our knowledge, particularly that concerning the condensation of phenols with three reactive positions on the nucleus. However, the well-established facts can be summed up as follows:

1. The initial reaction of formaldehyde with phenol yields a phenol alcohol. The methylol groups enter the ring in ortho and para positions to the phenolic hydroxy group.

2. In the presence of an acid catalyst, and when less than 0.86 mole of formaldehyde is used per mole of phenol, the primary phenol alcohols instantly condense to give a series of diphenylmethane chains, having from two to nine phenolic nuclei. These acid-condensed products are called novolacs, and do not undergo further curing reactions unless more methylol groups are supplied.

3. In the presence of an alkaline catalyst, the phenol alcohols (resoles) go through a complicated series of reactions. When the phenol has three reactive positions, the curing reactions eventually end in the production of an insoluble and infusible resin (resite).

4. The curing reactions are by no means simple, and a number of competing reactions take place at the same time.

5. Substitution in the phenolic nucleus has a profound effect not only on the nature of the curing reaction, but also on its kinetics. Alkyl groups meta to the phenolic hydroxy group greatly increase the speed of the addition reaction and the curing reactions. Substitution in ortho or para positions reduces the speed of the reactions.

6. The curing reaction which predominates depends upon the type and degree of substitution (i.e., the number of reactive positions) of the phenolic nucleus, and on the reaction conditions (temperature, catalyst, etc.)

7. The principal reaction in the early stages of curing appears to be the formation of dibenzyl ether linkages between phenolic nuclei.

8. The next principal reaction appears to be the splitting out of formaldehyde from the dibenzyl ether linkages, with the formation of methylene bridges between the phenolic nuclei.

9. In the case of phenols with three reactive positions, the formation of methylene linkages appears to take place almost instantly from the dibenzyl ether linkages; the cured resin has principally methylene bridges.

10. In addition to methylene linkages, the cured resin may contain some ethylene and stilbene linkages, resulting from the reactions with methylenequinone bodies. It is also possible, but not definitely proved, that some propylene linkages may be present.

11. Either the phenol alcohols or the dibenzyl ethers may form a methylenequinone body, which then forms larger molecular aggregates by polymerization.

12. The cured resin is cross linked in three dimensions, and has a high, but undetermined, molecular weight.

III. PHENOPLASTS FROM HIGHER ALDEHYDES

The discussion in Chapter II on the chemical structure of phenoplasts has covered only condensations with formaldehyde. Higher aldehydes are occasionally used in the manufacture of phenoplasts, although by far the greatest percentage of these resins is made from formaldehyde. There are two reasons for this: (*1*) Condensation with formaldehyde gives, in general, resins which have shorter curing times than those of higher aldehydes, and (*2*) formaldehyde is subject to few, if any, side reactions in the presence of the condensation catalysts. The latter consideration is important from the chemical viewpoint. The Cannizzaro reaction is the only side reaction which takes place to any extent in the case of formaldehyde under ordinary conditions of phenoplast manufacture. This reaction involves the reduction of one molecule of formaldehyde accompanied by the oxidation of a second, and is normally catalyzed by alkalis:

$$2\,CH_2O + H_2O \xrightarrow{NaOH} CH_3OH + HCOOH \qquad (20)$$

With sodium hydroxide and formaldehyde alone the reaction takes place slowly at room temperature, but the velocity approximately triples for every rise of 10°C. in temperature,[1] and is very rapid at 100°C. The presence of appreciable quantities of phenols greatly retards the Cannizzaro reaction with formaldehyde, and virtually no Cannizzaro reaction takes place, even at refluxing temperatures, when the molar ratio of phenol to alkali is greater than six to one. Other aldehydes not only undergo the Cannizzaro reaction, but take part in more complex reactions. For example, acetaldehyde may undergo an aldol condensation as follows:

$$2\,CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO \qquad (21)$$

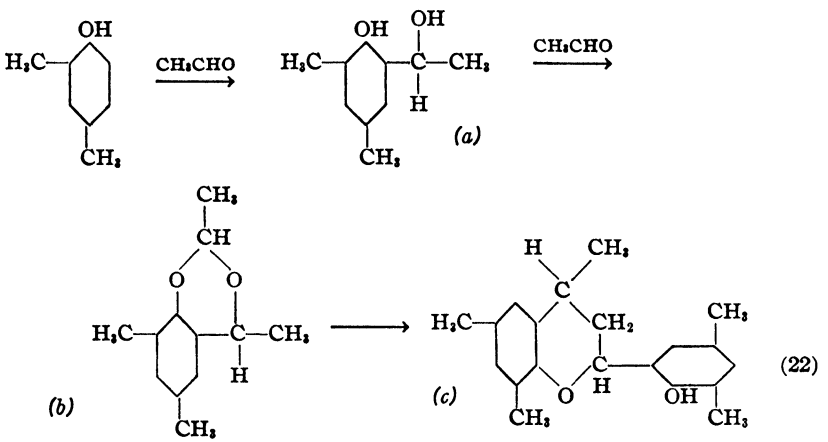
Acetaldehyde, and most of the higher aldehydes, also undergo self-resinification when treated with strong acids or bases. The facility with which such side reactions take place limits the usefulness of the higher aldehydes in the manufacture of phenoplasts.

[1] H. Euler and A. Euler, *Ber.*, **38**, 2551–2560 (1905).

1. Acetaldehyde

Acetaldehyde was condensed with phenol to form a resin by Baeyer[2] as early as 1872. Fabinyi[3] mixed an excess of phenol with paraldehyde, added stannic chloride slowly, and formed a dark brown resin, which distilled over, in part, under a pressure of less than 10 mm. The distillate was crystallized from benzene and yielded dihydroxydiphenylethane. Lunjak[4] obtained a similar result using hydrochloric acid as catalyst. Claus and Trainer[5] dissolved two moles of phenol and one mole of acetaldehyde in ether, and passed in hydrochloric acid gas. After removal of the ether, a dark brown resin was left which could not be crystallized. The ultimate analysis corresponded to dihydroxydiphenylethane. Baekeland and Bender[6] obtained a similar result. It will be noted that these were all rather vigorous chemical treatments.

Under mild conditions, however, initial condensation products may be isolated. Thus, Adler, von Euler, and Gie[7] have shown that in the presence of dilute aqueous hydrochloric acid at room temperature, the primary condensation of acetaldehyde with phenol produces a carbinol (Eq. 22,*a*) which then adds another mole of acetaldehyde to give the cyclic acetal, benzodioxin (Eq. 22,*b*). When the phenol has two or more reactive posi-



[2] A. Baeyer, *Ber.*, **5**, 25–26, 280–282, 1094–1100 (1872).

[3] R. Fabinyi, *ibid.*, **11**, 283–286 (1878).

[4] A. Lunjak, *J. Russ. Phys.-Chem. Soc.*, **36**, 301–311 (1904).

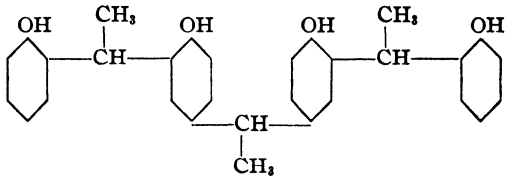
[5] A. Claus and E. Trainer, *Ber.*, **19**, 3004–3011 (1886).

[6] L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225–237 (1925).

[7] E. Adler, H. v. Euler, and G. J. Gie, *Arkiv Kemi Mineral. Geol.*, **A16**, No. 12, 1–20 (1943).

tions, polycondensation can take place with the formation of resins. When the phenol has only one reactive position, as in the case of 2,4-dimethylphenol, treatment with warm hydrochloric acid decomposes the benzodioxin to yield first an ortho vinyl phenol, which rapidly dimerizes to yield the chroman derivative (Eq. 22,*c*).

In view of our present knowledge on novolacs, it seems probable that the acid condensation of phenol with acetaldehyde under technical conditions yields a series of linear polymers, in which the phenol groups are linked together by ethane bridges, as shown in Formula XVIII. The bridges



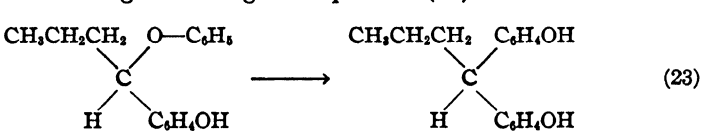
(XVIII)

may occur in a random manner either ortho or para to the phenolic hydroxy group. The arrangement in Formula XVIII, is, of course, highly idealized.

The resins from the acid condensation of phenols with acetaldehyde are soluble and permanently fusible, just as are the novolacs. Like the latter, the acetaldehyde–phenol resins may be converted to the insoluble resites by alkaline condensation with formaldehyde, or by heating with a source of methylene groups, such as hexamethylenetetramine. It is much more difficult to condense acetaldehyde with phenol in the presence of an alkaline catalyst, because the acetaldehyde tends to undergo aldol condensations and self-resinification.

2. Butyraldehyde

Baekeland and Bender[6] studied the condensation of phenol with normal butyraldehyde, in the presence of hydrochloric acid. They obtained a resin which on heating and vacuum distillation gave a fairly good yield of dihydroxydiphenylbutane. The authors concluded that the primary reaction was the formation of 1-phenoxy-1-*p*-hydroxyphenyl *n*-butane, which rearranged on heating according to Equation (23). When heated with



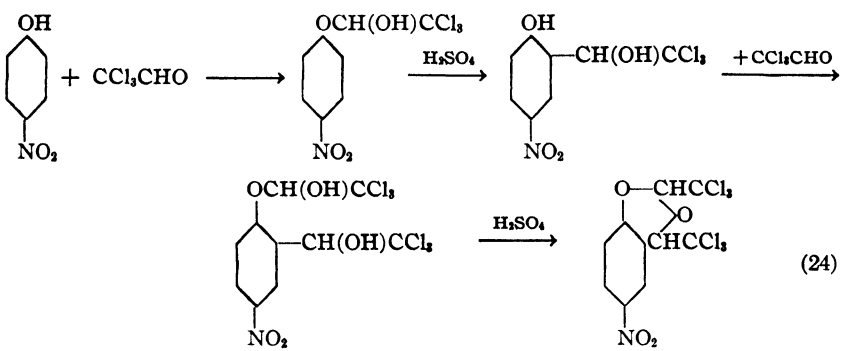
(23)

paraformaldehyde, an insoluble and infusible resin was obtained from the initial resinous condensation product of phenol and butyraldehyde.

3. Chloral

Chattaway and co-workers[8–10] studied the condensation of chloral with various phenols in the presence of sulfuric acid. When phenol itself was added to chloral suspended in concentrated sulfuric acid, an immediate reaction occurred, and an oily liquid separated which rapidly changed to an opaque white solid. The latter readily dissolved in alcohol and gave a colorless solution from which no crystalline matter could be obtained. On evaporating the solvent, a viscous liquid was left which solidified to a colorless, transparent resin. The constitution of the latter was not determined.

When a para substituent was present on the phenol nucleus, no resin was obtained. Instead, a good yield was obtained of a crystalline compound. For example, *p*-nitrophenol yielded anhydro 5-nitro-2-(β,β,β-trichloro-α-hydroxyethoxy) β,β,β-trichloro-α-hydroxyethylbenzene. Chattaway postulated that the reaction proceeded according to the scheme of Equation (24). Harden and Reid[11] also condensed a number of phenols with chloral, in order to study the bactericidal efficiency of the products.



(24)

4. Furfural

Of all the higher aldehydes which have so far been discussed, furfural probably has the most commercial importance in the manufacture of phenoplasts. It had been known since 1860 that furfural could be condensed with

[8] F. D. Chattaway, *J. Chem. Soc.*, **1926**, 2720-2727.
[9] F. D. Chattaway and A. A. Morris, *ibid.*, **1927**, 2013-2017.
[10] F. D. Chattaway and F. Calvet, *ibid.*, **1928**, 1088-1094.
[11] W. C. Harden and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 4325–4334 (1932).

phenols to give resinous bodies. In 1921, Novotny covered practical details of the condensation in U. S. Pat. 1,398,146. Trickey, Miner, and Brownlee[12] studied the condensation in 1923 and came to the following conclusions:

In the case of *acid* condensed resins:

1. In order to obtain an infusible, insoluble resin, the molecular proportions preferably should be slightly in excess of 1 mole of furfural to 1 mole of phenol.

2. The resin obtained when an excess of phenol is used is soluble in acetone and alcohol, and is permanently fusible.

3. The resins obtained by the use of varying amounts of acid as a condensing agent were similar but the time necessary to complete the reaction varied from two weeks when 0.2% of hydrochloric acid was used (based on the weight of the total reaction mass) to ten hours in the case of 0.6% acid.

In the case of *alkaline* condensed resins:

1. In order to obtain an insoluble resin, the proportions are preferably about 1.25 moles of furfural to 1 mole of phenol.

2. The resins formed by an excess of phenol are solid and brittle when cold, melt easily, and are readily soluble in acetone, alcohol, and furfural. When heated with enough furfural to bring the molecular proportions up to 1.25 of furfural to 1 of phenol, the resins pass over to the infusible state.

By careful condensation of furfural with phenol in dilute acid solution,[13] it is possible to prepare the primary product, hydroxyphenyl furyl carbinol, as shown by the reaction in Equation (25). The position of the carbinol

$$C_4H_3OCHO + C_6H_5OH \longrightarrow C_4H_3O{-}\underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}C_6H_4OH \qquad (25)$$

group has not been established. It appears, then, that the behavior of furfural in phenoplast condensations is very similar to that of formaldehyde. There are, however, certain differences between the formaldehyde and furfural condensation products. The phenoplasts from furfural have a dark, purplish black color, which differs from the yellow or brown color of the phenoplasts made from formaldehyde. The condensation of the phenols

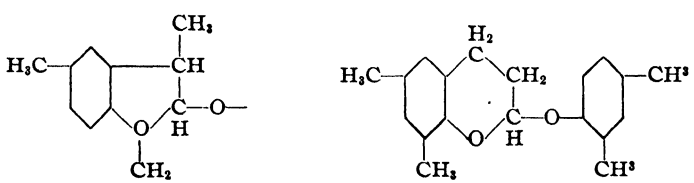
[12] J. P. Trickey, C. S. Miner, and H. J. Brownlee, *Ind. Eng. Chem.*, **15**, 65–66 (1923).

[13] A. Porai-Koschutz, N. Kudryanzeff, and B. Maschkileison, *Kunststoffe*, **23**, 97–100 (1933).

with furfural is initially more sluggish than with formaldehyde, and furfural itself has a marked tendency to polymerize under acid conditions.

5. Acrolein

One of the early phenoplasts was made by the condensation of phenol with acrolein.[14] McIntosh[15] developed a similar resin by the condensation of phenol with glycerol and sulfuric acid, under which conditions acrolein is formed. However, the products so obtained appear to have had no special advantages, and are no longer commercially manufactured. The technical aspects of their preparation have been covered in a somewhat empirical manner by Maksorow and Andrianow.[16] The condensation has been studied from the theoretical viewpoint by Adler and Tingstam,[17] who found that the course of the condensation, under carefully controlled acidic conditions, was quite different from that usually obtained with the saturated aldehydes. Thus, when 2,4-dimethylphenol (2 moles) was condensed with 1 mole of acrolein in acetic acid solution, with hydrochloric acid as a catalyst, 2-(2,4-dimethylphenoxy)-3,5,7-trimethyl coumaron, was formed melting at 89°C. (Formula XIX*a*). A small amount of another product, melting at 185°, was also obtained; this was probably the chroman derivative shown in Formula XIX*b*.



(a) (XIX) *(b)*

[14] C. Moureu and C. Dufraisse, German Pat. 382,903.

[15] J. McIntosh, *Ind. Eng. Chem.*, **19**, 111 (1927).

[16] B. V. Maksorow and K. A. Andrianow, *ibid.*, **24**, 827–833 (1932).

[17] E. Adler and S. Tingstam, *Arkiv Kemi Mineral. Geol.*, **B16**, No. 18, 1–7 (1943).

IV. PHENOPLASTS FROM POLYHYDRIC PHENOLS

The discussion so far has concentrated upon the monohydric phenols—that is, phenols which have only one hydroxy group upon the nucleus. From the commercial point of view, the monohydric phenols are by far the most important, since they are more readily available and less expensive. The theoretical studies leading to our knowledge of structure have dealt mostly with the monohydric phenols—and particularly, as explained in Chapter II, with monohydric phenols which have been highly substituted in order to decrease their reactivity. The polyhydric phenols are, in general, much more reactive than the monohydric phenols, since the effect of the second hydroxy group is to activate the benzene ring further. This is particularly true in the case of resorcinol, where the hydroxy groups are meta to one another. The resonance produced by this arrangement activates the ortho and para positions of the nucleus; as a result, the resorcinol resins are very rapidly cured.

Baeyer in 1872[1] condensed resorcinol and pyrogallol with various aldehydes. When the aldehyde was relatively inactive, crystalline compounds could be obtained. For example, benzaldehyde and pyrogallol gave a crystalline product. With resorcinol and acetaldehyde or formaldehyde, resinous products were obtained. Caro[2] in 1892 condensed an excess of resorcinol with formaldehyde in the presence of dilute hydrochloric acid; the product obtained was identified as tetrahydroxydiphenylmethane (Formula XX). The product obtained in a similar manner with pyrogallol was hexahydroxydiphenylmethane.

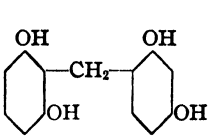
Boehm and Parlasca[3] prepared methylol derivatives of resorcinol by reduction of the corresponding dicarbomethoxy aldehydes. The compound shown in Formula XXI*a* was stable and not sensitive to acids, while compound *b* could not be prepared in a pure form, but always occurred as a resin. From this time on, no studies were made on the structure of the

[1] A. Baeyer, *Ber.*, **5**, 25–26, 280–282, 1094–1100 (1872).

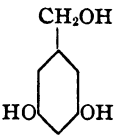
[2] N. Caro, *ibid.*, **25**, 939–949 (1892).

[3] T. Boehm and H. Parlasca, *Arch. Pharm.*, **270**, 168–182 (1932).

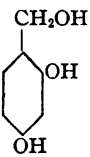
resins from polyhydric phenols until von Euler and associates included this type of condensation product in their work.[4-6]



(XX)



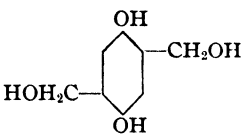
(a)



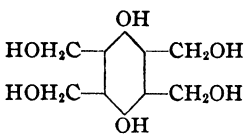
(b)

(XXI)

In the case of hydroquinone, it was shown that alkaline condensation with two moles of formaldehyde gave the dialcohol illustrated in Formula XXII*a*, while four moles of formaldehyde gave the tetraalcohol illustrated in Formula XXII*b*. Both the di- and tetraalcohols resinified on heating.



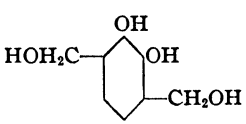
(a)



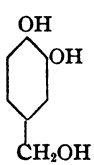
(b)

(XXII)

On treatment with a weak acid, the dialcohol quickly resinified to an insoluble amorphous product, to which von Euler, Adler, and Gie ascribe a methylene bridge structure.



(XXIII)



(XXIV)

The alkaline condensation of catechol with formaldehyde gave only catechol dialcohol, in which the position of the methylol groups was established by von Euler, Adler, Kispeczy, and Fagerlund[5] according to Formula XXIII. The catechol dialcohol also resinified on heating. Rosenmund and Boehm[7] prepared the monomethylol derivative of catechol (Formula XXIV) by reduction of the corresponding aldehyde.

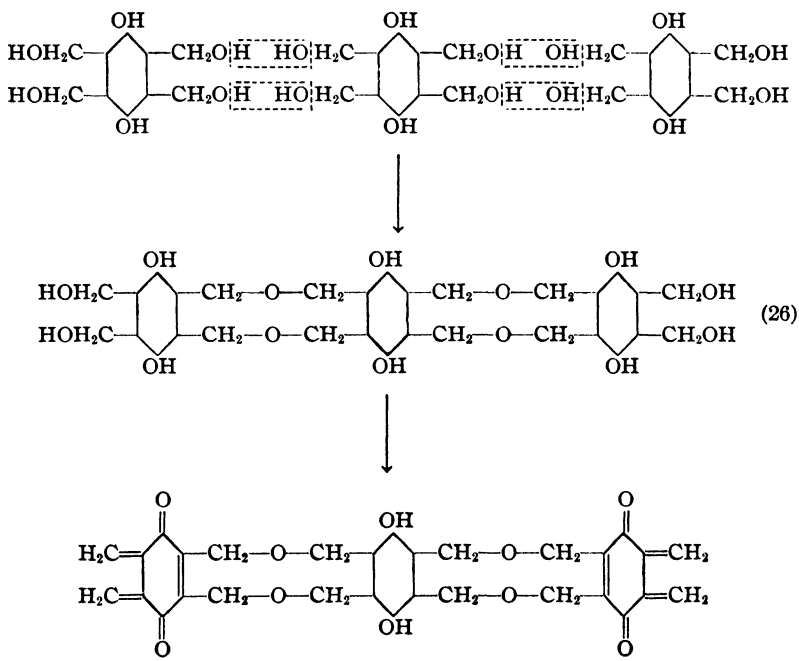
[4] H. v. Euler, E. Adler, and G. J. Gie, *Arkiv Kemi Mineral. Geol.*, **B14**, No. 9, 1-7 (1940).

[5] H. v. Euler, E. Adler, S. de Kispeczy, and A. Fagerlund, *ibid.*, **A14**, No. 10, 1-20 (1940).

[6] S. Kyrning, *ibid.*, **B15**, No. 11, 1-8 (1942).

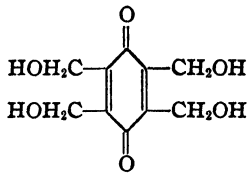
[7] K. W. Rosenmund and T. Boehm, *Arch. Pharm.*, **264**, 448-459 (1926).

Kyrning[6] studied the mechanism of curing of the di- and tetraalcohols from hydroquinone and catechol. The dialcohol of hydroquinone apparently went through a number of reactions involving ether formation, methylenequinone formation, and the formation of methylene bridges. The tetraalcohol of hydroquinone (Formula XXII*b*) was particularly interesting. It has no free nuclear positions and hence diphenylmethane formation cannot take place. When cured at 210°C., it gives off about



three moles of water per mole of tetraalcohol. This indicates methylenequinone formation in addition to the development of ether linkages, as shown in Equation (26).

Kyrning also studied the tetraalcohol from *p*-quinone (Formula XXV) and showed that at 180°C. it lost slightly less than two moles of water, indicating the formation of ether linkages only. Methylenequinone formation could not take place because no phenolic hydroxy group was present. This experiment showed that the quinone groups conferred a reactivity similar to that obtained when the hydroxy groups were present. However, methylation of the phenolic hydroxy groups in hydroquinone tetraalcohol gave a product which was completely stable at 180°C.



(XXV)

Dubusay and Papault[8] studied the rate of gel formation in alkaline-catalyzed resorcinol–formaldehyde resins. They concluded that the ratio of aldehyde to resorcinol had a marked effect upon the curing time; as the ratio increased, the gel time passed through a minimum and then increased. The position of the minimum gel time was affected by the concentration of sodium hydroxide present. Von Euler and co-workers point out that the methylol derivatives of the polyhydric phenols will produce infusible and insoluble resins when reacted with phenols which have only two reactive positions, though the latter normally give only soluble and fusible resins. This is because the dihydroxyphenols behave as tetrafunctional compounds, and when combined with the difunctional phenols, the dihydroxyphenols supply a sufficient number of reactive positions to cause the formation of three-dimensional, cross-linked molecules.

Because of its great reactivity, resorcinol and its methylol derivatives are used commercially today either as such[9] or in combination with other resins to increase the rate of curing of phenoplasts. The addition of from 3 to 20% of resorcinol will either decrease the time of cure required at high temperatures, or will permit curing at relatively low temperatures, even at room temperatures. Methods for accomplishing this have been described in British Pat. 221,475,[10] by Kessler,[11] and by Novotny.[12] Shiskov[13] has shown that chemically resistant resins for coatings may be prepared from 15 parts of phenol to 12 parts of resorcinol. In this proportion, the resin hardens rapidly and has physical properties which are only slightly inferior to those obtained when pure resorcinol is used.

[8] R. Dubusay and R. Papault, *Compt. rend.*, **215**, 348–350 (1942).

[9] P. H. Rhodes, *Modern Plastics*, **22**, 160–161, 198 (1944).

[10] Riben-Record Akt. Ges., British Pat. 221,475.

[11] J. J. Kessler, U. S. Pat. 1,889,751.

[12] E. E. Novotny, U. S. Pat. 1,802,390.

[13] B. P. Shiskov, *J. Chem. Ind.* (*U.S.S.R.*), **8**, 21 (Jan., 1941).

V. THE PHYSICAL STRUCTURE OF THE PHENOPLASTS

A. INTRODUCTION

The discussion in Chapter II regarding the chemical structure of the phenoplasts has shown that the cured resin has by no means a simple chemical structure. The information on chemical structure has been obtained chiefly from studies of the reactions of highly substituted phenols, which generally do not yield insoluble and infusible cured resins. The commercial phenoplasts are usually prepared from phenols with three reactive positions, and the cured resin has a high degree of three-dimensional cross linking. We then are concerned not only with a complex chemical structure, but also with a physical structure which is equally complex and difficult to describe accurately. These difficulties were recognized by the early investigators, and their theories of the physical structure of the phenoplasts were based upon reasoning rather than experimental evidence. The conventional methods for the study of resin structure give little or no information in the case of the cross-linked resins, and it has been necessary to develop specialized techniques in order to acquire even our present meager information.

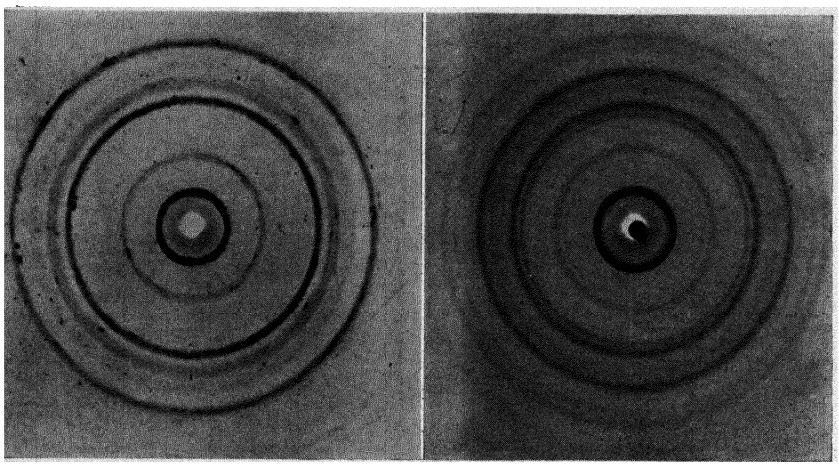
B. X-RAY EXAMINATION

The x-ray is a powerful tool for the determination of resin structure, when the structure is of a regular pattern. Unfortunately, the cured phenoplasts appear to be entirely amorphous and give x-ray patterns which cannot be used to interpret structure, at present, although in the future some interpretation may be obtained through diffraction analysis.[1] Mark and Fankuchen[2] recently suggested that the technique of low-angle scattering might be applied to phenoplasts. This technique utilizes a long distance between the specimen and the recording film. In this manner, it is

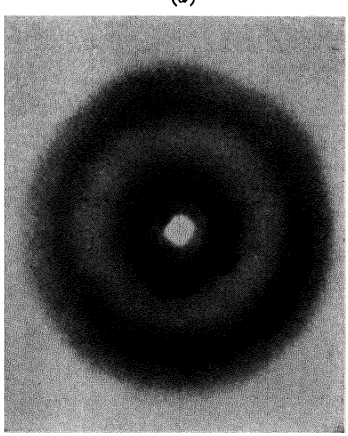
[1] W. T. Astbury, *Chemistry & Industry*, **23**, 114–116 (April 14, 1945).

[2] H. Mark and I. Fankuchen, Polytechnic Institute of Brooklyn, May, 1944, *private communication.*

possible to record the low-angle scattering which would be caused by crystal facets, fibrils, or other reflecting surfaces of relatively large dimensions. This technique has been successfully used in other investigations of macro-



(*a*) (*b*)



(*c*)

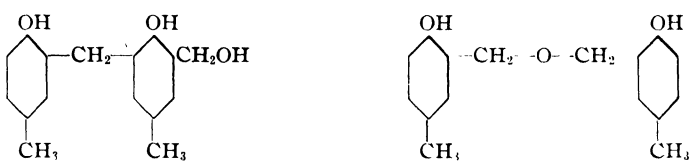
Fig. 2. X-ray diagram of *p*-cresol monoalcohol before and after heating: (*a*) initial material diagram; (*b*) intermediate compound stage; (*c*) final resin.[3]

molecular structure, such as that of cellulose. When this technique was applied to a number of phenoplast films in various stages of cure, no definite evidence of structure could be obtained. On the basis of such

[3] N.J. L. Megson and W. A. Wood, *Nature*, **140**, 642–643 (1937).

x-ray evidence, it was concluded that any structure which may exist within the cured films is probably of an order of magnitude larger than 400 Å.

Megson and Wood[3] examined the x-ray transmission spectrum of *p*-cresol monoalcohol, and noted an interesting change in the diagram as the alcohol was heated. The original alcohol is a crystalline compound, melting at 105°C., and gave a sharp diagram. After heating for 30 minutes at 130° under a pressure of 17 mm. of mercury, a new diagram was obtained, which also had a crystalline form. Megson and Wood were able to crystallize the new compound from petroleum ether, with a melting point of 99–100°C., and ascribed to it a dicresylmethane alcohol structure, as shown in Formula XXVI*a*. (In view of the work discussed in Chapter II,



(*a*) (XXVI) (*b*)

it is possible that the intermediate compound may have been the ether illustrated by *b*.) On further heating, a resin was obtained which showed only an amorphous diagram, but with strong central and outer halos similar to those which are present as rings in the crystal diagrams. From this evidence, Megson and Wood conclude that the resin is formed by small relative displacements of the molecules from the crystalline formation and not by radical rearrangement of a random nature. The diagrams are reproduced in Figure 2.

C. ELECTRON MICROSCOPE EXAMINATION

The electron microscope is the most recent tool which has been developed for the study of microscopic structure. In the hope that the high magnification of the electron microscope might reveal some details of structure, Barkhuff and Reynolds[4] studied cured phenoplast films. They prepared a resin by refluxing equimolar quantities of phenol and formaldehyde for 15 minutes at 100°C., using as catalyst 0.2 mole of sodium hydroxide per mole of phenol. The screens usually employed as supports in electron microscope technique were dipped in the alcoholic solution of resin, the excess solution was drained off, and the screen with its thin film of resin was heated

[4] R. A. Barkhuff and D. Reynolds, *private communication* from Monsanto Chemical Co., April, 1944.

for 16 hours at 80°C. The screens were mounted in the electron microscope, in the usual manner, for observation.

Figure 3 shows a typical electron photomicrograph of the resin film. Note that there are a series of dark spots throughout this film. These spots represent zones of high electron density and may be caused either by

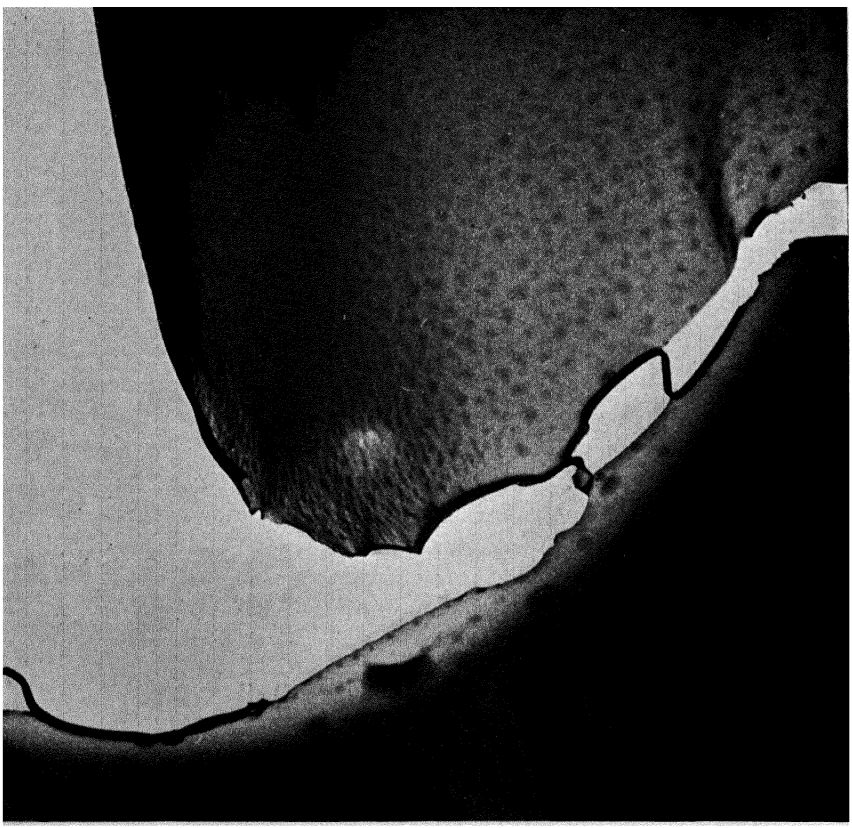


Fig. 3. Electron photomicrograph of a phenoplast film (×5500).

increased local resin content or by an agglomeration of impurities. Close examination of the curled edge of this film reveals a series of lumps in the lower right corner. Since these films are actually part of a concave lens formed within the screen opening, surface tension forces would make it improbable that such lumps of resin would form unless bound to that position by forces of appreciable energy. It is possible that these spots are highly

cross-linked nuclei which have grown into a somewhat spherical shape in a matrix of lower molecular weight material which binds the nuclei together. Measurements on a number of these spots indicate that they have an appreciable diameter—of the order of 2500 Å. If such an interpretation can be accepted, it indicates that the cross-linked portion of the phenoplast reaches a size which represents a tremendous molecular weight.

D. THE ISOGEL THEORY OF PHENOPLAST STRUCTURE

Wolfgang Ostwald in 1922 coined the term *isogel* to denote a colloidal gel in which the dispersed particles have the same chemical composition as the continuous phase. Houwink has developed the theory that a cured phenoplast has an isogel structure, in which the dispersed particles are highly cross-linked nuclei, while the continuous phase is a matrix of less highly polymerized material (German, *Harzbrei*). In calling this structure an isogel, Houwink assumes that the chemical structure is uniform throughout. The latest chemical studies discussed in Chapter II indicate that the phenoplasts may contain a number of chemical types. It would therefore seem preferable to speak of the phenoplasts as mixed isogels.

In 1936 Houwink[5] gave the following description of the structure of a cross-linked, thermosetting resin:

"It is supposed that condensation polymers in the A stage are not very highly polymerized, because at the beginning many nuclei are formed immediately, each growing rapidly so that practically no molecule will have the chance to become much bigger than its neighbours. For 3-dimensionally hardening condensations, however, this situation will change as soon as the small polymeric molecules, which have formed and grown at the expense of the monomeric molecules, find no more monomeric 'food' for further growth; they are then obliged to begin interlinking with each other. Thus it becomes comprehensible why at this stage of the process, corresponding to B stage of resin formation, a sudden change in physical properties may occur."

A schematic picture (Fig. 4) taken from Houwink,[5] shows the four stages through which a three-dimensionally hardening resin, the product of a condensation reaction, is assumed to pass between the liquid-resin stage and the so-called C stage.

"A fusible and soluble resin, the A stage, can be distinguished as a liquid A resin (an iso-sol, Fig. 4*a*), or as a solid A resin (an iso-gel, Fig. 4*b*), according to the stage of aggregation at room temperature. If the polymerization has gone so far that the resin is no longer fusible, but can only be weakened by heating, it will

[5] R. Houwink, *J. Soc. Chem. Ind.*, **55**, 247–259T (1936).

be said to be in the B stage (Fig. 4*c*); moreover B resins are only partly soluble. Finally, if the polymerization has gone so far that the resin has become infusible nd insoluble it will be said to be in the C stage (Fig. 4*d*)."

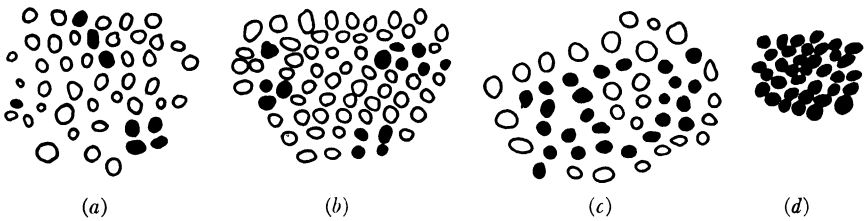


Fig. 4. Schematic picture of phenoplast condensation.[5]

The dispersed particles of the isogel are three-dimensionally cross-linked spherocolloids and are connected by primary valence bonds, presumably methylene links, as indicated by the solid lines of Figure 5. Houwink[6,7] has elaborated this theory of structure in other papers and Figure 5, taken from one of these,[6] shows what might be considered a magnification of Figure 4*d*. Figure 5 shows clearly the spherocolloidal aggregates, the primary bonds connecting them, and the secondary bonds which also play a part in binding the structure. The space between the spherocolloidal particles must be assumed to be filled with material of a lower degree of polymerization and cross linking.

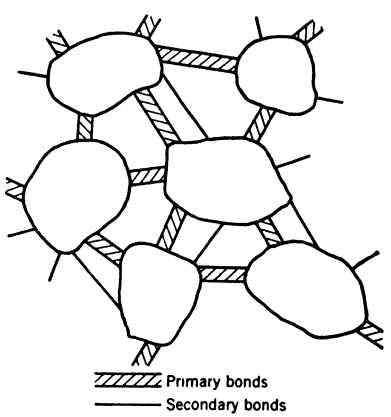


Fig. 5. Structure of a cured phenoplast.[6,7]

Klaasens and Houwink[8] developed additional evidence for the spherical form of the phenoplast molecule by a study of viscosity changes as the condensation proceeded. It was shown that up to a concentration of 5%, the resin solutions obeyed the Einstein formula for spherical molecules:

$$y = y_0 (1 + kc_v)$$

[6] R. Houwink, *Trans. Faraday Soc.*, **32**, 131–148 (1936).

[7] R. Houwink, *ibid.*, **32**, 122–131 (1936).

[8] K. H. Klaasens and R. Houwink, *Kolloid-Z.*, **76**, 217–223 (1936).

where y is viscosity of the solution, y_0 is viscosity of the solvent, c_v is volume concentration of the dispersed particles, and k is a constant. At concentrations of from 5 to 40%,

$$\log N_r = k \cdot c_v^{1.18}$$

where N_r is equal to y/y_0' or relative viscosity, and k is a constant. The constant k is a function of the time of the reaction and the type of phenol.

Hetényi,[9] basing his general ideas on those of Houwink, attempted to demonstrate the theory of the molecular structure of the phenoplasts by photoelastic tests at elevated temperatures. A bar of cured phenoplast was heated to, say 110°C., and loaded. The deformation was observed, and the bar was cooled under load. A permanently deformed sample was then obtained which exhibited, in polarized light, an isochromatic fringe pattern corresponding to an elastic state of stress. Thin slices were cut off and these showed in polarized light the stress pattern existing in the original three-dimensional piece. Hetényi then discusses the structure of the resin as follows:

"In the A stage the material is fusible and soluble and its molecules adhere only by the secondary loads of the van der Waals forces. Upon heating the A stage, the chemically active spots will react one with another, creating thus a strong primary bond among them. As this reaction proceeds, a strong molecular network will be built up throughout the whole bulk of the resin. The molecules of this network will be then in primary bond with one another, being thus in an infusible and insoluble state. Because of some particular features of the structure, however, not all the possible chemically active spots will be able to react, and within the globular micelles of the 3-dimensional network there will be material which is still in the fusible and soluble state. This state is termed isogel, because there is no difference in the chemical composition between the fusible and infusible part of the material.

"When a piece of such resin is heated, the A-stage material within the walls will be gradually fused, becoming liquid at a certain temperature. At that point, the only load-carrying element of the material will be its skeleton given by the primary network throughout the resin. The strength and elasticity of this material will not be affected by the temperature which was able to melt the A-stage material. When we load such a piece at the elevated temperature, the load will be carried completely by the primary network and consequently the deformation in all its characteristics will be purely elastic."

This description seems to represent an ideal condition which in fact is never realized in the phenoplast structure. The lower polymerized portions can hardly "fuse" and become liquid. The primary network is not completely elastic, as careful creep measurements show (see Chapter VIII).

[9] M. Hetényi, *J. Applied Phys.*, **10**, 295–300 (1939).

E. THE SPHEROCOLLOID THEORY OF PHENOPLAST STRUCTURE

In 1939, H. Stäger and co-workers[10-15] at the Technische Hochschule in Zurich introduced a new technique for the examination of cured phenoplast films, and their work has been described in a series of papers. They prepared a series of alkaline-catalyzed phenoplasts from formaldehyde and phenol or cresol. The uncured resin was poured into shallow metal pans and cured in an oven. Thin films, 0.02 to 0.04 mm. thick, were prepared from the cast disks by a modification of the grinding technique described in Weigel.[16]

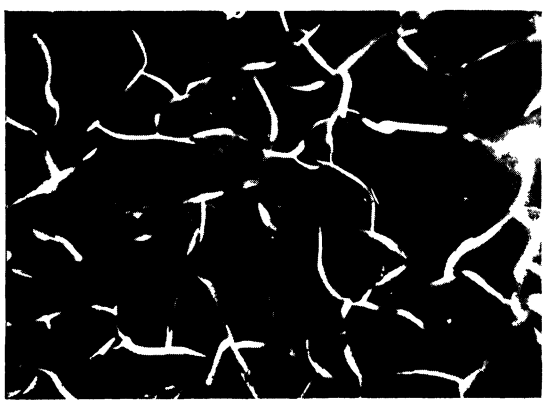


Fig. 6. Phenoplast swelling pattern.[17]

These films were then swollen in acetone, and examined under the microscope in polarized light. A network appeared as shown in Figure 6 (taken from the work of Barkhuff and Carswell as described below),[17] which Stäger interpreted as representing grain boundaries between the spherocolloids and the less highly polymerized matrix.

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[10] H. Stäger, R. Sänger, and W. Siegfried, *Helv. Phys. Acta*, **12**, 561–580 (1939).

[11] H. Stäger and W. Siegfried, *Kunststoff-Tech. u Kunststoff-Anwend.*, **10**, 193–212 (1940).

[12] H. Stäger, W. Siegfried, and R. Sanger, *Schweizer Arch. angew. Wiss. Tech.*, **7**, 130–139 (1941).

[13] H. Stager, W. Siegfried, and R. Sänger, *ibid.*, **7**, 153–174 (1941).

[14] H. Stäger, W. Siegfried, and R Sanger, *ibid.*, **7**, 201–208 (1941).

[15] W. Siegfried, *ibid.*, **8**, 255–262 (1942).

[16] W. Weigel, *Kunst- und Presstoffe*. I. V.D.I. Verlag, Berlin, 1937, pp. 2–7.

[17] R. A Barkhuff and T. S. Carswell, *Ind. Eng. Chem.*, **36**, 461–466 (1944).

Stäger and co-workers[11] developed the following structural picture for the phenoplasts:

> The three-dimensional intermeshed sphero colloidal constituents are imbedded in lower molecular portions having a one- or two-dimensional structure. From this, we can get a picture of the formation of phenolic resins that reverses the previously depicted isogel structure. Furthermore, the heterogeneous structure is influenced by electrolytes as condensation agents. By these the surface tension at the boundaries is influenced and also the structure.

In other papers, Stäger amplifies his theory to indicate that the more highly polymerized three-dimensional network forms small clumps, or spherocolloids, which are surrounded by a continuous phase of the lower molecular weight, viscous resin (*Harzbrei*). In this theory, there is no need to assume that the isocolloidal particles are fully linked by primary valence bonds to give a rigid sponge skeleton. Gelation is assumed to be the result of association and interpenetration of the molecules. Stäger interpreted the results of his swelling experiments as supporting the spherocolloid theory, in that the solvent selectively attacks the less cured portions of the phenoplast, revealing definite grain boundaries, similar to those which one finds in metal alloys or the cross section of wood pith. Koslov[18] developed a similar theory of the structure of the cured phenoplasts; unfortunately, his original papers were published in Russian journals which are not readily available. Dubusay[19] in 1928 studied the development of gel particles in a resorcinol formaldehyde resin, catalyzed by hydrochloric acid. The ultramicroscope revealed that the resin first separated in the form of small colloidal particles, which coalesced to larger groups as resinification proceeded.

F. FURTHER SWELLING EXPERIMENTS

Barkhuff and Carswell[17] studied the swelling technique intensively in order to use it as a tool for the further study of resin structure. They came to the conclusion that the exact pattern formed, as shown in Figure 6, could not be correlated with resin structure. However, it was observed that the time of immersion in acetone which was required to develop the pattern varied directly with the extent of cure. It was therefore possible to use the swelling technique as a tool for studying the development of cross linking in advanced stages of cure. No satisfactory technique for follow-

[18] P. M. Koslov, *Brit. Plastics*, 16, 168–169 (April, 1944).

[19] R. Dubusay, *Chimie & industrie*, April special number, 666–669 (1928).

ing the growth of cross linking from the B to the C stage had previously been developed.

Barkhuff and Carswell modified Stäger's technique, in that the liquid resin was simply spread on microscope slides in a thin layer and cured at the desired temperature. The tops of the resulting cured films were polished with graded emery papers, and then with a paste of pumice in mineral oil. The film thickness was checked with a micrometer. The cured films were treated with anhydrous acetone for various periods and intermittent microscopic examinations were made to determine when the netlike pattern was first visible. The pattern was most readily observed using dark-field illumination.

Figure 7[17] is typical of the relationship between the time required for appearance of the swelling pattern and the time of cure for two typical resins. It will be noted that the curves have three characteristic sections:

(*1*) An initial level section which is characteristic of all resins. Here the resin is only slightly advanced and in transition through the B stage. Swelling takes place rapidly in this region. In the early portions gelation rather than pattern formation may result.

(*2*) A second section of steep slope preceded by a rather sharp change in slope. This break appears to represent completion of the B stage and initiation of the C stage, in which three-dimensional cross linking predominates. The ascending linear section represents the progression of cross linking into a three-dimensional resin.

(*3*) A third virtually level section preceded by a second change in slope which appears to represent substantial completion of the curing reaction. Beyond this point the swelling time required for pattern formation is practically independent of the time of cure.

It is interesting to note that Schmid and de Senardens[20] also divided curing into three stages, basing their conclusions upon the results of an entirely different technique. These authors studied the change in the refractive index of a resole during curing. At temperatures of 72° to 85°C., the curve of refractive index versus time of cure changed smoothly from about 1.505 to about 1.620. However, when the first derivative of the curve (i.e., rate of change of the refractive index) was plotted against time, two inflexion points were evident, dividing the curve into three segments. Schmid and de Senardens interpreted the first section of the curve as representing a condensation reaction, and the later sections as polymerization.

From the results of their swelling experiments, Barkhuff and Carswell

[20] A. Schmid and G. de Senardens, *Helv. Chim. Acta*, **16**, 10–19 (1933).

drew the following conclusions regarding the effect of different variables upon the cure: (*a*) The rate of cure increased rapidly with increase in curing temperature; below 78°C., however, the resin appeared never to pass beyond the B stage, and that portion of the curve, which corresponded to the development of the C state, was not obtained. (*b*) The rate of cure increased rapidly as the catalyst (NaOH) concentration increased. (*c*) The rate of cure increased rapidly as the ratio of formaldehyde to phenol increased (up to 1.5 moles formaldehyde per mole phenol, beyond which no experiments were made). (*d*) When initial condensation of phenol and formaldehyde is conducted at a relatively low temperature, the resin cures faster than when the initial reaction takes place at a higher temperature.

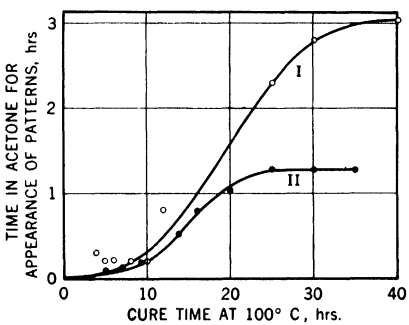


Fig 7. Relationship between degree of cure and rate of swelling pattern formation.[17]

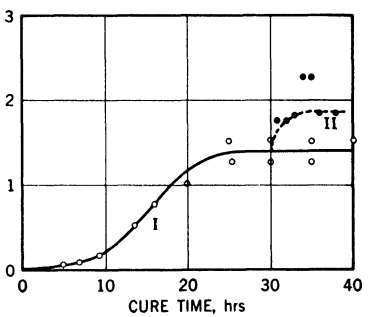


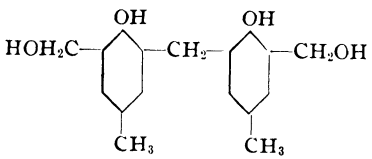
Fig. 8. Effect of increased temperature on rate of pattern formation: I, cured at 100°: II, at 150°C.[17]

One very interesting temperature effect is shown in Figure 8.[17] As mentioned above, at constant curing temperature the latter portions of the curves in Figure 7 become level, indicating that no further progression of cure takes place. However, when the temperature is raised after the level section of the curve has been reached, somewhat further curing takes place.

It is interesting to compare Figures 7 and 8 with some details from the work of von Euler, Adler, and Tingstam.[21] These authors studied the rate at which water and formaldehyde were given off when di-*p*-cresylmethane dialcohol (Formula XXVII) was heated for varying periods of time at different temperatures. They obtained the series of curves reproduced in Figure 9. At any given temperature, the curves reach a limiting

[21] H. v. Euler, E. Adler, and S. Tingstam, *Arkiv Kemi Mineral. Geol.*, **A15**, No. 10, 1-11 (1941).

value rather quickly, and continued heating at that temperature does not increase the amount of water or formaldehyde given off. Von Euler and co-workers checked the degree of cure for the dialcohol of Formula XXVII



(XXVII)

by determining the solubility of the cured product in chloroform. The results are shown in Figure 10. The same phenomenon is shown, in that at the temperature of heating (170°C.), the insolubility reaches a maximum

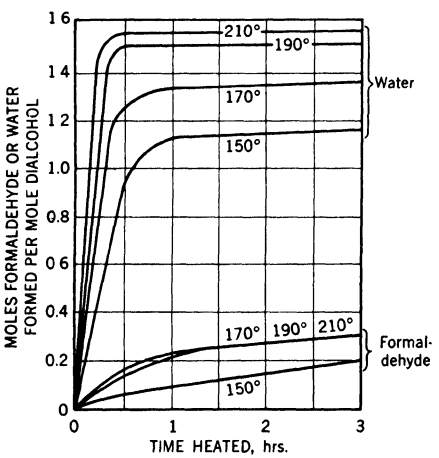


Fig. 9. The evolution of water and formaldehyde on heating di-*p*-cresylmethane-dialcohol.

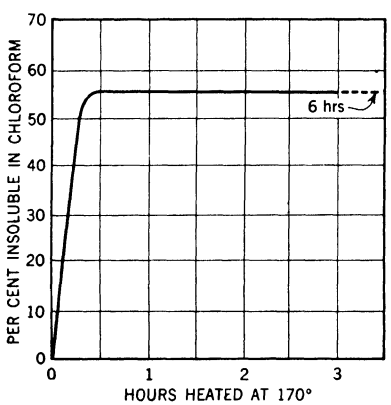


Fig. 10. The formation of insoluble material on heating di-*p*-cresylmethane dialcohol.

in about half an hour, and does not increase on further heating. The authors attributed the insolubility to the splitting of soluble ether bridges to yield a methylenequinone, which then polymerizes to a chloroform-insoluble product. It is therefore possible that there is a chemical as well as a physical explanation of the swelling-time curves; that is, the increase in the degree of cure may be due not only to the formation of larger cross-linked spherocolloids, but also to a change from cross linking through ether bridges to cross linking through polymerized methylenequinone molecules.

G. DEVELOPMENT OF STRUCTURE IN A-STAGE RESIN

The swelling-time experiments described above are most useful in giving information concerning the transition from B stage to C stage. They do not give much information about the very advanced stages of cure, nor do they give any information about the early stages of resin formation, while the resin is still soluble in acetone. It is not feasible to measure the molecular size of the A-stage resin by accepted methods for macromolecules, such as viscosity determinations at low dilutions. This is because the molecular size, while the resin is still soluble, is quite small—perhaps in the order of six to twelve phenolic nuclei. Consequently, the increase in viscosity of a dilute solution over that of the solvent is very small. In order to study the development of structure during the A stage, Barkhuff and Bierwert[22] have adapted the precipitation method. Other workers[23–25] have shown that, in the case of both thermoplastic and condensation resins, it is possible to obtain an idea of the molecular sizes present by dissolving the polymer in a solvent, adding a nonsolvent gradually, and observing the change in light transmission through the solution.

In the technique employed by Barkhuff and Bierwert, 50 g. of the essentially water-free soluble phenoplast (washed free of catalyst or other salts) were dissolved in 50 cc. of anhydrous methanol. The solution was then adjusted to a *p*H of about 4. The methanol solutions so obtained were diluted at 20°C., with a mixture of three parts of water to one part of methanol by weight. Periodically during these additions of nonsolvent the solution was transferred to a turbidimeter cell for the measurement of turbidity. The light transmission was measured by means of a photoelectric cell and expressed as microamperes, which vary inversely with the turbidity. Repeated additions of nonsolvent in 10-cc. portions were made until the turbidity reached a maximum. At this point the solution usually separated into two layers and further dilution was discontinued.

Figure 11 illustrates a typical result with the dilution method. In this figure, the reading in microamperes is plotted against the *dilution ratio.* The latter is defined as the volume ratio of nonsolvent (water) to solvent (methanol). In order to fix a definite point as the total precipitation point for any one resin, a value called the *critical dilution ratio* was chosen. This value is the point of inflection between the maximum and minimum values

[22] R. A. Barkhuff and D. V. Bierwert, *private communication* from the Plastics Division, Monsanto Chemical Co.

[23] J. G. McNally, Gibson Island High Polymer Conference, 1942.

[24] *Private communication,* Owens-Corning-Fiberglas Corp., Newark, Ohio (1943).

[25] B. Jirgensons, *J. prakt. Chem.*, **161**, 30–48 (1942).

of the steeply descending portion of the dilution curve. It is indicated by point *A* on Figure 11.

It was shown that such dilution curves were quite reproducible, even when the solid resin had been stored for several weeks. It was further shown that dilution curves, in the case of phenoplasts, characterize principally *only the higher molecular weight portion of the resin.* That is, the high molecular aggregates in the soluble phenoplast tend to precipitate much more rapidly than the low molecular weight portions. While this detracts somewhat from the overall value of the method, it does give a good picture of the large aggregates which are present. By the application of this technique to resins prepared in various ways, Barkhuff and Bierwert reached the following conclusions: (*a*) An increase in catalyst concentration (sodium hydroxide) results in a decrease in the molecular weight of the A-stage resin. This means that a larger number of small aggregates are present when the catalyst concentration is high. (*b*) A reduction in the initial reaction temperature produces a larger number of small aggregates. These conclusions check with those drawn from the swelling-time experiments.

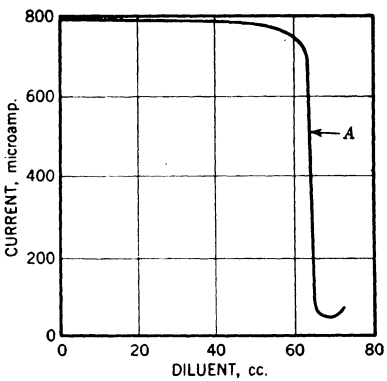


Fig. 11. Typical dilution curve.

H. GENERAL PICTURE OF PHENOPLAST STRUCTURE

As a result of the above studies, combined with those of previous investigators, the following picture can be drawn of the development of the physical structure of the phenoplasts during curing of the resoles.

The initial stage of the alkaline condensation of phenol and formaldehyde results in the formation of simple molecules—phenol alcohols. These phenol alcohols soon condense to larger units—although still not yet of macromolecular dimensions. These aggregates are dispersed throughout a mass of the lower homologues. These molecules form the nuclei of the isocolloidal state and may be diagrammatically represented by the crosses in Figure 12*a*.[17] The number and configuration of these nuclei are influenced by the initial reaction temperature, the amount of catalyst, the ratio of reactants, and other environmental factors. It must be noted that the phenoplast condensation, by its very nature, leads to highly

branched macromolecules, which probably have a more or less spherical form, and differ in this respect from the long-chain molecules which are present in addition polymerizations and in polyester condensations.

As the reaction proceeds, the nuclei grow at the expense of the less polymerized portions and occasionally by the union of the nuclei. This process continues until steric considerations and the amount of available reactants remaining terminate the growth. At this point, which corresponds to the completion of the B stage of resin formation, a structure very much like

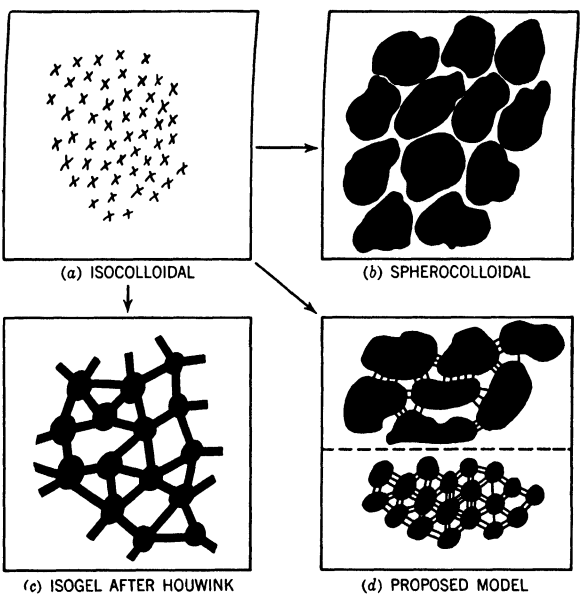


Fig. 12. Diagrammatic states of resin cure according to various points of view.[17]

the spherocolloid picture is visualized (Fig. 12*b*). Under certain conditions of reaction the nuclei form slowly and attain a relatively large size; under other conditions a large number of relatively small nuclei are formed. This process may be compared to that of crystallization, where the size and number of crystals depend upon the number of centers of crystallization which are present, and upon the influence of the environment upon crystal growth. As curing goes on, C-stage resin formation takes place, and cross linking among the macromolecules is the predominant reaction. Since most of the methylol groups are consumed in the formation of the three-

dimensional macromolecules, there will ultimately be a deficiency of reactants capable of forming methylene (or methylene ether) bridges in the interface between the spherocolloids. These bridges will then be formed primarily through methylol groups already present on the macromolecules

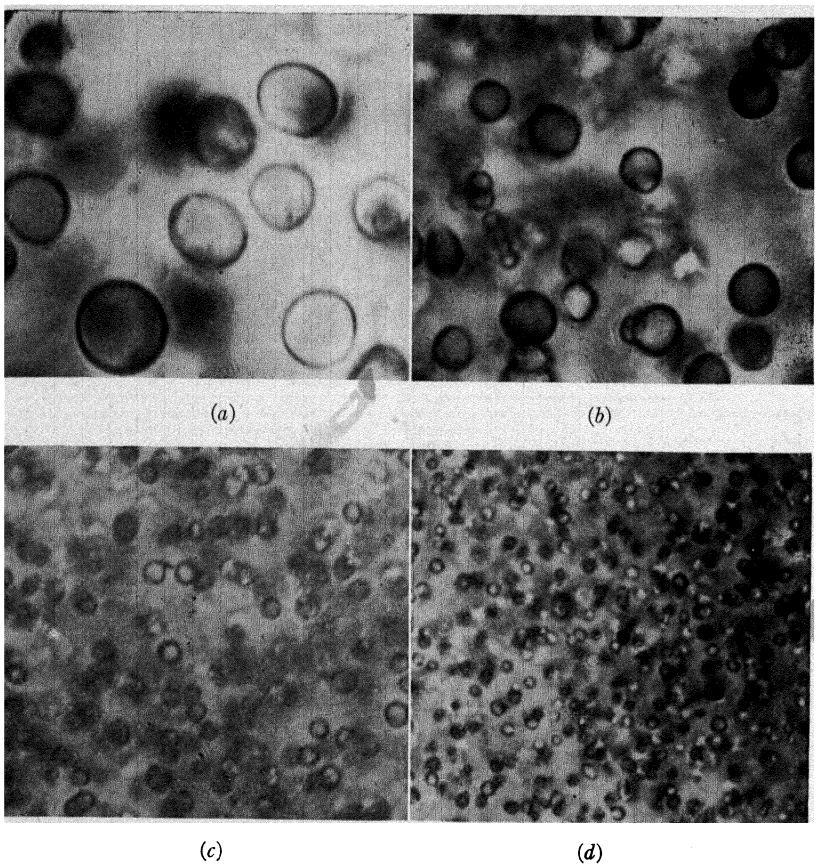
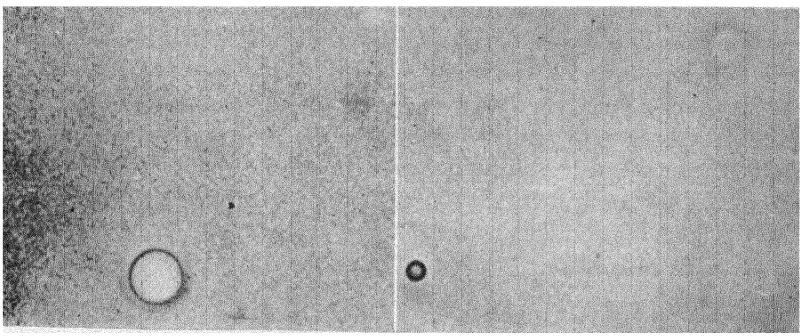


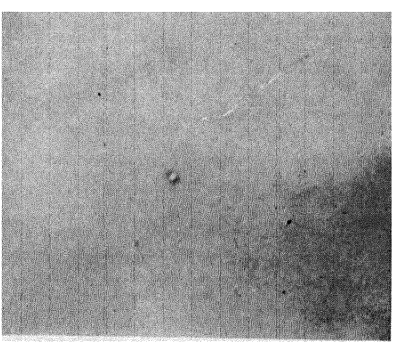
Fig. 13. Photomicrographs (×1000) of cast phenolic resins, showing variation in size of water droplets with water content.[27]

as such or formed by the splitting of existing ether bridges. The bridges formed in this final stage of resin structure will be limited in number by steric considerations and by available reactive positions containing methylol groups. It is evident[7] that the methylene bridges formed when large aggregates are present will be relatively few in number as represented

diagrammatically in the upper half of Figure 12*d*. In general, any factor which promotes the formation of numerous nuclei will favor increased bridging and a higher degree of cure. For example, an increased formaldehyde ratio, an increased catalyst concentration, and an increased tempera-



(*e*) (*f*)



(*g*)

Fig. 13 (*continued*).

ture of *cure* will all increase the number of nuclei formed. The increased number of nuclei will be reflected in the structure by a smaller macromolecular size as shown in the lower half of Figure 12*d*. These smaller macromolecules result in a close packing and give a thinner interface of the lower polymerized material between the spherocolloidal aggregates. These trends are reflected in resins which cure faster and to a higher degree of cross linking. It is to be noted that, while a higher temperature of *cure* speeds up cross linking, a lower *initial* reaction temperature gives a faster

curing resin, because the lower initial temperature gives time for numerous nuclei to form but does not permit their growth to a large size at too early a time in the life of the resin.

Figure 12*c* represents Houwink's concept of the isogel structure of the phenoplasts. The only difference between this concept and the one which has been detailed above lies in the relative importance of the methylene bridges. Houwink considers the methylene bridges to represent a major portion of the structure, giving rise to the elastic sponge network. The concept above regards the spherocolloidal particles as the major component of the structure, and the methylene bridges as a secondary but important part of the cured resin. In either case, the space about the aggregates is filled with less highly cross-linked material. In a well-cured resin, however, the actual percentage of the *Harzbrei* is probably small. The *Harzbrei* probably consist to a large extent of products of the less important curing reactions.

I. STRUCTURE OF CAST PHENOPLASTS

Cast phenoplasts for ornamental purposes are prepared in quite a different way from resins which are intended to be used for molding powders. A high initial ratio of formaldehyde is employed, so that ultimately a little more than two moles of formaldehyde are combined with one mole of phenol. The initial condensation is made under alkaline conditions; the excess of water is then removed under vacuum, and the resin is neutralized with an organic acid. The thick syrup which results is poured into molds and hardened at 80–100°C. The mold is usually of rather large size, and the water of condensation formed during the curing cannot escape.

It may be assumed that the chemical and physical structure of the cast phenoplasts follows the pattern already described in so far as the organic constituents are concerned, but differs in that the water of condensation is still present. Thompson[26,27] has studied the cast phenoplasts, and has

Figure No	13*a*	13*b*	13*c*	13*d*	13*e*	13*f*	13*g*
Water content, %	14.15	12 64	10.52	10.33	9.46	9.00	8 60
Particle size, μ	6–8	3–4	1.5–2	1 00	0.5	0.2	.

shown that the water separates as a highly dispersed colloidal phase. The size of the water particles depends upon the concentration of water in the

[26] W. R. Thompson, *Chem. Industries*, **48**, 450-456 (April, 1941).

[27] W. R. Thompson, *Modern Plastics*, **17**, 30–33 (Oct., 1939).

syrup before it is cast into the molds. (That is, all the water present from the initial condensation may not be removed under vacuum, so that the water content of the finished resin will be the sum of that present in the casting syrup plus that formed during curing.) The table on page 72, and photomicrographs in Figure 13 (taken from Thompson[27]) show the manner in which the particle size of the water droplets varies.

The particle size of the water droplets has a considerable effect upon the optical properties of the resin. When the water droplets are large the resin is translucent; as the particle size of the dispersed water decreases, the resin becomes more opaque, and the opacity becomes a maximum at about 9.5 to 9.0% water content. The resin then has a chalk-white appearance. As the water content drops below 9.0%, the opacity again decreases, due to the fact that the particle size of the dispersed water approaches the wave length of light.

VI. FILLERS FOR PHENOPLAST MOLDING POWDERS

A. INTRODUCTION

The idea of adding a filler to a phenoplast resin in order to produce a combination which could be molded satisfactorily originated with Baekeland, and was one of his pioneer contributions to the art. A filler is any substance, either organic or inorganic, which is mixed with a resin to produce a *nonhomogeneous* mixture which can subsequently be molded. The filler facilitates the molding process, which is usually very difficult with pure resin, and also improves the physical properties of the molded article.

The selection of the proper filler for a molding powder has an importance which is secondary only to the selection of the phenoplast resin. The filler is of most importance in controlling *mechanical* and *strength* properties of the finished molded product; to a lesser extent it affects the electrical qualities and heat resistance. The resin is important because it must give the proper flow and the proper bond, and must also permit curing to a well-finished piece in a reasonable length of time. The exact nature of the resin is important in securing the most desirable electrical properties. This point will be discussed further in a later chapter.

The general requirements for a satisfactory filler have been classified[1-3] into two groups, primary and secondary, with the idea that the primary requirements are essential for satisfactory molding, while some compromise is possible for certain uses in the case of the secondary requirements. The classification is as follows:

PRIMARY REQUIREMENTS

1. Good impact and tensile strength in the molded piece.
2. Low moisture absorption.
3. Low specific gravity in the molded piece.

[1] V. Meharg, *Modern Plastics*, **15**, 46–54 (Oct., 1937).

[2] Anon., *Plastics Catalog*, **1943**, pp. 231–242.

[3] V. Meharg, *Modern Plastics*, **16**, 30–31, 146–152 (Oct., 1938).

4. Easy wetting by resins and dyes.
5. No chemical or physical effects on steel dies, and particularly, no abrasive effects.
6. Low cost and adequate supply.
7. Nonflammability or low burning rate.
8. Freedom from odor.
9. Supplies must be readily obtainable and of uniform quality.

SECONDARY REQUIREMENTS

1. Good electrical characteristics in the molded piece.
2. Light color which is retained at elevated temperatures and in the presence of chemical materials used in the preparation of the molding powder.
3. Inertness to acids, alkalis, and solvents.
4. Easy machinability.
5. Heat resistance.
6. Availability in controlled mesh size and bulk factor.

B. TYPES OF FILLER

Fillers are usually classified primarily according to their general chemical nature—organic or mineral—and then are further divided into subdivisions according to their chemical composition and physical structure. Such a classification is as follows:

ORGANIC FILLERS

(A) Cellulose derivatives
  (a) Ground flours
    1. Wood flour
    2. Walnut-shell flour
    3. Cottonseed hulls
  (b) Cellulosic fibers
    1. Cotton flock
    2. Purified wood cellulose
    3. Sisal fiber
  (c) Comminuted paper
    1. Chopped paper
    2. Diced resin board
  (d) Creped paper
  (e) Pulp preforms
  (f) Textile by-products
    1. Macerated fabric
    2. Chopped tire cord

(B) Lignin and lignin-extended fillers

(C) Proteinaceous fillers
  (a) Soybean meal
  (b) Keratin

(D) Carbon fillers
  (a) Graphite
  (b) Carbon black

MINERAL FILLERS

(A) Asbestos
(B) Mica
(C) Diatomaceous silica
(D) Lead oxide
(E) Barium sulfate
(F) Glass fiber

C. EFFECT OF FILLER ON IMPACT STRENGTH AND DAMPING

The principal mechanical effect which is produced by different fillers is a change in the *impact resistance* of the molded plastic. The change in im-

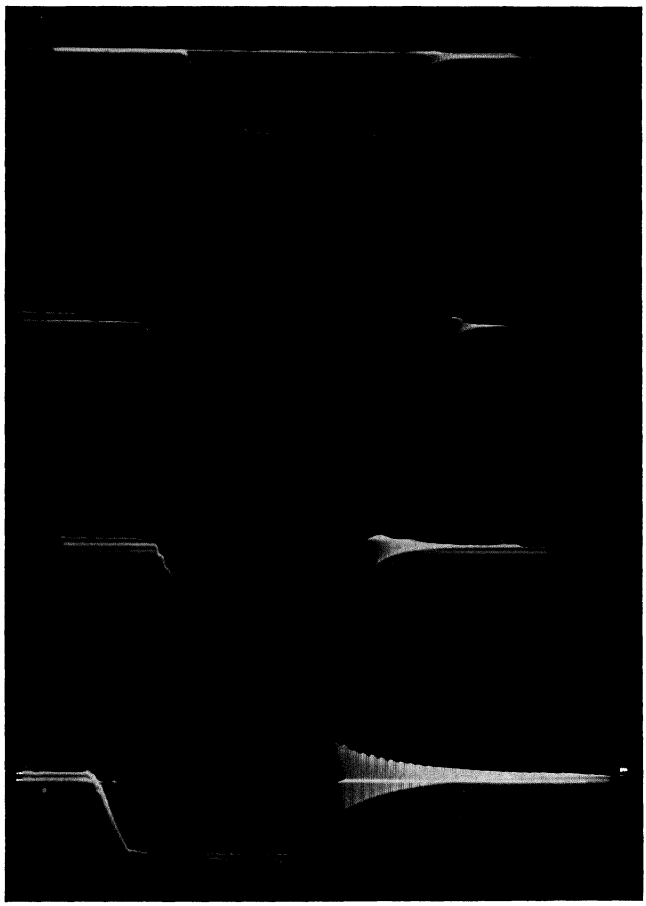


Fig. 14. Rate of decrease of torsional oscillations with various fillers.[4] Top to bottom; cord material, fabric molding material, wood flour material, and unfilled Bakelite resin.

pact resistance results from an increase in the capacity of the molded specimen to *absorb* mechanical shock waves, and thus prevent their amplifica-

[4] H. Leaderman, *J. Applied Mechanics*, 6, A79, A85 (1939).

tion at certain points through resonance. The ability to absorb mechanical-shock waves and transform them into heat is known as damping. In order to obtain a high degree of damping, it is necessary to have a high degree of nonhomogeneity in the molded plastic; this is usually best accomplished by the use of fibrous fillers. The filler itself must have very high tensile strength, so that it may resist the disruptive tensile forces which are created by the shock wave.

De Bruyne and Maas,[5] in 1936, studied the effect of damping and pointed out that the increase in shock resistance of fiber-filled molding compounds was connected with their greater damping capacity. De Bruyne[6] has also emphasized the importance of high damping capacity in assuring freedom from vibration. On the other hand, a high damping capacity involves a high energy absorption in the part which is subject to vibration, and the energy absorption is necessarily accompanied by the development of heat, which may of itself be destructive to the plastic. Leaderman[4] has studied the damping capacity by the decrement of free oscillations, using solid cylindrical specimens tested in torsion. Four grades of phenoplast molding materials were employed; (*a*) phenol–formaldehyde resin, white, transparent, and unfilled; (*b*) commercial phenoplast molding material with wood flour filler; (*c*) shock-resisting material, with a filler consisting of fabric snippings, impregnated with phenol–formaldehyde resin; and (*d*) shock-resisting material, with a filler consisting of closely packed cords running parallel to the axis of the specimen.

Figure 14, taken from Leaderman,[4] shows the rate at which free torsional oscillations decreased when these four fillers were used. From these data, the mean specific damping capacity in torsion was computed (in per cent), and is given in Table X. To illustrate the relation between damping capacity and impact resistance, Table X also contains the approximate im-

TABLE X

RELATION BETWEEN DAMPING CAPACITY AND IMPACT RESISTANCE

Molding powder composition	Damping capacity, % (dynamic test)	Impact resistance (notched Izod) ft lb /in of notch
Unfilled	8.9	0.25
Wood flour-filled	31.1	0.3
Fabric-filled	33.2	2.4
Cord-filled	36.6	7.0

[5] N. A. De Bruyne and J. N. Maas, *Aircraft Eng*, **8**, 289–290 (1936).

[6] N. A. De Bruyne, *J. Roy. Aeronaut. Soc.*, **41**, 523–40 (1937).

pact resistance for these various materials, as measured by the standard A.S.T.M. test.

D. MICROSCOPIC STRUCTURE OF FILLERS

The microscopic structure of both cellulosic and inorganic fillers has been examined in detail by Kent and Seiberlich.[7] They have demonstrated that the resilient fibrous fillers vary considerably in particle size. In the cellulosic fillers, the fibers are frequently split—in many cases, the microscopic examination showed that only 20 to 30% of the fibers were intact.

E. RATIO OF RESIN TO FILLER

The ratio of resin to filler has a profound effect upon the molding qualities of the powder and upon the physical and chemical properties of the molded plastic. (In all cases in this chapter *weight* ratios are meant.) When cellulosic fillers are employed, the molding composition usually contains approximately equal parts, by weight, of resin and filler. With this proportion, the best general combination of molding qualities, strength properties, and water resistance is obtained. When less resin is employed, molding becomes more difficult because the combination has less flow. Some strength properties, such as tensile and flexural strength, tend to drop off rather rapidly. Impact strength values usually rise to a maximum at about 30% resin content, and then decrease rapidly. However, whatever virtue there may be to this gain in impact strength is offset by the loss in tensile and flexural strength. Water resistance and resistance to other chemical agents decrease as the resin content decreases, because the particles of filler are not thoroughly covered and protected by a film of resin. For the same reason the appearance of the piece is poor, because the filler particles are exposed.

If the resin content is increased much above 50%, when a cellulosic filler is used, the molding tends to become more difficult because of excessive flow of the combination. There is not much change in tensile or flexural strength, but the impact strength decreases because the molded piece tends to become more homogeneous in composition, and consequently has less damping capacity.

When fillers are used which contain much natural resin, such as lignin-extended wood flour or redwood flour, the ratio of phenoplast resin to filler may be decreased. The natural resin present compensates for the lower quantity of phenoplast, and the total quantity of resin present in the com-

[7] R. J. Kent and J. Seiberlich, *Modern Plastics*, **19**, 65–69, 102 (June, 1942).

bination is still approximately 50%. When mineral fillers, such as mica or asbestos, are used, a higher *weight* ratio of filler is usually employed—about 70% filler to 30% resin. These mineral fillers have a higher specific gravity than the cellulosic fillers, and consequently the *volume* ratio of filler to resin is about the same as in the case of the cellulosic fillers.

F. STANDARD CLASSIFICATION OF PHENOPLAST MOLDING POWDER ACCORDING TO FILLER

There are several standard classifications of phenoplast molding materials, in which the method of classification is based upon the nature of the filler. Where cellulosic fillers are used, the impact strength of the molding also varies with the nature of the filler. Such classifications therefore also give an indication of the strength of the composition. It is important to note that the word *strength*, as affected by the nature of the filler, applies principally to *impact strength*, and not to other strength properties such as tensile or flexural strength. As a matter of fact, in so far as phenolic filled molding plastics are concerned, the tensile strength is scarcely altered in changing from wood flour (the weakest of the cellulosic fillers in impact resistance) to tire cord (the strongest in impact resistance), while the flexural strength is increased only slightly.

1. United States Navy Classifications

The United States Navy Classification for molded phenolic material is based primarily upon the type of filler employed. The following seven types are set up in Bureau of Ships Specification 17P4:[8]

TABLE XI

U. S. NAVY CLASSIFICATION FOR MOLDED PHENOLIC MATERIAL

Type	Impact strength[a]	Nature of filler
CFI- 5	0.60	Wood flour with cotton flock
CFI-10	1.1	Light macerated cotton fabric
CFI-20	2.3	Heavy macerated cotton fabric
CFI-30	4.0	.....
CFI-40	5.2	Cotton tire cord

[a] Specification 17P4, impact strengths are computed by a formula used only by the Bureau of Ships. In order to compare the impact figures with those obtained by A. S, T. M. methods, the figures given in 17P4 have been recomputed on the basis of ft. lb. per inch of notch.

[8] "Bureau of Ships ad Interim Specification 17P4 (INT)," Navy Dept., Washington, D. C., April 1, 1943.

TABLE XII

BULKING AND MOLDING PROPERTIES OF PHENOPLAST MOLDING POWDERS

Properties	Units	A.S.T.M. standard	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6	Type 7	Type 8	Type 9	Type 10
Particle size	Mesh	D-392-38	14–18	10–16	10–16	..	..	..	12–20	12–20	..	12–20
Pourability	Sec. (max.)	D-392-38	30	25	...	..	..	..	35	35	..	25
Apparent density	G./cc. (min.)	D-392-38	0.50	0.50	0.40	0.20	0.08	..	0.65	0.65	..	0.70
Bulk factor	G./cc. (max.)	D-392-38	2.5	3.0	3.5	10	18	18	3.0	3.0	12.5	2.8

TABLE XIII

MECHANICAL AND ELECTRICAL PROPERTIES DETERMINED ON COMPRESSION MOLDED SPECIMENS OF A.S.T.M. TYPES

Properties	Units	A.S.T.M. standard test	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6	Type 7	Type 8	Type 9	Type 10
General												
Water absorption	Per cent	D-48-42T	0.15	0.80	0.80	1.50	1.75	1.75	0.07	0.07	0.20	0.10
Specific gravity	(Max.), av.	D-570-40T										
	(Max.), av.	D-71-27	1.27	1.45	1.42	1.45	1.45	1.45	2.00	2.00	1.95	1.95
Strength properties												
Flexural strength	P.s.i. (min.), av.	D-48-42T	12,000	9,000	9,000	9,000	9,000	9,000	8,000	8,000	9,000	7,500
Impact strength (Izod)	Ft. lb./in. of notch (min.), av.	D-48-42T D-256-41T	0.36	0.24	0.34	0.80	1.75	4.00	0.34	0.34	0.75	0.30
Tensile strength ($^1/_8$ in. specimen)	P.s.i. (min.), av.	D-48-42T D-651-41T	7,000	7,000	7,000	5,500	6,000	6,000	5,500	5,500	4,500	5,000
Compressive strength	P.s.i. (min.), av.	D-48-42T D-649-41T	....	25,000	25,000	25,000	25,000	25,000	15,000	15,000	15,000	15,000
Thermal properties												
Mold shrinkage	In./in.	D-551-41T	0.010–0.014	0.006–0.008	0.005–0.008	0.002–0.007	0.003–0.006	0.004–0.006	0.001–0.004	0.001–0.004	0.001–0.005	0.003–0.006
Electrical properties												
Insulation resistance	Megohms (min.), av.	D-257-38	100	100	100	100	100	100	300	300	300	300
Dielectric strength	Volts/mil (min.), av.	D-48-41T (S/T)	300	300	300	200	200	200	350	400	225	300
		D-149-40T (S/S)	...	250	200	75	75	50	300	300	150	200
Dielectric constant	60 cycles (max), av.	D-150-42T	...	...	...	...	...	...	6	6	...	...
Dielectric constant	1 megacycle (max.), av.	D-150-42T	...	...	...	...	...	...	5 0	5.0	...	...
Power factor	60 cycles (max.), av.	D-150-42T	...	...	...	...	...	...	0.030	0.025	...	...
Power factor	1 megacycle (max.), av.	D-150-42T	...	...	...	...	...	...	0.015	0.009	...	...
Loss factor	60 cycles (max.), av.	D-150-42T	...	...	...	...	...	...	0.150	0.138	...	...
Loss factor	1 megacycle (max.), av.	D-150-42T	...	...	...	...	...	...	0.075	0.045	...	...

Type CFE—cellulose filler, electrical properties (radio)
Type CFG—cellulose filler, best general use, including electrical
Type CFI —cellulose filler, best impact strength
Type MFE—mineral filler, electrical properties (radio)
Type MFG—mineral filler, best general use, including electrical
Type MFH—mineral filler, best heat resistance
Type MFM—mineral filler, best moisture resistance

The CFI type is then subdivided further depending on the impact strength. Table XI lists the four subdivisions together with their impact strength and the general nature of the filler.

2. United States Air Corps Classification

The United States Air Corps Specification No. 32212A of December 19, 1940, lists three types of phenoplast molding powder, according to the filler employed:

Type I—cellulose filler, best general use
Type II—cellulose filler, best impact strength
Type III—mineral filler, best general use

3. American Society for Testing Materials

Subcommittee VI on Specifications of Committee D-20 on Plastics of the A.S.T.M. and Subcommittee 2 on Specifications of Committee D-9 on Electrical Insulating Materials have collaborated in the preparation of a joint specification[9] for thermosetting molding materials, in which phenolic molding compounds are classified in accordance with their filler and electrical, mechanical, and heat-resisting characteristics. The types are as follows:

Type 1—An unfilled transparent or translucent molding material suitable for both electrical and mechanical applications.

Type 2—General purpose wood flour-filled molding material suitable for both electrical and mechanical applications.

Type 3—General-purpose molding material with a cellulose filler which may be wood flour and cotton flock. It is somewhat higher in impact strength than Type 2 and suitable for both mechanical and electrical applications.

Type 4—Moderate impact strength molding material with cotton rag or other suitable forms of cellulose filler to give the required strength for this grade.

[9] American Society for Testing Materials, "Tentative Specification for Phenolic Molding Compounds, A.S.T.M. Designation: D700-43T."

Type 5—Medium impact strength molding material with cotton rag or other suitable forms of cellulose filler to obtain the required strength for this grade.

Type 6—High impact strength molding material with cotton rag or other suitable forms of cellulose filler to obtain the required strength for this grade.

Type 7—An electrical high frequency low loss molding material with a mineral filler.

Type 8—A superior electrical high frequency low loss molding material with a mineral filler.

Type 9—General-purpose mineral-filled molding material for both electrical and mechanical applications.

Type 10—Heat-resistant mineral-filled molding material.

Specific tests for all these types are described in A.S.T.M. Method D48–41T. Tables XII and XIII list the general properties of these types of material.

4. German Classification

The classification employed in Germany before about 1942 was based entirely upon the nature of the filler employed, and had nothing to do with

TABLE XIV

GERMAN DESIGNATIONS FOR FILLED RESINS

Filler	Type designation	Exact description of filler	Resin content, %
Powder	11	Powdered stone	70
Short fiber	12	Short asbestos fiber	70
Woven	M	Asbestos cloth cuttings	30–45
Wood flour	O	Wood flour	50
	S/C	Flocklike wood flour	40–50
	S/W	Finely ground wood flour	40–50
Textile fiber	T_1	Cotton flock	45–50
	$Z_{1/6}$	Long-fiber cotton flock	40–50
	$Z_{1/F}$	Fine cotton flocks	40–50
Woven fiber	T_2	Macerated canvas	40–50
Cellulosic	Z_{3B}	Long cotton-paper fibers	40–50
	Z_{3W}	Laminated paper ribbons	40–50
	Z_{3C}	Laminated cellulose ribbons	40–50

the impact strength, except in so far as this was influenced by the filler which was used. Table XIV shows the old German classification. Since about 1942, all German plastics have been reclassified into separate numerical classes, each with a code number, for which minimum mechanical properties are prescribed. Each class has ten units and special properties

are indicated by a single decimal figure following the code number. The following is the general classification for the hot-pressed phenoplasts:

00 to 09—without filler	50 to 69—cellulose filler
10 to 29—inorganic filler	70 to 89—textile filler
30 to 49—wood filler	90 to 99—other fillers

5. British Standards Designations

The field of phenol–formaldehyde moldings is broadly covered by B.S.S. 771 and deals with five types or grades of material:

Type G—general type
Type GX—improved general type
Type MS—medium shock-resistant type
Type HS—high shock-resistant type
Type HR—heat-resistant type

Although no mention is made of fillers, presumably Types G and GX are wood-filled, MS and HS fabric-filled, and HR asbestos- or mica-filled.

G. PROPERTIES OF INDIVIDUAL FILLERS

1. Cellulose Derivatives

The cellulose derivatives, and wood flour in particular, are by far the most widely used fillers in phenoplast molding powders. There are a number of reasons for this. As Meharg[1] has pointed out, the molder buys on a price-per-pound basis, but sells his moldings for so much per piece—that is, on a volume basis. The *molded specific gravity*, therefore, becomes of great importance from a cost standpoint. In this respect cellulose derivatives enjoy a marked advantage over mineral fillers. This is well illustrated by the following figures which represent the *molded specific gravity* of phenolic molded pieces containing a few common fillers:

Wood flour.....1.36	Mica.....1.90
Cotton.....1.36	Asbestos.....2.00

The cellulosic fillers have another great technical advantage in the manufacture of impact resistant plastics. As was shown in the discussion on damping, impact resistance is achieved *only by those fillers with appreciable fiber length;* and as a rule, the better the fiber length and strength, the higher is the impact resistance. The common fibrous fillers today are generally cellulosic in nature, with the exception of fibrous asbestos and glass fibers. Recently, some application has been made of synthetic fibers,

such as nylon, and it is possible that these may become important fillers in the future.

2. Wood Flour

Wood flour[10,11] is by far the most widely used filler for phenoplast molding powder—probably 70% of the phenolic molding powder used today is filled with this material. The reason for this lies partly in the low cost of wood flour ($20 to $30 per ton) and partly because wood flour is easily incorporated into the resin. The resulting combination can easily be molded, and gives a finished product with excellent surface finish and strength which is satisfactory for most uses.

Wood flour for use in plastics is nearly always obtained from the softer woods such as varieties of pine (*Pinus ponderosa*, sugar), Norway fir (*Abies balsamea*), spruce, poplar, basswood, and cottonwood. More recently, wood from Douglas fir (*Pseudotsuga taxifolia*) has been successfully employed. It is important that the wood be selected to insure the minimum contamination with knots, bark, and resin spots. These impurities when ground into the wood flour, and eventually incorporated into the molding powder, cause spots and surface imperfections in the finished molding. The possible advantages of a special type of wood flour from redwood (*Sequoia sempervirens*) have recently been described.[12] This wood contains tannins and phlobophanes of a phenolic nature. These give the wood a certain degree of flow and moldability. The latter properties are enhanced when the redwood chips are heated with high pressure steam for a few seconds, followed by a sudden release of the pressure. The resultant product, when ground to a fine powder, may be mixed in the customary manner with the proper grade of phenoplast. However, because of the flow properties imparted by the natural resins, somewhat less than the normal quantity of phenoplast may be employed. Lewis[13] has described molding compositions prepared by mixing redwood flour with phenoplast resins. The general properties of such compositions appear to be similar to those of general-purpose wood flour molding compounds.[12]

The grinding of the wood flour is an important part of its preparation. A type of attrition grinding is used; this has the advantage that the wood structure is not entirely destroyed, and a certain portion of its fibrous nature is retained. Despite these precautions, the fact remains that in

[10] M. H. Fischer, *Modern Plastics*, **14**, 50 (Oct., 1936).
[11] W. S. Dahl, *Woodflour*. W. S. Dahl, London, 1944.
[12] Anon., *Modern Plastics*, **20**, 77–81, 136 (Jan., 1943).
[13] H. F. Lewis, *ibid.*, **20**, 91–92, 134 (July, 1943).

wood flour a large part of the fiber structure is almost completely removed.[7] The wood flour is usually ground so that nearly all of it passes through an 80 or 100 mesh screen. The average length of the individual wood fibers is from 0.002 to 0.007 in.[14] The use of coarser material results in a poor finish of the molded article. Experiments have been made in the use of a more finely ground wood flour, but no advantage has been demonstrated. Wood flour was formerly largely imported from the Scandinavian countries but today is produced mostly in the United States.

When wood flour is used for the manufacture of a general-purpose phenoplast molding powder, approximately 50 parts of phenolic resin are used to 50 parts of wood flour. The resulting molding compound shows the following properties at 25°C. when molded and tested according to A.S.T.M. D-48 procedure:

Tensile strength, p.s.i.	6500–9500
Flexural strength, p.s.i.	9000–12000
Impact strength (Izod), ft. lb./in. of notch	0.24–0.40

3. Walnut-Shell Flour

Walnut-shell flour is a cellulosic type of filler which is used in place of wood flour when some special properties are desired. As compared to wood flour, walnut-shell flour gives a more lustrous finish to a molded phenoplast, and slightly better water resistance. Lougee[15] has described its use in detail and ascribes the improved water resistance to the presence of 1.7 to 6.3% of cutin, a natural wax. The physical properties of a molded phenoplast containing walnut-shell filler are in general quite similar to a general-purpose product filled with wood flour. The impact strength is about 10% lower, due to the less fibrous nature of the walnut-shell flour.

4. Cottonseed Hulls

Rosenthal[16] and Van Deventer[17] have described the possible use of cottonseed hulls as a filler for phenolic plastics. Rosenthal reached the following conclusions: (*a*) The absorbing power of cottonseed hulls is a function of their particle size and fiber content. (*b*) A maximum impact strength is obtained when the cottonseed-hull filler has a particle size of 100 mesh and 10% fiber content. (*c*) A maximum modulus of rupture is obtained in

[14] E. E. Halls, *Plastics (London)*, **6**, 304–311, 352–358, 384–394 (1942).

[15] E. F. Lougee, *Modern Plastics*, **19**, 35–37, 100–102 (Feb., 1942).

[16] F. Rosenthal, *Ind. Eng. Chem.*, **33**, 980–983 (1941).

[17] C. Van Deventer III, *Modern Plastics*, **18**, 68, 96–98 (June, 1941).

cottonseed hulls of 60 mesh and no fiber content. (*d*) The modulus of elasticity seems to vary in proportion to the modulus of rupture. (*e*) The control of particle size and fiber content permits the preparation of phenolic cottonseed-hull molding compounds whose strength characteristics compare favorably with commercial phenolic compounds. (*f*) Maximum strength characteristics are obtained at specific particle sizes and fiber contents. This versatility with respect to particle size and fiber content is a unique characteristic of cottonseed hulls.

Although cottonseed hulls have not as yet found much practical application as fillers for phenoplast molding compositions, the above analysis is interesting since it shows the manner in which filler characteristics may be chosen to give optimum properties in the molding powder.

5. Cellulosic Fibers

Cotton Flock.—This is obtained either by cutting from new cotton clippings or, to a lesser extent, from the fine particles which are left from the sorting of cotton linters. The fiber particles are longer and stronger than in the case of wood flour, and consequently moldings which contain this filler have greater impact strength.[18] The price is higher than wood flour, and molding powders which contain this filler tend to be bulky and fluffy and so do not mold quite so readily as when wood flour is the filler. However, the strength improvement is such that these minor disadvantages must be overlooked for many purposes.

Cotton flock for use as a filler must be free from foreign matter such as oils, grit, dirt, and metallic particles. A basic specification for cotton flock is as follows:

Moisture, maximum per cent	4.0
Ash, maximum per cent	0.5
Bulk, cc. per 10 g	40–50
Oil absorption, cc. per 10 g	20–30
Acetone-soluble material, maximum per cent	3.0

Molding powders containing cotton flock usually consist of about 50% filler and 50% resin. Standard test bars molded from such a composition show the following strength values at 25°C.:

Tensile strength, p.s.i.	6500–8500
Flexural strength, p.s.i.	9000–11,500
Impact strength, notched Izod, ft. lb./in. of notch	0.32–0.50

[18] F. Steinfield, *Modern Plastics*, **14**, 62 (Oct., 1942).

Purified Wood Cellulose.—Purified wood-cellulose filler (alpha flock) is obtained from bleached sulfite Kraft paper by treatment with dilute sodium hydroxide solution. Its advantages as a filler are its pure white color, permanence, cleanliness, controlled *p*H, and low density as compared with inorganic, pure-white fillers. Alpha flock is not widely used in the manufacture of phenoplast molding powder, but is more widely employed as a filler for the urea–formaldehyde resins. Alpha flock does find some use in phenoplasts to obtain certain special properties such as improved dielectric strength, shock resistance, improved flow during molding, superior surface appearance, and reduced shrinkage and distortion.[19]

Sisal Fiber.—The use of sisal fiber in the preparation of phenoplast molding compositions has been described by Koon.[20] To obtain the best impact strength, a woven mat of sisal fiber is prepared in the form of a fluffy batting, which is then consolidated by a needling operation which drives tufts of fiber through the mass. The mat is then impregnated with phenoplast resin. The resulting composition does not mold as readily as a standard wood flour-filled material, but has sufficient flow for many purposes. The molded composition is characterized by high impact strength.[21] Nelson and Reed[22] have described the technique for molding a composition containing 60% of sisal fiber and 40% of phenoplast resin. It is pointed out that the density of the finished molding can be varied by varying the amount of material charged to the mold, or by changing the molding pressure. Table XV from Nelson and Reed shows the relation between the physical properties of the molded sisal–resin combination and the specific gravity of the molded product.

TABLE XV

PHYSICAL PROPERTIES OF MOLDED SISAL FIBER OF VARIOUS SPECIFIC GRAVITIES[a]

Specific gravity	1.33	1.12	0.90	0.71
Impact strength (Charpy) ft. lb./in. of notch	8	9.6	8	4
Flexural strength, p.s.i.	18,000	21,000	13,500	7,800
Modulus of elasticity, p.s.i.	800,000	870,000	695,000	450,000
Tensile strength, p.s.i.	11,000	12,000	8,300	5,600

[a] H. C. Nelson, Jr., and L. D. Reed, *Modern Plastics*, 19, 52–53, 90 (March, 1942).

[19] R. K. Eskew, *Modern Plastics*, 14, 59–62 (Oct., 1936).

[20] A. W. Koon, *ibid.*, 18, 63–64, 84 (Aug., 1941).

[21] Anon., *Can. Plastics*, 1, 34 (Aug., 1943).

[22] H. C. Nelson, Jr., and L. D. Reed, *Modern Plastics*, 19, 52–53, 90 (March, 1942).

Comminuted Paper.—Chopped paper has been used as a filler for phenoplast molding powders to some extent in the United States and more extensively in Germany. The impact strength of moldings containing chopped paper is somewhat less than when macerated fabric is employed, and the molding technique required is more difficult. When chopped paper is used, it is customary to impregnate the paper web first, and then to chop it into fragments of the required size.

Diced Resin Board.—This material is considered to be a filler of the same category as chopped paper. In the case of the latter, paper is made first, then chopped up and mixed with resin. Diced resin board is made by preparing a suspension of pulp (usually from rag waste) and resin, and forming this, on a paper machine, into uncured and unpressed board.[23] The latter is then cut into rectangular chips which pass a U. S. Standard 6 mesh screen. As a high strength phenoplast molding powder, the product has special advantage in that its bulk factor is quite low. The physical properties, of course, depend largely upon the stock from which the board is made. When a high quality rag stock is used, the usual properties are:

Tensile strength, p.s.i.	4500–5500
Flexural strength, p.s.i.	7100–8500
Impact strength (Izod), ft. lb./in. of notch	0.85–1.2

Creped Resin-Treated Paper.—It is difficult to decide whether creped resin-treated paper should be considered as a laminating material or as a molding material. Actually, it bridges the gap between molding powders and laminates. Resin-impregnated paper cannot be used for molding where an appreciable amount of deep drawing is required during the process, because under such conditions the paper fibers tear and produce an imperfect molding. This has been overcome to some extent by creping the paper in two directions after it has been saturated with phenoplast resin. The creped paper can then adjust itself by flowing within the mold, thus permitting the formation of large objects with compound curves. The use of such creped resin-treated paper has been described by Morris[24] and by Calvin.[25]

Resin-Pulp Preforms.—Resin-pulp molding consists simply of making a uniform dispersion of resin and pulp in water, preforming this mixture into a shape which closely approximates the finished article, and subsequently curing it in the mold using heat and pressure. Alternatively, a

[23] Anon., *Modern Plastics*, **20**, 56–57, 144–146 (Jan., 1943).
[24] W. A. Morris, *ibid.*, **18**, 39, 92–94 (March, 1941).
[25] V. E. Calvin, *ibid.*, **22**, 136–139, 192–194 (Oct., 1944).

pulp preform may be made without resin, and then impregnated by dipping in a resin solution. In either case, the pulp can be considered to be the *filler*. The process is obviously an adaptation of the old papier-mâché process. The manufacture of dish-shaped and boxlike objects containing resin by such a process was described by Baekeland as early as 1910 and 1915 in U. S. Pats. 949,671 and 1,160,362. However, it has not been until recently that the process has been perfected and placed into large-scale operation.[26-32]

A typical pulp preforming operation may be described in the following way: The pulp stock is thoroughly dispersed in water to give a uniform suspension containing from 3 to 6% of fiber. A beater may be used for preparing the pulp suspension, although in many cases a simple, well-agitated tank will serve if the pulp stock has already gone through a beater. Many varieties of pulp stock may be used, and the strength and other properties of the finished article will depend to a large extent on the starting pulp. For example, Kraft stock, ground up rags, bleached pulp, and many combinations of these may be employed. The stock is then transferred to a preform tank where the concentration is reduced to 0.2 to 1.0% fiber. The preform tank contains a felting screen of approximately the same dimensions as the finished article. The pulp stock may be forced to pass through the felting screen either by suction or pressure. The suction technique is useful for relatively flat objects, while pressure may have to be employed in cases where sharp contours are encountered. The finished felted preform is then withdrawn from the tank and dried.

Drying may be accomplished either by heating in an oven or by placing the preforms between two perforated dies having the shape of the finished object and forcing heated air through the preform. The latter method has many advantages in that shrinkage and warping are largely prevented and the drying process is accelerated.

The dried preform may then be impregnated with a resin solution. The amount of resin absorption depends on the concentration of the resin solution and the length of time the preform is immersed. A more recently developed technique eliminates the use of a resin solution. In this process a

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[26] F. Ohl, *Wochbl. Papierfabr.*, **70**, 527–529, 541–543 (1939).
[27] W. E. Parsons, *Modern Plastics*, **19**, 45, 118 (Oct., 1941).
[28] W. E. Parsons, *ibid.*, **20**, 61, 138–140 (Aug., 1943).
[29] J. Delmonte, *Pacific Pulp & Paper Ind.*, **18**, 32 (April, 1944).
[30] R. U. Haslanger and R. Mosher, *Modern Plastics*, **20**, 76–77 (July, 1943).
[31] S. M. A. Young and R. J. Box, *ibid.*, **21**, 116, 166–168 (Dec., 1943).
[32] Anon., *ibid.*, **19**, 38–40, 78 (Sept., 1941).

TABLE XVI

EFFECT OF FIBER TYPE ON THE PHYSICAL PROPERTIES OF FIBER–RESIN PREFORMED MATERIAL[a]

Preformed fiber resin	Per cent resin	Molding pressure, p.s.i.	Sp. gr.	Flexural strength				Edgewise compress strength, p.s.i.	Impact strength (notched Izod), ft. lb./in. of notch		Tensile strength, p.s.i.	Water absorption, %
				Parallel[b]		Perpendicular						
				Flexural, p.s.i.	Deflection, in.	Flexural, p.s.i.	Deflection, in.		Perp.	Par.[c]		
Kraft (unbleached)	45	2200	1.33	17,140 ± 1008	0 081	17,120 ± 676	0.077	27,400 ± 333	3.11 ± 0.10	0.85 ± 0.05	11,400 ± 740	0.58
Alpha	45	2200	1.35	17,100 ± 700	0.071	19,300 ± 775	0.088	25,540 ± 804	1.91 ± 0.09	0.85 ± 0.03	11,260 ± 1243	0.43
Defibered rag	45	2200	1.35	17,000 ± 775	0.097	16,200 ± 533	0.093	26,400 ± 1200	2.67 ± 0.15	1.54 ± 0.04	10,000 ± 320	0.66
Sulfite (unbleached)	45	2200	1.35	15,930 ± 252	0.067	15,260 ± 328	0.060	26,500 ± 1300	2.69 ± 0.32	0.78 ± 0.04	9,500 ± 480	0.69
Ground wood	45	2200	1.34	11,800 ± 220	0.055	10,820 ± 234	0.059	22,400 ± 1243	1.21 ± 0.07	0.55 ± 0.04	8,400 ± 809	0.43
Waste paper	45	2200	1.35	11,600 ± 1732	0.044	12,320 ± 864	0.046	28,000 ± 943	1.54 ± 0.09	0.61 ± 0.21	8,100 ± 807	0.55
Asbestos glass fiber (85:15)	45	2200	1.72	17,700 ± 525	0.050	17,970 ± 1155	0.050	27,000 ± 640	2.94 ± 0.19	2.10 ± 0.05	9,300 ± 1400	0.14

[a] T. S. Carswell, *Pacific Plastics*, **2**, 26–29, 39 (Sept., 1944).
[b] Broken parallel to molding pressure.
[c] Notch runs parallel to molding pressure.

properly formulated phenol–aldehyde resin is added directly to the beater or dispersing tank and is intimately mixed with the pulp suspension. According to Martin,[33] sodium aluminate may be added to precipitate the resin, followed by the addition of aluminum sulfate to adjust the *p*H to 4.6–5.0. The resin is then uniformly dispersed together with the pulp during the preforming operation. This technique has an advantage in that it eliminates the separate impregnation operation and it also eliminates drying following the impregnation. It also eliminates the need for any resin solvent. However, it has not been as thoroughly developed as the impregnation operation and it can be employed only with specially formulated phenolic resins which are virtually insoluble in water. Since some resin is dissolved, re-use of the white water is essential. The pulp preform, containing resin, is then molded after removal of the water by appropriate drying methods. The preform will undergo only a very limited amount of flow during molding, and it must be pointed out that the extent to which the preform will flow to fit the mold is very much less than will conventional molding powder. It is therefore important *that the screen which is used to make the preform and the mold both be designed at the same time*, keeping in mind the fact that the preform which comes from the screen must conform closely to the mold dimensions.

If a fine finish is desired on both sides of the molded article, polished steel molds must be employed for both the male and female dies. However, there are many cases where only the outside of the finished article needs a high polish, such as in the case of housings for vacuum cleaners, adding machines and similar products. In these cases a type of expanding rubber die may be used. The use of such a die decreases the cost of the mold considerably and at the same time permits the manufacture of objects having a considerable side wall area. In fact, such a form of bag molding is the only process by which adequate pressure can be applied to objects having a very deep draw. An exterior finish may be obtained on the outside of the molded object by increasing the quantity of resin on the surface of the preform. This may be accomplished in a number of ways; the simplest is deposition by spraying a uniform resin dispersion on the outside of the resin-bearing pulp preform.

Haslanger and Mosher[30] have presented data (see page 92) for strength properties at 25°C. for pulp-resin preforms molded at 880 p.s.i. Kraft pulp was used, the resin content was 55%, and the preforms were impregnated with an alcoholic solution of resin.

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[33] H. C. Martin, *Plastics* (*London*) **8**, 520–529 (Nov., 1944).

Tensile strength, p.s.i.	13,400
Flexural strength, p.s.i.	18,200
Impact strength, Izod, ft. lb./in. of notch	1.09

The strength properties vary considerably with the type of pulp employed, and depend decidedly upon the fiber length.[34] The strength also varies, depending on whether the sample is taken with or across the direction of flow during felting. Table XVI[35] (page 90) shows the variation with different types of pulp and with direction.

6. Textile By-Products

Fabric.—Macerated fabric is employed as a filler when the impact strength required is higher than can be obtained with cotton flock. This use was first described by Kempton in U. S. Pat. 1,513,323 (Oct. 28, 1924). The type of fabric used varies from a light muslin or shirting stock to a heavy canvas. The impact strength increases with the weight of the fabric, but so does the difficulty of molding. Complete specifications for a filler will include the weight of fabric, the particle size of the fabric, and the percentage of fines. The amount of inorganic matter, dirt, metallic particles, and oil must be held at a minimum in order to avoid damage to the molds or spoilage of the finished article.

The strength properties of test bars molded from macerated fabric-filled phenoplasts vary, depending on the weight of fabric used. However, the list below tabulates these properties at 25°C. when a rather heavy grade of canvas is used. The bars were molded for 10 minutes at a mold temperature of 170°C. and a molding pressure of 4000 p.s.i.

Tensile strength, p.s.i.	6,370
Flexural strength, p.s.i.	12,000
Impact strength, ft. lb./in. of notch	2.4

Cotton Tire Cord.—The maximum in impact resistance with cellulosic fillers may be attained by the use of chopped cotton tire cord, as described by Whitlock and Haslanger.[36] When macerated fabric is employed as a filler, the impact strength is dependent on the particle size, the weight of the cord or thread, and the thread count. However, when the weight of thread and fabric chosen is too great, the flow and molding characteristics of the composition become quite poor. In molding compounds utilizing

[34] R. Mosher and J. B. Griffin, *Modern Plastics*, 22, 147–152 (Feb., 1945).
[35] T. S. Carswell, *Pacific Plastics*, 2, 26–29, 39 (Sept., 1944).
[36] C. H Whitlock and R. U. Haslanger, *Modern Plastics*, 19, 70–71 (June, 1942).

individual fibers as the filler, it was found that a satisfactory molding composition could be obtained using fibers of much greater weight than were possible with woven fabrics. After evaluating a wide range of fibrous fillers, a special twisted cotton cord was found to be the one best suited for use in producing a material with very high impact strength. When such fibrous fillers are employed, the impact strength of the resulting product is largely dependent upon the length of the fiber or cord used. Table XVII gives quantitative data concerning this point.

TABLE XVII

EFFECT OF FIBER LENGTH ON STRENGTH

(Approximately 50% fiber, 50% resin in all cases)

Nature of fiber	Flexural strength, p s.i.	Izod impact, ft. lb./in. of notch
Ramie fiber cut to 1 in.	9,500	0.96
Ramie, long fibers, about 4 in.	14,500	2.40
Sisal fiber, short, 1/8–1/4 in.	...	3.90
Sisal fiber, long, 1–2 in.	19,000	10.00
Tire cord, short, 1/2 in.	...	10.10
Tire cord, long, 1 in.	15,000	17.00

Lignin and Lignin-Extended Fillers.—About 30% of the weight of wood is lignin, a complex phenolic body of rather high molecular weight. Lignin apparently serves as the cementing agent between the cellulose chains in the wood structure. It is removed in the process of making chemical pulp, and in the course of removal its chemical nature is changed considerably. For example, in the manufacture of sulfite pulp the lignin is removed as lignosulfonic acid. Very large quantities of lignin or lignosulfonic acid are thrown away during paper manufacture, and attempts have been made to use these materials, in combination with wood flour, as fillers for phenoplasts.

Lignin and lignosulfonic acid are thermoplastic, and have a certain degree of flow and moldability. However, they do not make satisfactory molding powder when used alone with wood flour, because the limited flow demands unusually high pressure in molding and the thermoplastic nature requires a chilled mold. To overcome these disadvantages, a lignin-enriched wood flour may be mixed with a certain proportion of phenol–aldehyde resin. The combination then behaves very much like a general purpose phenoplast molding powder, although it contains a smaller amount of the phenol–aldehyde resin. Whereas the usual general-purpose molding

powder contains 45 to 50% of resin, the lignin-extended materials may contain as little as 30% of resin.[37]

Two methods are generally employed in the manufacture of lignin-enriched fillers. In one method, lignin-extended filler is produced by cooking waste lignosulfonic acid solution, from the sulfite paper process, with ground wood.[38] The lignosulfonic acid is precipitated on the wood. The resulting product is washed, screened, and dried. In another method of preparing a lignin-enriched filler, as described by Katzen, Reynolds, and Othmer,[39] the wood is first hydrolyzed by treatment with dilute sulfuric acid. This treatment removes part of the cellulose in the form of sugars, but leaves the lignin and part of the cellulose in fibrous form. The lignin-extended fillers were used to some extent during the war, when resins were scarce due to the shortage of phenol. The mechanical properties of phenoplast molding compounds containing lignin-extended fillers are very similar to those of general-purpose wood flour-filled compounds. The impact strength tends to be somewhat lower.

7. Proteinaceous Fillers

Soybean Meal.—Brother and McKinney[40,41] showed that soybean meal may be used as a filler for phenoplast molding compounds. The addition of some fibrous filler, such as wood flour, was necessary to improve the impact strength. In practice, it is usually found that phenoplast molding compositions containing proteinaceous fillers are somewhat deficient in water resistance as compared to standard wood flour-filled compositions.

Keratin.—Brother, Binkley, and Brandon[42] have described the use of keratin, derived from chicken feather, cattle hoof, and hog bristle. In order to obtain sufficient flow, it was necessary to calcine the keratin before incorporation in the molding powder mixture. The keratin acted as an extender for the resin, and permitted reduction of the resin content to about 35% of the total weight of the molding powder. A typical formulation contained 35% acid-catalyzed phenoplast resin, 25% keratin, 25% wood flour, and minor quantities of pigment, hexamethylenetetramine, and lubricants. Improved arc resistance is claimed for such a formulation.

[37] Anon., *Modern Plastics*, 19, 46–47 (May, 1942).

[38] J. G. Meiler, *ibid.*, 20, 64–66, 128–130 (Sept., 1942).

[39] R. Katzen, A. O. Reynolds, and D. F. Othmer, *ibid.*, 20, 91–97, 122–124 (Oct., 1942).

[40] L. L. McKinney and G. H. Brother, *ibid.*, 18, 69–71, 106–108 (May, 1941).

[41] G. H. Brother and L. L. McKinney, *Plastics (London,)* 4, 93–95 (1940).

[42] G. H. Brother, C. H. Binkley, and B. Brandon, *Modern Plastics*, 22, 157–160 (March, 1945).

8. Carbon Fillers

Carbon Black.—The use of carbon black is well known in compounding natural rubber, where it increases the tensile strength and the abrasion resistance. A similar effect is obtained by the use of acetylene black in GRS synthetic rubber. It might therefore be natural to suppose that carbon fillers would have some special virtue in plastics. In fact, such reinforcing action is not observed, and phenoplasts when filled with graphite, carbon black, or acetylene black are more brittle than the original resin, but otherwise have about the same strength properties. The action of a carbon filler is apparently quite different in the case of a phenolic resin as compared to an elastomer. Acetylene black as a filler does cause the molding composition to become a fairly good conductor of electricity. This application has advantages for some special purposes. Carbon black is frequently used as a pigment in the manufacture of black molding compositions which must be resistant to solvents. In such cases other fillers are used and the real function of the carbon black is that of a coloring material.

Graphite.—This material has been used as a filler in special cases where self-lubrication is required, as in the case of molded bearings for heavy-duty machinery or marine use.

9. Mineral Fillers

Mineral fillers are employed where high heat resistance, exceptional electrical properties, or minimum moisture absorption characteristics are required in the molded products. Mineral-filled phenoplasts frequently cause more abrasion on the molding dies than the cellulosic fillers.

Asbestos.—This is the only mineral composition which has a natural fibrous structure. It comes from the mineral, *chrysotile*, which is a hydrated magnesium silicate which corresponds in composition to the formula $H_4Mg_3Si_2O_9$, or $3\,MgO \cdot 2\,SiO_2 \cdot 2\,H_2O$. The fiber length of the material which is used as a plastic filler varies from one-half inch to a fine powder. The use of asbestos as a filler in plastic compositions has been discussed in some detail by Cummins.[43] When very short fibers are used, the impact strength of an asbestos-filled molding powder is of the same order of magnitude as a wood flour-filled composition. When the longer fibers are used, impact strengths can be obtained which approach those obtained with light macerated fabric. The resistance to either short-time or continuous heat is much improved when asbestos is used as a filler. This point will be discussed in detail in later chapters.

[43] A. B. Cummins, *Modern Plastics*, 14, 50–56 (Oct., 1936).

Mica.—Mica is employed as a filler in electrical grades of phenoplasts and is used in a powdered form. As described by Halls,[14] the two chief sources of reliable mica are India and Canada. The first of these supplies is the muscovite or potash group of micas, chemically formulated $H_2KAl_3(SiO_4)_3$. This group has a specific gravity of 2.76 to 3.0 and resists temperatures to 500°C. The second locality provides the phlogopite micas, chemically $HK(MgF)_3Mg_3(AlSiO_4)_3$. The specific gravity of these lies between 2.78 and 2.85. They can be safely used between 900° and 1000°C. Electrically, those of the muscovite group have superior resistance, higher permittivity, and somewhat better breakdown strength. Either of them is admirably suited to incorporation in plastics, but where better electrical characteristics are required the muscovites are advocated. Table XVIII is a summary of data for mica.

TABLE XVIII

SUMMARY OF DATA ON MICA[a]

Characteristic	Muscovite group	Phlogopite group
Chemical formula	$H_2KAl_3(SiO_4)_3$	$HK(MgF)_3Mg_3Al$
General name	Potash or white mica	Amber mica or magnesia mica
Chief source	India	Canada
Chemical analysis (typical), per cent		
Silica	45.2	40.8
Alumina	38.4	26.9
Potash	11.8	12.7
Magnesia	...	7.6
Ferric oxide	...	12.0
Water	4.6	...
Specific gravity	2.75–3.0	2.75–2.85
Moh's hardness	2.8–3.2	2.5–2.7
Maximum safe working temperature	500°C.	1000°C.
Permittivity	4.2–5.0	2.9–3.0
Specific resistance, ohms $\times 10^{12}$	10–100	0.5–20
Electrical strength, v./mil at 20°C.	3000–6000	3500–4500
Loss of water, per cent on ignition at:		
450°C.	0.03	Nil
650°C.	0.06	Nil
750°C.	1.69	Nil
800°C.	3.29	Nil
900°C.	4.20	0.20
1100°C.	4.30	1.0 (max.)

[a] Data from E. E. Halls, *Plastics* (*London*), **6**, 304–311 (1942).

Incorporating mica into plastics presents difficulties which differ from those encountered with the cellulosic filler in that mica is nonabsorbent

and very difficult to wet. The resin must be specially formulated to overcome this latter problem, and great care must also be taken in the rolling operation. McMurray[44] has described a finely ground mica recovered from schist ores which appears to have inherently better electrical properties than ground scrap micas. Thus, the dielectric strength of a disk molded from 70% ground scrap mica and 30% phenoplast resin was 405 v. per mil; the same composition with schist mica gave 482 v. per mil.

Diatomaceous Silica.—Diatomaceous silica is the amorphous fossil remains of diatoms. As provided for the plastics industry,[45] the material

TABLE XIX

PROPERTIES OF SILICA-FILLED PHENOPLASTS[a]

Property	50% Celite 110	50% Asbestos floats	50% Wood flour	25% Celite 110, 25% asbestos floats	25% Celite 110, 25% wood flour
Sp. gr., molded	1.62	1.73	1.35	1.67	1.49
Hardness, Brinell, load 500 kg.	55–57	44–46	34–40	50–51	48–49
Flexural strength, modulus of rupture, p.s.i.	8,500–12,000	5,000–8,000	8,500–11,000	8,000–10,000	7,000–9,000
Compressive strength, p.s.i.	20,000–24,000	15,000–20,000	20,000–24,000	21,000–23,000	24,000–26,000
Tensile strength, p.s.i.	4,900–6,400	3,800–4,000	4,800–5,500	4,400–5,900	4,400–5,600
Impact strength, ft. lb./in. squared	1.4–1.7	1.3–1.6	1.9–2.2	1.5–2.0	1.4–1.75
Water absorption, 38 hr. immersion, room temperature	0.04–0.05%	0.06–0.24%	0.50–0.90%	0.06–0.07%	0.50–0.60%
Water absorption, 30 min. boiling water	0.04–0.05%	0.12–0.20%	0.40–0.50%	0.05–0.09%	0.30–0.38%
Dielectric strength, step (v./mil)	280–370	280–315	240–350	280–315	260–290
Power factor, audio frequency, 1000 cycles	3–5	13–15	3–10	8–10	5–6
Power factor, radio frequency, 1,000,000 cycles	1.5–1.6	...	3.5–4.5	...	...
Resistance to arcing (times to produce continuous path)	9–12	4–6	7–8	...	...
Resistivity, megohm/cm.	19–20 × 10^5	...	1–5 × 10^5	...	...

[a] A. B. Cummins, *Modern Plastics*, **14**, 57–58 (Oct., 1936).

is an impalpable powder of extreme lightness and high absorptive capacity. It is chemically inert and heat stable at all temperatures up to 2200°F.

[44] L. L. McMurray, *Modern Plastics*, **18**, 61–63, 98 (March, 1941).

[45] A. B. Cummins, *ibid.*, **14**, 57–58 (Oct., 1936).

The silica content ranges from 90 to 94% SiO_2. Plastic compositions employing this filler have low water absorption, good electrical properties, and heat and chemical resistance. Cummins[45] has discussed the properties and uses of diatomaceous silica in detail. Table XIX, taken from his work, shows the properties of phenoplast molding compounds containing a commercial silica filler (Celite 110), alone and in mixture with other fillers.

Lead Oxide.—Lead oxide (litharge) has occasionally been used as a filler when a molding of exceptionally high density is required. For this purpose, lead oxide is the most useful filler, since it combines a very high specific gravity (9.53) with ready availability and a reasonably low price. Since molding powders from lead oxide and resin alone are very brittle, some proportion of cellulosic filler, such as cotton flock, is frequently added.

Barium Sulfate.—When a reasonably high specific gravity is required barium sulfate (barytes) may be employed as a filler. Barytes is less effective in increasing the density of phenoplast moldings since barium sulfate has a lower specific gravity than lead oxide (4.50 in contrast to 9.53).

Glass Fiber.—Glass fibers have been used to a limited extent in the manufacture of special types of high impact material, where nonflammability is important. The molding of material prepared with this filler is difficult, due to the stiff nature of the fiber.

VII. FILLERS AND RESINS FOR PHENOPLAST LAMINATES

The fillers for laminated phenoplasts differ from those used in molding powders principally in that the fillers for laminates are continuous webs rather than discrete particles. The chemical nature of fillers is quite similar—they may be paper, cotton, or linen fabric, sisal mat, or woven asbestos. More recently, woven glass fiber has become available for applications in which exceptionally high strength is required. The filler greatly increases the strength properties of the laminate over those of the pure resin; the increase is greater than is obtained with molding powders because of the continuous web which is present. The filler has the same type of damping effect upon impact waves as has been described in the case of molding powders.

The resin, usually in the form of an alcoholic impregnating solution, is applied to the filler. Aqueous solutions, however, are frequently used, particularly in the case of paper base laminates. The impregnated sheet, which may contain from 25 to 65% resin (usually about 40%) is then dried and pressed between metal plates at a high temperature. In cases in which a highly polished finish is required on the surface of the laminate, the surface sheets may contain a higher resin content—approximately 50%. For standard flat laminates, the usual pressing temperature ranges from 140° to 180°C. and the molding pressure is from 1000 to 2500 p.s.i. Laminated phenoplast tubing may be formed by rolling the impregnated sheet material upon mandrels between heated pressure rolls and then either oven baking or pressing in a heated mold to complete the curing of the resin.

In recent years[1] there have been important developments in the molding of laminates into more intricate forms, such as seats for airplane pilots, air ducts, ammunition boxes, and similar articles. There are two general methods by which such contoured laminates may be formed: (*1*) Layers of laminate, cut to the proper size, are formed in a mold under heat and pressure. The amount of draw, or the degree of contour, is usually limited, since the base of the laminate will tear if subjected to too much strain in

[1] H. J. Luth, *Modern Plastics*, 20, 91, 138–140 (March, 1943).

molding. The molding pressures may vary from a high range (1200 to 2000 p.s.i.) down to a low range (100 to 250 p.s.i.). Somewhat better strength properties are obtained at the higher pressures, but the lower pressures permit the use of cheaper dies and less expensive presses. (*2*) By selection of the proper resin and careful control of the curing cycle during lamination, it is possible to produce a flat laminate which can be heated and reshaped under relatively low pressures. Such a process is known as post-forming.[2–5] It was originally thought that the resin used in bonding the laminate should be undercured; later work has indicated that a fully cured resin can be formed just as well, and the use of a well-cured resin is, in fact, desirable.[6] The filler is a cotton fabric, with a weave chosen especially so that some stretch is possible in two directions. As in the case of low-pressure laminating, post-forming permits the production of relatively large articles with cheap dies and light presses. A certain amount of draw is possible when molding by this process; Guhl[7] has stated that the maximum draw may be determined from an index (r/R), which is calculated by dividing the cup radius (r) by the blank radius (R) of the piece to be drawn. This index should lie between 0.67 and 0.77 for satisfactory hot drawing of laminated phenoplast sheets in thicknesses of from $^1/_{32}$ to $^1/_{16}$ in.

A. CLASSIFICATION OF LAMINATES

Standard laminated sheets and tubes are classified according to properties and functional use, which in turn are dependent upon the type of filler. Paper has been the most important single filler used; according to Hanson and Wilson,[8] the laminating industry produces about 70,000,000 lb. of finished stock per year. Prior to the war, 80% of this material had paper used as a base; this represented an annual consumption of 28,000,000 lb. of paper.

In the United States, the National Electrical Manufacturers Association (NEMA)[9] has set up standard classifications for laminates made under high pressure (i.e., 1000 to 2500 p.s.i.). The standard NEMA grades are listed below. These grades do not include recent developments in high strength

[2] E. F. Lougee, *Modern Plastics*, **20**, 69–71, 143 (June, 1943).
[3] Anon., *ibid.*, **20**, 70 (Aug., 1943).
[4] H. C. Guhl, *Mech. Eng.*, **67**, 175–179 (1945).
[5] E. E. Halls, *Plastics (London)*, **9**, 266–271 (June, 1945).
[6] W. I. Beach, *Modern Plastics*, **22**, 132–135, 206–208 (Nov., 1944).
[7] H. C. Guhl, *Plastics Resins Ind.*, **3**, 7 (Aug., 1944).
[8] N. D. Hanson and F. P. Wilson, *Paper Trade J.*, **118**, 48–50 (1944).
[9] NEMA Publication No. 39–57, Nov., 1939.

paper, glass fabric, and low pressure laminates. These new materials will be described in separate paragraphs.

1. Laminated Phenolic Sheets

Grade X—A strong paper-base laminated material primarily intended for mechanical applications where electrical requirements are of secondary importance. Should be used with discretion when high humidity conditions are encountered. Not equal to fabric-base grades in impact strength.

Grade P—A paper-base laminated material primarily intended for punching. More flexible and not quite as strong as *Grade X*. Moisture-resistance and electrical properties intermediate between *Grades X* and *XX*

Grade XX—A paper-base laminated material suitable for usual electrical applications.

Grade XXP—A paper-base laminated material similar to *Grade XX* in electrical and moisture-resisting properties, but more suitable for hot-punching. Intermediate between *Grades P* and *XX* in punching and cold flow characteristics.

Grade XXX—A paper-base laminated material, suitable for radio frequency work, for high humidity applications, and with minimum cold flow characteristics.

Grade XXXP—A paper-base laminated material similar to *Grade XXX*, but having lower dielectric losses and being more suitable for hot punching. This grade has greater cold flow than *Grade XXX*, and is intermediate between *Grades XXP* and *XXX* in punching characteristics.

Grade C—A fabric-base laminated material made throughout from cotton fabric weighing over 4 oz. per sq. yd. and having a count, as determined from inspection of the laminated plate, of not more than 72 threads per in., in the filler direction, nor more than 140 threads per in. total, in both warp and filler directions. A strong, tough material suitable for gears and other structural forms exposed to high impact. The heavier the fabric base used the higher will be the impact strength, but the rougher the machined edge; consequently, there may be several subgrades in this class adapted for various sizes of gears and types of mechanical service. Should not be used for electrical applications except for low voltages.

Grade CE—A fabric-base laminated material of the same fabric weight, and

thread count as *Grade C*. For electrical applications requiring greater toughness than *Grade XX*, or mechanical applications requiring greater resistance to moisture than *Grade C*. Exceptionally good in moisture resistance.

Grade L—A fine weave fabric-base laminated material made throughout from cotton fabric weighing 4 oz. or less per sq. yd. As determined by inspection of the laminated plate, the minimum thread count per inch in any ply shall be 72 in the filler direction and 140 total in both warp and filler directions. For purpose of identification, the surface sheets shall have a minimum thread count of 80 threads per in. in each of the warp and filler directions. This grade is suitable for small gears and other fine machining applications, particularly in thickness under $^1/_8$ inch. Not quite as tough as *Grade C*. Should not be used for electrical application except for low voltage.

Grade LE—A fine weave fabric-base laminated material of the same fabric weight, and thread count as *Grade L*. For electrical applications requiring greater toughness than *Grade XX*. Better machining properties and finer appearance than *Grade CE*—also, available in thinner sizes. Exceptionally good in moisture resistance.

Grade A—An asbestos paper-base laminated material. More resistant to flame and slightly more resistant to heat than other laminated grades because of high inorganic content. Suitable for only low voltage applications. Minimum dimensional changes when exposed to moisture.

Grade AA—An asbestos fabric base laminated material. Similar to *Grade A* but stronger and tougher. Minimum dimensional changes when exposed to moisture.

2. Laminated Phenolic Tubes (NEMA Classification)

There are two types of tubes: rolled and molded. The rolled are oven baked after rolling on mandrels while the molded are cured in molds under pressure. The rolled tubes are less dense and generally less resistant to moisture than molded tubes but are of uniform strength around the circumference, whereas molded tubes have mold seams which are a source of weakness both mechanically and electrically, particularly in thin walled tubes. Each type has its own particular applications and characteristics.

X-Rolled—A high mechanical strength paper-base tubing with good punching and fair machining qualities. Low power factor and high dielectric strength under dry conditions.

XX-Rolled—A paper-base tubing with good machining, punching, and threading qualities. Not as strong mechanically as *X-Rolled* but better moisture resistance. Best grade for low dielectric losses particularly on exposure to high humidity.

X-Molded—Better in moisture resistance and machining qualities than *X-Rolled*. Strongest paper base except in thin walls. Dielectric strength may be low at molded seams.

XX-Molded—Best paper-base grade from moisture resisting standpoint. Good machining and good electrical properties except in very thin wall forms.

C-Rolled—A fabric-base tubing made from a cotton fabric weighing more than 4 oz. per sq. yd. As determined by inspection of the laminated tube, the thread count shall not be more than 72 threads per in. in the filler direction. The total thread count per inch in both warp and filler direction shall not exceed 140. This tubing is intended primarily for mechanical purposes. Dielectric strength is relatively low and moisture absorption greater than for other fabric-base grades.

CE-Molded—A fabric-base tubing made of same fabric weight and thread count as *Grade C-Rolled*. For use when a tough, dense, fabric-base material is required, having fair electrical properties along with excellent mechanical properties and good resistance to moisture. Dielectric strength may be low at molded seams, especially in thin walls.

LE-Rolled—Made from a fine weave cotton fabric weighing 4 oz. or less per sq. yd. As determined by inspection of the laminated tube, the minimum thread count per inch shall be 72 in the filler direction and 140 total in both warp and filler directions. Best concentricity and dielectric strength of any fabric base grade. For use when the seams from a molded tube may be objectionable and when the application requires good machining qualities, together with good electrical and mechanical properties.

L-Molded—Made from a fine weave cotton fabric of the same weight, and thread count as *Grade LE-Rolled*. Has high density and good moisture resistance. For mechanical applications, primarily when finer machined appearance than with *CE-Molded* is desired or when tougher material than *LE-Molded* is required. Should not be used for electrical applications, except for low voltage.

LE-Molded—Made from a fine weave cotton fabric of the same weight and thread count as *Grade L-Molded*. Has excellent machining and moisture resisting characteristics. For use in electrical applications even under

humid conditions when a tougher material than *Grade XX* tubing is required at some sacrifice of electrical properties. Dielectric strength may be low at molded seams, especially in thin wall forms. *Grade LE-Molded* is better electrically than *Grade CE-Molded*, but not quite as tough.

3. High Strength Paper Laminates

In recent years a new type of paper base for phenoplast laminates has been developed, which gives higher tensile strength properties than the usual paper bases. This type of filler is not included in the NEMA specifications. This new base was principally developed because of the need for paper laminates of improved strength characteristics in the construction of component parts for aircraft, particularly when molded at low pressure ranges (i.e., 50 to 200 p.s.i.). The paper is made from Mitscherlich spruce sulfite pulp, because, with a minimum of mechanical treatment, it gives a sheet of paper with exceptionally high tensile strength.[10,11] The fibers are laid on the paper machine so that they are largely oriented in the direction of the machine. A thin sheet gives the best results, and the weight of the paper is generally held to 35 lb. per ream. For best results, the gauge of the paper must be uniform in all directions. Although spruce is ideal for the purpose, a number of other softwoods yield pulps of about the same characteristics. In place of Mitscherlich pulp, that from the Kraft process can be used satisfactorily provided the papermaking conditions are altered to suit the pulp.[12]

When such a paper is used as a laminate, and the plies are all oriented in the same direction, an ultimate tensile strength as high as 35,000 p.s.i. *in the direction of the fibers* may be obtained. The strength in the opposite direction, however, is rather low. The paper is usually used by laying the plies in alternate directions, so that the strength properties are substantially the same in any direction. Stamm[13] has given the data in Table XX to illustrate the strength properties obtained with this base as compared with standard NEMA classifications. Erickson and Mackin[14] in a later paper have described the properties of a highly developed laminated paper pheno-

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[10] G. K. Dikermann, *Paper Trade J.*, 118, 33–36 (1944).

[11] C. F. Marschner, *Pacific Pulp & Paper Ind.*, 18, 22–26 (1944).

[12] T. A. Howells and H. F. Lewis, *Ind. Eng. Chem.*, 37, 264–268 (1945).

[13] A. J. Stamm, *Paper Trade J.*, 118, 39–41 (1944).

[14] E. O. Erickson and G. E. Mackin, *Trans. Am. Soc. Mech. Eng.*, 67, 267–277 (May, 1945).

TABLE XX[a]

PROPERTIES OF CROSS-LAMINATED PHENOPLASTS WITH DIFFERENT BASES

Property	Mitscherlich high strength paper	Kraft paper, NEMA *Grade XX*	Cotton fabric, NEMA *Grade C*	Cotton fabric, NEMA *Grade L*	Asbestos paper, NEMA *Grade A*	Asbestos fabric, NEMA *Grade AA*
Sp. gr.	1.38	1.34	1.34	1.34	1.8	1.8
Tensile strength, ultimate, p.s.i.	18,200	11,400	9,000	10,800	6400	6,400
Compressive strength, edgewise, p.s.i.	13,100	17,500	20,600	18,800	5500	11,700
Impact strength (notched Izod)						
Face	4.0	2.1	2.8	4.1	4.5	...
Edge	0.7	0.6	1.9	1.9	2.0	...

[a] A. J. Stamm, *Paper Trade J.*, **118** 39–41 (1944).

TABLE XXI[a]

STRENGTH PROPERTIES OF NOMINAL ONE-EIGHTH INCH PAPREG

Properties and tests	Parallel laminated				Cross laminated	
	Lengthwise		Crosswise		Lengthwise and crosswise	
	Average	Stand. deviation	Average	Stand. deviation	Average	Stand. deviation
Sp. gr.	1.41	...	1.41	...	1.41	...
Tension						
Ultimate strength, p.s.i.	35,610	2321	20,010	853	27,160	1591
Yield strength at 0.2% offset, p.s.i.	32,780	2575	14,560	838	23,160	1665
Elongation immediately before fracture, %	1.20	0.16	1.88	0.30	1.29	0.14
Static bending (flatwise)						
Modulus of rupture, p.s.i.	36,590	1171	24,300	785	30,540	1153
Bearing ($^1/_8$ in. diam. pin, tensile loading)						
Bearing strength (4 to 6 tests), p.s.i.	24,290	...	22,940	...	25,920	...
Ultimate bearing stress, p.s.i.	35,060	...	31,300	...	34,280	...
Shear (Johnson-type shear tool)						
Shearing strength (flatwise), p.s.i.	16,980	700	14,010	733	15,550	415

[a] E. O. Erickson and G. E. Mackin, *Trans Am. Soc. Mech. Eng.*, **67**, 267–277 (May, 1945).

plast, to which the name *Papreg* has been given. This laminate was made from a sulfite pulp having the following specifications:

Ream weight (25 × 40—500), lb.....25–40
Thickness, in.....0.001–0.004
Density, g./cc.....0.60–0.75
Minimum tensile strength, p.s.i.
in grain.....10,000
cross grain.....4000
Porosity (Gurley densometer, 100 cc.), sec.....less than 30

The resin content was about 36%, and the volatile content (of the impregnated paper) was 4.5%. The laminates were pressed at 250 p.s.i. and 350°F.

Tables XXI and XXII, taken from the above authors, show the strength properties of *Papreg* in two thicknesses ($^1/_8$ in. and $^1/_2$ in.) at room temperature (75°F.).

Marschner[15] has presented the data in Figure 15 to illustrate the vari-

TABLE XXII[a]

STRENGTH PROPERTIES OF NOMINAL ONE-HALF-INCH PAPREG

Properties and tests	Parallel laminated				Cross laminated	
	Lengthwise		Crosswise		Lengthwise and crosswise	
	Average	Stand. deviation	Average	Stand. deviation	Average	Stand. deviation
Sp. gr.	1.41	...	1.41	...	1.41	...
Compression (edgewise)						
Ultimate strength, p.s.i.	22,530	727	19,430	729	20,790	911
Yield strength at 0.2% offset, p.s.i.	14,040	421	9,730	462	11,290	439
Compression (flatwise)						
Ultimate strength, p.s.i.	42,200	...	...	...	45,600	...
Static bending (flatwise)						
Modulus of rupture, p.s.i	31,170	1371	19,540	2489	28,710	1522
Static bending (edgewise)						
Modulus of rupture, p.s.i.	28,870	1502	20,790	1239	26,590	1319
Shear (Johnson-type shear tool)						
Shearing strength (edgewise), p.s.i.	20,500	581	17,840	684	18,670	922
Impact strength (Izod)						
Flatwise, notched on face, ft. lb./in. of notch	4.69	...	2.43	...	3.82	...
Edgewise, notch on edge, ft. lb./in of notch	0.67	...	0.60	...	0.66	...

[a] E. O. Erickson and G. E. Mackin, *Trans. Am. Soc. Mech. Eng.*, **67**, 267–277 (May, 1945).

[15] C. F. Marschner, *Modern Plastics*, **21**, 81–85, 168–170 (March, 1944).

ation of tensile strength with the angle at which the specimen is cut from the paper, for both cross- and parallel-laminated panels.

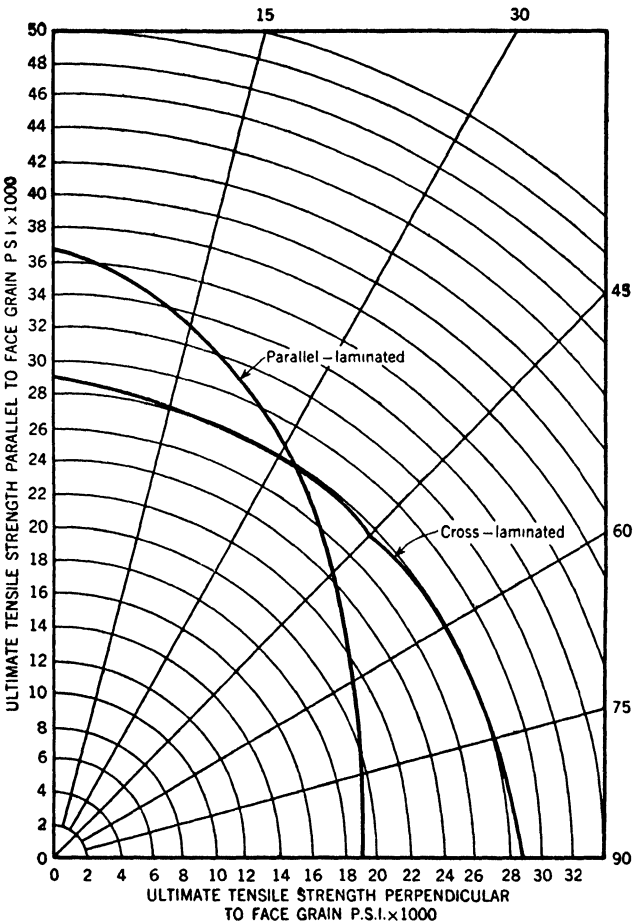


Fig. 15. Ultimate tensile strength properties through complete range of angles to face grain of both parallel- and cross-laminated high strength paper-base phenoplasts.[15]

4. Plastic Bonded Cotton Fiber

It is possible to prepare a laminate by using as a filler cotton fibers which have all been laid in a parallel direction. The laminate then develops very high tensile strength (up to 35,000 to 40,000 p.s.i.) in the direction of the

fiber, although the strength properties across the fiber are low. Such laminates have been described by Goldman and Olsen.[16,17]

5. Glass Fabric Filler

Woven glass fabric has recently become available as a filler for laminates and this type of filler is also not included in the NEMA specifications.[18-20] The grade most commonly used has the glass fibers running in one direction, and is woven together by a fine cotton fiber. To obtain equal strength properties in both directions, the laminates are *cross banded*—that is, the alternate layers of fabric are oriented at an angle of 90° to each other. With this filler, it is possible to obtain an ultimate tensile strength in the neighborhood of 30,000 p.s.i. at room temperature. The high strength is, to some extent, offset by the relatively high specific gravity of the laminate —1.67 as compared with 1.34 for a paper laminate with comparable resin content. The impact strength of the laminated glass fabric is particularly high; the notched Izod value at room temperature is 22 ft. lb. per inch of notch, as compared to 1 ft. lb. per inch of notch for the usual paper laminate.

B. RESINS USED FOR LAMINATES

In general, the resins used in laminates are very similar to those used for molding powders. Where exceptionally good electrical properties are required, cresylic acid is frequently used as the base instead of phenol, or some special type of extender is added to the phenolic resin.[9] The proportion of resin to filler is usually lower than in the case of molding powders; it may be as low as 25% based on the weight of the finished laminate, and usually averages about 40%. Less resin can be used because less flow is required in the molding operation—there are no sharp corners in the mold to be filled out by flow of the resin and filler. The effect of the quantity of resin on physical properties is further discussed in the chapter on the physical properties of laminated phenoplasts.

Cox and Pepper[21] have shown that the degree of impregnation obtained in a paper filler varies markedly with the molecular complexity of the resin; as the molecualr size is reduced, an improvement in the impregna-

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[16] M. A. Goldman and G. A. Olsen, *Modern Plastics*, **20**, 100, 130–132 (May, 1943).

[17] M. A. Goldman and G. A. Olsen, *Textile Research*, **13**, 2, 25–32 (1942).

[18] T. S. Rogers, *Modern Plastics*, **18**, 69–70, 96–98 (July, 1941).

[19] G. Slayter, *ibid.*, **21**, 100–103 (May, 1944).

[20] C. W. Armstrong, *Iron Age*, 152, 51–54 (1943).

[21] H. L. Cox and K. W. Pepper, *J. Soc. Chem. Ind.*, **63**, 150–154 (1944).

tion is observed. There is considerable difference between the impregnation achieved by a low molecular weight resin dissolved in water and a more highly condensed resin which must be dissolved in a solvent such as alcohol. The more highly condensed resin does not penetrate the fibers to the same extent as the water-soluble resin.

It is desirable to use a resin which will not cure too rapidly at the drying temperature, as this makes the drying time very critical. On the other hand, the resin should cure rapidly at the pressing temperature. Thus, a resin with a high temperature coefficient of cure is desirable.

Table XXIII, taken from a paper by Wilson and Hanson,[22] gives data on the range of phenoplast resins that are available for low pressure molding.

TABLE XXIII

TYPES OF PHENOPLAST RESIN USED FOR LOW PRESSURE MOLDING

Resin type	Hardening temperature, °F.	Molding time	Molding pressure, p.s.i.
Cold-hardening	70–140	30 min. to 12 hr.	Contact to 75
Warm-hardening	140–220	15 min. to 2 hr.	Contact to 250
Hot-hardening	280–360	5 min. to 1 hr.	Contact to 250

Gordon[23] has presented some evidence, based upon the microscopic examination of cellulose-filled laminates, to indicate that a possible chemical combination, or at least a very close association, takes place between the cured resin and the cellulosic filler. The change, whatever its nature, increases as the cure time is increased. The experimental data, while necessarily fragmentary, are interesting and worthy of further amplification. It is obvious that the principle applies not only to laminates, but to all types of cellulose–phenoplast combinations, and may be a possible explanation of the excellent adhesive qualities of the phenoplasts for woods, as demonstrated in the manufacture of exterior-grade plywood.

[22] F. P. Wilson and N. D. Hanson, *Modern Plastics*, **20**, 57–60, 144 (Aug., 1943).

[23] C. M. Gordon, *J. Soc. Chem. Ind.*, **63**, 272–277 (1944).

VIII. MECHANICAL PROPERTIES OF MOLDED PHENOPLASTS

A. INTRODUCTION

During the first few years after the art of phenoplast molding became well developed, the largest proportion of molded objects was used by the electrical industry. There were a number of reasons for this. Primarily, the phenoplasts had many natural advantages; they had excellent electrical resistance and could be molded into fairly complex shapes. The electrical industry was growing rapidly and needed just such a material. The strength and shock resistance of the general-purpose material, filled with wood flour, was adequate for most electrical purposes. Subsequently, the inexpensiveness and ease of molding of the phenoplasts promoted their use in mechanical parts and there developed a need for higher strength products. This need was met by the use of fillers which had greater fiber length and strength than wood flour.

Serious studies on the mechanical properties of molded phenoplasts were initiated as soon as the industrial usefulness of these products became apparent. Such studies were accelerated and intensified in the United States by the advent of World War II. German scientists, realizing that molded plastics could, in many places, be used to supplant metals which were available in only limited quantities, had published many studies on mechanical properties in the period just before the war. The war also emphasized our need for knowledge concerning the effect of temperature on the mechanical properties of plastics. Temperatures ranging from $-40°$ to $+120°$F. are commonly encountered in the continental United States. Since the development of high altitude flying, temperatures as low as $-70°$ may be reached in less than an hour over nearly any spot on the globe, and even lower readings have been reported. Metal equipment exposed to the sun can easily reach temperatures of $+160°$F. in the southern parts of the United States, and temperatures exceeding 200°F. have been measured inside the wing structures of metal aircraft on the North African desert. Designers of military matériel now consider that temperatures from $-60°$ $+160°$F. are routine limits which may be encountered by any piece of

equipment. In the past few years studies have been made of the effect of temperature on molded phenoplasts containing many different fillers.

B. MECHANICAL PROPERTIES COVERED

There are many mechanical properties which could be considered in the case of any structural material. Only the following more important ones are considered in this chapter, in the order given: tensile strength, modulus of elasticity, compressive strength, flexural strength, shear strength, bearing strength, impact resistance, creep and stress endurance, and fatigue characteristics.

The scope of this book will not permit an exhaustive discussion of the nature of these properties, nor of the test methods used in evaluating them. For such information the reader must be referred to standard textbooks on the subject, and particularly to publications in this series by Alfrey[1] and Nason.[2] The publications of the American Society for Testing Materials describe the methods of testing which have been adopted as standard in the United States.

C. PHENOPLAST PROPERTIES AT ROOM TEMPERATURE

A molded phenoplast is ordinarily a very nonhomogeneous mass. Pure resin without filler is very rarely used for molding, and only limited quantities are employed in the form of cast resin. The filled, molded resin has a structure consisting of filler particles more or less impregnated by resin, depending on the nature of the filler, and bound together by resin. It is obvious that the mechanical properties will be influenced to a large extent by the nature and quantity of filler present. The common types of filler have already been described in Chapter VI, and some indication of the more common mechanical properties has been given. The effect of the filler in influencing strength properties, particularly through fiber length and strength, and the effect of the filler on damping have also been discussed in Chapter VI.

A molded test bar of filled phenoplast is obviously a nonhomogeneous structure. The arrangement of the filler is not identical in each individual molded bar, and the chance of random arrangement increases with the size of the filler particles. For example, wood flour is used in very finely divided form. The resin is intimately mixed with the wood flour by blend-

[1] T. Alfrey, *Mechanical Behavior of High Polymers*. Interscience, New York, 1947.

[2] H. K. Nason, *The Testing of Organic Plastics* (in preparation). Interscience, New York.

ing and rolling. Consequently, any small volume such as a $^1/_4$-inch cube, taken from one point in a piece molded from a wood flour-filled phenolic, will have almost the identical composition as a similar volume taken from some other point in the molding. The case is quite different when a high impact composition made from macerated canvas is considered. In this case, the canvas particles are present in pieces about $^3/_4$ inch square, and these pieces are impregnated with resin. When molded, the pieces of canvas are obviously distorted and pushed out of shape in an entirely random manner. Consequently, a small volume taken at any one point in a molding from macerated canvas material may have quite a different composition from a piece taken from another point, and the composition may vary both as to the quantitative relationship between resin and filler, and also in respect to the spatial arrangement of the filler. This means that small specimen bars of macerated canvas material will show a variation in physical properties which is much wider than that shown by a similar series of bars from a wood flour-filled phenolic. Table XXIV shows

TABLE XXIV

SCATTER OF IMPACT DATA ON MOLDED PHENOPLASTS WITH VARIOUS FILLERS

(Data expressed in foot-pounds per inch of notch)

Wood flour	Coarse cotton flock	Macerated fabric	Chopped cotton tire cord
0.46	2.06	3.00	11.0
0.52	2.04	3.52	6.8
0.46	2.02	3.52	13.3
0.42	1.96	3.12	8.2
0.52	2.00	3.34	6.6
0.48	2.56	3.28	5.8
0.50	2.34	2.68	7.7
0.46	1.88	2.56	8.3
0.52	2.00	2.44	7.7
0.46	1.82	3.12	7.5

the manner in which these results may be scattered in a series of ten consecutive tests by the standard A.S.T.M. Izod impact test on phenoplasts containing various fillers. It will be seen that the results with wood flour are reasonably uniform, but the amount of scatter increases with the size of the filler. The recognition that this condition may exist is important in evaluating test results on high strength materials. To obtain the same degree of accuracy in evaluation, it is necessary to examine a much larger

number of specimens. The average should be computed by proper statistical methods, and the probable error indicated. While such an average is satisfactory for laboratory studies, it should not be used where the strength property is to be used in design calculations. For such purposes, the *minimum* strength value should be employed.

1. Effect of Degree of Cure on Physical Properties

The degree of cure has considerable effect upon the physical properties of a phenoplast; if the piece is undercured, the maximum strength is not developed. Overcure also tends to reduce strength properties, as charring of an organic filler may easily occur if the piece is held for too long a time or at too high molding temperatures. Nitsche[3] has pointed out that undercuring of a phenoplast has bad effects in that the piece is not of uniform structure, and contains strains, it is more water sensitive, and the mechanical properties are impaired. Undercure may be demonstrated in several ways: (*a*) the piece has a high content of acetone-soluble material, (*b*) it tends to blister when dipped into boiling water, and (*c*) it can be easily deformed when hot.

Grush[4] studied the effect of cure time on the impact strength of a commercial phenoplast when molded at 320°F. and 3000 p.s.i. The data indicated that with the particular size molding employed in this study, the maximum impact resistance was obtained with a cure time of 15 minutes. However, the impact resistance changed very little over a range of from 5 to 30 minutes cure time. These data can be regarded as illustrative of only the general effect of cure, since the optimum cure at any temperature depends upon the size of the piece. Fortunately, in so far as mechanical properties are concerned, cure is not very critical and may be varied over a wide range without changing the strength values significantly.

In a study of shear strength, Delmonte[5] graphically demonstrated the effect of cure time on this property, and also showed the greater softening effect of acetone on undercured plastic. The results are further discussed in this chapter under shear strength (page 118), and are reproduced in Figure 16.

No exact rule can be stated for determining the proper time of cure for any one piece; the time depends on the type of molding powder em-

[3] R. Nitsche, *Kunststoff-Tech. u. Kunststoff-Anwend.*, **10**, 313–322 (1940).
[4] F. Grush, *Plastics Trends*, **2** (March, 1942).
[5] J. Delmonte, *ASTM Bull.* **No. 114**, 25–27 (Jan., 1942).

ployed, the thickness of the piece, and the design, type of heating, and temperature of the mold. Thick sections, when molded in the usual manner, show variations in the degree of cure between the surface layers and

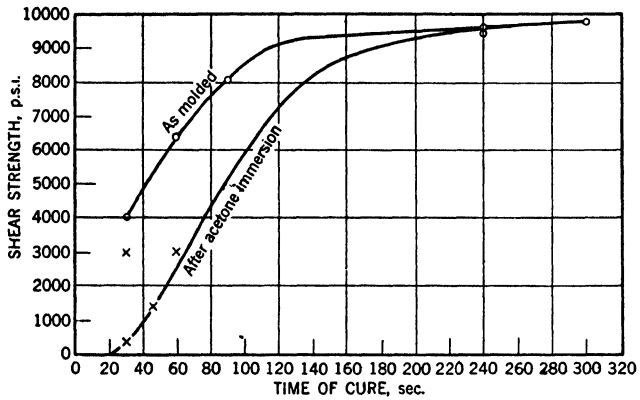


Fig. 16. Effect of cure time on shear strength of a phenoplast at 2000 p.s.i. molding pressure and 310°F.[5]

the inner sections, with a corresponding change in strength properties.[6] If the preforms for such thick moldings are uniformly preheated, for example, by electronic heating, a much more uniform cure results.

2. Tensile Strength

Information regarding the behavior of a material under tension can best be obtained by careful examination of the stress–strain curve. The stress–strain curve of nearly any plastic material at equilibrium with any environment can be represented by a portion of Figure 17, provided that: (*1*) the curve is obtained by a constant-rate-of-straining type of test and (*2*) the point of rupture of the test specimen may occur at any point on the curve.[7] The behavior of a typical ductile material, such as cellulose acetate under room conditions, may be represented by the entire curve, with the break occurring at point B. Molded phenoplasts are relatively stiff and nonductile, and consequently show only the early part of the typical curve of Figure 17, with the break occurring at or before point A. Stress–strain curves for typical molded phenoplasts are shown in Figure 18 on page 116.

[6] R. Meikrantz, *Plastics Trends*, **3**, No. 4 (Feb. 15, 1943).

[7] T. S. Carswell and H. K. Nason, *Modern Plastics*, **21**, 121–126, 158–160 (June, 1944); **21**, 125–130, 160–162 (July, 1944).

Table XXV lists the usual values obtained for tensile strength at failure for phenoplasts with various fillers. These values are taken from a recent publication of the Plastics Materials Manufacturers Association,[8] and are obtained by A.S.T.M. test method D48-42T. A range of values is given in all cases, since the exact value is influenced by minor variations in the filler and by the molding technique.

Tensile strength data for phenoplasts have also been reported by Riechers,[9] Imhof,[10] Jacobi and Thum,[11] Oberg, Schwartz, and Shinn,[12] Moyer,[13] Findley,[14,15] and Siegfried.[16]

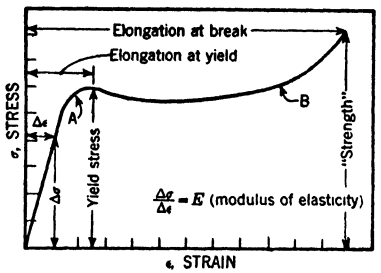


Fig. 17. Generalized tensile stress–strain curves.[7]

TABLE XXV

TENSILE STRENGTH VALUES FOR MOLDED PHENOPLASTS

Type of phenoplast	Tensile strength, p.s.i.
General-purpose, cellulose-filled	7000–9500
Low shock resistant, cellulose-filled	7000–8500
Low to intermediate shock resistant, flock-filled	5000–8500
Intermediate shock resistant, fabric-filled	5000–7000
Intermediate to high shock resistant, fabric-filled	5000–7000
High shock resistant, fabric-filled	5500–7500
Very high shock resistant	6000–8000
Shock and heat resistant, mineral-filled	4500–8000
Heat resistant, mineral-filled	3500–5000
High frequency insulation, mineral-filled	5500–7000
Arc resistant, semiflexible	3500–5000
Transparent, no filler	7000–8000

[8] *Technical Data on Plastic Materials*, Plastics Materials Mfrs. Assn., Washington, D.C., May, 1943.

[9] K. Riechers, *Z. Ver. deut. Ing.*, **82**, 665–671 (1938).

[10] A. Imhof, *Schweizer Arch. angew. Wiss. Tech.*, **4**, Nos. 4 and 5, 99–104, 112–27 (1938).

[11] H. R. Jacobi and A. Thum, *Ver. deut. Ing., Forschungsheft* 396, supplement to "Forschung auf dem Gebiete des Ingenieurwesens," Part B, **10** (May/June, 1939).

[12] T. P. Oberg, R. T. Schwartz, and D. A. Shinn, *U. S. Air Corps Tech. Rept.* No. 4648, June 6, 1941.

[13] H. R. Moyer, *Product Eng.*, **13**, 379–381 (1942).

[14] W. N. Findley, *N.A.C.A. Report on Contract NA W-1243* (Oct. 5, 1942).

[15] W. N. Findley, *Advance Restricted Report, N.A.C.A.* (June, 1943).

[16] W. Siegfried, *Schweizer Arch. angew. Wiss. Tech.*, **8**, 255–262 (1942).

3. Modulus of Elasticity

The modulus of elasticity, or *Young's modulus* is a property which is derived from the stress–strain curve, and is represented by the slope ($\Delta\sigma/\Delta E$) of the initial straight line portion of the curve. For phenoplasts, when the rate of straining is constant and relatively fast (i.e., 0.05 in. per min.), the stress–strain curve is essentially a straight line up to the yield point. The modulus is commonly used as a measure of stiffness. The modulus of various types of filled phenoplast moldings is given in Table XXVI.

TABLE XXVI

MODULUS OF ELASTICITY FOR MOLDED PHENOPLASTS

Type of filler	Modulus, p.s.i.
No filler	8.9×10^5
Wood flour	14.6×10^5
Chopped tire cord	12.0×10^5
Asbestos	24.3×10^5
Mica	28.0×10^5

4. Compressive Strength

When a load is applied to any material in compression, it is possible to obtain a stress–strain diagram similar to that of Figure 17 (page 115). In

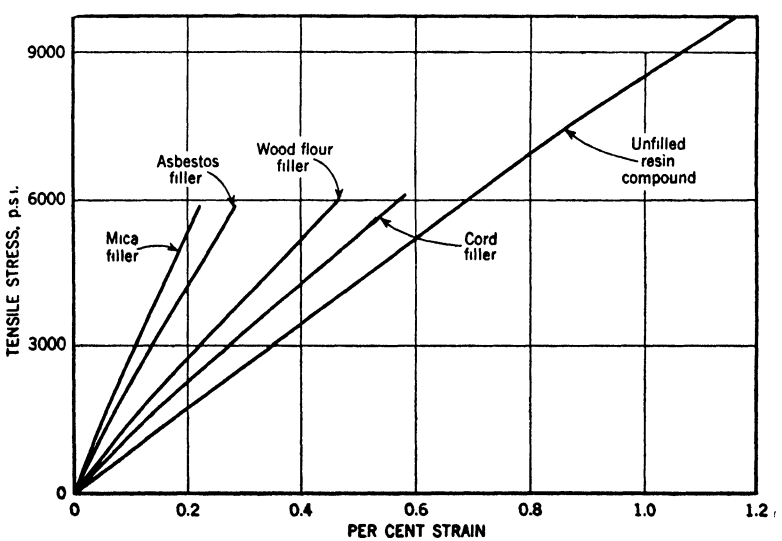


Fig. 18. Typical stress–strain curves for molded phenoplasts.

fact, the tensile stress–strain and compressive stress–strain diagrams are really two parts of a complete stress–strain diagram for the material as it passes from tensile to compressive stresses.

Table XXVII gives the ultimate compressive strength for molded phenoplasts containing various fillers. The method of testing is that given in A.S.T.M. D48-42T.

TABLE XXVII

COMPRESSIVE STRENGTH OF MOLDED PHENOPLASTS

Type of phenoplast	Compressive strength, p.s.i.
General-purpose, cellulose-filled	24,000–30,000
Low shock resistant, cellulose-filled	25,000–30,000
Low to intermediate shock resistant, flock-filled	25,000–30,000
Intermediate shock resistant, fabric-filled	25,000–30,000
Intermediate to high shock resistant, fabric-filled	25,000–30,000
Very high shock resistant, fabric-filled	15,000–30,000
Shock and heat resistant, mineral-filled	10,000–15,000
Heat resistant, mineral-filled	20,000–25,000
High frequency insulation, mineral-filled	7,000–20,000
Arc resistant, semiflexible	10,000–20,000

5. Flexural Strength

Flexural strength is determined by A.S.T.M. test D48-42T. Table XXVIII gives values for this property as published by the Plastics Materials Manufacturers Association.

TABLE XXVIII

FLEXURAL STRENGTH OF MOLDED PHENOPLASTS

Type of phenoplast	Flexural strength, p.s.i.
General-purpose, cellulose-filled	9,500–14,000
Low shock resistant, cellulose-filled	9,500–11,000
Low to intermediate shock resistant, cellulose-filled	7,000–11,000
Intermediate shock resistant, fabric filled	9,000–11,000
Intermediate to high shock resistant, fabric-filled	8,500–12,500
High shock resistant, fabric-filled	9,000–11,000
Very high shock resistant	10,000–15,000
Shock and heat resistant, mineral-filled	10,000–13,000
Heat resistant, mineral-filled	6,500– 8,000
High frequency insulation, mineral-filled	7,000–10,000
Arc resistant, semiflexible	5,000– 7,000
Transparent, no filler	13,000–15,000

Flexural strength data for phenoplasts have also been given by Oberg, Schwartz, and Shinn,[12,17] Moyer,[13] Findley,[14] Calm, Davis, and Hauth,[18] and Fuller.[19]

6. Shear Strength

Very little information has been published on the shear strength of molded phenoplasts. Delmonte[5] determined the shear strength of a commercial molding powder as a function of the time of cure. The values were obtained with the aid of a punch and die which measured 0.106 inch in diameter. The punch was forced through a flat sample of the material being tested and the load was measured. The shear strength was then calculated according to the formula:

$$\text{shear strength} = \frac{\text{load required to force punch through sample}}{11 \times 0.106 \times \text{thickness of specimen}}$$

The data obtained by Delmonte were presented in Figure 16 (page 114). In discussion, W. N. Findley pointed out that the values obtained in this test were not true shear because of the unequal distribution of stresses over such a small area.

Schwartz and Dugger[20] determined the shear strength of a cast phenolic resin by the method of Federal Specification LP 406; the average value at 77°F. was 9200 p.s.i.

7. Bearing Strength

There is likewise very little information on the bearing strength of molded phenoplasts. Bond[21] determined values for a macerated canvas-filled material. The method chosen as most useful was the determination of the load causing a deformation equal to 4% of the bearing pin diameter. The data obtained for bearing strength in p.s.i. under various conditions were as follows: at 70°F. and 55% R.H. 26,900; at 160°F., 31,800; and at 70°F. in water, 25,900.

8. Impact Resistance

The impact test is used to measure the toughness or shock resistance of a plastic. Of the several methods which have been developed, the notched Izod test has been adopted by the A.S.T.M. (Test D48-42T) and data ob-

[17] T. P. Oberg, R. T. Schwartz, and D. A. Shinn, *Modern Plastics*, **20**, 87–100, 122–128 (April, 1943).

[18] H. Calm, R. Davis, and R. Hauth, *Plastics Trends*, **2**, No. 22 (Nov. 15, 1942).

[19] F. B. Fuller, *Modern Plastics*, **20**, 95–97, 130 (June, 1943).

[20] R. T. Schwartz and E. Dugger, Jr., *ibid.*, **21**, 117–121, 164–166 (March, 1944).

[21] J. Bond, *ibid.*, **19**, 70–73, 110 (July, 1942).

tained by this method only will be discussed in this chapter. As Telfair and Nason[22,23] have pointed out, the standard impact tests are not reliable as indications of the behavior of a plastic part when subjected to impact stresses in service, nor do they rank accurately different plastic materials with respect to their ability to resist fracture when exposed to such stresses. However, until better methods are developed, the data obtained by the notched Izod must be accepted as giving a relative rating of the impact resistance.

The data, presented in Table XXIX, on the impact resistance of various grades of molded phenoplasts, are quoted from the Plastics Materials Manufacturers Association.

TABLE XXIX

IMPACT RESISTANCE OF MOLDED PHENOPLASTS[a]

Phenoplast type	Impact strength, Izod, milled notch, ft. lb./in.
General-purpose, cellulose-filled	0.24–0.32
Low shock resistant, cellulose-filled	0.30–0.45
Low to intermediate shock resistant, flock-filled	0.50–1.00
Intermediate shock resistant, fabric-filled	1.00–1.80
Intermediate to high shock resistant, fabric-filled	2.00–3.50
High shock resistant, fabric-filled	3.00–4.00
Very high shock resistant	6.00–9.00
Shock and heat resistant, mineral-filled	0.70–1.50
Heat resistant, mineral-filled	0.24–0.32
High frequency insulation, mineral-filled	0.40–0.50
Arc resistant, semiflexible	0.40–0.50
Transparent, no filler	0.40–0.50

[a] *Technical Data on Plastic Materials*, Plastics Materials Mfrs. Assn., Washington, D.C., May, 1943.

The above data appear to indicate that the general-purpose, cellulose-filled (i.e., wood flour) material has the same impact strength as a heat resistant mineral (i.e., asbestos powder) filled type. This is because the standard test does not show up small differences in the low range. By measuring the minimum energy required to fracture such pieces, Nason and Telfair[22] have demonstrated that the wood flour-filled product has almost twice the shock resistance of the asbestos-filled phenoplast.

The effect of the filler in damping the impact shock wave has already been discussed in Chapter VI.

The value obtained for the impact strength varies with the speed at which the stress is applied. Carswell and Nason,[7] and Telfair and Nason,[23] have reported data for a fabric-filled molded phenoplast, containing ap-

[22] D. Telfair and H. K. Nason, *Modern Plastics*, **20**, 85–88 (July, 1943).

[23] D. Telfair and H. K. Nason, *ibid.*, **22**, 145–149, 186–188 (April, 1945).

proximately 50% resin, over a wide range of impact velocities. The data of Telfair and Nason are reproduced in Figure 19.

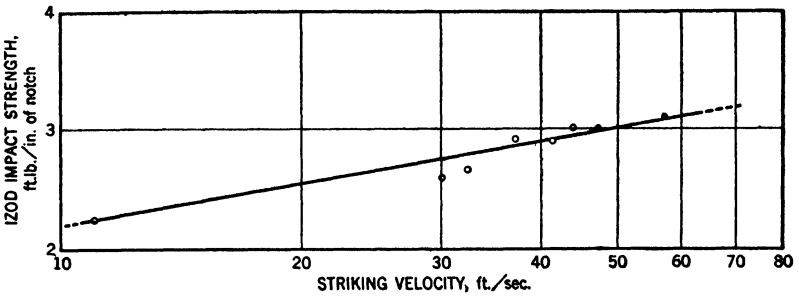


Fig. 19. Effect of striking velocity on impact strength of fabric-filled phenoplast.[23] ◒ A.S.T.M. D256 impact test (Bell Labs. Tester) with broken-end correction; O steel projectile (106 g.), broken-end mass considered; ● aluminum projected (39 g.), broken-end mass considered.

9. Creep and Stress Endurance

When an object is stressed the resulting deformation may, in general, be thought of as being composed of an instantaneous elastic deformation, plus a delayed deformation. The first is independent of time and depends only on the stress and the elastic modulus of the material. This is the elastic strain which is considered in the classical theory of elasticity, and corresponds to the straight-line portion of the curve in Figure 16 (page 114), where the time of stress application is short. The second, or delayed deformation, depends upon time as well as stress. It may be divided into (*a*) delayed elastic deformation, and (*b*) viscous flow, or nonrecoverable deformation. Most plastics, including the phenoplasts, are characterized by relatively large delayed deformation even for stresses far below their ultimate tensile strengths. As a result, strains lag behind the applied stresses by an appreciable quantity, and so these materials exhibit high damping capacity. Figure 20 will serve to illustrate and clarify the terms, *elastic deformation, creep* or *delayed deformation, elastic recovery, delayed recovery,* and *permanent set.*

At first, little work had been done on the accurate determination of creep in the phenoplasts. Recently, Findley[15,24] obtained some valuable data on the creep of various phenoplasts for times as great as 8000 hours.

[24] W. N. Findley, *Modern Plastics*, 22, 153–59, 194–96 (Dec., 1944).

Weibel[25] reported creep tests of limited duration (2 hours or less) on photoelastic plastics. Perkuhn[26] studied the creep of laminated phenoplasts.

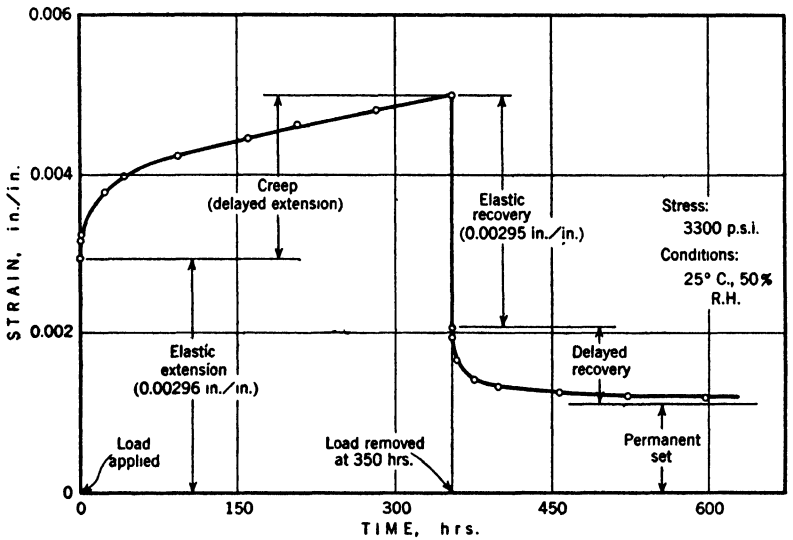


Fig. 20. Typical strain–time curve for a cord-filled phenoplast at room temperature.[7]

Telfair, Carswell, and Nason[27] have studied the creep properties of an unfilled phenoplast, and also five compositions containing as fillers, wood flour, chopped fabric, cotton cord, asbestos, and mica. The filled materials contained 50% phenol–formaldehyde resin and 50% filler, by weight, with the exception of the asbestos-filled material which contained approximately 40% resin and 60% filler.

All the materials were compression molded using a 6 min. cure at 170°C. and a pressure on the specimen of 4000 p.s.i. (A.S.T.M. D638-44T test specimens). The total deformation for the molded phenoplasts was very small (of the order of magnitude, 0.5%), and so it was necessary to use a very sensitive and accurate method of measuring strain. In cooperation with A. C. Ruge, an electrical resistance type (SR-4) of gauge was developed, with which strains as small as 0.055% could be easily detected.

[25] E. E. Weibel, *Trans. Am. Soc. Mech. Engrs.*, **56**, 637 (1934).

[26] H. Perkuhn, *Luftfahrt-Forsch.*, **18**, No. 1 (Feb. 28, 1941).

[27] D. Telfair, T. S. Carswell, and H. K. Nason, *Modern Plastics*, **21**, 137–144, 174–176 (Feb., 1944).

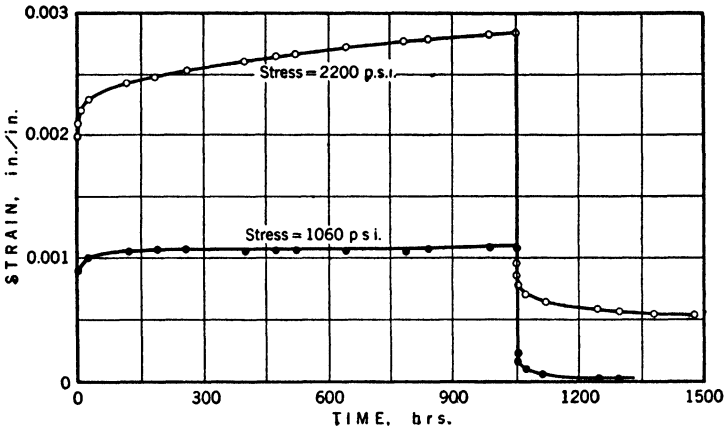


Fig. 21*a*. Creep and recovery curves at 25°C. and 50% R.H. for wood flour-filled phenoplasts.[27]

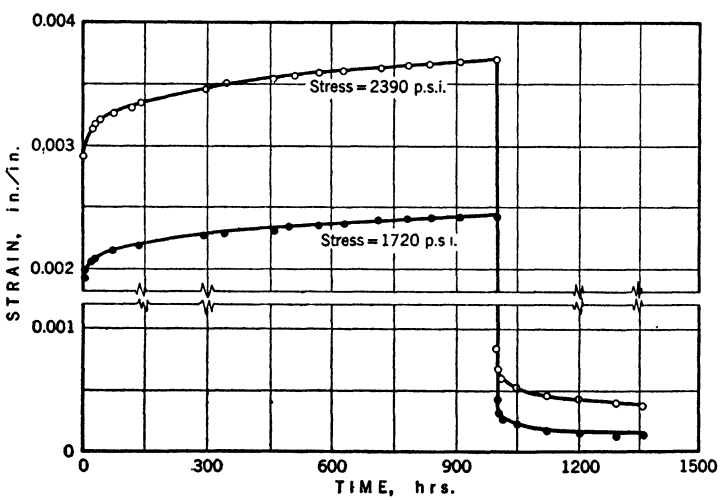


Fig. 21*b*. Creep and recovery curves at 25°C. and 50% R.H. for unfilled resin phenoplasts.[27]

Creep and recovery curves, up to 1000 hours of constant stress, are given in Figures 21*a*–*f* for six molded phenolic compositions. Figure 22 (p. 125)

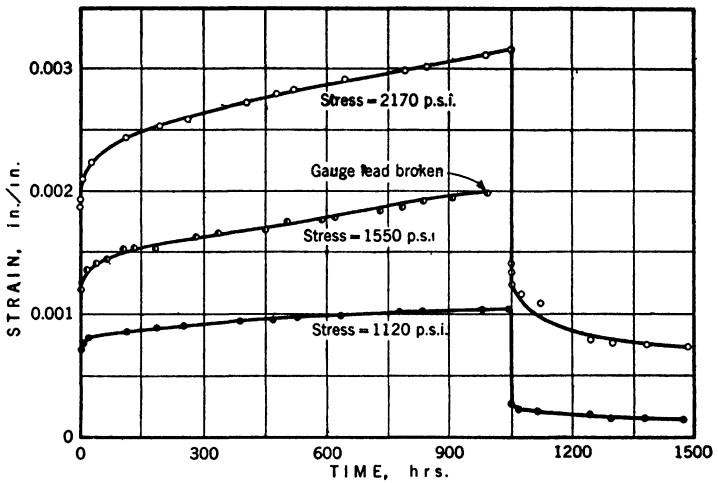


Fig. 21*c*. Creep and recovery curves at 25°C. and 50% R.H. for macerated fabric-filled phenoplasts.[27]

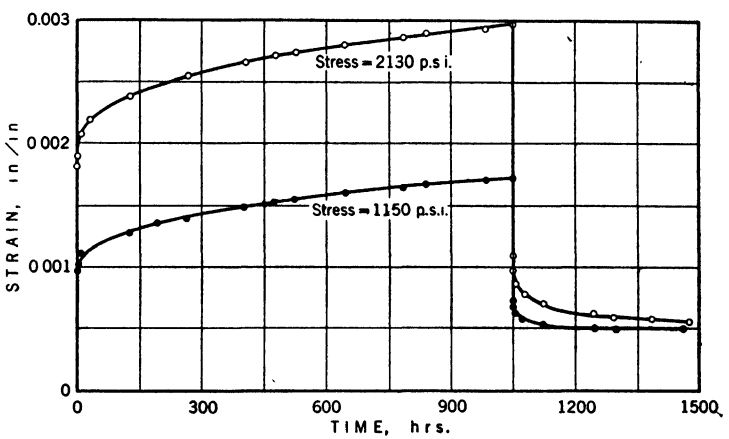


Fig. 21*d*. Creep and recovery curves at 25°C. and 50% R.H. for cord-filled phenoplasts.[27]

shows the average total inelastic deformation after 1000 hours of constant stress, plotted against the applied stress. From these curves, the stress re-

quired to produce a total creep of 0.003 in. per in. during a 1000 hr. test may be estimated roughly as follows:

Cord-filled	500 p.s.i.
Rag-filled	900 p.s.i.
Wood flour-filled	1100 p.s.i.
Unfilled resin	1400 p.s.i.
Asbestos-filled	1900 p.s.i.
Mica-filled	2500 p.s.i.

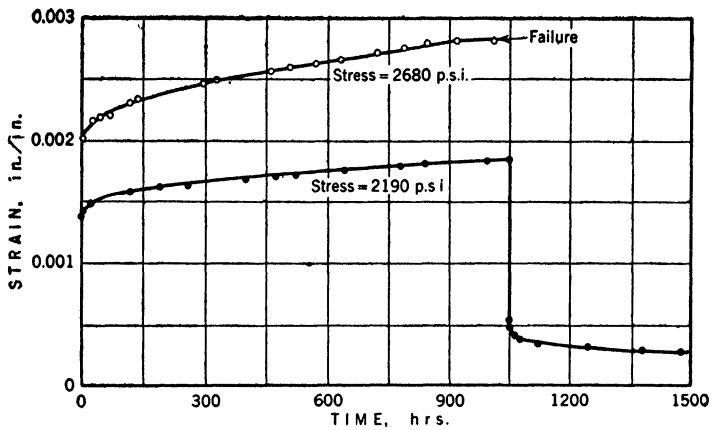


Fig. 21*e*. Creep and recovery curves at 25°C. and 50% R.H. for asbestos-filled phenoplasts.[27]

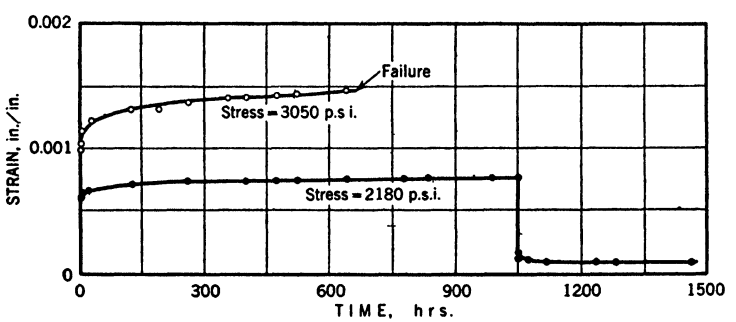


Fig. 21*f*. Creep and recovery curves at 25°C. and 50% R.H. for mica-filled phenoplasts.[27]

Qualitatively, all the materials tested possess the same general type of creep and recovery curves. A pseudoelastic deformation follows the application of the load almost instantaneously, and merges into rapid creep

which gradually decreases in rate and eventually appears to approach a constant rate for long times and high stresses. For a number of the specimens, recovery curves were plotted for 300 or more hours after unloading.

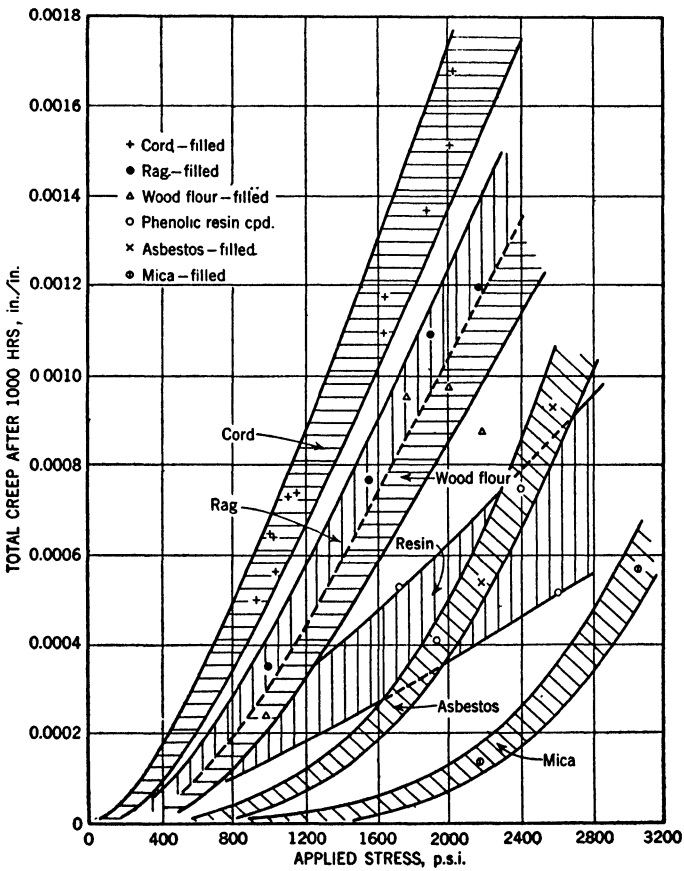


Fig. 22. Average total inelastic deformation (creep) for various phenoplasts, after 1000 hours constant stress, plotted *vs.* applied stress (at 25°C., 50% R.H.).

All the materials tested showed an *instantaneous* elastic recovery which was numerically equal (within a few per cent) to the *instantaneous* elastic deformation produced by the original loading. This was followed by a period of *delayed elastic recovery*. In most cases it seemed that a significant permanent set had been produced. Table XXX presents data for the

creep rate after 500 hours and the total creep in 1000 hours for the phenoplasts at 25°C.

TABLE XXX

CREEP RATE AFTER 500 HOURS AND TOTAL CREEP IN 1000 HOURS OF PHENOLIC PLASTICS AT 77°F.

Material	Stress, p.s.i.	Approximate creep rate after 500 hrs., $\times 10^{-6}$ in./in./hr.	Total creep in 1000 hrs., $\times 10^{-4}$ in./in.
Cord-filled	1000	32	5.8
	1500	53	10.4
	2000	72	15.3
Rag-filled	1000	21	3.5
	1500	40	7.2
	2000	63	11.2
Wood flour-filled	1000	10	2.3
	1500	23	6.0
	2000	47	9.3
Resin-compound	1000	11	2.3
	1500	19	3.5
	2000	26	4.8
	2500	35	6.5
Asbestos-filled	1500	8	2.0
	2000	21	4.3
	2500	45	8.1
Mica-filled	2000	3	1.0
	2500	6	2.6
	3000	10	5.4

Telfair, Carswell, and Nason[27] have pointed out that the tendency to creep may be correlated to a fair degree with the notch sensitivity of the material and with its impact strength as measured by an energy-to-fracture method. The correlation is shown in Table XXXI. The notch sensi-

TABLE XXXI

CORRELATION BETWEEN CREEP RATE, TOTAL CREEP, NOTCH SENSITIVITY, AND IMPACT STRENGTH OF PHENOLIC PLASTICS AT 77°F.

Material	Approximate creep rate after 500 hrs. at 1800 p.s.i. $\times 10^{-6}$ in./in./hr.	Average total creep after 1000 hrs. at 1800 p.s.i., $\times 10^{-4}$ in./in.	Notch sensitivity[a]	Energy-to-fracture impact strength, ft. lb./in.
Cord-filled	64	13.2	1.1	1.60
Rag-filled	53	9.6	1.1	1.10
Wood flour-filled	37	7.9	3.6	0.11
Resin-compound	22	4.3	12.0	0.05
Asbestos-filled	13	3.2	4.1	0.06
Mica-filled	2	0.6	5.0	0.10

[a] The ratio of the energy-to-fracture impact strength of an unnotched specimen to that of a notched specimen of thickness equal to the depth under the notch.

tivity refers to the ratio of the impact strength (energy-to-fracture) of the unnotched to that of the notched specimen. This type of correlation is to be expected because the ability of the material to undergo plastic deformation makes possible a relief of local stress concentrations in the vicinity of the notch.

From the nature of the creep curve, it is evident that when a sufficient load is applied for a long time, the specimen will fail under a much lower load than in the short time tensile test, data for which have been given in Table XXV. Telfair, Carswell, and Nason estimated the long time tensile strength for the phenoplasts studied, and the figures are given in Table XXXII.

TABLE XXXII

LONG TIME TENSILE STRENGTH OF PHENOPLASTS AT 77°F. AND 50% RELATIVE HUMIDITY

Material	Short time tensile strength, A.S.T.M. D638-41T, p.s.i.	Estimated limiting long time tensile strength, p.s.i.	Percentage of short time strength
Cord-filled	6000	2400–3000	45
Rag-filled	6100	2400–3000	45
Wood flour-filled	6100	2000–2500	36
Resin-compound	8900	1600–2400	23
Asbestos-filled	5700	1900–2300	37
Mica-filled	5400	1600–2100	34

10. Fatigue Resistance

In the fatigue, or endurance test, relatively small loads are alternately applied to the specimen and then removed. The process is repeated for thousands or even millions of cycles, and under such conditions failure will occur at stresses far below those which are required to produce failure in the usual short time tensile test. Such cyclic fatigue tests are especially important for the evaluation of materials which are to be used in the construction of machinery, since cyclic stress conditions are prevalent in such apparatus. Materials for use in aircraft, especially, must have good fatigue strength; vibrations are common in aircraft, and fatigue failures in such structures are likely to prove disastrous.

The technique of performing fatigue tests on phenoplasts has not been standardized. There are a number of ways in which the alternating stress may be applied—in torsion, flexure, or tension. There are indications that the shearing stress may be the governing stress which initiates the fatigue crack,[17] after which failure takes place. The temperature of the test specimen always increases during the cyclic application of stress, and this factor has not yet been fully considered in interpreting fatigue data.

Fatigue data on the molded phenoplasts are rather scarce; most of the recent work has been on laminated rather than molded products, and will be further referred to in Chapter IX. Jacobi and co-workers[28-30] have shown that the fatigue resistance of a molded phenoplast depends on the type of filler, the condition of the surface of the sample, and the resin content. Removal of the mold polish increases the fatigue resistance; notches or holes decrease the fatigue resistance. In general, the fatigue strength of a fiber-filled phenoplast, at about 10^7 cycles, is from 27 to 31% of the strength obtained in a short time tensile test.

D. INFLUENCE OF TEMPERATURE ON MECHANICAL PROPERTIES

The mechanical properties listed in the previous section have all been determined at room temperature—approximately 25°C. The need for knowledge of these properties over a wide range of temperature has been explained. It is important to note that the action of heat or cold on plastics may be divided into three categories: (*1*) *short term effects*, wherein the plastic is heated to a high temperature just long enough to come into thermal equilibrium with the environment; (*2*) *long term effects*, wherein the plastic is held at an elevated temperature for an extended period of time; and (*3*) *cyclic effects*, wherein the plastic is subjected to alternating heat and cold for many cycles. Very little data on cyclic effects have as yet been published, but a considerable amount of data has become available within the past few years on short and long term temperature effects.

The variation of flexural strength and the deflection at failure for a number of compression molded plastics at temperatures from −70° to 200°C. was described by Nitsche and Salewski,[31] while a determination of static tensile strength, compressive strength, stiffness, and bending properties, and fatigue strength of three laminated phenolic materials at −39°, −18°, and 25°C. are included in Air Corps Technical Report No. 4648.[10] Kistler,[32] Kozlov,[33] Küch,[34] Nitsche,[35] and Nitsche and Salewski[36] have also

[28] A. Thum, A. Greth, and H. R. Jacobi, *Kunststoffe u. Pressstoffe*, **2**, 16–24 (1937).

[29] A. Thum and H. R. Jacobi, *Ver. deut. Ing., Forschungsheft* 396, supplement to "Forschung auf dem Gebiete des Ingenieurwesins," Part B,**10**, (May/June, 1939).

[30] A. Thum and H. R. Jacobi, *Z. Ver. deut. Ing.*, **83**, 1044–1048 (1939).

[31] R. Nitsche and E. Salewski, *Kunststoffe*, **29**, 209–220 (1939).

[32] S. S. Kistler, *J. Applied Phys.*, **11**, 769–778 (1940).

[33] P. M. Kozlov, *Trudy Sessii Akad. Nauk Org. Khim.* **1939**, 91–97.

[34] W. Küch, *Jahrb. deut. Luftfahrtforsch.*, **1**, 561–573 (1938).

[35] R. Nitsche, *Z. Ver. deut. Ing.*, **83**, No. 6, 161–164 (1939).

[36] R. Nitsche and E. Salewski, *Kunststoffe*, **31**, 381–388 (Nov., 1941).

reported data on the effect of temperature on the mechanical properties of plastics.

Carswell, Telfair, and Haslanger[87] made a systematic study of the change of impact, tensile, and flexural strengths over the temperature range −80° to 250°C. Molded compositions employing wood flour, asbestos, macerated fabric, and cord fillers as well as a pure resin composition were evaluated.

Three common types of phenol–formaldehyde resins were evaluated in connection with the wood flour filler; (*1*) a typical one-stage, base-catalyzed resin, (*2*) a typical novolac (two-stage, acid-catalyzed resin), and (*3*) a resin made first with an acid catalyst, followed by the addition of methylol groups under alkaline conditions.

No appreciable difference in properties was exhibited over the entire temperature range studied, and therefore the novolac resin (with added hexamethylenetetramine) was used in connection with the other fillers and for the preparation of the pure resin molding compound.

Test bars of the various compositions were molded, and prior to testing were conditioned at the desired temperature for 4 to 5 hours. Tests were run immediately upon removal of the test specimen from the conditioning chamber. Figures 23 to 28 demonstrate the effect of temperature upon the

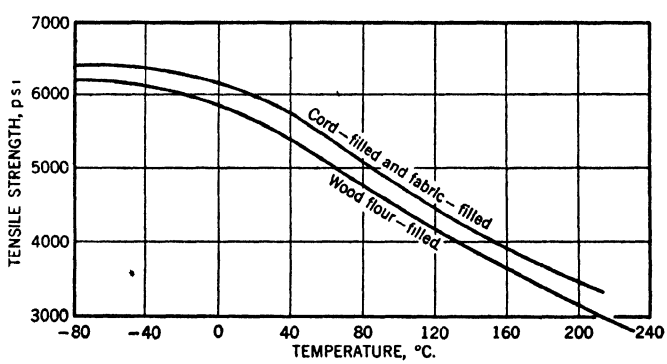


Fig. 23. Change of ultimate tensile strength with temperature for molded phenoplasts with wood flour, cord, and fabric fillers.[87]

following properties: tensile strength, flexural strength, and impact strength.

[87] T. S. Carswell, D. Telfair, and R. U. Haslanger, *Modern Plastics*, 19, 65–69 (July, 1942).

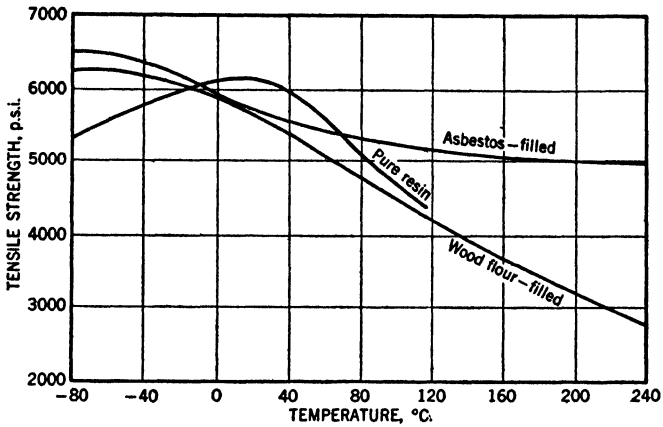


Fig. 24. Change of ultimate tensile strength with temperature for molded phenoplasts of low impact strength.[37]

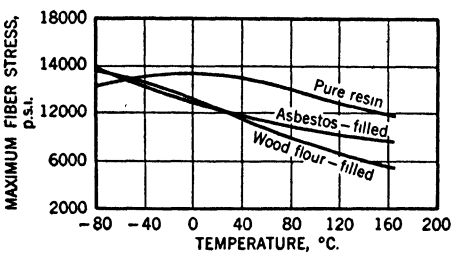


Fig. 25. Change of the maximum fiber stress (in flexure) with temperature for molded phenoplasts of low impact strength.[37]

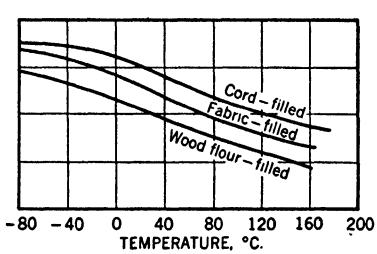


Fig. 26. Change of the maximum fiber stress (in flexure) with temperature for molded phenoplasts with wood flour, cord, and fabric fillers.[37]

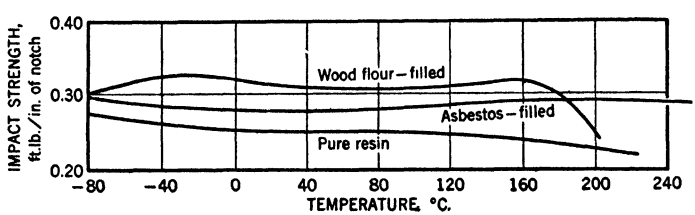


Fig. 27. Change of the notched Izod impact strength with temperature for molded phenoplasts of low impact strength.[37]

Delmonte[5] has studied the effect of temperature on the shear strength of a commercial molded phenoplast, using the punch method which has been previously described. Figure 29 illustrates the data obtained.

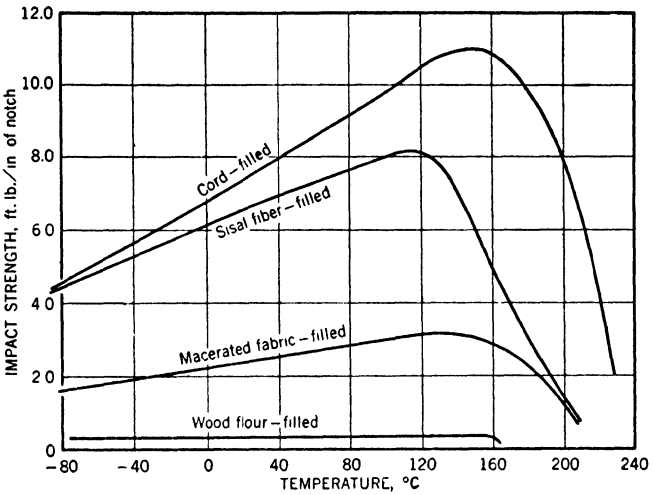


Fig. 28. Change of notched Izod impact strength with temperature for molded phenoplasts with fibrous fillers.[37]

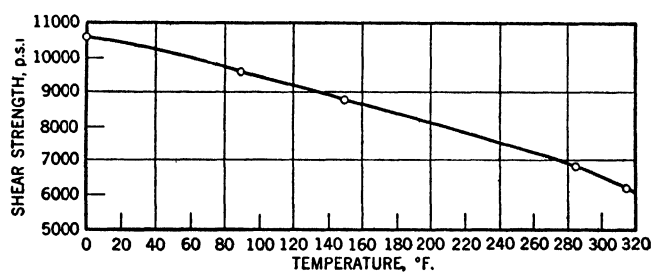


Fig. 29. Effect of temperature on shear strength of a commercial molded phenoplast.[5]

From the data presented above, it can be seen that, in short term tests over the temperature range of normal use (−60° to +160°F.), the mechanical strengths of phenolic molding compositions deviate from the value at 25°C. (77°F.) by about 15%. The tensile and flexural strengths show a decrease with increasing temperature. The high impact materials show an

increase in impact strength with increasing temperature. The probable reasons for these changes will be discussed later. At about 160°C., all the materials containing cellulosic fillers have lost strength to such an extent that they no longer have structural utility, and this temperature may be regarded as the maximum practical limit for that type of phenoplast in short term exposures. The pure resin, and compositions containing asbestos filler, retain a large part of their strength properties even up to 240°C.

The A.S.T.M. heat distortion test D648-41T is a rather empirical method of determining the temperature to which a plastic can be subjected without undergoing excessive creep. The heat-distortion point of the plastic is defined as the temperature at which the deflection of the midpoint of a 0.5 × 0.5 × 5 in. bar, supported at both ends, reaches 0.010 in.; the bar is immersed in a bath, the temperature of which is raised 0.5°C. per minute. Sauer, Schweitz, and Wolf[38] have applied a refinement of this test to various phenolics, and found the accompanying values for cast, molded, and laminated phenoplasts.

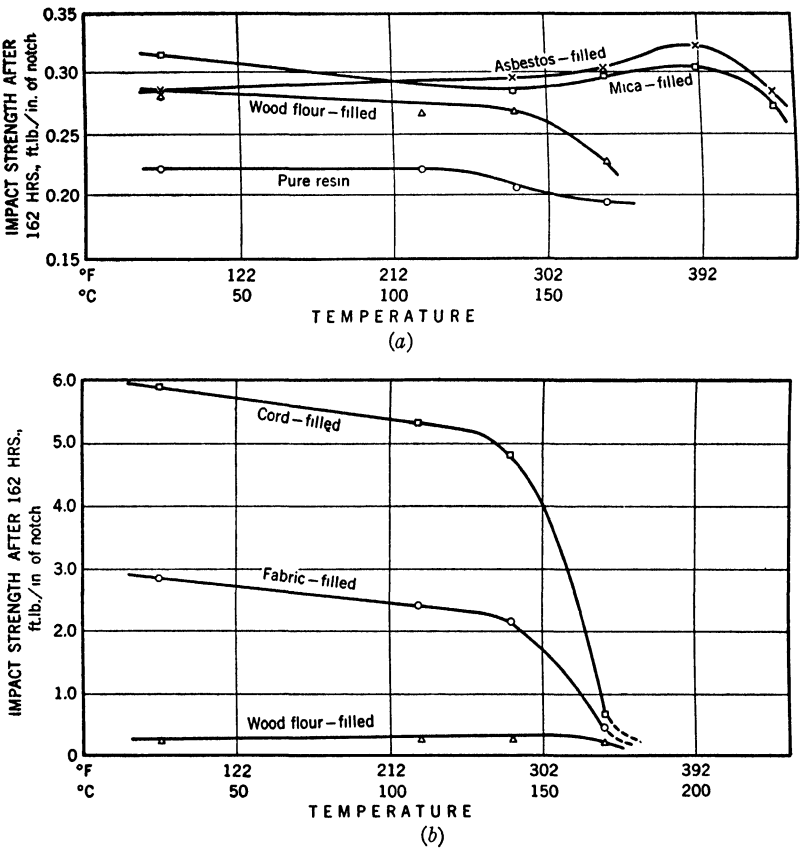
Type of phenoplast	Heat-distortion temperature, °C.
Cast	79.0
Molded, one type	121.0
Molded, second type	159.0
Laminate, asbestos-paper	154.3
Laminate, Kraft paper	193.0
Laminate, fine cotton-fabric	193.5
Laminate, Fiberglas-fabric	200.0
Laminate, for postforming	103.0

Carswell, Telfair, and Haslanger[39] have also determined the effect of long continued heating on the mechanical properties of pure phenolic and molded phenoplasts containing wood flour, fabric, cord, mica, and asbestos fillers. The cellulosic compositions and those with asbestos contained 50% filler and 50% resin. The molding powder with mica contained 60% filler and 40% resin. The two high impact grade materials, containing macerated fabric and cord fillers, were prepared by blending the resin and filler in a wet-mix process to assure a uniform mixture and to obtain optimum strengths. The other compositions were processed on a set of differential rolls in the manner customary for the preparation of phenolic molding compositions. Specimens were prepared in the usual way and were baked for 2, 6, 18, 54, 162 and 500 hours at temperatures of 110°, 140°,

[38] J. A. Sauer, F. A. Schweitz, and D. L. Wolf, *Modern Plastics*, **22**, 153–156, 192–194 (March, 1945).

[39] T. S. Carswell, D. Telfair, and R. U. Haslanger, *ibid.*, **20**, 79–82, 126 (Feb., 1943).

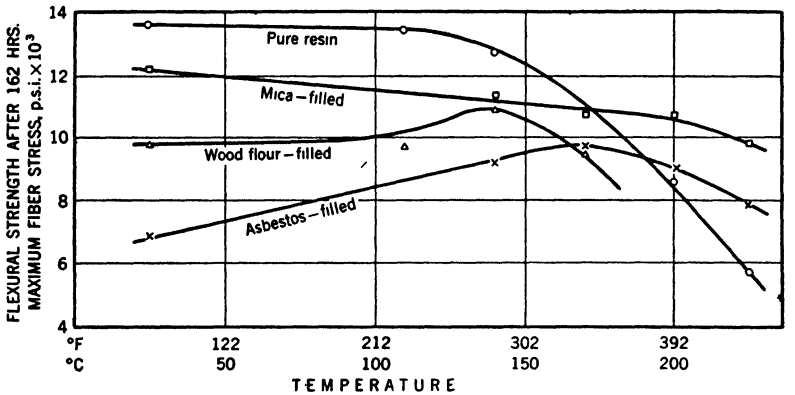
170°, 200°, and 225°C. After the desired baking time, the specimens were cooled to 25°C. in a desiccator and tested. It is important to note that in the short term tests described previously, the specimens were tested *at the conditioning temperature;* in the study of long continued heating, the



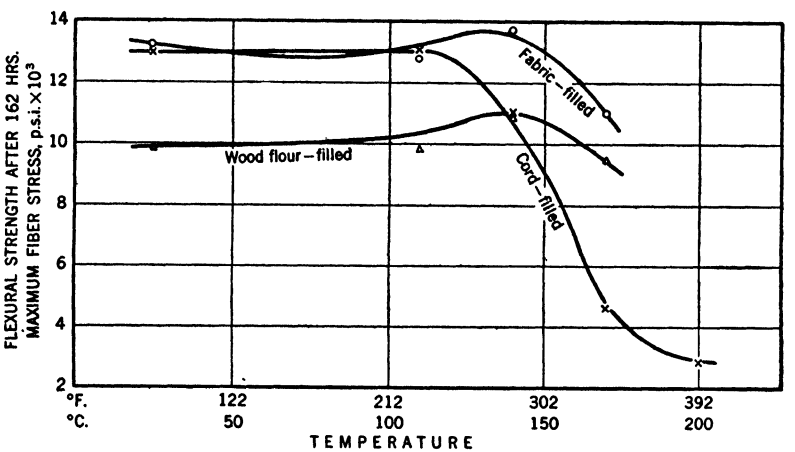
Figs. 30*a* and *b*. Effect of continuous heating on various phenoplasts.[39] Effect of heating for 162 hours on impact and flexural strength of various types. See also Figures 30*c* and *d*.

specimens were tested at room temperature. The data obtained are illustrated graphically in Figures 30*a–f*. Table XXXIII lists the six materials tested together with the approximate limiting temperatures. The latter are arbitrarily taken as the temperatures at which a 10% reduction in strength occurs after 162 hours of heating. It is obvious that the filler

plays a major part in determining the limits of serviceability. The organic fillers undergo a definite deterioration as exhibited both by a lowering of



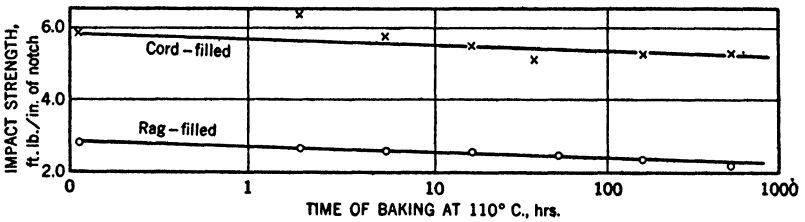
(*c*)



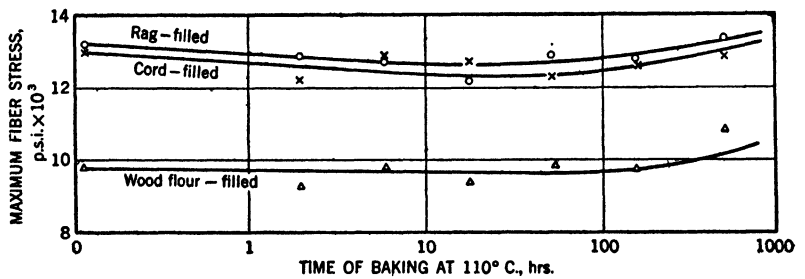
(*d*)

Figs. 30*c* and *d*. Effect of continuous heating on various phenoplasts.[89] Effect of heating for 162 hours on impact and flexural strength of various types. See also Figures 30*a* and *b*.

the strength characteristics and by a visual observation of disintegration of the molded specimen, at much lower temperatures than do the inorganic- or mineral-filled materials.



(*e*)



(*f*)

Figs. 30*e* and *f*. Effect of continuous heating on various phenoplasts.[39] Change of impact and flexural strength with time of heating at 110°C. for various types.

TABLE XXXIII

APPROXIMATE LIMITING TEMPERATURES FOR PHENOLIC PLASTICS ON BASIS OF 10% REDUCTION IN STRENGTH AFTER 162 HOURS OF HEATING

Material tested	Flexure		Impact	
	°C.	°F.	°C.	°F.
Pure phenolic resin	140	284	140	284
Wood flour-filled phenolic	170	338	150	302
Fabric-filled phenolic	150	302	130	266
Cord-filled phenolic	130	266	130	266
Mica-filled phenolic	200	392	200	392
Asbestos-filled phenolic	220	428	220	428

Influence of Temperature on Creep

An attempt to study the effect of temperature upon creep was made by Telfair, Carswell, and Nason[27] in the paper previously referred to. This early work was somewhat in error, as it was then not realized that the amount of shrinkage which takes place due to continued curing effects, during prolonged heating at high temperatures is relatively large. Further

study of creep was therefore made by Gailus and Telfair.[40] A temperature of 89°C. (192°F.) was chosen for this work, and the same series of molding compounds was chosen as in the work done at room temperature. As in the previous work, SR-4 strain gauges were used, mounted on opposite sides of each specimen with phenolic cement. It was found that the creep at high temperatures consisted of a balance between the opposing actions of strain due to load and shrink due to further curing of the resin.

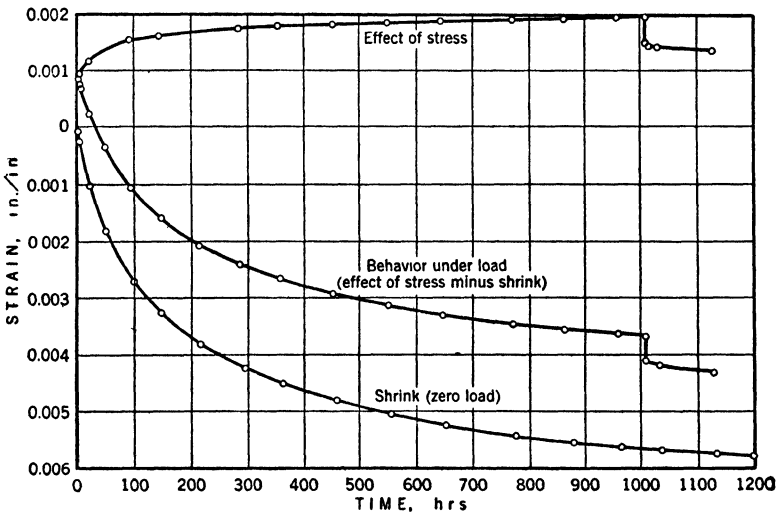


Fig. 31. Relationship between creep and shrink components at 194.1° ± 1.4°F. and 488 p.s.i.[40]

The term *behavior* was used to denote the observed effect due probably to the combined effects of stress (creep) and shrink. The relationship of these components for a wood flour-filled phenolic is illustrated in Figure 31. Figures 32 to 36 illustrate the creep (corrected for shrink) of the various phenoplasts tested at 89°C., while Figures 37 to 41 illustrate the observed behavior at this temperature. Table XXXIV presents a rough comparison of the stress required to produce a total strain (elastic plus inelastic) of 0.003 in. per in. during a 1000 hr. test at 89°C. as against 25°.

The unfilled resin would not bear a stress as low as 100 p.s.i. for more than 370 hours at 89°C.

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[40] W. J. Gailus and D. Telfair, *Modern Plastics*, **22**, 149–154, 192 (May, 1945).

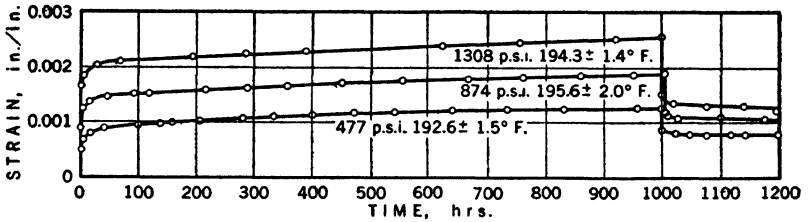


Fig. 32. True creep (corrected for shrinkage) of asbestos-filled phenoplast at 194°F.[40]

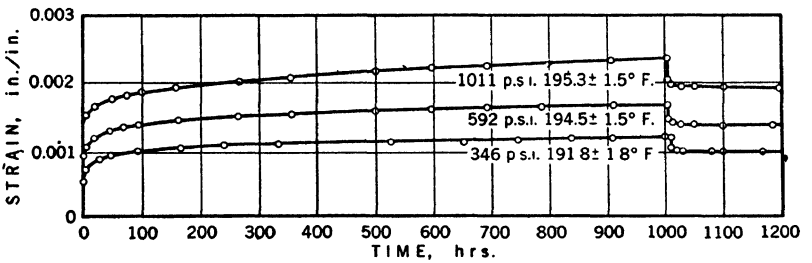


Fig. 33. True creep (corrected for shrinkage) of mica-filled phenoplast at 194°F.[40]

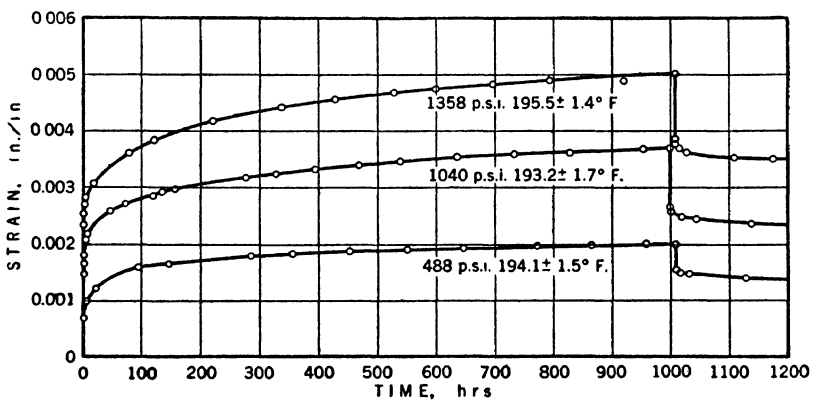


Fig. 34. True creep (corrected for shrinkage) of wood flour-filled phenoplast at 194°F.[40]

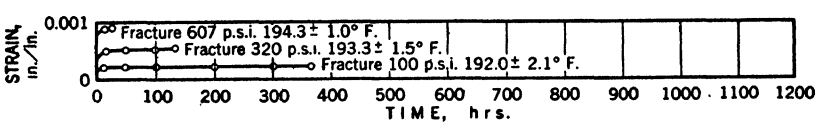


Fig. 35. True creep (corrected for shrinkage) of unfilled phenoplast resin at 194°F.[40]

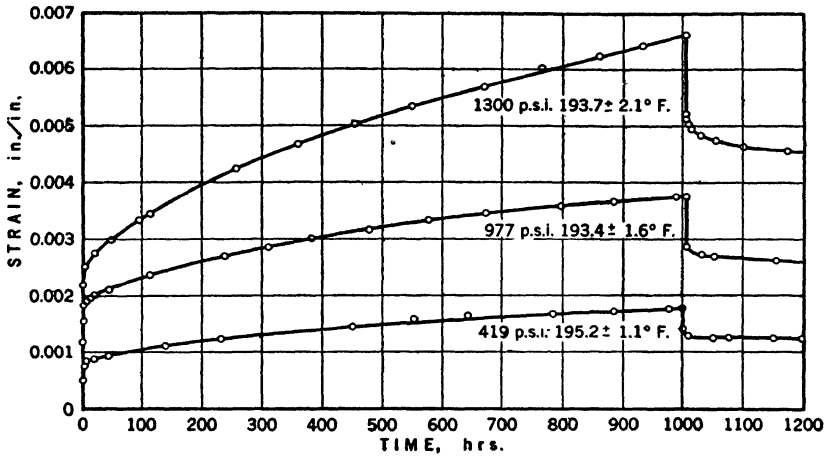


Fig. 36. True creep (corrected for shrinkage) of macerated fabric-filled phenoplast at 194°F.[40]

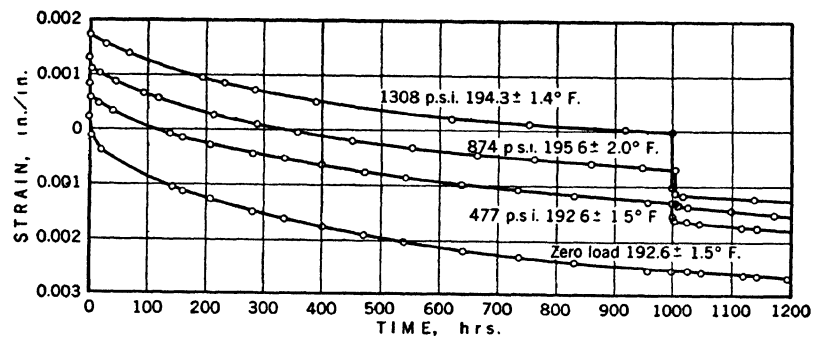


Fig. 37. Behavior under load of asbestos-filled phenoplast 194°F.[40]

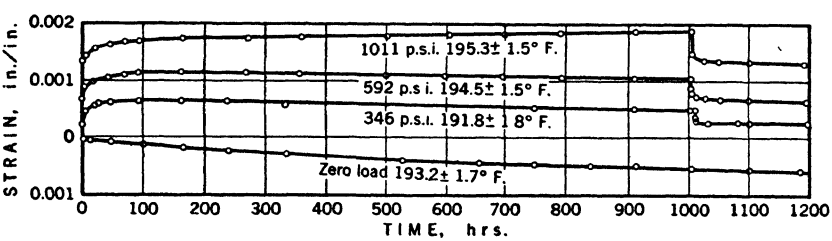


Fig. 38. Behavior under load of mica-filled phenoplast at 194°F.[40]

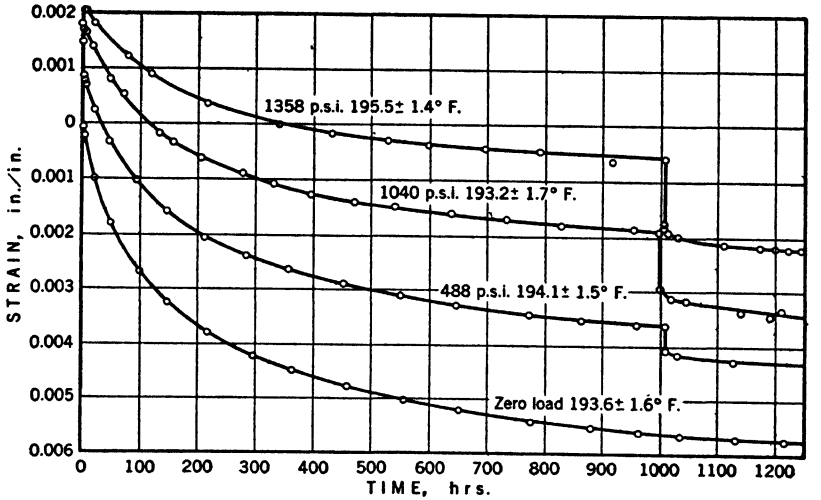


Fig. 39. Behavior under load of wood flour-filled phenoplast at 194°F.[40]

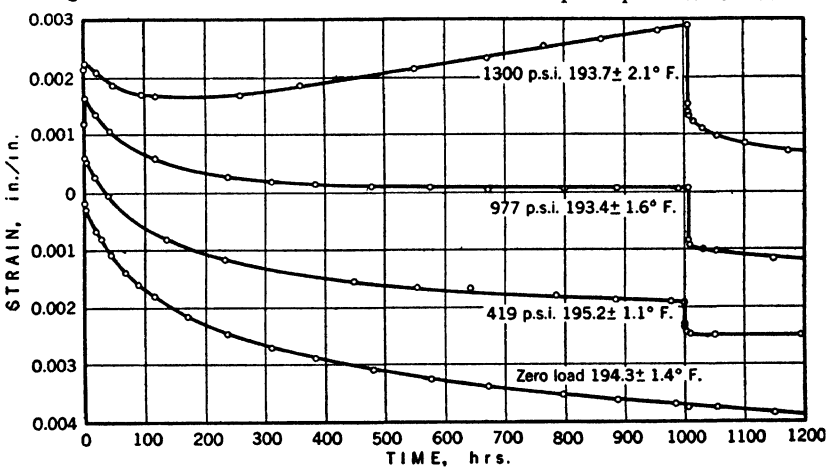


Fig. 40. Behavior under load of macerated fabric-filled phenoplast at 194°F.[40]

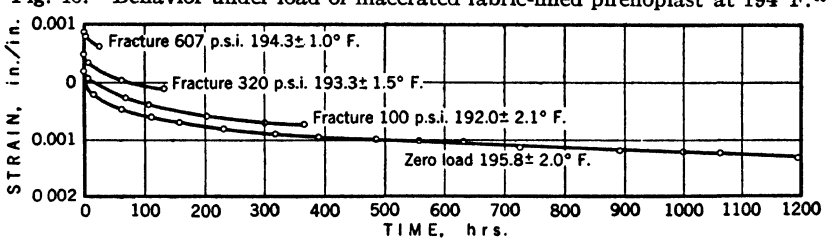


Fig. 41. Behavior under load of unfilled phenoplast resin at 194°F.[40]

TABLE XXXIV

COMPARISON OF STRESSES REQUIRED TO PRODUCE A TOTAL STRAIN OF 0.003 INCH PER INCH IN 1000 HOURS

Material	P.s.i. at 25°C.	P.s.i. at 89°C.
Cord-filled	2150	...
Rag-filled	2100	700–800
Wood flour-filled	2400	800
Unfilled resin	2100	...
Asbestos-filled	2700	1600
Mica-filled	4800	1400

Table XXXV presents values comparing the long time tensile strength at 89°C. with short time tensile strength at 25°C. and with the long time strength at 25°C.

TABLE XXXV

COMPARISON OF SHORT TIME TENSILE STRENGTH AT 25°C. WITH LONG TIME TENSILE STRENGTH AT 25° AND 89°

Type of phenoplast	Short time tensile strength by A S.T.M. D638-42 at 25°C. and 50% R.H., p.s.i.	Long time tensile limiting stress			
		At 25°C. and 50% R.H.	Per cent of short time at 25°C.	At 89°C.	Per cent of short time at 89°C.
Cord-filled	6000	2400–2800	43	900–1200	18
Macerated canvas-filled	6100	2400–2800	43	1200–1400	21
Wood flour-filled	6100	2600–2800	44	1300–1400	22
Unfilled resin	8900	...	..	2100	..
Asbestos-filled	5700	2800–3200	53	1300–1400	24
Mica-filled	5400	2200–2400	39	1200–1500	25

It is interesting to note that an appreciable amount of curing seems to take place on long heating at 89°C., as evidenced by the shrink data. The shrink observed for the unfilled phenolic resin during the creep test was 0.00123 in. per in., which corresponds to a density increase of 0.369%. During molding, the density was observed to increase about 1%. If the shrinkage during the creep test were due entirely to continued condensation, it would indicate that about one-third as much reaction takes place during a long time creep test as during molding.

E. THEORETICAL DISCUSSION OF STRENGTH PROPERTIES OF PHENOPLASTS

It is obvious that the strength properties of the molded phenoplasts are tied in with their physical structure. In the latter term, we must in-

clude not only the structure of the resin itself, but also the nonhomogeneous mass consisting of the resin and the filler.

The physical structure of the resin has been discussed in detail in Chapter III, and it has been shown that the probable structure is that of a cross-linked spherocolloid embedded in a matrix of less highly polymerized material; the spherocolloid particles are connected at touching points by primary valence (methylene) bonds, and possibly also by secondary bonds, due to van der Waals' forces.

De Boer[41] calculated the theoretical tensile strength of phenol–formaldehyde condensation products; his calculation was based upon the assumption that the products were united entirely by "primary bonds" (methylene groups). On this basis, a phenol–formaldehyde condensation product should have a tensile strength of about 4300 kg. per mm.^{2} (6100×10^3 p.s.i.), and a *m*-cresol–formaldehyde product about 3800 kg. per mm.^{2} (5400×10^3 p.s.i.). These values are about 1000 times greater than the experimentally determined values. De Boer also calculated the theoretical tensile strength based upon van der Waals' forces only, and arrived at values of more than 39 kg. per mm.^{2} (55,000 p.s.i.) and 32 kg. per mm.^{2} (45,000 p.s.i.) for phenol–formaldehyde and *m*-cresol–formaldehyde, respectively. Even these values are about one order of magnitude higher than the observed figures. Such a discrepancy between theoretical and experimental strength values is not at all unusual. Similar results have been obtained in the case of sodium chloride crystals, glasses, and other materials.

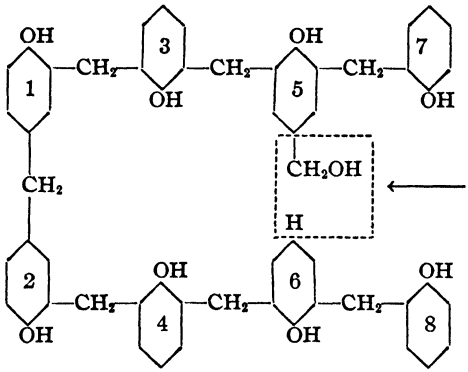
In order to account for such wide discrepancies, Smekal and others have developed the theory of flaws, or *Lockerstellen*. According to this theory, the molecular structure of crystals and glasses is not perfect, and minute flaws or voids occur at irregular points throughout the mass. When the body is strained, as in the tensile test, stress concentrations are set up about the flaws. Due to these stress concentrations, the load about the flaw soon becomes greater than the cohesive force of the material, and rupture takes place at a low apparent stress. Houwink[42] has adapted this theory to the phenoplasts. He points out that all the possible methylene bridges may not be formed, as illustrated in Formula XXVIII.

The benzene nuclei are irregularly arranged and do not all lie in one plane. Some spots, such as those designated by the dotted lines in the

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[41] J. H. de Boer, *The Phenomena of Polymerization and Condensation*. The Faraday Society, London, 1935, pp. 10–38.

[42] R. Houwink, *Trans. Faraday Soc.*, **32**, 122–131 (1936).



(XXVIII)

{flaw-forming groups, due to the fact that CH_2OH and H may not lie in one plane

formula, will occur when the benzene nuclei 5 and 6 are in such relative positions that a chemical reaction between the methylol group and the ring hydrogen is impossible. It is also possible that the presence of occluded reaction products, such as water, might give rise to flaws in the macromolecule.

If the theory of cross-linked spherocolloids is accepted as the fundamental physical structure of the resin, it is evident that there is another reason why the actual strength does not approach that calculated by de Boer. The number of methylene bonds *between* the spherocolloid particles are few compared to those uniting the phenyl groups *within* the spherocolloids. When a tensile stress is applied to the resin, it is probable that these primary bonds connecting the colloid particles rupture first, leaving the load to be borne by the *Harzbrei*, which presumably has lower strength properties. Kistler[32] has given an interesting word picture of this effect:

"The picture is somewhat as though one tied together here and there loops of a tangled mass of thread, then soaked the mass in heavy tar and applied tension at the ends. Here and there within the mass most of the tension would be localized on one or two threads where they were tied together. These would rupture quickly and the force required to stretch the mass would be largely that required to slide the threads over each other in the viscous tar. The forces required to produce flow in the tar represent the secondary forces between chains while the knots between the loops represent the primary bonds. It is easy to imagine that such a tangle of thread would show little more tensile strength due to the knots than it would have shown if these knots had not been tied."

The *Harzbrei* represents the heavy tar of Kistler's picture; it evidently plays an important part in determining the strength of the phenoplasts.

In similar manner, it is possible to explain the effect of temperature on the strength of the phenoplasts, and of the creep phenomena at both high and low temperatures. The *Harzbrei* must be considered as a supercooled liquid, with extremely high, non-Newtonian viscosity. As the temperature is raised, the viscosity of this material decreases, with a resultant decrease in all the strength properties which depend upon cohesive forces. Impact strength, on the other hand, increases due to better and more rapid stress distribution by the less viscous matrix.

The above discussion applies to pure resin only. When the molding composition contains filler, a new set of conditions is introduced. It is obvious that the nature of the resin itself is not changed, and the above remarks regarding the strength of the resin still apply. In addition, it is necessary that the resin be able to wet and have cohesion to the filler. As is indicated by the data in Tables XXV and XXVIII, the addition of filler

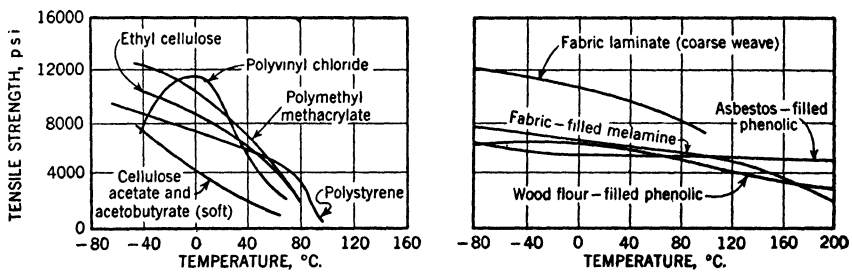


Fig. 42. Relative effect of temperature on (*a*) thermoplastics and (*b*) phenoplasts.[7]

tends to decrease the tensile and flexural strengths of the pure resin; the decrease is particularly marked when a mineral filler is used, with short fiber length and in itself of low tensile strength. However, as is shown in Table XXIX, the impact resistance can be greatly increased by the proper choice of filler. This improvement in impact resistance is principally due to the increased damping capacity of the more fibrous fillers. This point has been discussed in detail in Chapter VI.

The phenoplasts, and indeed all other cross-linked plastics such as the urea or melamine–formaldehyde condensation products, are generally superior in heat resistance to the thermoplasts. The thermoplastic polymers usually have a long chain structure, in contrast to the cross-linked spherocolloid structure of the thermosetting materials. As a result, the

thermoplastics show a greater rate of change in properties with temperature, and have a much lower ultimate temperature resistance. Figure 42 presents a good comparison of the relative rates of change of tensile strength with temperature for some thermoplastics and some phenoplasts, respectively.

F. STRENGTH–WEIGHT COMPARISONS WITH METALS

In recent years there has been a tendency to substitute plastics for metals in semistructural and functional parts of automobiles, aircraft, and military weapons. During the early days of World War II, a considerable part of this substitution was prompted by the shortage of light metals. The phenoplasts are particularly adapted to such substitutions because of their

TABLE XXXVI

TENSILE STRENGTH–WEIGHT RATIOS AND TENSILE MODULUS–WEIGHT RATIOS FOR PHENOPLASTS AND SOME COMMON STRESS-CARRYING METALS AT 25°C.

Materials	Average density	Weight per in.^{3}, lb.	Av. tensile strength–weight ratio, p.s.i.	Av. tensile modulus–weight ratio, p.s.i. × 10^6
Molded phenoplasts				
Wood flour-filled	1.38	0.0497	160,000	25
Macerated fabric-filled	1.41	0.0505	140,000	20
Mineral-filled	2.00	0.0720	(70,000)	20
Laminated phenoplasts				
Paper base (Grade X)	1.25	0.045	200,000	41
Cotton fabric base (Grade L)	1.25	0.045	145,000	20
Glass fabric base	1.67	0.060	390,000	19
High strength paper laminate	1.38	0.051	390,000	..
Metals				
Structural steels	7.7	0.28	210,000	105
Alloy steels	7.8	0.28	340,000	105
Cast iron, common gray, high strength	7.1	0.26	110,000	55
	7.7	0.28	180,000	75
Aluminum	2.7	0.10	300,000	100
Monel metal	9.0	0.32	310,000	75
Brass, annealed	8.7	0.31	290,000	33
Bronze, annealed	8.9	0.32	310,000	50
Aluminum alloy 24ST	2.8	0.11	200,000	...

general strength properties and their relative resistance to temperature changes in contrast to the thermoplastics. The intrinsic strength of the phenoplasts—for example, the tensile strength expressed as p.s.i.—is far less than that of the common metals. However, their specific gravity (approximately 1.38 for the cellulose-filled types) is also much less than the common metals. For this reason the specific strength, or strength–weight

ratio (that is, strength in p.s.i. divided by weight per unit volume), compares favorably with many of the metals.[43,44] The properties of laminates in particular show up to advantage over metals where the application is critical in respect to bending or buckling; the lower density of the plastic permits greater thickness, and this in turn confers a greater stiffness factor. It would be beyond the scope of this book to make an exhaustive comparison of the mechanical properties of the phenoplasts with metals. However, Table XXXVI is presented to illustrate the point for tensile strength and tensile modulus only.

In the practical use of phenoplast molding powders and laminates, combinations are frequently made between different types of material in order to get the maximum strength properties and greatest ease of molding. For example, a phenolic gear blank may be built up using laminated phenoplast plies for the rim, and macerated fabric phenoplast for the hub. The whole is molded in one operation. In this way, the best strength properties of the two types of material are utilized where they are most needed. A thorough study of the type and direction of the applied stress must be considered in making such combinations of phenoplasts.[45]

[43] H. Sang, *Aero Digest*, **43**, 163 (Aug., 1943).

[44] W. A. Norman and E. H. Schwartz, *A.A.F. Tech. Rept.* **4963**, July 6, 1943.

[45] H. R. Jacobi, *Kunststoffe*, **32**, 1 (Jan., 1942).

IX. MECHANICAL PROPERTIES OF LAMINATED PHENOPLASTS

A. INTRODUCTION

The laminated phenoplasts differ from the molded products principally in that the filler of the laminates consists of a continuous web. When the same type of filler is compared, the laminates are superior in strength to the molded products. The phenoplast resin and the filler combine, in a very practical way, the properties of both component parts in much the same way that steel and concrete in reinforced concrete structures support each other. The phenolic resin, which has low tensile strength, furnishes compressive strength and stiffness, fills the voids between the fibers of the filler, and bonds together the fibers and layers of the laminate. The fibers of the filler contribute the major portion of the composite tensile strength.[1]

Owing to their construction, the laminates have marked directional strength properties. Because of this, Caldwell[2] has emphasized that consideration must be given to methods of loading in order to obtain the greatest strength. Figures 43*a* to *d* illustrate the proper methods for loading laminates in order to develop the best mechanical properties.

The following definitions, taken from Caldwell, are a key to the directional loads referred to in Figure 43:

Flatwise (F)—The load is applied to the flat side of the plate, perpendicular to the laminations of the plastic.

Edgewise (E)—The load is applied to the edge of the plate, parallel to the laminations.

With Grain (WG)—The load is applied in the direction of the length of the plate, i.e., parallel to the cloth warp or lengthwise of the paper fiber.

Across Grain (CG)—The load is applied in the direction at right angles to the length of the plate, i.e., parallel to the cloth fill or crosswise of the paper fiber.

In the above definitions, the term *grain* is not synonymous with *laminations* but rather refers to the grain directions of the filler.

[1] R. W. Barber, *Mech. Eng.*, **64**, 888–890(1942).

[2] L. E. Caldwell, *Modern Plastics*, **20**, 82–87, 138 (Aug., 1943).

Compressive loads should be applied in the flatwise direction in order to take advantage of the greater compressive strength in this direction. However, edgewise loads are allowable, and, in some cases in which other factors must be considered, they may be desirable, as in the instances of certain marine bearings in which edgewise wear is more even than flatwise wear.

Tensile loads should be applied edgewise, preferably in the grain direction since the tensile strength in this direction is usually somewhat greater

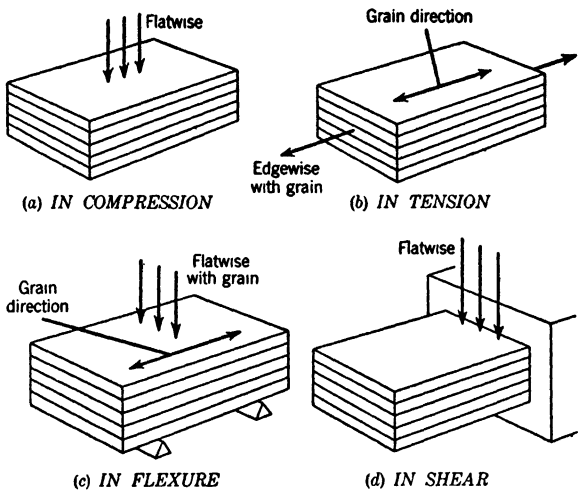


Fig. 43. Best methods for loading laminates.[2]

than it is across the grain. Flatwise tensile loads should be avoided, since the flatwise tensile strength is relatively low because of the lack of continuity of the filler in this direction.

Flexural, shear, and impact loads should be applied flatwise, preferably in the grain direction. However, these loads may be applied flatwise across the grain, edgewise with grain, and edgewise across grain, since the corresponding strengths are sufficiently high to allow considerable loads. These loads should not be applied parallel to the laminations since the corresponding strengths are relatively low in this direction.

Because of their superior strength properties, the laminates are more widely used than the molded phenoplasts in applications calling for resistance to stress. Their mechanical properties, both at room temperature

and over a wide temperature range, have been studied quite carefully within recent years.

As in the case of the molded phenoplasts, only the following more important mechanical properties of the laminates will be considered in this chapter, in the order given: tensile strength; modulus of elasticity; compressive strength; flexural strength; shear strength; bearing strength; impact resistance; creep and stress endurance; fatigue characteristics; abrasion resistance. Data for flat sheets or plates, only, have been included in this chapter; separate data for laminated tubes are supplied in the literature.[3]

B. MECHANICAL PROPERTIES AT ORDINARY TEMPERATURES

The physical properties of a laminate are influenced by several factors, including the type of filler used, the ratio of resin to filler, and the molding pressure. In the discussion which follows, consideration will, in general, be given first to the mechanical properties of the standard NEMA grades; the properties of laminates with new fillers, such as high strength paper and glass fiber, follow the description of the standard grades. The effect of molding pressure and resin content will then be described. It will be recalled that the principal fillers for laminates have been described in Chapter VII, together with the standard NEMA classification.

1. Tensile Strength

The tensile strength of a laminate is obtained from the stress–strain curve as illustrated in Figure 16 (page 114) of Chapter VIII. As in the case of the molded phenoplasts, the laminates are relatively nonductile, and show only the early straight line portion of the curve. Table XXXVII lists the minimum and average values for the tensile strength at failure for various types of laminates. These values are taken from the recent publication of the Plastics Materials Manufacturers Association,[3] and are obtained by A.S.T.M. test method D-229. These values hold for laminates from $^1/_{16}$ to 1 inch in thickness. The minimum values for laminates from 1 to 2 inches in thickness are 10% lower. The average values for thicknesses of $^1/_8$ inch and under will generally be higher than the figures given, while the average for thicknesses approaching 1 inch may be as much as 10% lower than those given.

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[3] *Technical Data on Plastic Materials.* Plastics Materials Mfrs. Assn., Washington, D.C., May, 1943.

TABLE XXXVII

TENSILE STRENGTH OF LAMINATED PHENOLIC PLATES AT 25°C.

Grade of laminate	Tensile strength, p.s.i.	
	Minimum	Average
Paper-base, Grade X	9,000	12,500
Paper-base, Grade P, 1/16 to 1/4	6,000	8,000
Paper-base, Grade XX	6,000	8,000
Paper-base, Grade XXP, 1/16 to 1/4 in.	6,000	8,000
Paper-base, Grade XXX	5,000	7,000
Paper-base, Grade XXXP, 1/16 to 1/4 in.	5,000	7,000
Fabric-base, Grade C	7,500	9,500
Fabric-base, Grade CE	6,500	8,000
Fine weave fabric-base, Grade L	7,000	9,000
Fine weave fabric-base, Grade LE	6,500	8,500
Asbestos-paper-base, Grade A	...	8,000
Asbestos-fabric-base, Grade AA	8,000	10,000

In addition to the standard NEMA grades listed in Table XXXVII laminates from high strength paper and glass fabric have become important. The properties of these materials will be discussed more exhaustively in later portions of this chapter; however, for comparison with the above figures the usual strength values of these fillers, when cross-banded, are:[4]

High strength paper.....18,000–24,000 p.s.i.
Glass fabric.....30,000–70,000 p.s.i.

2. Modulus of Elasticity

The modulus of elasticity in tension for various types of laminates has been described by Caldwell,[2] and the data are presented in Table XXXVIII.

TABLE XXXVIII

MODULUS OF ELASTICITY IN TENSION FOR VARIOUS LAMINATES

Type of filler and grade	Modulus, p.s.i.	
	With grain	Across grain
Asbestos fabric, Grade AA	1.3×10^6	1.3×10^6
Kraft paper, Grade X	1.7×10^6	1.1×10^6
Absorbent paper, Grade XX	1.0×10^6	1.0×10^6
Fine weave fabric, Grade LE	1.0×10^6	0.7×10^6
Fine weave fabric, Grade L	1.0×10^6	0.8×10^6
Absorbent paper, Grade P	0.9×10^6	0.7×10^6

[4] H. Sang and P. M. Field, *Modern Plastics*, 20, 107–109, 142 (Oct., 1943).

3. Compressive Strength

In Table XXXIX are listed the compressive strengths of standard laminates. These data have also been compiled from the Plastics Materials Manufacturers Association publication, and were obtained by A.S.T.M. method D-229. It is important to note that these compressive strength values were obtained in the flatwise direction.

TABLE XXXIX

FLATWISE COMPRESSIVE STRENGTH OF LAMINATED PHENOLIC PLATES AT 25°C.

Grade of laminate	Compressive strength, p s.i.	
	Minimum	Average
Paper-base, Grade X	....	35,000
Paper-base, Grade P, 1/16 to 1/4 in.	....	22,000
Paper-base, Grade XX	....	34,000
Paper-base, Grade XXP, 1/16 to 1/4 in.	....	25,000
Paper-base, Grade XXX	....	32,000
Paper-base, Grade XXXP, 1/16 to 1/4 in.	....	25,000
Fabric-base, Grade C	35,000	38,000
Fabric-base, Grade CE	34,000	36,000
Fine weave fabric-base, Grade L	30,000	35,000
Fine weave fabric-base, Grade LE	33,000	37,000
Asbestos-paper-base, Grade A	....	36,000
Asbestos-fabric-base, Grade AA	35,000	38,000

4. Flexural Strength

Table XL gives values for the minimum and average flexural strength as published by the Plastics Materials Manufacturers Association, and as determined by A.S.T.M. method D-229.

TABLE XL

FLEXURAL STRENGTH OF LAMINATED PHENOLIC PLATES AT 25°C.

Grade of laminate	Flexural strength, p.s.i.	
	Minimum	Average
Paper-base, Grade X	16,000	21,000
Paper-base, Grade P, 1/16 to 1/4 in.	11,000	15,000
Paper-base, Grade XX	12,000	16,000
Paper-base, Grade XXP, 1/16 to 1/4 in.	12,000	16,000
Paper-base, Grade XXX	12,000	15,000
Paper-base, Grade XXXP, 1/16 to 1/4 in.	12,000	15,000
Fabric-base, Grade C	16,000	20,000
Fabric-base, Grade CE	13,000	17,000
Fine weave fabric-base, Grade L	15,000	20,000
Fine weave fabric-base, Grade LE	15,000	19,000
Asbestos-paper-base, Grade A	....	16,000
Asbestos-fabric-base, Grade AA	16,000	20,000

5. Shear Strength

Schwartz and Dugger[5] studied the shear strength of a number of laminates at 77°F., using sheets of varying thickness. The shear strength was determined in various directions, and it was found that the shear values were not greatly different for both longitudinal and transverse shear planes of laminated phenolic materials (both paper- and fabric-filled) which showed marked directional properties in tension. The data in Table XLI are typical of the values obtained.

TABLE XLI

SHEAR STRENGTH OF LAMINATES AT 77°F.

Type of laminate	Direction	Shear strength, p.s.i.
Grade L	Longitudinal	12,600
	Transverse	13,500
	At 45° to longitudinal	13,400
Grade C	Longitudinal	13,000
	Transverse	14,900
	At 45° to longitudinal	12,700
Grade XX	Longitudinal	12,300
	Transverse	13,900
	At 45° to longitudinal	11,600
High strength paper	Longitudinal (flatwise)	11,900
	Longitudinal (edgewise)	15,200
Glass and cotton	Longitudinal	18,600
	Transverse	18,600
	At 45° to longitudinal	21,400

Data on shear strength have also been given by Keuch[6] and by Field.[7] The data of the latter are presented in this chapter in the discussion of temperature effects.

6. Bearing Strength

Schwartz and Dugger[8] studied the bearing strength of four types of laminate at 77°F. They defined bearing strength as the bearing stress when deformation of the hole was equal to 4% of the diameter. The effect of a number of variables was investigated, such as width of the specimen and diameter of the hole. The data are given in Table XLII.

Bond[8a] gives appreciably higher values for bearing strength of Grade XX, i.e., 33100 p.s.i. at 70°F. and 55% relative humidity.

[5] R. T. Schwartz and E. Dugger, Jr., *Modern Plastics*, **21**, 117–121, 164–166 (Mar., 1944).

[6] W. Keuch, *J. Roy. Aircraft Soc.* (*London*), 44–73 (Jan., 1940).

[7] P. M. Field, *Modern Plastics*, **20**, 91–102, 126–130 (Aug., 1943).

[8] R. T. Schwartz and E. Dugger, Jr., *ibid.*, **21**, 133–137, 180–184 (May, 1944).

[8a] J. Bond, *ibid.*, **19**, 70–73, 110 (July, 1942).

TABLE XLII

BEARING STRENGTH OF LAMINATES AT 77°F.

Type of laminate	Direction of specimen and loading	Bearing strength, p.s.i.
Grade L	Crosswise	18,600
	Lengthwise	20,000
Grade C	Crosswise	20,400
	Lengthwise	21,000
Grade XX	Crosswise	23,800
	Lengthwise	23,200
High strength paper	.....	31,100

7. Impact Resistance

Caldwell[2] has given the data in Table XLIII for the impact strengths of various types of laminate at 77°F.

TABLE XLIII

IMPACT STRENGTH AT 77°F. FOR VARIOUS LAMINATES DETERMINED BY THE CHARPY METHOD ON UNNOTCHED SPECIMEN 0.5 IN. THICK

Type of filler and grade	Impact strength, ft.lb./in.			
	Flatwise with grain	Flatwise across grain	Edgewise with grain	Edgewise across grain
Asbestos fabric, Grade AA	12.3	11.5	9.8	8.5
Kraft paper, Grade X	8.9	4.8	6.6	4.5
Absorbent paper, Grade XX	4.5	3.4	4.5	3.5
Fine weave fabric, Grade LE	10.4	9.8	8.6	7.8
Fine weave fabric, Grade L	15.4	10.9	10.3	9.1
Absorbent paper, Grade P	7.2	6.5	7.5	6.4

Field[7] determined the impact strength of various laminates at three different temperatures. These data are presented later in this chapter in the discussion under temperature effects.

8. Creep and Stress Endurance

The existing data on creep and stress endurance of laminates at room temperature are rather scanty. Field[7] has pointed out that laminates fail under repeated stresses at loads lower than the failure shown in a single short time test. Two possible causes for such failure are suggested: (*1*) brittle failure in the resin, which produces sharp edges or particles which gradually destroy the reinforcing fibers; and (*2*) poor adhesive bond between the resin and the reinforcing agent—this effect may be a factor when glass cloth is the filler. The ultimate tensile strength of a glass cloth filled laminate dropped 31% when stressed 100 times at two-thirds of the initial

ultimate strength; under the same conditions the ultimate tensile strength of a high strength paper laminate dropped 17%.

Chasman[9] studied the creep and long time tensile strength of two grades of standard laminates—Grade L and Grade XX. The data are reproduced in Table XLIV.

TABLE XLIV

COMPARISON OF SHORT AND LONG TIME TENSILE STRENGTH OF LAMINATES

Grade	Short time ultimate tensile strength, av. p.s.i.	Tensile strength to fracture after 1000 hrs. p.s.i.	Long time tensile strength as percentage of ultimate
Grade L	16,520	11,000	67%
Grade XX	16,540	11,000	67%

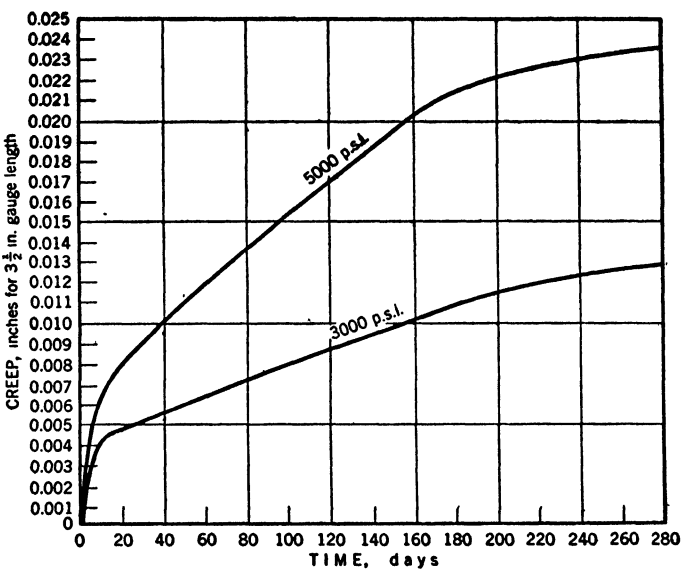


Fig. 44. Creep of a coarse weave fabric laminate at room temperature.[2]

Findley and Worley[10] made a very thorough study of the mechanical properties of a paper laminate made from high strength Mitscherlich paper

[9] B. Chasman, *Modern Plastics*, **21**, 145–148, 176 (Feb., 1944).

[10] W. N. Findley and W. J. Worley, *ibid.*, **22**, 143–150, 190–194 (June, 1945).

bonded with a low pressure type of phenoplast. Creep data, at room temperature, were obtained under various loadings for times up to 7000 hours. For any given time, the rate of creep, v, was shown to be related to stress σ by the exponentional equation:

$$v = C_2(e^{k\sigma} - 1)nt^{n-1}$$

where t is the time and C_2, k and n are constants.

Caldwell[2] has determined the creep of a coarse weave fabric laminate at room temperature under two loadings; Figure 44 is reproduced from this source. Additional data on the creep of laminates have been given by Perkuhn.[11]

9. Fatigue Resistance

As in the case of the molded phenoplasts, there are a number of methods by means of which the fatigue or endurance resistance of laminates may be determined, but no one method has as yet been standardized. An excellent discussion of the various methods of testing fatigue resistance, together with the significance of the results, has been given by Lazan and Yorgiodis.[12] Field[7] selected the Krause plate method of testing as the most satisfactory, because the stresses on the flat specimen more nearly simulated operating conditions in aircraft structures. No matter which method is selected, an appreciable temperature rise takes place during the test. With the Krause plate method, the temperature rise is from 25° to 35°F. In a torsional method, using a special type of oscillator to obtain rapid reversals, Lazan[13] found a rise of as much as 150°F. when a vibration of about 6000 radians was superimposed upon a torsional stress of 7.5 cps.; the specimen was a laminated canvas phenoplast. When fatigue tests are made on samples of plastic which are cooled by a stream of air, as many as 280% more reversals may be required than in the case of an uncooled specimen. In general, it can be only concluded that the rise in temperature during the fatigue test has some effect upon the numerical results, but the effect has not yet been fully evaluated.

The results of fatigue tests on various types of laminates are summarized in Table XLV, the data from which were taken from Field. In the fatigue test, minute cracks develop long before the specimen breaks; these cracks are, in fact, the first evidence of structural failure. Field showed that

[11] H. Perkuhn, *Luftfahrt-Forsch.*, **18**, No. 1 (1941).

[12] B. J. Lazan and A. Yorgiodis, *Modern Plastics*, **21**, 119–128, 164 (Aug., 1944).

[13] B. J. Lazan, *ibid.*, **20**, 83–88, 136–144 (Nov., 1942).

these cracks caused the specimen to show increased deflection under load, and considered the specimen to have failed when a marked increase took place in the rate of change of the deflection on successive applications of the initial load.

TABLE XLV

FATIGUE LIMITS OF LAMINATED SHEETS DETERMINED BY THE KRAUSE PLATE METHOD

(In cycles × 10^6 to produce failure)

Induced stress, p.s.i.	Type of laminate			
	Felted asbestos	Cotton fabric	Cross banded high strength paper	Unidirectional high strength paper
6,000	2.0[a]	2.0[a]	...	..
6,500	1.7	..	...	..
7,000	0.90	1.6	2.0[a]	..
7,500	0.55	0.35	...	..
8,000	0.65	0.05	0.64	2.0[a]
8,500	....	..	...	1.25
9,000	....	..	0.165	0.90
9,500	....	..	...	0.37
10,000	....	..	...	0.10
11,000	0.0047	..	0.027	..
12,000	0.0011	..	...	..

[a] Specimen did not fail; test discontinued.

10. Abrasion Resistance

The abrasion resistance of paper-base phenoplast laminates has been studied by Hoffman[14] using a Taber Abraser. The abrasion resistance varies considerably with the exact type of resin and filler used. However, the following general conclusions were drawn:

1. The abrasion resistance of thermosetting laminates is comparable to the softer metals, such as aluminum and copper, and better than wood or pressed boards.

2. In general, rag paper and bleached sulfite paper-base laminates have equal abrasion resistance and are better than unbleached sulfite paper-base laminates.

3. The abrasion resistance of paper-base laminates decreases as the number of impregnated sheets per panel increases up to a certain point and then remains constant.

4. Fiber orientation affects the abrasion resistance of the laminates.

5. The abrasion resistance of laminates is unaffected by conditioning

[14] E. R. Hoffman, *Paper Trade J.*, **120**, 45–48 (1945).

in atmospheres up to 75% relative humidity, but decreases rapidly at higher humidities.

C. INFLUENCE OF TEMPERATURE ON MECHANICAL PROPERTIES

Because of their high specific strength properties, the laminated phenoplasts are finding increasing use for structural and functional applications. A thorough knowledge of the effect of temperature on their mechanical

TABLE XLVI

CHANGE IN ULTIMATE TENSILE STRENGTH OF LAMINATES WITH TEMPERATURE

Type of laminate	Direction tested	Ultimate strength in p.s.i. at		
		−70°F.	+76°F.	+160°F.
Cross banded high strength paper	With grain, max.	30,700	25,500	18,050
	min.	28,000	24,600	17,880
	Cross grain, max.	29,200	26,150	17,420
	min.	29,200	25,750	17,120
Felted asbestos	With grain, max.	20,800	19,550	10,550
	min.	18,730	18,800	9,910
	Cross grain, max.	16,680	15,250	11,250
	min.	16,180	14,800	10,590
Glass cloth	With grain, max.	48,200	39,600	30,250
	min.	44,700	39,400	28,250
	Cross grain, max.	45,900	30,600	26,700
	min.	45,100	29,500	22,750

TABLE XLVII

CHANGE IN ULTIMATE COMPRESSIVE STRENGTH OF LAMINATES WITH TEMPERATURE

Type of laminate	Direction tested	Ultimate strength in p.s.i. at		
		−70°F.	+76°F.	+160°F.
Cross banded, high strength paper	With grain, max.	26,640	19,850	13,380
	min.	26,000	18,900	12,900
	Cross grain, max.	27,700	18,850	12,430
	min.	27,630	18,800	12,020
Felted asbestos	With grain, max.	22,900	18,960	12,340
	min.	22,700	18,900	12,230
	Cross grain, max.	23,630	19,730	13,370
	min.	22,200	19,250	10,060
Glass cloth	With grain, max.	39,900	29,400	27,700
	min.	36,900	27,000	26,940
	Cross grain, max.	40,400	30,760	27,600
	min.	40,250	29,700	....

properties is therefore very important. The information is still rather scanty, although data have been presented by Caldwell,[1] Place,[15] Norelli and Gard,[16] and particularly by Field.[7] Tables XLVI, XLVII, XLVIII, and XLIX, taken from the data of Field, show the ultimate tensile, compressive, shear, and bearing strength of various types of laminated phenoplasts at three different temperatures: −70°F., +76°F., and +160°F.

TABLE XLVIII

CHANGE IN SHEAR STRENGTH OF LAMINATES WITH TEMPERATURE

Type of laminate	Direction tested	Flatwise shear strength in p.s.i. at			Edgewise shear strength in p.s.i. at		
		−70°F.	+76°F.	+160°F.	−70°F.	+76°F.	+160°F.
Cross banded, high strength paper	With grain, max.	17,220	12,640	9,375	16,750	14,200	11,430
	min.	16,570	12,270	8,380	16,060	14,150	10,750
	Cross grain, max.	18,200	12,950	11,350	18,400	14,350	11,320
	min.	16,900	12,900	10,100	16,850	13,100	11,190
Felted asbestos	With grain, max.	17,410	15,700	15,700	16,530	13,650	10,270
	min.	17,070	15,030	15,030	16,110	13,500	9,960
	Cross grain, max.	17,850	16,120	16,120	17,920	14,460	10,460
	min.	17,180	16,020	16,020	16,520	13,525	10,220
Glass cloth	With grain, max.	19,000	17,950	16,730	14,300	13,900	14,000
	min.	18,900	16,470	15,730	13,500	13,000	13,710
	Cross grain, max.	22,000	18,430	16,450	17,150	16,120	15,100
	min.	20,400	17,400	15,920	16,500	15,260	14,940

TABLE XLIX

CHANGE IN BEARING STRENGTH OF LAMINATES WITH TEMPERATURE

Type of laminate	Direction tested	Bearing strength in p.s.i. at		
		−70°F.	+76°F.	+160°F.
Cross banded, high strength paper	With grain, max.	34,300	28,780	23,800
	min.	33,200	28,580	18,850
	Cross grain, max.	35,400	30,200	22,580
	min.	....	26,950	20,300
Felted asbestos	With grain, max.	41,900	31,200	26,400
	min.	38,500	30,500	24,600
	Cross grain, max.	31,900	31,100	21,900
	min.	31,600	29,600	20,200
Glass cloth	With grain, max.	41,400	28,800	19,900
	min.	37,300	28,100	15,700
	Cross grain, max.	38,700	31,900	28,000
	min.	34,700	31,300	24,800

[15] S. W. Place, *Modern Plastics*, **18**, 59–62 (Sept., 1940).

[16] P. Norelli and W. H. Gard, *Ind. Eng. Chem.*, **37**, 580–585 (1945).

Norelli and Gard[16] have studied the effect of a wide range in temperature on the tensile, compressive, and shear strength of a number of commercial laminates made with a cresylic acid resin. The grades examined were:

NEMA grade	Type of filler	Resin content, %
C	Coarse weave cotton fabric	35–40
X	Kraft paper	40–45
AA	Asbestos cloth	40–45
XX	Alpha paper	50–55
LE	Fine weave cotton fabric	50–55
..	Fiberglas fabric	35–40

Figure 45 illustrates the effect of temperature on the ultimate tensile strength of these laminates, while Tables L and LI present data for the ultimate compressive and shear strengths of the various laminates in both flatwise and edgewise directions.

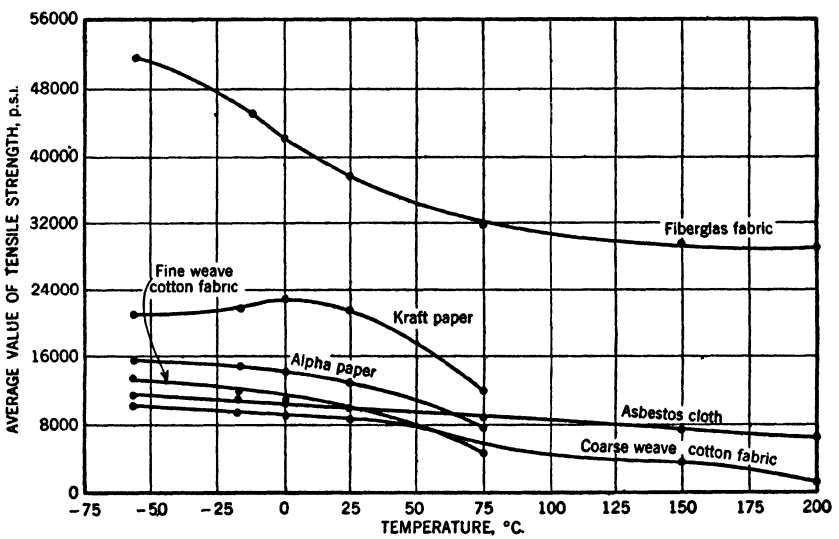


Fig. 45. Effect of temperature on ultimate tensile strength of laminates.[16]

Field has given data for the effect of temperature on the notched Izod impact strength of three types of laminate. As in the case of the molded

TABLE L

ULTIMATE COMPRESSIVE STRENGTH IN P.S.I. FOR VARIOUS LAMINATES AT −55° TO 200°C.

NEMA Grade	Temperature, °C.						
	−55	−20	0	25	75	150	200
	A. FLATWISE DIRECTION						
C	51,000	44,930	42,500	42,120	29,850	19,460	11,600
X	48,800	44,800	41,800	44,030	33,530	....	....
AA	54,960	48,700	43,630	48,550	38,430	25,300	30,780
XX	54,100	48,250	44,630	39,950	29,150	....	....
LE	54,100	45,300	43,900	43,200	31,730	....	....
Fiberglas	73,200	66,900	47,400	69,750	48,870	35,130	23,700
	B. EDGEWISE DIRECTION						
C	37,350	30,300	27,050	24,250	15,550	9,825	8,600
X	33,400	30,450	26,750	26,075	16,750	....	....
AA	22,250	22,450	19,800	20,575	15,225	12,260	11,675
XX	38,300	30,800	29,700	25,700	15,975	....	....
LE	39,850	33,900	33,100	27,900	19,900	....	....
Fiberglas	20,400	14,800	18,830	14,195	13,700	7,325	7,025

TABLE LI

ULTIMATE SHEAR STRENGTH IN P.S.I. FOR VARIOUS LAMINATES AT −55° TO 200°C.

NEMA Grade	Temperature, °C.						
	−55	−20	0	25	75	150	200
	A. FLATWISE DIRECTION						
C	20,660	17,420	16,630	15,320	10,080	5,770	2,150
X	18,030	12,060	13,010	13,460	9,340	....	....
AA	18,850	16,300	15,200	14,650	11,060	7,580	4,480
XX	11,275	11,320	10,530	11,480	8,400	....	....
LE	19,570	17,270	17,410	14,800	10,025	....	....
Fiberglas	27,900	25,420	22,850	20,970	15,000	10,550	8,350
	B. EDGEWISE DIRECTION						
C	10,250	8,065	8,250	8,175	6,070	3,950	3,330
X	12,650	8,290	8,275	10,450	6,960	....	....
AA	11,065	8,945	7,550	8,425	7,425	5,825	4,000
XX	10,650	8,975	9,070	9,300	7,460	....	....
LE	13,275	11,075	10,565	13,625	10,200	....	....
Fiberglas	13,200	13,200	11,265	9,870	8,240	6,130	6,575

phenoplasts, the usual effect of temperature is to increase the impact strength. In the case of the glass cloth laminates, an increase in tempera-

ture appears to decrease the impact strength. No fundamental explanation of this effect has yet been presented. Table LII presents the data given by Field.

TABLE LII

EFFECT OF TEMPERATURE ON NOTCHED IZOD IMPACT STRENGTH

Type of laminate	Direction tested	Impact strength per inch of notch					
		Edgewise at			Facewise at		
		−70° F.	+76° F.	+160° F.	−70° F.	+76° F.	+160° F.
Cross banded, high strength paper	With grain	1.0	1.0	1.0	4.0	4.5	4.5
	Cross grain	1.0	1.0	1.0	3.0	4.5	4.5
Felted asbestos	With grain	2.0	2.0	3.0	4.0	4.0	5.0
	Cross grain	3.0	2.0	3.0	5.0	5.0	5.5
Glass cloth	With grain	33.5	22.0	20.0	29.0	23.0	27.5
	Cross grain	31.0	22.5	20.5	31.5	32.5	31.0

Caldwell[2] has given data for the change of impact strength with temperature of a coarse weave cotton fabric.

1. Influence of Temperature on Creep

Gailus and Telfair[17] studied the creep of a cross banded, high strength paper laminate at 194°F. As in the case of the molded phenoplasts described in Chapter VIII, shrinkage took place during heating, and the effect of this obscured the true creep until the two components were separaated. Figure 46 illustrates the observed *behavior* of the laminate during heating, while Figure 47 illustrates the *true creep* which took place.

2. Effects of Long Continued Heating

Hausmann, Parkinson, and Mains[18] made a thorough study of the heat resistance of laminated phenoplasts, using chiefly the standard NEMA grades. Grades X, XXX, and C showed a decrease in flexural strength when tested at 90°C., although the loss in strength was much less when the laminate was cooled before testing. In all cases, the strength when tested at 90°C. continued to increase with increasing time of exposure to this

[17] W. J. Gailus and D. Telfair, *Modern Plastics*, **22**, 149–154, 192 (May, 1945).

[18] E. O. Hausmann, A. E. Parkinson, and C. H. Mains, *ibid.*, **22**, 151–154, 190–198 (Nov., 1944).

temperature. Figure 48 indicates these effects. The work was then extended to higher temperatures. Figures 50 and 51 show the loss in flexural strength for various grades when heated for seven-day periods at tempera-

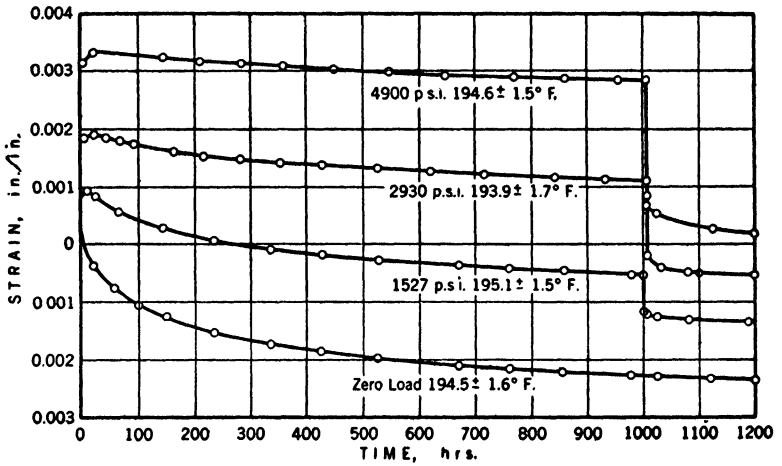


Fig. 46. Behavior of high strength paper laminate under load at 194°F.[17]

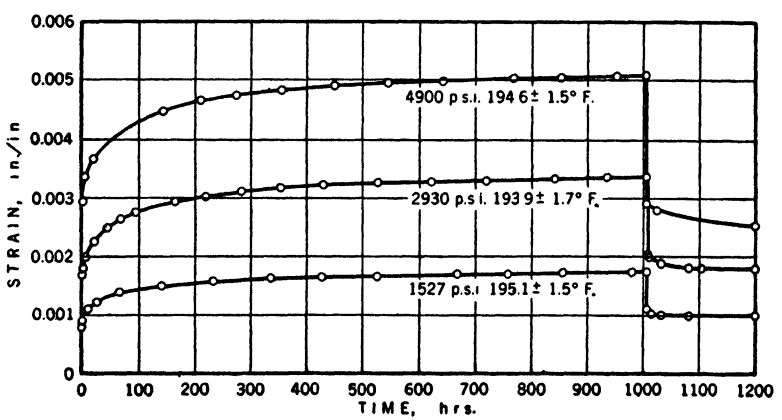


Fig. 47. True creep (corrected for shrinkage) of high strength paper laminate under load at 194°F.[17]

tures up to 250°C. Figure 49 shows the change in flexural strength for the more heat-resistant grades when heated for as long as four weeks at

150°C.; in all these figures, strength was measured after cooling the specimen to room temperature.

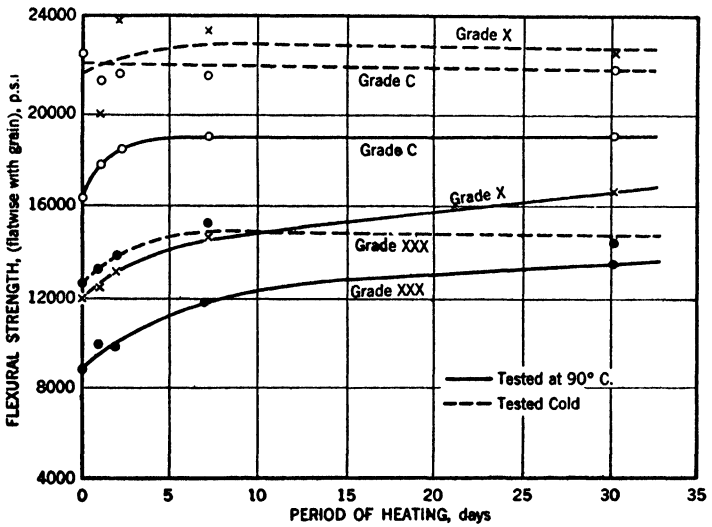


Fig. 48. Effect of heating at 90°C. on flexural strength of phenoplast laminates.[18]

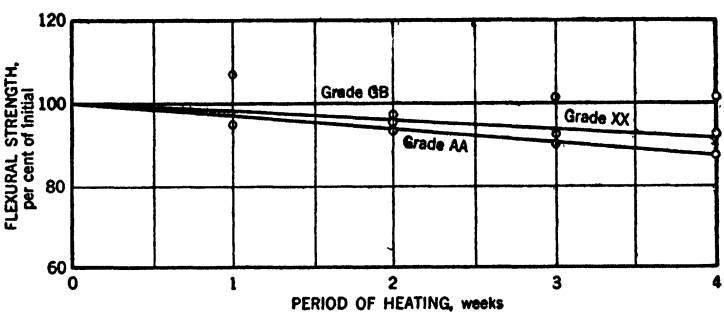


Fig. 49. Change in flexural strength for better heat-resisting grades of phenoplast laminates after heating to 150°C.[18]

The temperature at which the various laminates blistered was determined by heating at a constant rate of temperature rise in a period of 45 minutes. The data are presented in Figure 52.

It was generally concluded from these tests that glass-base laminates have the best heat resistance; they exhibit practically no change in flexural

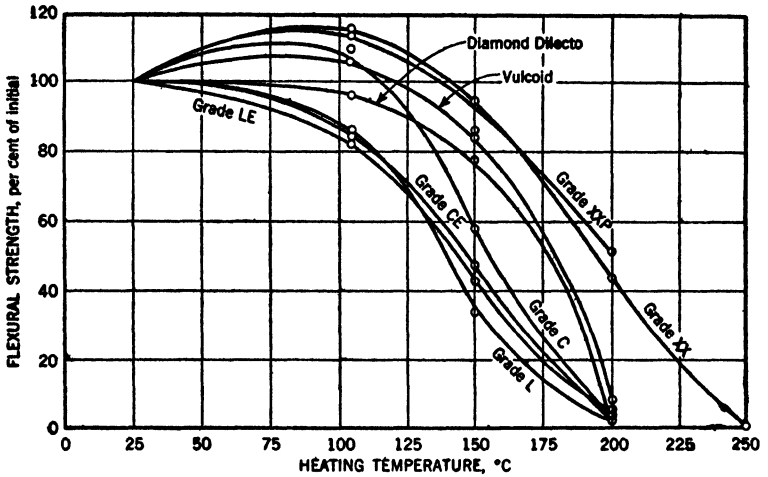


Fig. 50. Effect of heating for seven days at temperatures up to 250°C. on flexural strength of phenoplast laminates.[18]

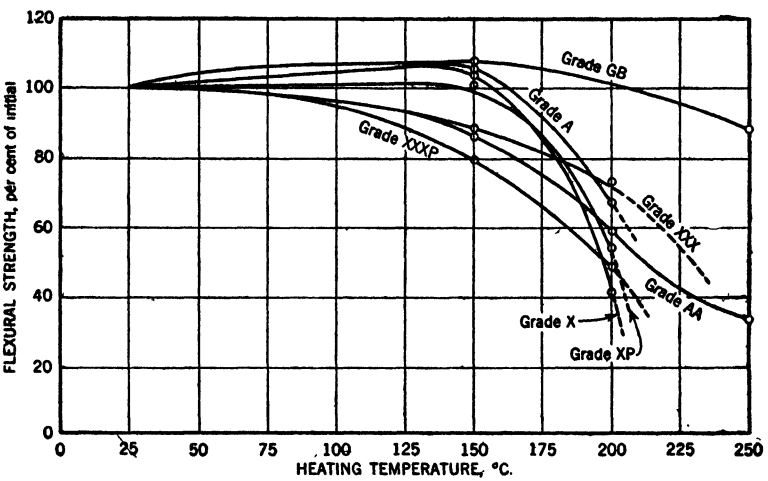


Fig. 51. Effect of heating for seven days at temperatures up to 250°C. on flexural strength of better heat-resisting grades of phenoplast laminates.[18]

or impact strength measured at room temperature for one week at temperatures up to 200°C. or for periods up to four weeks at 150°C. Asbestos

fabric base is next best in heat resistance. This applies specifically to the material made from Grade AA asbestos cloth containing 90% asbestos and 10% cotton. Materials made from the Underwriters' grade of asbestos fabric are definitely less heat resistant. High resin content paper-base

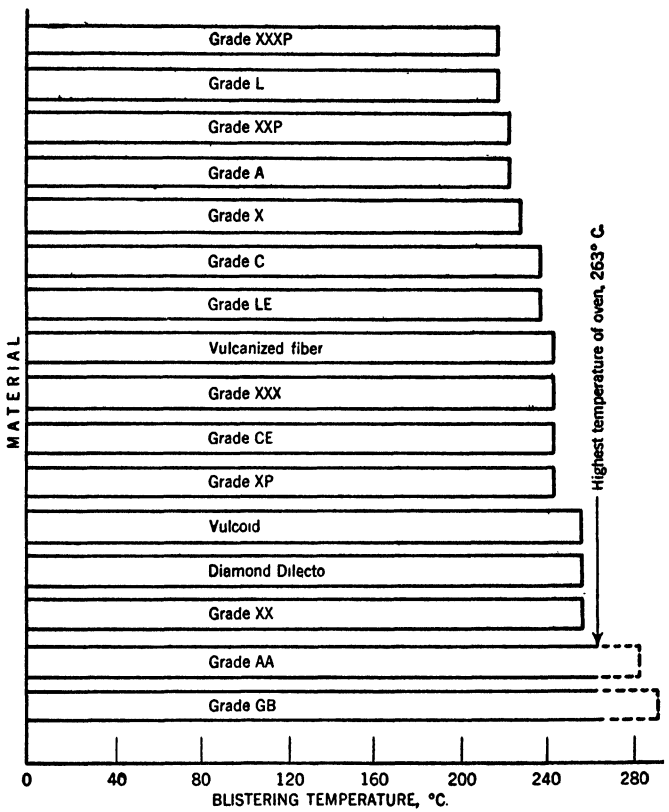


Fig. 52. Blistering temperature for various phenoplast laminates.[18]

grades of the XX or XXX type were third best. Asbestos paper base grades tended to blister at the higher temperatures, while cotton fabric base phenolic materials lost practically all flexural and impact strength in one week at 200°C. and showed a marked decrease in strength even at 150°C.

D. EFFECT OF RESIN CONTENT ON MECHANICAL PROPERTIES

The effect of resin content on mechanical properties has been studied by Cox and Pepper[19] and by Pepper and Barwell.[20] In the first work re-

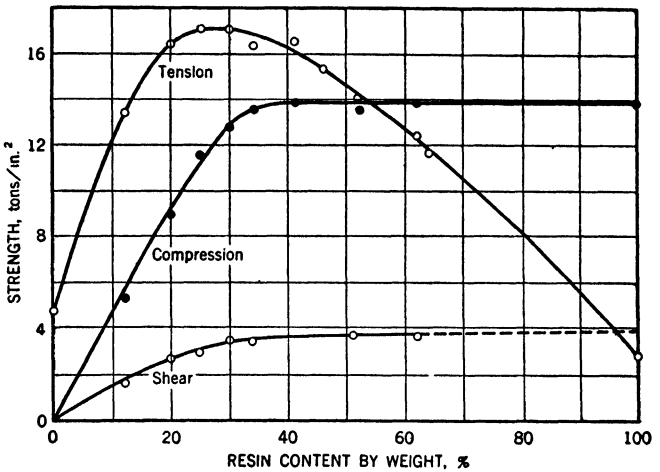


Fig. 53. Effect of resin content on strength properties of laminated manila-hemp paper.[19]

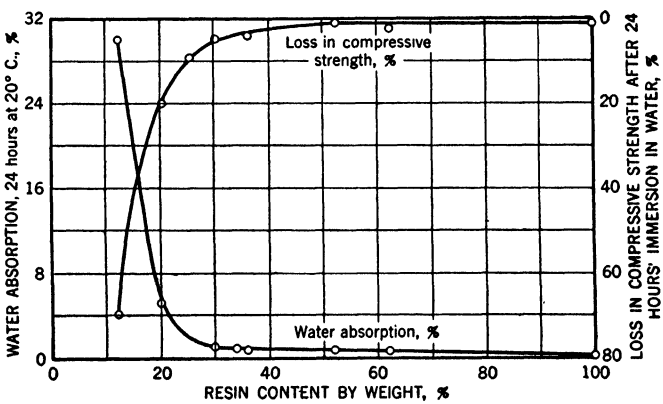


Fig. 54. Effect of resin content on water absorption of laminated manila-hemp paper.[19]

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[19] H. L. Cox and K. W. Pepper, *J. Soc. Chem. Ind.*, **63**, 150–154 (1944).

[20] K. W. Pepper and F. T. Barwell, *ibid.*, **63**, 321–329 (1944).

ferred to, the laminates were made from thin bleached manila hemp paper and an alcoholic solution of resin. The laminates were pressed at 2500

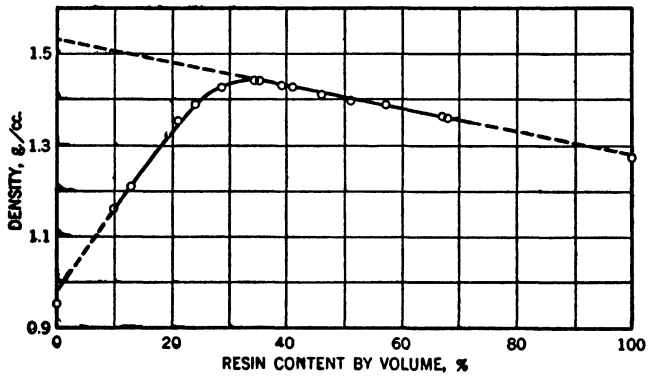


Fig. 55. Effect of resin content on density of laminated manila-hemp paper.[19]

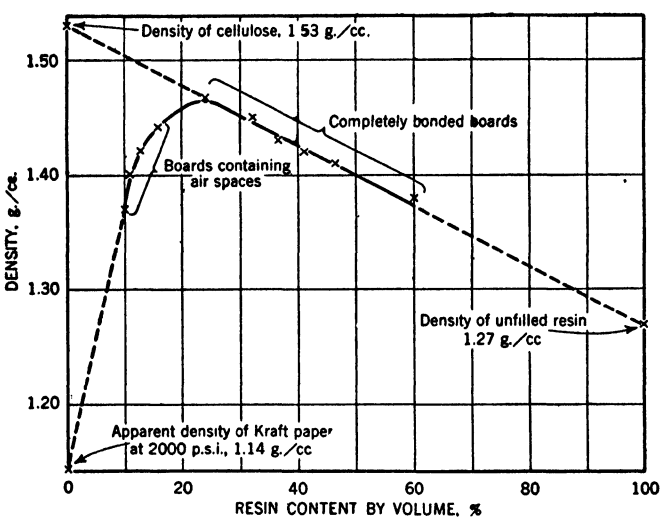


Fig. 56. Density variation with resin content of Kraft paper laminated at 2000 p.s.i.[20]

p.s.i. for 30 minutes at 145°C. Figures 53 to 55 show the effect of varying resin content upon strength properties, water absorption, and density, respectively.

Figure 55 indicates that as the resin content increases from zero, the density increases up to a maximum of 1.44 at 35% resin by volume (equivalent to 30% by weight), and then decreases linearly. The latter values lie on a straight line between the density of cellulose (1.53) and that of unfilled resin (1.27). Below 30% resin content, the density increases as resin is added to paper up to the point where the voids are just filled with resin.

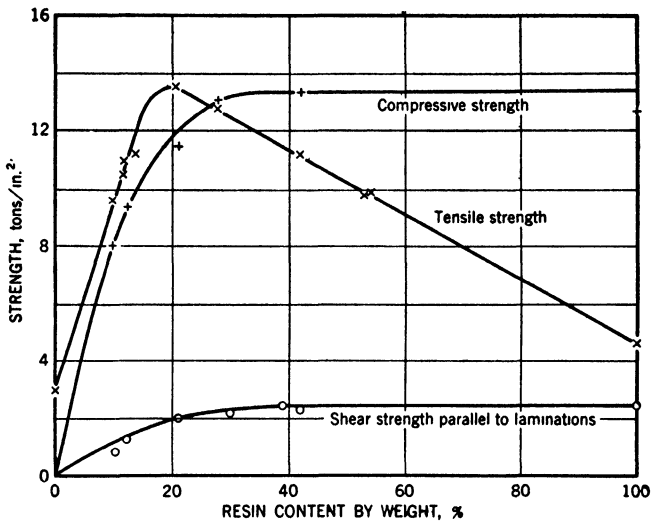


Fig. 57. Effect of resin content on strength properties of high density Kraft paper laminate.[30]

In the second reference given above, a high density Kraft paper was used as the base, impregnated with an aqueous solution of phenoplast resin. The laminating pressure was 2000 p.s.i. Figure 56 shows the change in density with increasing resin content; the form of the curve is similar to that of Figure 55, except that the maximum density occurs at 24% resin content by volume. This is due to the lower content of voids, which is estimated at 25% in the case of the high density paper. From the curves of Figures 55 and 56, it is concluded that the best combination of properties may be obtained when the laminate contains exactly the maximum amount of resin to fill the voids in the base.

Figure 57 shows the variation of strength properties with resin content in the case of the high density Kraft paper.

E. EFFECT OF MOISTURE CONTENT OF PAPER FILLER BEFORE LAMINATION

The moisture content of the paper filler before lamination appears to have a pronounced effect upon the physical properties of the resulting laminate. Experimental work reported by Croup[21] was done on a sulfite paper three mils thick, impregnated with a low pressure type alcohol-soluble phenoplast resin. The laminates, 1/8 in. thick, were pressed at 160°C. and 250 p.s.i. for twelve minutes. Table LIII presents data on the effect of moisture content on the physical properties.

TABLE LIII

EFFECT OF MOISTURE CONTENT IN THE IMPREGNATED PAPER ON THE PHYSICAL PROPERTIES OF LAMINATES

Moisture content at lamination, %	Ultimate tensile strength, p.s.i.	Ultimate flexural strength, p.s.i.	Edge impact strength, Izod, ft.lb./in.
0.7	33,000	33,000	0.64
1.8	31,800	28,900	0.66
2.7	30,600	26,800	0.70
4.0	27,500	26,100	0.74
4.7	26,400	23,500	0.78
6.6	24,400	20,000	0.82
7.9	22,700	17,900	0.99

F. EFFECT OF LAMINATING PRESSURE

As previously explained, the standard NEMA laminated grades are manufactured under relatively high pressure (1200–2000 p.s.i.). Production demands during the war years stimulated interest in laminating flat sheets and contoured articles at much lower pressures—in the range of 100 to 250 p.s.i. The use of lower pressures permits the use of less expensive dies and presses. In many cases, forming is accomplished by the use of hydraulic pressure; a rubber diaphragm or bag is used as the hydraulic membrane. This type of low pressure laminating is particularly useful for the manufacture of articles of irregular contour, such as aircraft fairings, fillets, housing, cowling, and ducts.[22]

The effect of a variation in pressure has been studied by Pepper and Barwell.[20] A Kraft paper was used, impregnated with 42% of phenol–formaldehyde resin in aqueous solution. The change of strength proper-

[21] A. H. Croup, *Paper Trade J.*, **118**, 43–46 (1944).

[22] J. D. Nelson, *ibid.*, **120**, 33–36 (1945).

ties with laminating pressure is shown in Figures 58 and 59. The strength increases up to about 250 p.s.i. laminating pressure, but above this there is little increase.

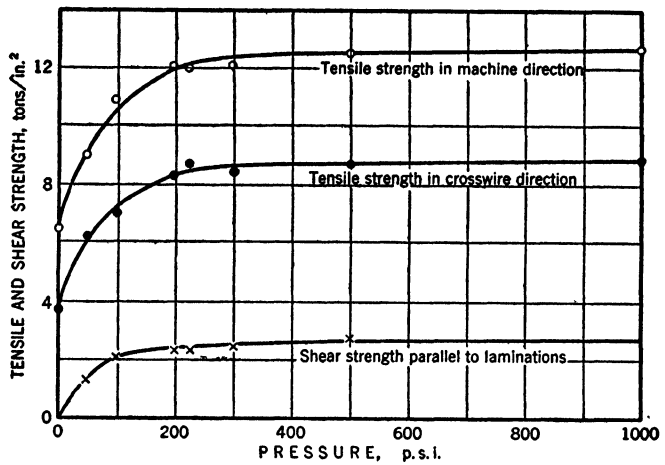


Fig. 58. Effect of laminating pressure on tensile and shear strength of Kraft paper laminates.[20]

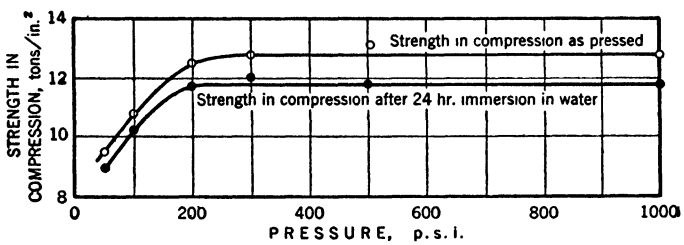


Fig. 59. Effect of laminating pressure on compressive strength.[20]

Field[7] has pointed out that low pressure laminates show increased water absorption as compared to high pressure laminates up to 24 hr. immersion, but the relative disadvantage decreases sharply on longer exposure.

G. EFFECT OF DEGREE OF CURE

Howells and Lewis[23] reviewed the subject of paper base laminates, and included new data on the effect of curing conditions on the physical proper-

[23] T. A. Howells and H. F. Lewis, *Ind. Eng. Chem.*, **37**, 264–268 (1945).

ties of commercial laminating paper containing 40% phenoplast resin. Table LIV is taken from their data; a laminating pressure of 100 p.s.i. was used in the preparation of the laminates referred to in this table. The authors emphasize that the optimum temperature of pressing depends upon the nature of the resin and the amount of catalyst in the resin; the time is likewise determined by the nature of the resin, the amount of catalyst and the temperature.

TABLE LIV

EFFECT OF CURING CONDITIONS ON PAPER-BASE LAMINATES

Property	Conditions					
	220°F., 20 min.	250°F., 10 min.	250°F., 20 min.	300°F., 10 min.	300°F., 20 min.	300°F., 30 min.
Specific gravity	1.34	1.36	1.35	1.36	1.36	1.35
Tensile strength, p.s.i.						
In machine direction	25,100	25,400	28,400	28,200	28,200	28,600
Across machine direction	9,500	10,500	14,200	17,000	16,300	16,800
Flexural strength, p.s.i.						
In machine direction	28,100	29,000	30,200	29,600	29,600	28,000
Across machine direction	18,500	20,300	20,900	21,200	22,400	20,800
Edge-notched Charpy Impact, ft.lb./in.						
In machine direction	0.81	0.79	0.71	0.73	0.61	0.63
Across machine direction	0.56	0.56	0.59	0.58	0.50	0.54
Water absorption, per cent in 24 hrs.	12.07	7.04	5.16	2.06	2.36	2.47
Acetone extract, %	30.4	12.9	8.0	0.9	1.0	0.7

H. EFFECT OF MOISTURE CONTENT ON PHYSICAL PROPERTIES

The moisture content of the laminate has a marked influence upon its physical properties; the dimensions of the laminate are also affected by changes in moisture content. Changes in dimension brought about by varying moisture content due to humidity variations are frequently more important than creep or cold flow, and this fact must be recognized in many applications of the phenoplast laminates.[24] The resin content is an important factor in controlling dimensional stability; according to Brown,[25] the minimum change in superficial dimensions is obtained at about 35% resin content in the laminate. The same author gives the following data for the change in tensile strength of a paper-base laminate under varying moisture conditions:

[24] J. J. Martin, *Symposium on Plastics*. American Society for Testing Materials, February, 1944.

[25] D. W. Brown, *Plastics (London)*, **8**, 177–187 (April, 1944).

Conditions	Tensile strength, p.s.i.
At 33%, relative humidity	25,200
At 75%, relative humidity	20,800
After immersion in water to constant weight	15,200

Further data on the moisture absorption of phenoplasts are given in Chapter XII.

I. MECHANICAL PROPERTIES OF POST-FORMED LAMINATES

The general principles of postforming of laminates have been discussed in Chapter VII. The mechanical properties of the postformed laminate may differ from that of the original flat sheet for two reasons:

1. The temperature required to soften the laminate may alter the physical properties. However, the chance of this is slight because the heating period is usually of short duration. For example, Beach[26] has given the following schedule for $^1/_{16}$ in. material:

Oven temperature, °F.	Heating period, min.
350	2.75–3.0
400	2.0 –2.25
450	1.0 –1.20
500	0.9 –1.00

From the preceding discussion on temperature effects, it is obvious that such short heating periods will have little or no harmful effects.

2. The forming operation distorts and stretches the threads of the laminate, particularly at the points of maximum draw. This will have some effect upon the properties at these points.

Beach[27] has discussed the effect of stretching upon a fabric-base laminate, prepared with a slightly plasticized phenol–aldehyde resin. The specimens were subjected to an elongation while hot of from 2.1 to 8.3%, and the physical properties were measured after cooling. The specimens were pulled in three different directions: (*a*) in the direction of the filler thread, (*b*) in the direction of the warp thread, and (*c*) in a direction 45° to the filler and warp threads.

The conclusions regarding strength properties are discussed in the following paragraphs.

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[26] W. I. Beach, *Modern Plastics*, **22**, 132–135, 206–208 (Nov., 1944).

[27] W. I. Beach, *ibid.*, **21**, 127–131, 186–188 (Jan., 1944).

1. Tensile Strength

There was a general drop in tensile strength of the specimens which were pulled in the direction of the filler thread, accompanied by a drop in the modulus. When pulled in the direction of the warp, the strength showed an increase up to 16%. When stretched on the bias, an appreciable increase in tensile strength took place, amounting to as much as 84.5% when the specimen was prestretched to 14.5%.

2. Flexural Strength

Stretching in any of the three directions tended to increase the flexura strength; the increases were not as marked as in the case of tensile strength

3. Shear Strength

The shear strength was appreciably lowered by stretching; the order of decrease was, in the direction on the bias, with the filler, and with the warp

4. Impact Strength

The impact strength was decreased by nearly 50% when the laminate was stretched either in the direction of the filler or the warp threads; when stretched on the bias, the decrease amounted to about 10%.

5. Water Absorption

Water absorption increased, up to about three times, when stretched to 8.3% in the warp and filler directions, and showed a slight increase at the same stretch in the bias direction.

X. ELECTRICAL PROPERTIES OF PHENOPLASTS

A. INTRODUCTION

In previous chapters, it was pointed out that the earliest important applications of the phenoplasts were in the electrical industry, where their excellent insulating qualities and ease of molding into complex shapes combined to give them a natural advantage. For these same reasons, the electrical industry is still an important outlet for all forms of the phenoplasts. There are a number of electrical properties which are commonly measured; in this chapter, the following will be considered: dielectric strength; volume resistivity; dielectric constant; power factor; loss factor; arc resistance and tendency to track.

B. THEORETICAL DISCUSSION

With the exception of the cast phenoplasts and pure resin molding compounds, all the commercial phenoplasts are mixtures of resin and filler. The electrical properties are influenced both by the resin and the filler, and by the proportions in which they are present. In addition, the commercial phenoplasts contain small quantities of ionizable salts, which come from the catalyst used in the preparation of the resin. The result is a complicated system, which is hardly subject to exact theoretical treatment. At the end of this chapter, tables are given which list the range of electrical properties for both molded and laminated phenoplasts. It will be noted that the range is rather broad in most cases; such latitude is required so that the large number of commercial products put out by the various manufacturers will be covered. It will usually be found that the individual manufacturers control their products quite closely; specific data on the actual figures for commercial phenoplasts must be obtained from the trade literature of the manufacturer.

In view of the above, it must be understood that any attempt to explain the electrical properties of the phenoplasts on theoretical ground must apply to the resin only, and not to the complicated system represented by a molding powder or laminate.

The *dielectric strength* of an insulating material such as a phenoplast is indicated by the voltage which is required to rupture or puncture the plastic. It represents the breakdown strength of the insulator. Fuoss[1] considers that it is not possible to discuss breakdown strength from a purely theoretical point of view, because the effect of electrical stress on organic compounds has not yet been treated fundamentally. Lusk[2] has shown that the degree of cure affects the dielectric strength, which reaches a maximum value only when the cure is complete.

The *dielectric constant*, *power factor*, and *loss factor* are subject to a theoretical discussion, and the groundwork for their understanding has been laid by Debye, Fuoss, and others. These properties of any organic molecule are controlled by the polar moment of the molecule, which in turn is dependent upon the atomic structure of the molecule and the balance between the distribution of the charges on the individual atoms. Thus, benzene, shown in Formula XXIX, has a balanced electrical struc-



(*a*) (*b*)

(XXIX)

ture and a zero moment. Phenol, as shown in *b*, has an unbalanced electrical structure due to the hydroxy substituent, and has a moment of 1.56 debye (one debye equals 10^{-27} coulomb). It is a polar molecule, and is said to have a dipole moment.

When a polar molecule such as phenol is brought into an alternating current field, the molecule tends to change polarity and to orient its dipole moment in phase with the alternating field. If the alternating polarization of the molecule were always in phase with the applied field, the polarizing process would be completely reversible and no energy would be lost. However, due to the viscous effects in solid and liquid bodies, the displacement of the molecule always lags behind the applied field. Electrical energy is then lost in the form of heat, which results in a temperature rise in the dielectric medium. The difference in phase be-

[1] R. M. Fuoss, *The Chemistry of Large Molecules*. Interscience, New York, 1943.
[2] W. Lusk, *Plastics Trends*, 2, No. 3 (Feb. 1, 1942).

tween the applied field and the effective current through the dielectric medium is the angle θ or phase angle; the angle $(90° - \theta)$ is conventionally referred to as δ or loss angle. The tan δ is known as the loss tangent or dissipation factor; it is equivalent to the ratio of loss current to charging current; in other words, it is equivalent to the ratio of energy dissipated per cycle to the energy stored per cycle. The tan δ is fundamentally a basic property. However, the *power factor*, or cos θ, is more commonly used by industrial testing laboratories. The power factor is equivalent to the ratio of the loss current to the total current. In the case of a good insulator (an effective dielectric), the total current is very nearly 90° out of phase with the field (δ is nearly 0°; θ is nearly 90°) and, therefore, the values of tan δ and of cos θ (power factor) are almost exactly identical. The *dielectric constant*, ϵ, of a dielectric is defined as the ratio of the capacitance of a given condenser with the dielectric between the condenser plates to its capacitance when the dielectric is replaced by a vacuum. The *loss factor*, ϵ'', is defined as the product of the loss tangent (tan δ) and the dielectric constant, but for reasons already explained the loss factor is commonly obtained by multiplying the *power factor* by the *dielectric constant*.

The magnitude of the dielectric constant and the power factor is normally influenced appreciably by the temperature of the plastic and the frequency ofthe alternating field. For most organic materials, the dielectric constant rises to a maximum at a certain temperature, after which it tends to decrease. The power factor at any given frequency also rises to a maximum at a certain temperature, after which it drops off; the temperature at which the maximum is reached depends upon the frequency, and the position of the maximum shifts upwards along the temperature axis with increasing frequency.

Hartshorn, Megson, and Rushton[3,4] studied the behavior of novolacs prepared from phenol, the cresols and *m*-5-xylenol; these studies were all made on the uncured resin, while it was still in the thermoplastic condition. The resins all behaved in the usual manner as described above for solid organic substances. Values of the loss factor at 1000 cycles, and at temperatures from 10° to 110°C., showed a maximum in the loss factor at various temperatures. The temperature at which the maximum occurred depended upon the phenol from which the novolac was prepared; the observed temperature values at which the maximum occurred, and the

[3] L. Hartshorn, N. J. L. Megson, and E. Rushton, *J. Soc. Chem. Ind.*, **59**, 129–133 (1940).

[4] L. Hartshorn, N. J. L. Megson, and E. Rushton, *Proc. Phys. Soc. (London)*, **52**, 796 (1940).

numerical value of the power factor at the maximum for the various novolacs are shown in Table LV. An increase in frequency shifted the curve along the temperature axis without materially altering the maximum value of the power factor.

TABLE LV

TEMPERATURE AT WHICH NOVOLACS SHOW MAXIMUM IN POWER FACTOR

Source of novolac	Temperature of maximum, °C.	Numerical value of power factor at the maximum
o-Cresol	37	0.17
p-Cresol	50	0.19
Phenol	60	0.17
m-Cresol	75	0.15
m-5-Xylenol	83	0.13

In contrast to the thermoplastic novolacs, the cured resin changed very slightly in either the dielectric constant or the loss factor as either temperature or frequency was varied.

Debing[5] has recently made a thorough study of the power factor and dielectric constant of a large number of novolacs at room temperature over a frequency range of 1 kilocycle to 45 megacycles (10^3 to 45×10^6 cycles). The novolacs were prepared from phenol and substituted phenols; both formaldehyde and higher aldehydes were used. In the case of the novolacs from phenol, it was found that both the power factor and dielectric constant could be reduced considerably by placing an alkyl or aryl group as a substituent in the methylene bridge. An even greater reduction in dielectric properties was obtained by placing a substituent group in the para position in the phenol nucleus. The power factors of phenol–formaldehyde novolacs were increased at low frequencies and decreased at higher frequencies through curing the novolac by heating with hexamethylenetetramine. When the novolac was cured, the dielectric constant increased approximately 9% over the entire range of frequency studied. Typical data are presented in Table LVI, which lists the power factor and dielectric constant for a phenol–formaldehyde novolac, the same resin after curing, for a cresol–formaldehyde novolac, and for the latter after curing by mixing 75% of the cresol–formaldehyde novolac with 25% of the phenol–formaldehyde novolac, plus sufficient hexamethylenetetramine to cure the mixture.

It is evident that, in a pure phenoplast resin, the phenolic hydroxy

[5] L. M. Debing, *Dissertation*, Columbia University, 1945.

fact, the tensile stress–strain and compressive stress–strain diagrams are really two parts of a complete stress–strain diagram for the material as it passes from tensile to compressive stresses.

Table XXVII gives the ultimate compressive strength for molded phenoplasts containing various fillers. The method of testing is that given in A.S.T.M. D48-42T.

TABLE XXVII

COMPRESSIVE STRENGTH OF MOLDED PHENOPLASTS

Type of phenoplast	Compressive strength, p.s.i.
General-purpose, cellulose-filled	24,000–30,000
Low shock resistant, cellulose-filled	25,000–30,000
Low to intermediate shock resistant, flock-filled	25,000–30,000
Intermediate shock resistant, fabric-filled	25,000–30,000
Intermediate to high shock resistant, fabric-filled	25,000–30,000
Very high shock resistant, fabric-filled	15,000–30,000
Shock and heat resistant, mineral-filled	10,000–15,000
Heat resistant, mineral-filled	20,000–25,000
High frequency insulation, mineral-filled	7,000–20,000
Arc resistant, semiflexible	10,000–20,000

5. Flexural Strength

Flexural strength is determined by A.S.T.M. test D48-42T. Table XXVIII gives values for this property as published by the Plastics Materials Manufacturers Association.

TABLE XXVIII

FLEXURAL STRENGTH OF MOLDED PHENOPLASTS

Type of phenoplast	Flexural strength, p.s.i.
General-purpose, cellulose-filled	9,500–14,000
Low shock resistant, cellulose-filled	9,500–11,000
Low to intermediate shock resistant, cellulose-filled	7,000–11,000
Intermediate shock resistant, fabric filled	9,000–11,000
Intermediate to high shock resistant, fabric-filled	8,500–12,500
High shock resistant, fabric-filled	9,000–11,000
Very high shock resistant	10,000–15,000
Shock and heat resistant, mineral-filled	10,000–13,000
Heat resistant, mineral-filled	6,500– 8,000
High frequency insulation, mineral-filled	7,000–10,000
Arc resistant, semiflexible	5,000– 7,000
Transparent, no filler	13,000–15,000

plasts, including paper-base laminates. After long drying at 110°C., all the laminates showed a maximum in the dielectric loss factor (measured at room temperature) just above 10^7 cycles. When the samples were tested after humidification, the high frequency maxima were still present and in the same order, but in addition there was a very large low frequency loss. The large increase in free ion conductivity which accompanied the increase of dielectric constant and dielectric loss at low frequencies in the humidified phenoplasts suggests that ionic effects are the principal cause of this loss. The mineral-filled phenoplasts are much less moisture sensitive in respect to dielectric properties, especially at low frequencies, than those of cellulose-filled resins.

The *volume resistivity* of the phenoplasts is, in general, quite high, and is one of the properties which makes them excellently suited for use in the electrical field. For a few special uses, high conductivity is required; this may be obtained by the addition of a large quantity of a conducting carbon, such as acetylene black. Stäger, Sänger, and Siegfried[8] have reported that the conductivity of a cured phenoplast may vary widely with the chemical nature of the phenol and the content of condensing agent present. Table LVII presents data from their work.

TABLE LVII

EFFECT OF PRESENCE OF CONDENSING AGENT ON CONDUCTIVITY OF PHENOPLASTS

Type of phenol used	Content of condensing agent	Conductivity, mho/cm. $\times 10^{-15}$
Phenol	Usual content present	7246.0
Phenol	Completely washed out	0.59
Cresol	Usual content present	0.56
Cresol	Completely washed out	0.37
m-Cresol	Completely washed out	0.25

Arc resistance and *tendency to track* refer to the ability of a plastic to withstand an arc across the surface without a breakdown of the insulating quality. The phenoplasts have a marked tendency to track, and where good arc resistance is required, better service is obtained from the aminoplasts—resins based on urea, melamine, or aniline. The passage of the arc tends to carbonize the phenoplast rapidly, after which a ready path or track is left for the passage of the current. Stäger, Sänger, and Siegfried studied the effect on arc resistance of various electrolytes on the surface

[8] H. Stäger, R. Sänger, and W. Siegfried, *Helv. Phys. Acta*, **12**, 561–580(1939).

of the resin. Certain salts, such as aluminum sulfate, tended to increase greatly the time required for the arc to form.

C. NUMERICAL DATA ON ELECTRICAL PROPERTIES

The following data on electrical properties at room temperature have been taken from those published by the Plastics Materials Manufacturers Association[9] and has been determined by A.S.T.M. method D48–43T.

Table LVIII lists the electrical properties of the molded phenoplasts. The values given for dielectric strength, volume resistivity, dielectric constant, power factor, and loss factor are for $^1/_8$ in. thick specimens molded of prewarmed material. If prewarming is omitted, the values for the dielectric strength and volume resistivity are usually lower, and the values for the dielectric constant, power factor, and loss factor are usually higher. In general, if good electrical qualities are to be maintained, the mold charges should be prewarmed or special care should be taken to keep the materials dry, as increases in the moisture content may decrease their value as insulation. This is particularly true for dielectric constant, power factor, loss factor, and resistivity, and for dielectric strength at elevated temperatures. At room temperature the power factor on certain grades may increase from 10 to 20% if the relative humidity reaches 90%.

Table LIX lists the dielectric strength of laminates of various thickness. The following standard sizes of specimens and electrodes were used in measuring the power factor, dielectric constant, and dielectric loss:

Thickness, in.	Diameter of disk electrodes, in.	Size of specimen, in.
Under $^1/_{16}$	3	6 × 6
$^1/_{16}$ to $^1/_8$	4.5	6 × 6
Over $^1/_8$ to $^1/_4$	6	8 × 8
Over $^1/_4$ to $^1/_2$	8	10 × 10
Over $^1/_2$ to 1	11	14 × 14

Table LX lists the dielectric constant, power factor, and loss factor for various grades of laminated phenoplasts. As in the case of the molded phenoplasts, the electrical properties of the laminates depend upon the type of filler, the resin content, and the exact type of resin. Generally speaking, the best electrical properties are obtained from the paper-base laminates.[10] The rag papers, or other papers high in alpha-cellulose con-

[9] *Technical Data on Plastic Materials*, Plastics Materials Mfrs. Assn., Washington, D.C., May, 1943.

[10] L. V. Larsen, *Paper Trade J.*, **120**, 34–36 (1945).

TABLE LVIII

PHENOL–FORMALDEHYDE AND FURFURALDEHYDE–PHENOL MOLDING MATERIALS
(A.S.T.M. TEST METHOD D48–43T)

Property	Test No.	Transparency, no filler	Cellulose-filled		Flock-filled	Fabric-filled		
			General-purpose	Low shock resistance	Low to intermediate shock resistance	Intermediate shock resistance	Intermediate to high shock resistance	High shock resistance
Dielectric strength, short time, v./mil.	1	300–400	300–375	250–350	200–350	200–350	200–340	200–325
Dielectric strength, step by step, v./mil.	2	.....	275–375	200–300	150–300	150–300	150–300	150–275
Volume resistivity, ohm-cm.	3	5–12 × 10^{11}	0.01–10 × 10^{11}	0.01–10 × 10^{11}	0.01–10 × 10^{11}	0.01–10 × 10^{11}	0.01–10 × 10^{11}	1–10 × 10^{11}
Dielectric constant, 60 cycles	5	5.0–6.5	5.5–7.0	6.0–9.0	6.0–9.0	6.0–9.0	6.5–10.0	7.0–10.0
Power factor, 60 cycles	6	0.06–0.10	0.03–0.12	0.08–0.20	0.08–0.25	0.08–0.25	0.08–0 25	0.10–0.25
Loss factor, 60 cycles	7	0.30–0.65	0.16–0.84	0.48–1.4	0.48–2.25	0.48–2.25	0.52–2.5	0.70–2.60
Dielectric constant, 1000 cycles	8	4.5–6.0	4.8–6.0	5.5–7.5	5.5–8.0	5.5–8.0	5.5–8.0	5.5–8.0
Power factor, 1000 cycles	9	0.03–0.08	0.03–0.06	0.04–0.08	0.04–0.10	0.04–0.10	0.04–0.10	0.04–0.10
Loss factor, 1000 cycles	10	0.14–0.48	0.14–0.36	0.22–0.60	0.22–0.80	0.22–0.80	0.22–0.80	0.22–0.80
Dielectric constant, 1,000,000 cycles	11	4.5–5.0	4.5–5.5	4.5–6.0	4.5–6.0	4.5–6.0	4.5–6.0	5.0–6.0
Power factor, 1,000,000 cycles	12	0.015–0.03	0.03–0.05	0.03–0.06	0.03–0.06	0.03–0.06	0.03–0.06	0.04–0.06
Loss factor, 1,000,000 cycles	13	0.07–0.15	0.13–0.28	0.14–0.36	0.14–0.36	0.14–0.36	0.14–0.36	0.20–0.36

TABLE LVIII (*Continued*)

PHENOL–FORMALDEHYDE AND FURFURALDEHYDE–PHENOL MOLDING MATERIAL

(A.S.T.M. TEST METHOD D48–43T)

Property	Test No.	Cord-filled	Mineral-filled				Flock-filled	Excellent chemical resistance
		Very high shock resistance	Shock and heat resistance	Heat resistance	High frequency insulation	Superior high frequency insulation	Arc resistance, semi-flexibility	
Dielectric strength, short time, v./mil.	1	200–275	200–275	300–350	325–450	350–500	350–450	225–275
Dielectric strength, step by step, v./mil.	2	150–250	150–225	200–350	275–375	300–400	300–400	175–225
Volume resistivity, ohm-cm.	3	$1–10 \times 10^{11}$	$0.01–10 \times 10^{11}$	$1–10 \times 10^{11}$	$1–10 \times 10^{12}$	$10^{11}–10^{14}$	$1–8 \times 10^{13}$	$0.5–1 \times 100^{11}$
Dielectric constant, 60 cycles	5	7.0–10.0	40.0–50.0	12.0–15.0	5.4–6.0	5.0–5.5	4.5–5.0	10.0–15.0
Power factor, 60 cycles	6	0.10–0.30	0.35–0.42	0.15–0.35	0.02–0.06	0.010–0.025	0.02–0.05	0.15–0.25
Loss factor, 60 cycles	7	0.70–3.1	14.8–23.0	1.8–5.6	0.11–0.36	0.05–0.11	0.09–0.25	1.5–3.75
Dielectric constant, 1000 cycles	8	6.0–9.0	20.0–30.0	8.0–12.0	5.0–5.5	4.5–5.0	4.5–4.9	9.0–12.0
Power factor, 1000 cycles	9	0.05–0.12	0.30–0.40	0.10–0.25	0.02–0.04	0.007–0.015	0.02–0.03	0.14–0.20
Loss factor, 1000 cycles	10	0.30–1.0	6.2–13.1	0.80–3.1	0.10–0.22	0.03–0.08	0.09–0.15	1.27–2.45
Dielectric constant, 1,000,000 cycles	11	5.0–6.0	5.7–8.0	5.5–7.0	4.5–5.2	4.5–5.0	4.0–4.3	5.5–7.0
Power factor, 1,000,000 cycles	12	0.04–0.06	0.12–0.20	0.05–0.10	0.01–0.03	0.005–0.009	0.03–0.04	0.04–0.085
Loss factor, 1,000,000 cycles	13	0.20–0.36	0.68–1.3	0.28–0.70	0.05–0.16	0.02–0.04	0.12–0.17	0.22–0.60

TABLE LIX

THE DIELECTRIC STRENGTH OF LAMINATED PHENOPLASTS[a]

Thickness, in.	Paper-base, Grade X Paper-base, Grade XX				Paper-base, Grade P Paper-base, Grade XXP				Paper-base, Grade XXX				Paper-base, Grade XXXP				Fabric-base, Grade C[b]			
	minimum standard		average value		minimum standard		average value		minimum standard		average value		minimum standard		average value		minimum standard		average value	
	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S
0.015 to 1/32	700	450	950	700	700	450	950	700	700	450	900	650	700	450	900	650	None	None	...	...
Over 1/32 to 1/16	500	300	700	500	500	300	700	500	500	300	650	450	500	300	650	450	None	None	200	120
Over 1/16 to 1/8	360	220	500	360	360	220	500	360	360	220	470	320	360	220	470	320	None	None	150	90
Over 1/8 to 1/4	250	150	360	250	250	150	360	250	250	150	340	225	250	150	340	225	None	None	100	60
Over 1/4 to 1/2	180	110	250	180	...	...	...	...	180	110	240	165	...	...	...	...	None	None	75	45
Over 1/2 to 3/4	145	90	205	145	...	...	...	...	145	90	200	135	...	...	...	...	None	None	60	35
Over 3/4 to 1	130	80	180	130	...	...	...	...	130	80	175	115	...	...	...	...	None	None	50	30
Over 1 to 2	90	55	130	90	...	...	...	...	90	55	120	85	...	...	...	...	None	None	35	20

Thickness, in.	Fabric-base, Grade CE				Fine weave fabric-base, Grade L[b]				Fine weave fabric-base, Grade LE				Asbestos paper-base, Grade A[b]				Asbestos fabric-base, Grade AA[b]			
	minimum standard		average value		minimum standard		average value		minimum standard		average value		minimum standard		average value		minimum standard		average value	
	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S	ST	S/S
0.015 to 1/32	...	...	...	...	None	None	250	150	560	350	700	450	...	...	...	...	...	...	...	...
Over 1/32 to 1/16	400	240	500	300	None	None	200	120	400	240	500	300	None	None	225	135	None	None	None	None
Over 1/16 to 1/8	240	170	360	220	None	None	150	90	240	170	360	220	None	None	160	95	None	None	50	30
Over 1/8 to 1/4	200	120	250	150	None	None	100	60	200	120	250	150	None	None	110	65	None	None	35	20
Over 1/4 to 1/2	145	85	180	110	None	None	75	45	145	85	80	110	None	None	80	50	None	None	25	15
Over 1/2 to 3/4	120	70	145	90	None	None	60	35	120	70	145	90	None	None	65	40	None	None	20	12
Over 3/4 to 1	105	60	130	80	None	None	50	30	105	60	130	80	None	None	55	35	None	None	18	10
Over 1 to 2	75	40	90	55	None	None	35	20	75	40	90	55	None	None	40	25	None	None	13	8

[a] This table gives the dielectric strength in volts per mil in oil at approximately 25°C. for varying thicknesses of laminates. The thickness is given in inches. The abbreviations, ST and S/S, indicate short time and step-by-step methods of A.S.T.M. D-149

[b] Grades C, L, A, and AA are primarily mechanical grades and are not held to minimum electrical properties.

TABLE LX

ELECTRICAL CHARACTERISTICS OF LAMINATED PHENOPLASTS AT 10^6 CYCLES

(DATA DETERMINED BY A.S.T.M. METHOD D–150)

Grade	Range	Dielectric constant	Power factor	Loss factor
Paper base, Grade X	....	...	...	...
Paper base, Grade P	....	...	...	...
Paper base, Grade XX[a]	Min. or max.	5.5	0.045	0.25
	Average	5.0	0.040	0.20
Paper base, Grade XXP[b]	Min. or max.	5.5	0.045	0.25
	Average	5.0	0.040	0.20
Paper base, Grade XXX[a]	Min. or max.	5.2	0.035	0.18
	Average	4.8	0.032	0.15
Paper base, Grade XXXP[b]	Min. or max.	5.2	0.030	0.16
	Average	4.5	0.027	0.12
Fabric base, Grade C[a]	Min. or max.	None	None	None
	Average	7.0	0.10	0.70
Fabric base, Grade CE[a]	Min. or max.	6.0	0.065	0.40
	Average	5.5	0.055	0.30
Fine weave fabric base, Grade L[a]	Min. or max.	None	None	None
	Average	7.0	0.10	0.70
Fine weave fabric base, Grade LE[a]	Min. or max.	5.5	0.055	0.30
	Average	5.0	0.045	0.22
Asbestos paper base, Grade A	....	...	...	...
Asbestos fabric base, Grade AA	....	...	...	...

[a] Data hold for all thicknesses up to 1 inch.
[b] Data hold for all thicknesses.

tent, give the lowest power factor and dielectric constant under high frequencies. A high resin content (50 to 60%) protects the fibers of the laminate, and, by reduction of the moisture absorption, improves the electrical properties under wet or humid conditions. In general, the higher the resin content, the better is the resistance to water and hence the better are the electrical properties not only when dry, but particularly in humid or wet environment. As the resin content is increased to obtain lower power factor and dielectric constant, the impact strength becomes somewhat lower.

D. EFFECT OF HEATING ON ELECTRICAL PROPERTIES

Hausmann, Parkinson, and Mains[11] studied the effect of heat on the electrical properties of laminates; the samples were kept at an elevated temperature for as long as seven days. The work was done on $^1/_{16}$ inch thick panels of Grade XX laminate, and temperatures of 75°, 100°, and

[11] E. O. Hausmann, A. E. Parkinson, and C. H. Mains, *Modern Plastics*, **22**, 151–154, 190–198 (Nov., 1944).

150°C. were reached. Tests were made after cooling the specimens down to 25°C. The dielectric strength increased, while the power factor, dielectric constant, and loss factor decreased. It is probable that this improvement was due to further curing of the resin, accompanied by the elimination of water and small quantities of other volatile polar substances. Table LXI is reproduced from the reference cited, and shows the detail of the results.

TABLE LXI

EFFECT OF HEAT ON THE ELECTRICAL PROPERTIES OF GRADE XX PHENOPLAST LAMINATE

Period of exposure prior to test, days	Exposure temperature, °C.	Short time dielectric strength, v./mil.	Power factor at 10^6 cycles	Dielectric constant at 10^6 cycles	Loss factor at 10^6 cycles
0	...	887	0.0324	5.34	0.173
1	75	927	0.0294	4.95	0.145
2	75	898	0.0284	4.95	0.141
3	75	904	0.0251	4.87	0.123
4	75	932	0.0288	4.76	0.137
5	75	932	0.0272	4.71	0.128
6	75	965	0.0260	4.74	0.123
7	75	948	0.0262	4.65	0.122
0	...	887	0.0324	5.34	0.173
1	100	919	0.0302	4.88	0.148
2	100	946	0.0254	4.64	0.118
3	100	943	0.0216	4.56	0.0989
4	100	937	0.0253	4.50	0.114
5	100	950	0.0241	4.45	0.109
6	100	955	0.0244	4.55	0.110
7	100	951	0.0227	4.39	0.100
0	...	887	0.0324	5.34	0.173
1	150	936	0.0245	4.61	0.113
2	150	956	0.0237	4.54	0.107
3	150	944	0.0232	4.47	0.102
4	150	942	0.0239	4.54	0.108
5	150	961	0.0244	4.56	0.111
6	150	917	0.0241	4.57	0.111
7	150	901	0.0246	4.64	0.114

The insulation resistance drops rapidly as the temperature rises; in the case of most phenoplasts, the resistance at 120°C. is only about 0.1% of the value at 30°C.[12] The insulation resistance may be improved by either preheating the molding compound before molding, or by afterbaking the molded part.

The A.S.T.M. publication[9] gives the following incomplete data (Table

[12] T Hazen, *Elec. Eng.*, **62**, 191–197 (1943).

LXII) for electrical properties of general-purpose cellulose-filled and superior high frequency insulation (mineral-filled) phenoplasts at 180°F. All measurements were made at 60 cycles.

TABLE LXII

ELECTRICAL PROPERTIES OF MOLDED PHENOPLASTS AT 180°F.

Type	Dielectric strength, short time, v./mil.	Dielectric constant	Power factor at 60 cycles	Loss factor
General-purpose, cellulose-filled	250–300	7.0–9.0	0.35	2.8
Superior high frequency insulation, mica-filled	500–550	6.0	0.025	0.15

XI. THERMAL PROPERTIES OF PHENOPLASTS

A. INTRODUCTION

By the thermal properties of the phenoplasts are meant the coefficient of expansion, the heat conductivity, and the specific heat of the various types. There is relatively little information on these points in the literature. The data in Table LXIII are taken from the tables published by the Plastics Materials Manufacturers Association[1] and cover molding

TABLE LXIII

THERMAL PROPERTIES OF PHENOPLAST MOLDING MATERIALS

Type	Linear coefficient of expansion per °C.	Thermal conductivity, cal./cm²/sec./°C./cm.	Specific heat, cal./g.
Transparent, no filler	.....	.....	0.38–0.42
General-purpose, cellulose-filled	$3.0–3.5 \times 10^{-5}$	4.7×10^{-4}	0.35–0.40
Low shock resistance, cellulose-filled	$3.0–4.4 \times 10^{-5}$	4.7×10^{-4}	...
Low to intermediate shock resistance, flock-filled	$3\ 3 \times 10^{-5}$	....	...
Intermediate shock resistance, fabric-filled	Up to 2.93×10^{-5}	....	...
Intermediate to high shock resistance, fabric-filled	.....	....	...
High shock resistance, fabric-filled	$1.0–2.0 \times 10^{-5}$	4.7×10^{-4}	...
Very high shock resistance, cord-filled	.....	....	...
Shock and heat resistance, mineral-filled	$1.5–2.0 \times 10^{-5}$	$8–16 \times 10^{-4}$	0.28–0.32
Heat resistance, mineral-filled	2.12×10^{-5}	$8–16 \times 10^{-4}$	0.28–0.32
High frequency insulation, mineral-filled	.....	$10–14 \times 10^{-4}$	0.28–0.32
Superior high frequency insulation, mineral-filled	1.9×10^{-5}	$10–14 \times 10^{-4}$	0.28–0.32
Arc resistance, semiflexible, mineral-filled	$4.0–5.0 \times 10^{-5}$	....	0.38–0.42
Excellent chemical resistance	4.3×10^{-5}	....	...

[1] Plastics Materials Manufacturers Assn., publication of May, 1943.

materials only. The thermal conductivity was determined by A.S.T.M. method D325–31T. It should be noted that the coefficient of linear expansion is quite low, and consequently changes in dimension produced by simple expansion or contraction with heat or cold may be overshadowed by changes resulting from gain or loss in moisture.

B. COEFFICIENT OF EXPANSION

The coefficient of expansion of the phenoplasts is, in general, somewhat higher than that of metals. A recent publication[1a] has listed the following data for the thermal expansion of metals and phenoplasts, in the range from 30° to 60°C. It will be noted that the method of classification and the data given for thermal expansion of the various phenoplasts differ slightly from that in Table LXIII.

Material	Linear coefficient of thermal expansion per °C. ($\times 10^{-6}$)
Phenoplasts:	
General-purpose	39
Medium impact	38
Medium impact, CFI-5	33
High impact, CFI-10	29
High impact, CFI-20	22
Medium heat resistance	34
High heat resistance	26
Electrical general-purpose	35
Low loss	19
Arc resistance	49
Metals:	
Aluminum 2S, 99.2% Al	23.94
Copper, 99.9+	17.71
Phosphor bronze 30, 95.5 Cu, 4 Sn, 1 Zn	18.90
Phosphor bronze	16.8
Brass, ordinary, 67 Cu, 33 Zn	18.5
Bronze, commercial, 90 Cu, 10 Zn	18.8
Steel, 99 Fe, 1 C	12.
Stainless steel, 90-2 Fe + 8 Cr, 0.4 Mn, 0.12 C	11.
Nickel	12.9
Monel, 60 Ni, 12 Fe, 11 Cr, 2 Mn	14.
Silver, standard, 92.5 Ag, 7.5 Cu	18.
Zinc, 95 Zn, 5 Al	28.

For this reason, attempts to use metals such as steel wire in the reinforcement of phenoplast structures have not been successful. In large moldings under wide temperature variations, the stresses which result

[1a] *Design Standards for Inserts—Their Application in Plastics Parts.* The Society of the Plastics Industry, Inc., Jan., 1946.

from the difference in dimensional change between the metal and the plastic tend to tear loose the reinforcement.

The difference between the coefficient of expansion of the phenoplasts and metals must also be considered when metal inserts are used in molded articles. Phenoplasts are ordinarily molded at about 160°C., and when the ejected moldings are cooled to room temperature, the piece will shrink from 0.003 to 0.012 inch per inch. A metal insert made of brass will shrink only 0.002 inch per inch. If the part is again heated, there is similar difference in the expansion which takes place. This difference in thermal behavior sets up considerable stress in the neighborhood of the insert, and cracking may occur if the stresses set up are excessive. If the mold and insert are designed so that excessive stresses are avoided, the elasticity of the phenoplast can compensate for the strain imposed. Shepard and Sontag[2] have dealt with this aspect of the problem and they state that field experience has shown that certain grades of molding compounds with improved elastic properties have remedied a number of obstinate cases of cracking around inserts. The improved elasticity has been obtained by modification of the phenoplast resin.

Erickson and Mackin[3] have reported that the coefficients of linear thermal expansion of a high strength paper laminate from Mitscherlich spruce pulp (Papreg) were greater in the direction of compression perpendicular to the laminations than in the plane of the lamination. The test specimens, prior to test, were heated for 24 hours at 105°C., and then stored in a desiccator over phosphoric anhydride. The linear coefficients for laminates in which the grain of the paper was all parallel were, in the range between −50° and +50°C., in centimeters per centimeter per degree Centigrade:

5.73×10^{-6} in the plane of the laminations, lengthwise
15.14×10^{-6} in the plane of the laminations, crosswise
65.10×10^{-6} perpendicular to the plane of the laminations, flatwise

Cross-laminated paper gave the following coefficients:

10.89×10^{-6} in plane of laminations parallel to the fiber direction of half of laminations
62.20×10^{-6} perpendicular to the plane of the laminations, flatwise, between +52.3° and −25.2°C.

The authors point out that the linear coefficient of thermal expansion in the plane of the laminations for the cross laminated material lies mid-

[2] A. F. Shepard and L. A. Sontag, *Modern Plastics*, **17**, 48, 78, 80 (Feb., 1940).

[3] E. O. Erickson and G. E. Mackin, *Trans. Am. Soc. Mech. Eng.*, **67**, 267–277 (May, 1945).

way between that of the lengthwise and crosswise linear coefficients of parallel laminated Papreg, in the same manner as the tensile and flexural properties do.

Vieweg and Schneider[4] studied the linear coefficients of expansion of several types of German laminates, and obtained the data listed in Table LXIV. They state that the coefficient in the plane of the laminations is practically the same in either the lengthwise or crosswise directions, but the coefficient perpendicular to the plane of the laminations is much greater. The coefficients of expansion were practically uniform over the entire temperature range.

TABLE LXIV

COEFFICIENTS OF EXPANSION FOR GERMAN LAMINATES

Filler	Average linear coefficient of expansion		Temperature range, °C.
	In plane of laminations	Perpendicular to plane of laminations	
Fine textile fabric	45×10^6	70×10^6	30–120
Coarse textile fabric	50	67	30–120
Paper (sheet)	25	140	40–120
Paper (rod)	25	200	50–100

Norelli and Gard[5] have studied the coefficient of thermal expansion of a paper-filled laminate. They state that a change in the coefficient takes place at approximately 60°C., and appears to indicate a second-order transition point. The temperature at which this transition occurs lies within the range where a critical variation in the physical properties of the laminate was noted. However, the authors point out that the phenomenon will have to be studied more thoroughly before any general conclusions can be drawn.

Wiley[6] studied the volume expansion of phenoplasts among other plastics, and found transition temperatures in the neighborhood of 45–75°C. for both wood flour-filled, molded phenoplasts and cast phenoplasts.

C. FLAME RESISTANCE

Gale, Stewart, and Alfers[7] have studied the flame resistance of a number of molded and laminated phenoplasts. The test method employed

[4] R. Vieweg and W. Schneider, *Kunststoffe*, **32**, 295–297 (1942).

[5] P. Norelli and W. H. Gard, *Ind. Eng. Chem.*, **37**, 580–585 (1945).

[6] F. E. Wiley, *ibid.*, **34**, 1052–1056 (1942).

[7] J. A. Gale, R. W. Stewart, and J. B. Alfers, *Am. Soc. Testing Materials Bull.*, **131**, 23–27 (Dec., 1944).

was developed by the Material Laboratory of the U. S. Navy Yard in New York and consisted of exposure of the plastics under standard conditions in the center of an electrically heated coil. In general, the mineral-filled materials were found to be least affected by exposure to test conditions. They retained some semblance of mechanical strength after burning and resisted the effect of flame to a greater extent than did the cellulose-filled materials. All the cellulosic type specimens either carbonized completely or continued to smolder after being tested. Mechanical strength was nil in both instances. Melamine resin-filled plastics, tested at the same time as the phenoplasts, showed better flame-resistant characteristics.

Table LXV gives pertinent data on the flame resistance of the various plastics studied by Gale, Stewart, and Alfers.

TABLE LXV

FLAME RESISTANCE OF PHENOPLASTS

Classification	Characteristics after burning	Time required for ignition sec.	Time required to burn, sec.	Temperature required for ignition, °C.
A. MOLDED PLASTICS				
U. S. Navy[a]				
CFG	Carbonized, brittle	86–107	260–315	340–385
CFI-5	Smoldered	128	282	420
CFI-10	Smoldered	150	262	450
CFI-20	Smoldered	74–142	259–303	310–440
CFI-40	Carbonized, brittle	121	257	410
MFE	Surface charring	120–153	213–244	410–455
MFG	Surface charring	315	52	600+
MFI	Surface charring	177	214	490
B. LAMINATED PLASTICS				
NEMA				
Grade XXX	Carbonized, brittle	108	437	385
X	Carbonized, brittle	99	427	370
LE	Carbonized, brittle	121	356	410
CE	Carbonized, brittle	120–150	260–406	410–450
C	Smoldered	88	388	350
AA	Surface charring	175	199	485
Glass fabric-base	Surface charring	222	140	540

[a] See Chapter VIII.

XII. CHEMICAL RESISTANCE OF PHENOPLASTS

A. INTRODUCTION

Phenoplast resins are relatively resistant to the action of most chemical reagents. At room temperature, or below, the unfilled resin of the molding powder type is almost unaffected by most of the common reagents except strong alkaline solutions. At higher temperatures, the effects of reagents are more pronounced. The resin is decomposed by hot dilute alkalis, converted to picric acid and other oxidation products by nitric acid, and dissolved at very high temperatures by some organic chemicals such as naphthols. Filled resins may be more sensitive to the action of reagents, depending upon the nature of the filler which is used. For example, resins containing cellulosic fillers are affected by reagents which tend to destroy the filler, such as sulfuric acid. The degree of this effect is dependent upon the ratio of filler to resin; when a high proportion of resin is present and when the filler is well covered by a resin film, the destructive actions of reagents are minimized.

B. WATER ABSORPTION

Phenoplasts absorb water to some extent when immersed; the degree of absorption depends upon the time of immersion, the nature of the filler, the resin content, and the size of the test sample. A standard test specimen of the pure resin absorbs about 0.2% of water at room temperature, and this absorption is only slightly changed by the presence of mineral fillers. The addition of cellulosic fillers usually increases the degree of water absorption. Kline, Martin, and Crouse[1] present the data in Table LXVI for the water absorption of various phenoplasts at 25°C.

The effects of the type of filler on moisture absorption, and of resin content, are shown quantitatively in Tables LXVII and LXVIII, respectively. The data for these tables were obtained in accordance with the A.S.T.M. D48–41T procedure, and water absorption is expressed as per cent increase by weight.

[1] G. M. Kline, A. R. Martin, and W. A. Crouse, *Modern Plastics*, **18**, 119–123, 152–154 (Oct., 1940).

TABLE LXVI

MOISTURE ABSORPTION BY PHENOPLASTS AT 25°C.

Type of phenoplast	Gain during immersion in water, %			
	24 hrs.	48 hrs.	7 days	8 weeks
Molded, wood flour-filled	0.25	0.40	0.91	4.69
Cast	0.16	0.25	0.54	1.87
Laminated, paper-base	0.44	0.84	2.24	6.38

TABLE LXVII

EFFECT OF THE TYPE OF FILLER ON WATER ABSORPTION OF PHENOPLASTS

Type of filler	Filler, %	Resin, %	Water absorption after		
			24 hrs. at 25°C.	48 hrs. at 25°C.	48 hrs at 50°C.
Wood flour	50	50	0.50	..	1.75
Wood flour (15%) mixed with cotton flock (30%)	45 (total)	55	0.60	1.10	2.25
Cotton flock	45	55	0.70	1.25	2.75
Wood flour (19%) mixed with asbestos (41%)	60 (total)	40	0.20	..	..
Asbestos	60	40	0.08	..	..
Mica	60	40	0.03	..	0.07
Chopped fabric	50	50	0.55	..	3.00
Cotton cord	50	50	1.10	..	3.75

TABLE LXVIII

EFFECT OF RESIN CONTENT ON WATER ABSORPTION OF WOOD FLOUR-FILLED PHENOPLASTS

Wood flour, %	Resin, %	Water absorption after		
		24 hrs. at 25°C.	1 month at 25°C.	6 months at 25°C.
50	50	0.55%	4.0%	10 – 15%
40	60	0.51	...	...
10	90	0.15	0.7	2.0

Wakeman[2] studied the gain in weight and the dimensional changes which took place after long immersion in boiling water. Table LXIX is taken from these data.

Busch[3] made a thorough study of the effect of high humidity over a long period of time on wood flour-filled phenoplasts. In order to simulate tropical atmospheres, the molded specimens were held for four months at 42°C.

[2] R. L. Wakeman, *Modern Plastics*, **18**, 65–68, 86 (July, 1941).

[3] J. Busch, *Kunststoffe*, **33**, 265–267 (1943).

and 90 to 95% relative humidity. The moisture take-up varied, depending upon the exact resin content and the pressing conditions, from 1.6 to 6.5%; the dimensional change varied from about 1 to 5% in the direction of pressing and from 0.7 to 3% perpendicular to the direction of pressing. Both

TABLE LXIX

WEIGHT INCREASE OF PHENOPLASTS AFTER IMMERSION IN BOILING WATER

Type of phenoplast	Per cent increase in weight after	
	4 days	2 years
Molded samples		
Pure resin, no filler, mold polished surface	1.97	4.79
Chopped fabric-filled	4.19	3.54
Mica-filled	1.34	1.71
Laminates		
Fabric-base, Grade C	6.15	3.94
Fabric-base, Grade L	5.28	3.43
Paper-base, Grade XX	6.38	4.22

flexural and impact strength decreased as the moisture take-up increased; the decrease after four months varied from 10 to 40%. There was very little difference in the behavior of samples containing from 40 to 50% of resin; there was also little difference in the behavior of wood flour from either soft or hard woods.

C. EFFECT OF REAGENTS

A laboratory study of the effects of various reagents on molded (wood flour-filled) phenolic, cast resin, and a paper base laminate has been made by Kline, Rinker, and Meindl.[4] In the case of the paper base laminate, specimens 1 in. × 3 in. were cut from sheet material approximately $^1/_8$ in. thick. The molded specimens used were disks 2 in. in diameter by $^1/_8$ in. thick. The specimens were immersed for 60 days in 60 ml. of reagent, according to the method specified by A.S.T.M. D–543. Table LXX lists the changes in weight, length, and thickness which were measured immediately after removal from the reagent. The specimens were then allowed to condition for four weeks at 25°C. and 50% relative humidity, and were again measured. In many cases negative values were observed, which were attributed to removal of a portion of the plastic composition by the chemical reagent. The data obtained after conditioning are shown in Table LXXI.

[4] G. M. Kline, R. C. Rinker, and H. F. Meindl, *Am. Soc. Testing Materials*, **41**, 1246–1257 (1941).

TABLE LXX

PER CENT CHANGE IN WEIGHT AND DIMENSIONS OF PHENOPLASTS IMMERSED FOR SEVEN DAYS IN CHEMICAL REAGENTS AT 25°C.

Reagent used	Per cent change								
	In weight			In length ±0.03%			In thickness ±0.08%		
	Laminate	Cast	Molded	Laminate	Cast	Molded[a]	Laminate	Cast	Molded
30% Sulfuric acid	1.9	0.1	0.5	0.05	0.03	0.00	1.6	−0.08	1.5
3% Sulfuric acid	1.6	0.5	2.1	0.15	0.10	0.07	1.6	0.08	3.0
10% Nitric acid	6.2	0.4	1.7	0.05	0.00	0.07	6.4	0.0	4.6
10% Hydrochloric acid	4.8	0.3	1.4	0.40	0.07	0.02	6.3	−0.08	2.7
5% Acetic acid	1.0	0.6	1.8	0.20	0.10	0.05	1.6	0.0	2.2
Oleic acid	0.2	0.1	0.2	0.00	0.03	−0.02	0.0	0.0	0.4
10% Sodium hydroxide	43	[b]	92	3.8	[c]	0.73	57	[c]	110
1% Sodium hydroxide	1.3	6.4	5.0	0.15	0.42	0.08	1.6	14.0	8.4
10% Ammonium hydroxide	1.0	4.7	2.6	−0.05	0.23	0.07	1.6	4.7	4.4
2% Sodium carbonate	1.4	0.6	2.0	0.20	0.00	0.10	0.8	0.0	3.8
10% Sodium chloride	0.5	0.4	1.4	−0.25	0.07	0.04	0.0	0.8	1.9
10% Hydrogen peroxide	1.3	1.0	2.5	−0.25	0.07	0.07	1.6	0.8	1.5
Distilled water	0.8	0.5	2.2	0.40	0.09	0.08	0.8	0.0	2.5
50% Ethyl alcohol	0.6	1.5	0.9	0.15	0.10	0.07	1.6	1.6	1.4
95% Ethyl alcohol	−0.5	0.04	0.03	0.20	0.20	0.00	0.8	−0.4	2.3
Acetone	−0.2	0.6	13.0	0.00	0.11	0.18	0.8	4.2	4.3
Ethyl acetate	−0.1	−0.3	0.4	0.00	−0.03	0.02	−1.6	0.0	0.8
Ethylene dichloride	−0.07	−0.1	−0.07	−0.25	0.02	0.02	0.8	−0.04	0.4
Carbon tetrachloride	0.00	0.01	0.03	0.00	0.04	0.01	0.8	0.0	0.4
Toluene	0.2	−0.02	0.04	0.05	−0.03	0.02	−0.8	0.0	1.0
Gasoline	0.07	−0.04	−0.01	0.00	−0.07	0.03	1.6	0.8	0.0

[a] For these specimens, the value in the column is the change in diameter.
[b] Dissolved.
[c] Action of the reagent made measurements of dimensional changes impractical or impossible.

Riley[5] has studied, in similar manner, the effect of reagents on a commercial C grade laminate, containing a 10-ounce canvas duck filler and approximately 50% of resin. Specimens measuring $^1/_4 \times 1 \times 3$ in. for all tests were cut from a single large sheet, so that all results were comparable. Tests

[5] H. E. Riley, *Ind. Eng. Chem.*, **28**, 919–922 (1936).

TABLE LXXI

PER CENT CHANGE IN WEIGHT AND DIMENSIONS OF PHENOPLASTS AFTER IMMERSION FOR SEVEN DAYS IN CHEMICAL REAGENTS AT 25°C. AND SUBSEQUENT EXPOSURE TO AIR AT 25°C. AND 50% R.H. FOR FOUR WEEKS

Reagent used	Per cent change								
	In weight			In length ±0.03%			In thickness ±0.08%		
	Laminated	Cast	Molded	Laminated	Cast	Molded[a]	Laminated	Cast	Molded
30% Sulfuric acid	1.2	0.0	0.2	0.0	0.1	0.0	0.8	0.8	0.0
3% Sulfuric acid	0.7	0.1	0.5	0.1	0.0	0.0	1.6	0.0	0.0
10% Nitric acid	2.6	0.2	0.8	−0.2	−0.1	0.0	4.0	0.4	2.3
10% Hydrochloric acid	1.8	0.1	0.5	−0.1	0.0	0.0	3.9	0.0	0.0
5% Acetic acid	0.3	0.1	0.6	0.1	0.0	0.0	0.0	−0.8	0.4
Oleic acid	0.4	0.1	0.2	0.0	0.0	0.0	0.0	0.0[b]	0.0
10% Sodium hydroxide	16.0	[b]	30.0	1.9	[b]	−0.8	30	[b]	53
1% Sodium hydroxide	0.7	−2.5	0.9	0.0	0.0	0.0	0.0	2.7	1.9
10% Ammonium hydroxide	0.0	1.2	0.6	0.0	0.1	0.0	0.0	0.8	0.0
2% Sodium carbonate	0.7	0.1[c]	0.5	0.2	0.0[c]	0.0	−0.8	0.0[c]	0.0
10% Sodium chloride	0.3	0.1	0.5	0.1	0.0	0.0	0.0	−0.8	0.4
3% Hydrogen peroxide	0.6	0.3[c]	0.5	−0.1	0.0[c]	0.0	0.8	0.8[c]	0.0
Distilled water	0.4[c]	0.2	0.6	0.3[c]	0.0	0.0	0.0[c]	−0.4	0.8
50% Ethyl alcohol	−0.2	−0.01	0.3	0.0	−0.1	0.0	0.8	0.0	0.7
95% Ethyl alcohol	0.1	−0.1	0.1	0.1	0.0	0.0	0.0	−0.4	0.0
Acetone	0.0	0.0	4.3	−0.1	0.0	0.0	0.8	1.2	8.6
Ethyl acetate	0.1	0.1	0.4	0.1	0.0	0.0	−1.6	0.0	0.4
Ethylene dichloride	0.0	−0.0	0.0	−0.1	0.0	0.0	0.0	0.0	0.4
Carbon tetrachloride	−0.2	0.1	0.2	−0.3	0.0	0.0	0.8	−0.4	0.3
Toluene	−0.1	−0.1	0.2	−0.1	0.1	0.0	0.0	0.0	0.4
Gasoline	0.0	0.0	0.1	0.1	0.0	0.0	0.8	0.8	0.0

[a] For these specimens, the value in the column is the change in diameter.
[b] Action of the reagent on the sample made measurements of dimensional changes impractical or impossible.
[c] Values obtained seven days after removal from the reagent.

were made both at room temperature and at 140°F. The data obtained are listed in Table LXXII. In a discussion of the results, it was pointed out that weight change may ordinarily be considered a measure of the permeability of the sample and an indication of the degree of protection of the fiber by the resin bond. The most striking feature of the data, with some exceptions, was the similarity of total weight change which (after completion of a 180 day immersion) lies generally in the range 2.5 to 4% for all concentrations of chemical solution and for normal and elevated temperatures.

TABLE LXXII

EFFECT OF IMMERSION OF CANVAS-BASE PHENOPLAST LAMINATE IN SOLUTIONS OF VARIOUS CHEMICALS

Reagent	Concentration, weight per cent	Temperature, °F.	Per cent increase after 10 days		Condition of sample at 180 days[a]
			In thickness	In weight	
Sulfuric acid	1	77	1.20	1.88	Slightly darkened and dulled.
	1	140	2.00	3.07	Dark, dull, mottled; no attack apparent but slight loss in weight
	20	77	0.39	1.05	Darkened.
	20	140	1.54	1.82	Blistered and losing wt. at 106 days; removed.
Nitric acid	1	77	1.15	1.50	Slightly pimpled.
	1	140	2.26	2.52	Surface fibers swollen.
	20	77	2.68	1.57	Pimpled and very rough at 160 days; removed.
	20	140	7.28	5.38	Surface soft and mushy at 10 days; removed.
Chromic acid	1	77	1.93	1.25	Slightly rough.
	1	140	2.69	3.07	No attack apparent.
	20	77	..	..	Surface soft, losing wt. at 1 day; removed.
	20	140	..	..	Same.
Hydrochloric acid	1	77	1.56	1.46	Dull and darkened.
	1	140	2.29	2.60	Dull and darkened, mottled, slight wt. loss.
	20	77	0.77	0.60	Blistered at 106 days; removed.
	20	140	1.92	1.36	Blistered and losing wt. after 10 days; removed.
Hydrofluoric acid	1	77	1.94	1.68	No change in 30 days; test stopped.
	20	77	1.16	1.78	Same.
Phosphoric acid	1	77	1.95	1.55	Slightly rough.
	1	140	1.50	2.59	Dark, dull, mottled; slight wt. loss.
	20	77	1.15	1.25	Slightly rough; no attack apparent, final wt. increase 4.8%.
	20	140	1.13	2.13	Dark, dull, mottled, loss of wt. after 30 days but no attack apparent. Final wt. gain 2.6%.
Acetic acid	1	77	1.57	1.43	Surface rough.
	1	140	1.50	2.65	Dark, dull, and mottled.
	20	77	1.56	1.19	Slightly rough.
	20	140	2.63	2.35	Dark, dull, and mottled.
Citric acid	1	77	1.90	1.42	Slightly rough.
	1	140	1.12	2.56	Dark and mottled.
	20	77	1.95	1.31	Slightly rough.
	20	140	1.12	2 32	Dark and mottled.
Aluminum chloride	1	77	1.97	1.48	No attack.
	1	140	1.90	2.59	Dark and mottled, no attack apparent, but slight loss in wt.
	20	77	0.41	0.67	No attack.
	20	140	1.15	1.04	Dark and mottled.
Zinc chloride	1	77	2.68	1.34	Dark and dull.
	1	140	2.21	2.24	Surface fibers slightly swollen.
	20	77	1.19	1.12	Dark and dull.
	20	140	1.53	2.25	Same.

TABLE LXXII (*Continued*)

Reagent	Concentration	Temperature, °F.	Per cent increase after 10 days		Condition of sample at 180 days[a]
			In thickness	In weight	
Ferric chloride	1	77	1.10	1.84	No attack.
	1	140	2.29	2.78	Dark and dull, mottled; slight loss in wt.
	20	77	1.55	0.96	No attack.
	20	140	1.53	1.99	Same.
Sodium hydroxide	1	77	1.58	1.89	Rough, edges showed slight erosion.
	1	140	2.27	2.92	Dark and dull.
	20	77	3.53	2.16	Swelled and blistered; 5.3% wt. increase at 30 days; 14% wt. increase at 106 days; removed.
	20	140	11.8	9.43	Rough and blistered at 10 days, greatly swollen; removed.
Potassium permanganate	0.35	77	2.53	1.82	Slightly rough.
	0.35	140	2.24	2.91	Dark coating, fibers slightly swollen.
	7.1	77	2.36	2.57	Slightly rough, dark coating; removed at 106 days because of loss of liquid from test tube.
	7.1	140	1.87	3.70	Dark coat, removed at 30 days because of loss of liquid from test tube.
Potassium bichromate	0.67	77	1.55	1.44	Dull and darkened.
	0.67	140	2.26	2.68	Dull, darkened, and mottled.
	13.5	77	1.56	1.48	Dark and mottled.
	13.5	140	2.32	2.85	Dark, mottled, and dull.
Sodium hypochlorite	(1% available chlorine)	77	1.54	1.62	Slightly rough.
		140	2.68	2.55	Slightly rough, dark, and dull.
Sodium carbonate	1	77	1.17	1.42	Dark and mottled.
	1	140	2.26	2.67	No attack.
	20	77	1.52	1.11	Dark and mottled.
	20	140	1.12	2.08	Dark, mottled, and dull.
Trisodium phosphate	0.68	77	1.58	1.61	No attack apparent.
	0.68	140	2.61	2.80	Same.
	13.7	77	1.97	1.51	Same.
	13.7	140	2.30	2.83	Same.
Sodium sulfite	1	77	1.14	1.37	Dull, dark, and mottled.
	1	140	2.00	3.16	Dull and dark.
	20	77	0.87	1.15	Dull, dark, and mottled.
	20	140	1.18	2.17	Same.
Sodium thiosulfate	1	77	1.57	1.46	Same.
	1	140	2.68	2.75	Same.
	20	77	1.19	1.27	Same.
	20	140	1.96	2.20	Same.
Salt water	...	77	1.98	1.50	Dull and dark.
	...	140	1.96	2.67	Same.
Tap water	...	77	2.30	1.41	Dull, dark, and mottled.
	...	140	2.37	2.87	Same.
Ethyl lactate	...	77	0.00	0.10	Same.
	...	140	0.79	0.70	Dull and darkened.

[a] Weight loss refers to a decrease from the maximum weight gained.

The rate of increase in weight was initially more rapid at elevated temperatures and the maximum was reached after fewer days, but the final condition of absorption was only slightly different from that obtained at normal temperatures. The rate and amount of absorption depend to some extent on the ratio of the area of cut surface to total area exposed. In general, the greater the area of cut surface to the total area, the higher was the absorption. This was due to the fact that on the cut edges the filler fibers were exposed, and those fibers which were not completely impregnated by resin tended to act as a wick. In practical use, a resistant varnish could be applied to protect the cut edges.

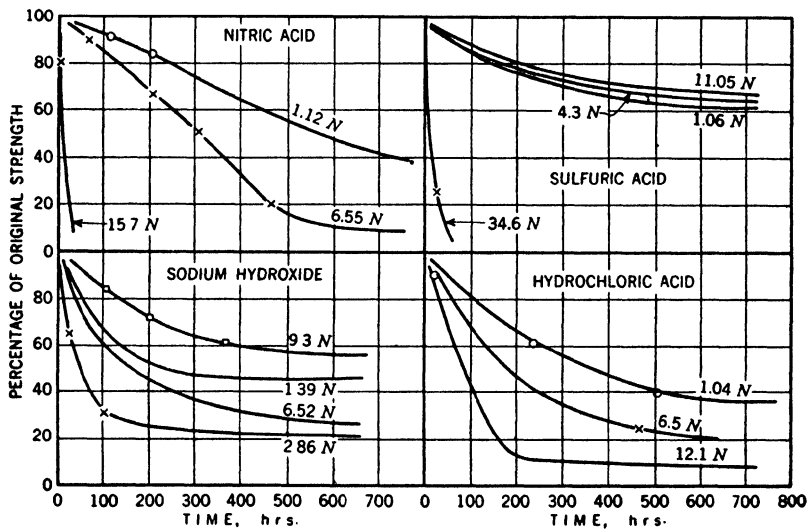


Fig. 60. Effect of various reagents on strength of paper-base phenoplast laminate.[6]

Delmonte[6] studied the chemical action of reagents on laminated phenoplasts in a different manner, in that the change in a strength property was chosen as the measure of the effect of the reagent. Two phenoplasts were studied: (*1*) laminated phenolic, paper-base, Grade XX, $^1/_{16}$ in. thick; and (*2*) laminated phenolic, glass-base, 0.055 in. thick. The change in shear strength was measured by the punch method described in Chapter VIII. Figures 60 to 62 illustrate the data obtained.

[6] J. Delmonte, *Modern Plastics*, **20**, 91–94, 146–148 (Dec., 1942).

The effect of reagents on strength properties has also been studied by Enz[7] and by Straka.[8] Figures 63 to 66 are reproduced from the latter, and

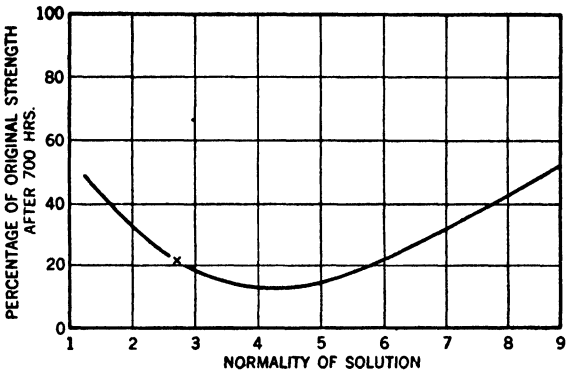


Fig. 61. Effect of strength of sodium hydroxide solution on strength of paper-base phenoplast laminate.[6]

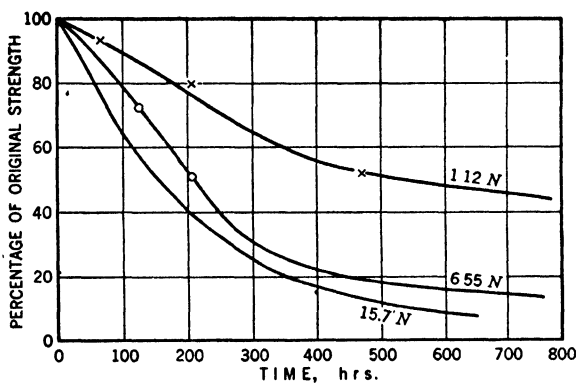


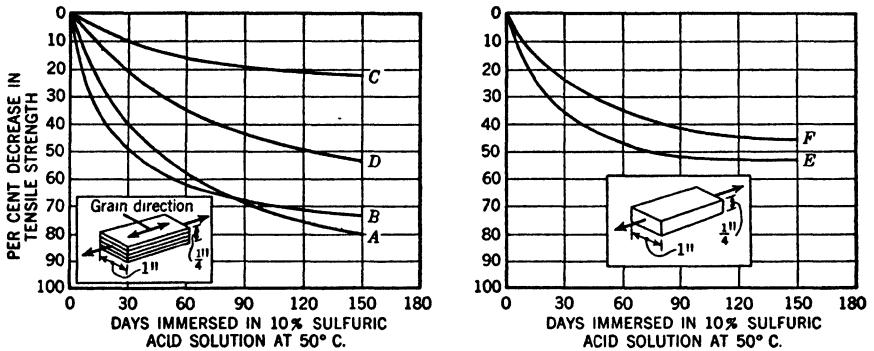
Fig. 62. Effect of nitric acid on laminated, woven glass-base phenoplast.[6]

show the effect of 10% sulfuric acid solution at 50°C. on the tensile and impact strengths of several laminates. In every case the letters shown on the figures refer to the following types of laminates: *A*, asbestos fabric, regular type of phenoplast resin; *B*, heavy cotton cloth, regular type of phenoplast resin; *C*, fine weave cotton cloth, chemically resistant phenoplast resin;

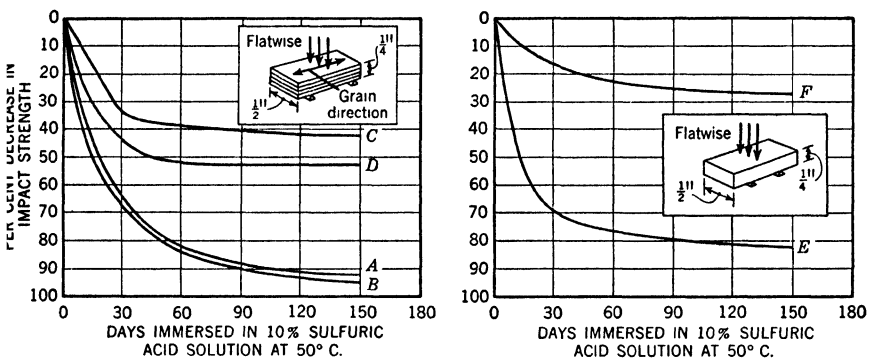
[7] V. E. Enz, *Chem. Industries*, **51**, 200–201 (1942).

[8] C. J. Straka, *Modern Plastics*, **20**, 80–84, 136–138 (July, 1943).

D, medium weave cotton cloth chemically resistant phenoplast resin; *E*, chopped laminated heavy cotton cloth, regular type of phenoplast resin;



Figs. 63 and 64. Change in tensile strength of laminates after immersion in 10% sulfuric acid.[8]



Figs. 65 and 66. Change in impact strength of laminates after immersion in 10% sulfuric acid.[8]

F, chopped laminated fine weave cotton cloth, chemically resistant phenoplast resin.

1. Chemical Applications for Phenoplasts

Because of its excellent resistance to many reagents, the phenoplasts are widely used in domestic equipment and even in chemical plant apparatus. A variety of chemical engineering uses have been described by Carswell and

Haslanger[9] and by Lombardo.[10] One of the most important applications is Haveg, the trade name of the Haveg Corporation for a phenolic-asbestos composition which finds considerable use in the chemical processing industry. Haveg is a finished material available in the form of complete units of equipment or parts molded to shape.[11,12] There are three grades of the material available: Haveg "41" contains a long-fiber asbestos filler and is resistant to almost all inorganic acids except nitric and concentrated sulfuric acids. It is not resistant to oxidizing agents, to strong bases, or to acetone and similar solvents. Haveg "43" contains a carbonaceous filler in place of asbestos and is resistant to hydrofluoric acid; its use is almost always restricted to fluorine compounds. Haveg "50" contains a special type of resin which is primarily resistant to the strong bases such as sodium and potassium hydroxides and compares favorably with Haveg "41" in its resistance to most inorganic acids. These materials are not affected by temperatures up to 265°F., and are not subject to damage caused by rapid temperature changes.

An acid-pump impeller molded of a phenolic molding composition to replace rubber-covered bronze has been used with outstanding success.[13] The use of the molded impeller has resulted in longer life of the part because of the increased chemical resistance, a 20–25% increase in efficiency because of a better finish, a 5% increase in head, and a decrease in torque because of a 50% reduction in weight. In addition, balancing of the impeller is no longer necessary because of the uniformity of the molded part. Parts for a bilge pump are molded of a phenolic plastic.[14] This light-weight pump is resistant to salt water, oil, and abrasion and is resistant to electrolytic action.

Straka[8] has reported that compressor rings of phenolic laminates are superior to cast-iron rings in ammonia equipment and in handling propane, butane, and pentane in the petroleum industry. In the electroplating industry baskets and barrels manufactured of laminates, and laminated gears, are superior to other chemical resistant materials because they possess better insulation properties and consequently the current loss is lowered. Laminated hold-down rolls are used in pickling tanks. In the paper indus-

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[9] T. S. Carswell and R. U. Haslanger, *Trans. Am. Inst. Chem. Engrs.*, **39**, 755–767 (1943).

[10] G. Lombardo, *Plastics (London)*, **7**, No. 76, 391–399 (1943).

[11] D. H. Killeffer, *Ind. Eng. Chem.*, **25**, 1217–1219 (1933).

[12] W. H. Adams, Jr., *Modern Plastics*, **18**, 53–57, 80–82 (Dec., 1940).

[13] Anon., *ibid.*, **18**, 51 (Aug., 1941).

[14] Anon., *ibid.*, **17**, 39, 92 (July, 1940).

try, white-water suction boxes, doctor blades, and similar equipment are made of laminates because of their resistance to weak acid and alkaline white water.

Considerable technical information is available on the use of phenolic laminates or high strength moldings for bearings.[15-23] Where slow movements, high pressures, and corrosive conditions are involved, as in steel-rolling mills and marine installations, laminated bearings are not affected by salt water, solvents, oil, and stream pollution. They have a low coefficient of friction; and as a result they wear longer than bronze bearings. They possess high shock resistance, no grain as in wood, and only half the weight of aluminum. Performance is equivalent to that of lignum vitae and bronze and the life is longer. Bearings for screw conveyors operate under high working temperatures, critical friction at low velocities, and are subjected to serious soiling of the lubricant. Phenolic laminated bearings operated satisfactorily for this duty and gave a remarkable reduction in wear over bronze and cast iron. In other heavy-duty applications, bearings of this type have performed so well that nonferrous bearings of other types will not be used again, according to Arens.[15] The bronze bearings in a citrus fruit press were replaced with a laminated bearing because of increased resistance to the fruit juices which lubricate the bearings.

Soot and gaseous products resulting from coal combustion create a serious corrosion problem in ventilating equipment construction. Pulleys of nonferrous metals and alloys, mild steel protected by metal coats and by paint, cast iron, stainless steel, and a molded fabric-filled phenolic plastic were exposed in the ventilating shaft of a steam-operated railway tunnel. After three and one-fourth years the molded phenolic pulley was the only specimen unaffected.[24]

Laminated plastic pipes and valves have been used to advantage in many applications. Enz[7] has reported that some laminated pipes handling 5 to 15% acid at 75 lb. pressure have outlasted all other products tried; in some cases where bronze was previously used they have had a life three times that

[15] J. Arens, *Kunststoffe*, **32**, 237 (1942).
[16] J. Arens, *Stahl u. Eisen*, **59**, 213 (1939).
[17] F. Bechtold, *Brit. Plastics*, **14**, No. 168, 640 (1943).
[18] D. W. Browne, *Plastics (London)*, **6**, No. 65, 333 (1942).
[19] E. Gilbert and K. Laurenbaum, *Z. Ver. deut. Ing.*, **86**, No. 9/10, 139 (1942).
[20] H. C. Irvin, *Modern Plastics*, **19**, 33–34, 120 (April, 1942).
[21] K. T. MacGill, *ibid.*, **20**, 76, 112–114 (Nov., 1942).
[22] Anon., *Chem. Revs.*, **1**, No. 3, 6 (1943).
[23] O. Eilbensteiner, *Fertigungstech.*, 31–33 (1943); see *C. A.*, **38**, 6005.
[24] S. C. Britton, *Brit. Plastics*, **12**, No. 144, 380 (1941).

of the bronze. In the paper industry valves and pipes of phenolic laminates are being used to work with wet chlorine. Laminated pipes handling kaolin clay in a filter press where the *p*H is 4–5 outlast silicon bronze by 300%. Because of its resistance to petroleum products, resin-treated laminated-paper pipe has been used in oil prospecting, and its possible use in the construction of low pressure oil or gasoline pipe lines has been suggested.[25]

From the above discussion, it is evident that the phenoplasts possess chemically resistant properties which make them of interest in applications in which resistance to corrosion and chemical reagents is important. They are particularly valuable where resistance to acids is required. It may be expected that such uses will continue to expand as engineers and designers become more familiar with their properties. As in the case of all materials of construction, specific corrosion tests should be conducted before deciding on the exact type of material for all uses where chemical attack is a major factor.

2. Resistance to Microorganisms

Under normal conditions in temperate climates, the phenoplasts are quite resistant to attack by fungi or other microorganisms. The resin is not attacked at all, and the growth is usually confined to cut edges. Laminated phenolics with cellulosic fillers are more readily attacked. Very little growth is noted on molded specimens filled with mica or asbestos.[26] Under severe tropical conditions, serious attack may occur on phenoplasts containing organic fillers. The experiences of the Armed Forces in the Pacific theater of operations during the early days of World War II showed that the heat and high humidity encountered in tropical climates furnished a very favorable environment for the growth of fungi. One of the materials which was attacked was a cellulose-filled molded phenoplast. The fungous growths on electrical parts molded from these phenoplasts not only impaired the action of switches and other moving parts, but caused short circuits due, probably, to the moisture which was absorbed by the spongy growths. Because of this, the useful life of the electrical equipment of our fighting forces in the South Pacific campaigns was alarmingly short. For example, a Signal Corps radio set had an average useful life of three days early in the war. Proper fungicidal treatment of the organic filler will control attack by microorganisms.

[25] H. W. Richter, *Modern Plastics*, **20**, 48–49 (Sept., 1942).

[26] Anon., *Plastics (London)*, **9**, 317–318 (1945).

XIII. OIL-SOLUBLE PHENOPLASTS

A. INTRODUCTION

In the early chemical development of the phenol–formaldehyde condensation products, that is, from 1900 to 1910, many attempts were made to use the phenoplasts as shellac substitutes. These attempts were unsuccessful as the phenoplasts did not possess all the good properties of shellac. The work of Baekeland pointed the way to the successful molding of the phenoplasts, and work during 1910 to 1920 was largely devoted to the expansion of the molding, laminating, and casting phases of the industry. Some attempts were made to use the phenol–aldehyde condensation products with natural oils or in synthetic coatings, but no great success was achieved.

In about 1910 the firm of Kurt Albert in Wiesbaden, Germany, developed a series of substitutes for the fossil resins, e.g., kauri and copal; these products were made by dispersing phenol–aldehyde resins in rosin, followed by complete esterification of the abietic acid with glycerine. The fundamental process was covered by Albert and Berend in German Pat. 254,411 (1910). Rights to the process for the United States were acquired by the Resinous Products Company of Philadelphia, an affiliate of the Röhm and Haas Company, and introduction of the resins to the American market was begun in 1924. The resins were not well received as mere substitutes for the fossil gums. However, it was soon found (1926) that, when the resins were combined with tung oil, the resulting varnish would dry to a tack-free surface after about four hours. The discovery of this rapid drying quality enabled the oil varnishes to compete with the nitrocellulose lacquers, which were then just coming into widespread use. In addition, the tung-oil phenoplast varnishes and enamels had excellent resistance to outdoor exposure. A short time later, in 1928, the Bakelite Corporation introduced pure oil-soluble phenolic resins, unmodified with natural resins. Oil solubility was accomplished by condensing formaldehyde with a para-substituted phenol, such as *p-tert*-butylphenol or *p*-phenylphenol.

The growth of the oil-soluble resins has been rapid. Mattiello[1] esti-

[1] J. J. Mattiello, *Protective and Decorative Coatings*. Wiley, New York, 1941.

mates that approximately 20,000,000 lb. of phenolic resins were consumed by surface coatings industry in 1937. This estimate covers both the pure and modified resins, and would be appreciably less on the basis of 100% phenoplast resin. Sollenberger[2] states that 44,000,000 lb. of phenoplasts were used for protective coatings in 1944.

When properly combined with drying oils, the phenoplast resins give coatings which are outstanding in durability, rapid drying, toughness, alkali resistance, acid resistance, and waterproofing.[3,4] During the introduction of the oil-soluble phenoplasts, tung oil was the principal drying oil used. The shortage of tung oil in recent years has prompted the use of other oils, such as linseed, oiticica, perilla, and dehydrated castor oil, and phenoplasts have been developed which work successfully with these.[5,6] The pure phenolic resin varnishes possess particularly excellent durability, and the Baltimore Paint and Varnish Production Club has reported[7] that the results from the 100% phenolic varnishes included in their study indicated that with all oils and all proportions of oil to resin, the durability far exceeds that of any other oil–resin combination used. When used in baking finishes, the phenolic resins give excellent protection against corrosion, and are used for coating beer tanks, milk storage tanks, transformers, and tank cars.[8] Where a very high degree of protection against corrosion is required, baked phenoplast coatings of the non-oil-soluble type are frequently used; new types of these resins have been described by McCullough.[9]

The technology of oil-soluble phenoplasts has been very highly developed. There are many different types of these resins, and the type of coating produced can be varied widely depending on the type of resin employed, the nature of the oil, the length of the varnish, the time and temperature of cooking, and other variables. It is not the purpose of this chapter to go into this technology deeply; readers interested in this field should consult the various special texts on varnish making. An attempt will be made to describe the general nature of the oil-soluble phenoplasts, and to

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[2] G. H. Sollenberger, *Modern Plastics*, **22**, 101–102, 200–202 (April, 1945).

[3] V. H. Turkington, R. C. Shuey, and W. H. Butler, *Ind. Eng. Chem.*, **22**, 1177–1180 (1930).

[4] V. H. Turkington, R. C. Shuey, and W. H. Butler, *ibid.*, **23**, 791–797 (1931).

[5] R. C. Shuey, *ibid.*, **32**, 921–930 (1940).

[6] V. H. Turkington, R. J. Moore, W. H. Butler, and R. C. Shuey, *ibid.*, **27**, 1321–1325 (1935).

[7] Baltimore Paint and Varnish Production Club, *Paint Oil Chem. Rev.*, **102**, 36–45, 66 (1940).

[8] R. L. Norum, *Chem. Industries*, **54**, 524–528 (1944).

[9] K. V. McCullough, *Paint Ind. Mag.*, **59**, 336–343 (Oct., 1944).

show the probable nature of the reactions which they undergo when cooked with unsaturated oils.

The oil-soluble phenoplasts are divided into two major categories: (*1*) The *pure* or *100%* phenolic resins. These resins are made by condensation of substituted phenols with formaldehyde, and contain no modifying or solubilizing agents. (*2*) The modified phenolic resins. These resins are made by dispersion of a phenoplast in a natural resin, such as rosin. The phenoplast, in pure form, might not be soluble in oil, but the dispersed resin is soluble.

B. PURE OIL-SOLUBLE PHENOPLASTS

Phenoplasts made from trifunctional phenols, such as phenol itself or *m*-cresol, are generally not soluble in the varnish oils. In order to obtain oil solubility, it is necessary to use a phenol which is substituted in either the ortho or para position by an aryl or alkyl group. This substitution accomplishes two things: (*1*) It yields a bifunctional phenol, which will not give a highly cross-linked resin even on advanced curing. (*2*) It has a favorable physicochemical influence on solubility in the oil, because the aryl or alkyl groups are oleophyllic.

Both ortho- and para-substituted phenols yield oil-soluble products, but in practice the para derivatives are generally used because they produce varnishes which have the least discoloration on weather exposure. The ortho derivatives always tend to a pronounced yellowing, either during the cooking operation or on subsequent light exposure. The exact reason for this yellowing is not certain, but it is usually ascribed to the formation, under light and heat, of a *p*-quinone structure. Such a structure cannot be formed when the para position is occupied by an aryl or alkyl group.

Substitution in the phenol nucleus by groups with a high oxygen content, such as carboxy (e.g., salicylic acid, *p*-hydroxybenzoic acid, the cresotinic acids), does not yield oil-soluble resins, and therefore these are not used in the manufacture of the pure oil-soluble phenoplasts. However, as Turkington and Allen[10] and Mehta[11] have pointed out, these acids become soluble when modified with rosin or fatty acids and esterified, and are therefore useful for the preparation of certain modified resins. The latter combine the good properties of both phenolic and alkyd type resins within the same molecule, and therefore form more homogeneous products than can be obtained by simply mixing phenolic and alkyd resins.

[10] V. H. Turkington and I. Allen, *Ind. Eng. Chem.*, **33**, 966–971 (1941).

[11] T. N. Mehta, *Paint Oil Chem. Rev.*, **107**, 9–12, 46 (May 4); 9, 20–25 (July 27); 12–14 (Aug. 10); 14–16 (Aug. 24, 1944); **108**, 18, 22–24 (Jan. 11, 1945).

The condensation of the substituted phenols with formaldehyde may be conducted either with acid or alkaline catalysts. When an acid catalyst is used, typical novolacs are formed, which are permanently fusible. When an alkaline catalyst is used, a mono or dimethylol compound is formed, depending upon the molar quality of formaldehyde which is used in the condensation. On further heating, these methylol compounds condense to ethers and diphenylmethane derivatives of the types described in Chapter II. If the condensation is allowed to progress too far, even the para-substituted phenols may in some cases yield products which are insoluble in oil. The condensation during resin manufacture is therefore usually stopped at an intermediate stage, and the remainder of the condensation is effected during heating in the varnish kettle with the oil. The possible nature of the reaction with the oil will be discussed in a later section of this chapter.

There are a large number of substituted phenols which may be used to produce oil-soluble phenoplasts. The physical properties of sixty such phenols have been described by Pardee and Weinrich;[12] general methods for the preparation of many of these have been described by Britton.[13] Turkington and Allen[10] have described the properties of resins and varnishes from forty-four phenolic compounds. However, many of these are either not commercially available or do not yield satisfactory varnishes. The most important substituted phenols for the manufacture of oil-soluble phenoplasts are, at present, as follows: *p*-cresol; *p*-ethylphenol; *p-tert*-butylphenol; *p-tert*-amylphenol; *p-tert*-octylphenol; *p*-phenylphenol; *p,p'*-dihydroxydiphenylmethane; 4,4'-dihydroxydiphenyldimethylmethane.

Table LXXIII, abstracted from the paper of Turkington and Allen, lists the properties of resins and varnishes from phenoplasts derived from the above, with the exception of 4,4'-dihydroxydiphenyldimethylmethane and *p-tert*-octylphenol. In place of the latter, the properties of isooctylphenol resins are given.

C. THE MODIFIED PHENOPLASTS

The modified oil-soluble phenoplasts are made by dispersing a phenol–formaldehyde condensation product in a natural resin, such as rosin, the principal constituent of which is abietic acid. The phenol–aldehyde condensation product may be gradually added to the hot rosin, or the condensation may be accomplished *in situ* by adding the phenol and formaldehyde to the hot rosin. Complete esterification is usually accomplished at

[12] W. A. Pardee and W. Weinrich, *Ind. Eng. Chem.*, **36**, 595–603 (1944).
[13] E. C. Britton, *ibid.*, **33**, 965 (1941).

TABLE LXXIII

PROPERTIES OF PHENOPLAST RESINS AND VARNISHES FROM COMMON SUBSTITUTED PHENOLS[a]

Phenolic compound	Resin reaction conditions				Resin properties				Varnish properties[c]			
	Catalyst	Mole ratio, formaldehyde:phenol	Time, hrs.	Temp., °C.	Type	Melting point, °C.[b]	Color	Light resistance	Oil solubility	Gelation time, min.	Drying time, hrs.	Color stability
p-Cresol	Acid	1.0:1	3	100	P.F.	104	L.	Fair	Sol.	24	5	Fair
	Alkali	4.0:1	48	25	H.H.	Crystals	L.	Good	Sol.	..	6	Good
p-Ethylphenol	Acid	1.0:1	3	100	P.F.	86	L. yellow	Fair	Sol.	27	6	Fair
	Alkali	2.0:1	24	25	H.H.	Crystals	L. yellow	Good	Sol.	..	6	Good
p-*tert*-Butylphenol	Acid	1.0:1	12	100	P.F.	96	L. yellow	Fair	Sol.	34	5	Fair
	Alkali	2.0:1	40	25	H.H.	Liquid	W.W.	Good	Sol.	35	6	Good
p-*tert*-Amylphenol	Acid	1.0:1	17	100	P.F.	88	Yellow	Fair	Sol.	32	5½	Fair
	Alkali	2.0:1	46	25	H.H.	Liquid	L. yellow	Good	Sol.	26	6	Good
p-Isooctylphenol	Acid	1.1:1	13	100	P.F.	91	Sl. yellow	Fair	Sol.	39	6	Fair
p-Phenylphenol	Acid	1.5:1	3	130	P.F.	110	L. yellow	Fair	Sol.	24	3	Fair
	Alkali	3.0:1	24	35	H.H.	Crystals	L. yellow	Good	Sol.	16	4	Good
p,*p*′-Dihydroxydiphenylmethane	Acid	1.0:1	6	100	H.H.	...	L. yellow	Fair	Insol.	..	...	...

[a] The following abbreviations are used: H.H., heat hardening; P.F., permanently fusible; Sl., slight; W.W., water white; L. light.

[b] All melting points were determined by the ring and ball method.

[c] All varnish properties were determined on the basis of 100 parts resin to 200 parts tung oil; gelation tests were made at 250°C.; the drying time is the approximate time to reach the *print free* stage.

the same time by adding glycerol, pentaerythritol, or ethylene glycol. Woodruff[14] has pointed out that by adjusting the ratio of polyhydric alcohol to rosin, certain of the hydroxy groups can be left in the finished resin. This yields a resin containing polar hydroxy groups, and it is claimed that varnishes made with these resins have improved adherence to metal and other surfaces.

The mechanism by which the methylolphenols are dispersed in natural resins is not clearly understood. The problem is similar to that of the general reaction of the oil-soluble phenoplasts, which is discussed in subsequent paragraphs. Whatever the mechanism, it is certain that in the modified form it is possible to use phenols which would not be oil soluble without modification. For example, 4,4′-dihydroxydiphenylmethane and 4,4′-dihydroxydiphenylpropane may be used in modified resins. As in the case of the 100% phenolics, a para-substituted phenol must be used if resistance to discoloration on exposure is required. Powers[15] has shown that up to 67 mole per cent of a trifunctional phenol, such as phenol, *m*-cresol, or 3,5-xylenol, may be co-condensed with a bifunctional phenol and formaldehyde, and the resulting product dispersed in rosin to yield a high viscosity, oil-soluble resin. However, the resulting resins cannot be esterified with glycerol, as insoluble gels are formed before the acidity is greatly reduced.

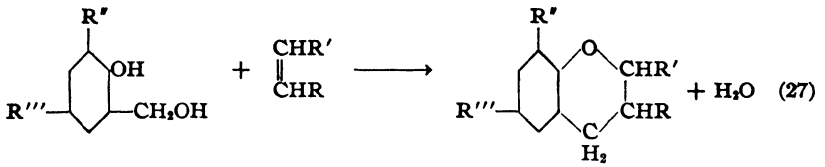
D. REACTIONS OF THE PHENOPLASTS WITH OILS

There are two schools of thought regarding the reactions which take place during the heating of phenoplasts with unsaturated oils. One school assumes that the phenoplast condensation takes place without any chemical reaction with the oil, and the resulting solution is a colloidal dispersion of the cured phenoplast in the bodied oil. If this line of reasoning were correct, the reactions which take place would be simply the normal curing reactions of the methylolphenols as described in Chapter II.

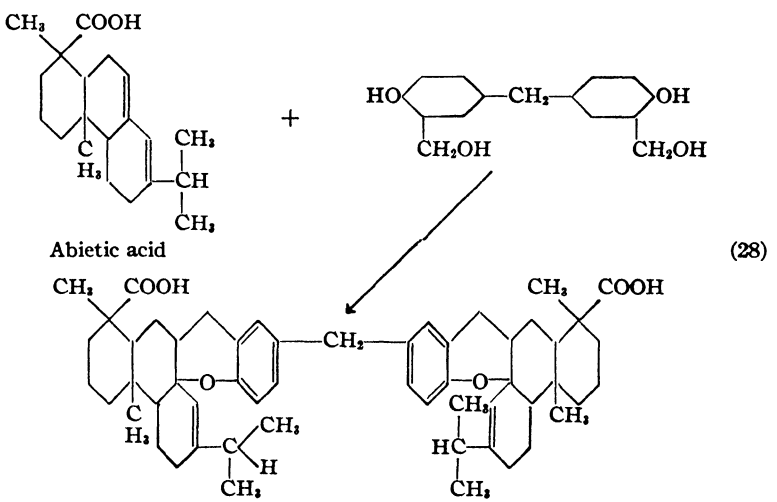
The other school considers that a chemical reaction takes place between the methylol phenol and the unsaturated glyceride. The exact nature of this reaction has not been demonstrated, but there are a number of possibilities. Thus, Hultzsch[16] has shown that chroman derivatives may be obtained by the condensation of a methylolphenol with an unsaturated bond, as shown by the reaction in Equation (27).

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[14] H. C. Woodruff, *Paint Oil Chem. Rev.*, **103**, 20–22 (1941).
[15] P. O. Powers, *Ind. Eng. Chem.*, **36**, 1008–1012 (1944).
[16] K. Hultzsch, *J. prakt. Chem.*, **158**, 275–294 (1941).



For example, styrene may be condensed with saligenin to yield 2-phenylchroman. This reaction occurs only with phenol–alcohols having a free phenolic hydroxy group and a methylol group ortho to each other—a condition which is met in the para-substituted phenol–alcohols. The reaction takes place only above 140°C., a condition which also is present during cooking in the varnish kettle. Hultzsch has represented the probable reaction of abietic acid with the dialcohol from *p,p'*-dihydroxydiphenylmethane as shown in Equation (28).



As Hultzsch has further pointed out,[17] the chroman condensation may take place through the diene addition of the very reactive *o*-quinonemethide which is formed during curing. In such a case, it is obvious that the phenol alcohol need react only in its simplest, uncondensed form. Condensation to a methylene or methylene-ether linked macromolecule might take place, after which a quinonemethide might form, with the resulting addition of the macromolecule to the unsaturated oil.

[17] K. Hultzsch, *Ber.*, 74, 898–904 (1941).

The condensation between 2,6-dimethylol-*p*-cresol and the esters of higher fatty acids was studied by Hilditch and Smith.[18] They showed that no reaction took place between the dimethylol derivative and aliphatic paraffins when heated together at 240°C.; similarly, no condensation takes place between the dimethylol compound and the simple (methyl) esters of saturated or monoethylenic acids, although there is a certain amount of displacement of the methyl group by the phenolic alcohol group. However, with polyethenoid esters, a condensation at the unsaturated centers proceeds to a considerable extent, especially in the case of elaeostearic esters. The interaction with linseed oil or tung oil is determined by the nature of the component fatty acids of these oils.

The condensation of the phenol alcohols is not limited to the unsaturated fatty acids, but appears to be general for organic compounds having this type of unsaturation. Thus, Cunneen, Farmer, and Koch[19] have shown that saligenin will condense with rubber when heated at 180°C. in toluene solution. The condensation goes more readily with highly oxidized rubber; this appears to be due merely to the greatly shortened, highly oxygenated chains of the oxidized rubber. A similar condensation takes place with the simple analogs of rubber, 1-methylcyclohexene and dihydromyrscene. A study of the absorption spectra of the resulting compounds indicated the presence of a chroman structure, such that an average number of one in every ten isoprene units in the rubber has reacted with a saligenin or an ortho substituted saligenin group.

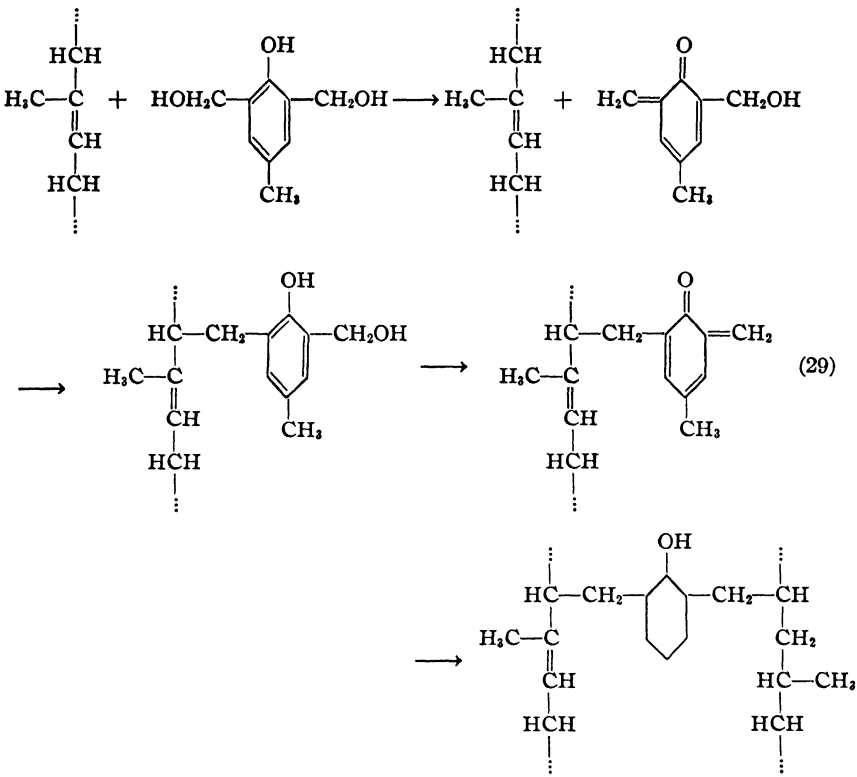
The vulcanization of rubber with phenol alcohols has been carefully studied by van der Meer,[20] who has shown that excellent results may be obtained by means of the phenol dialcohols, such as 2,6-dihydroxy-4-methylphenol from *p*-cresol. The reaction mechanism is ascribed to the formation of methylene quinones, which react with the rubber molecule as illustrated in Equation (29). The reaction takes place in four steps: (*1*) one methylol group of the phenol alcohol forms a methylenequinone; (*2*) the methylenequinone then adds on to a rubber molecule; (*3*) the second methylol group of the phenol alcohol then forms a methylenequinone; (*4*) the latter then adds on to a second rubber molecule and a bridge is formed between the two rubber molecules. Instead of the phenol alcohols, the pseudo phenol halides may be used. In the latter case, the hydrohalide, liberated when the methylenequinone is formed, combines with a

[18] T. P. Hilditch and C. J. Smith, *J. Soc. Chem. Ind.*, **54**, 111–115T (1935).

[19] J. I. Cunneen, E. H. Farmer, and H. P. Koch, *Rubber Chem. Tech.*, **17**, 277–284 (1944).

[20] S. van der Meer, *Rec. trav. chim.*, **63**, 147–169 (1944).

double bond in the rubber molecule. Phenol monoalcohols will not vulcanize, as only one addition can take place to one rubber molecule. In practice, a little vulcanization is observed, because the formaldehyde liberated during curing of the monoalcohol forms some dialcohol.



(29)

The preponderance of evidence seems clearly in favor of some reaction between the phenoplast and the unsaturated oil, although physical and colloidal effects of the dispersed resin no doubt are important in explaining the nature of such a complex system. Turkington, Shuey, and Schechter[21] showed that the alkali resistance and boiling water durability of linseed oil–phenoplast films increased with increasing content of para phenylphenol resins. Zeidler and Hesse[22] compared a reactive phenoplast with a

[21] V. H. Turkington, R. C. Shuey, and L. Schechter, *Ind. Eng. Chem.*, **30**, 984–990 (1938).

[22] G. Zeidler and H. Hesse, *Fette u. Seifen*, **47**, 146–151 (1940).

ıonreactive resin in linseed and linseed–tung oil varnishes at two oil engths. They showed that the films with the reactive resin were tougher, ged better, and had better water resistance. Buser[23] heated reactive henoplasts with linseed, tung, and paraffin oils and measured the water iberated. The amount of water liberated was the same regardless of the il but was proportional to the amount of resin used in the experiment. Buser thought that this indicated no reaction between the resin and the il; however, as reference to Equation (27) on page 210 shows, the amount f water split out is the same whether the phenol alcohol merely condenses vith itself or whether it adds on to the oil at a double bond.

Turkington and Allen[10] point out that there is strong evidence that certain types of phenoplast react chemically with drying oils, although the bility to combine varies greatly among the various phenoplasts. The hemical structure of the oil must also be considered. Those oils which ontain a conjugated double bond system show the greatest evidence of ombination, though even those oils which contain only isolated double onds show evidence of some chemical combination with the more active ypes of phenolic resins.

[23] K. Buser, *Farben-Ztg.*, **45**, 148–149, 165–167 (1940).

XIV. PHENOPLASTS AS ION-EXCHANGE RESINS

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A. INTRODUCTION

An ion-exchange material is an insoluble solid which permits an interchange between certain ions, located either in the crystalline structure of the solid or attached to its surface as functional groups, and other ions present in the solution with which the solid is brought into contact. The exchange is a reversible one and has fundamentally the same mechanism for all types of materials demonstrating this property.

Ion exchange as a physicochemical phenomenon was recognized many years ago. The first observations of base-exchange phenomena are generally accredited to Way,[1] who, in 1850, studied the adsorption of cations by soils. The earliest ion-exchange substances were the *zeolites*, and most chemists are familiar with the fact that certain complex sodium aluminosilicates, both natural and synthetic, contain, within their lattice, sodium ions which are exchanged, in stoichiometric fashion, for calcium and magnesium ions in aqueous solution. Ion exchange was originally employed for the removal of hardness elements from water supplies. Economical industrial applications have followed, because the *zeolites* may be used repeatedly by virtue of the fact that the reaction is reversible.

The siliceous zeolites will exchange with almost all cations. However, certain large ions and hydrogen ions place a severe stress upon the lattice which gradually leads to its rupture. Moreover, waters of high *p*H or of low silica content cause the loss of silica from the zeolitic structure and slow solution follows. Despite these limitations, greensands, which offer hard, dense structures with relatively low capacity, and synthetic gel zeolites with higher capacity, have been and still are being used successfully in many water-softening installations, both of the domestic and commercial types.

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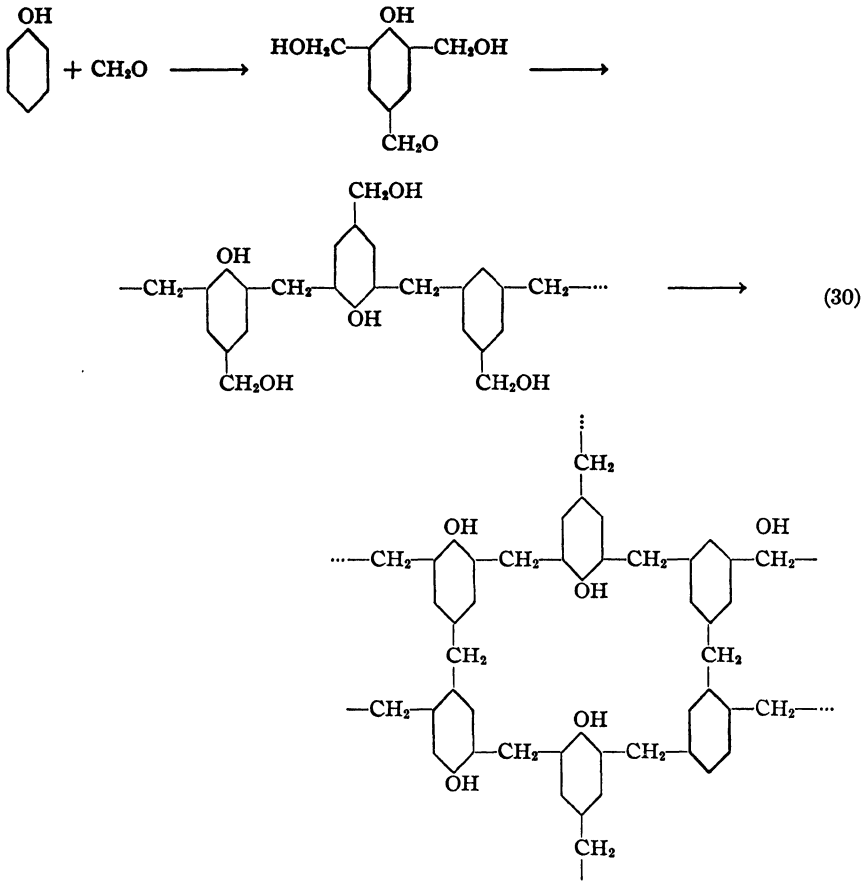
[1] J. R. Way, *Agr. Soc. Eng.*, **11**, 313 (1850); **13**, 123 (1852).

The second type of ion-exchange substance to be developed was the so-called *carbonaceous zeolite.* This material is usually prepared by sulfonation and oxidation of complex organic materials such as coal or lignite. The sulfonic acid group which is thereby introduced contains exchangeable hydrogen ions comparable to the sodium ions of a greensand. These materials first made hydrogen cycle operation possible because their stability to acids was assured by virtue of their mode of preparation. Hydrogen cycle exchangers are those ion exchangers which are capable of revivification by acid and which will replace all metallic cations in a solution by an equivalent number of hydrogen ions. Hydrogen cycle exchangers have been very important to the practical utilization of ion exchangers; if ion exchangers were limited to the exchange of metallic cations, their application would be indeed restricted. For example, all calcium bicarbonate in hard waters would be converted to sodium bicarbonate which is undesirable in boiler feed water and other applications. However, hydrogen cycle exchangers permit elimination from the water of all ions causing temporary hardness, leaving with the water only the relatively harmless carbon dioxide. Carbonaceous ion exchangers have been developed rapidly and are now employed in a number of ways in water treatment practice.

The third and newest class of ion-exchange substances was announced in 1935 by two English chemists, Adams and Holmes,[2] who pointed out that synthetic resins could be utilized. These workers reported to the London Section of the Society of Chemical Industry that certain polyhydric phenoplasts, when polymerized to the insoluble C stage, would exchange ions. Two types of ion-exchange resins are now available: (*1*) the cation-active resin which may be regenerated by brine or acid; and (*2*) the anion-active resin which may be revivified by alkali. Both are essentially macromolecules which contain certain active groups available for ion exchange; the cation-active types are phenoplasts, while the anion-active is obtained by the condensation of amines with formaldehyde. The phenoplast macromolecule, produced by the condensation of phenol and formaldehyde, may be represented by the typical structure of Equation (30).

Because of the known acidity of the hydrogen in the phenolic hydroxy group, Adams and Holmes were led to postulate that a lattice of this character would exhibit exchange of hydrogen atoms. This was readily confirmed. Practically all cations were exchanged for hydrogen ions when solutions of various salts were passed through a column of crushed resin. Acids were found to elutriate these metallic ions and repeated cyclic operation was therefore possible.

[2] B. A. Adams and E. L. Holmes, *J. Soc. Chem. Ind.*, **54**, 1–6 (1935).



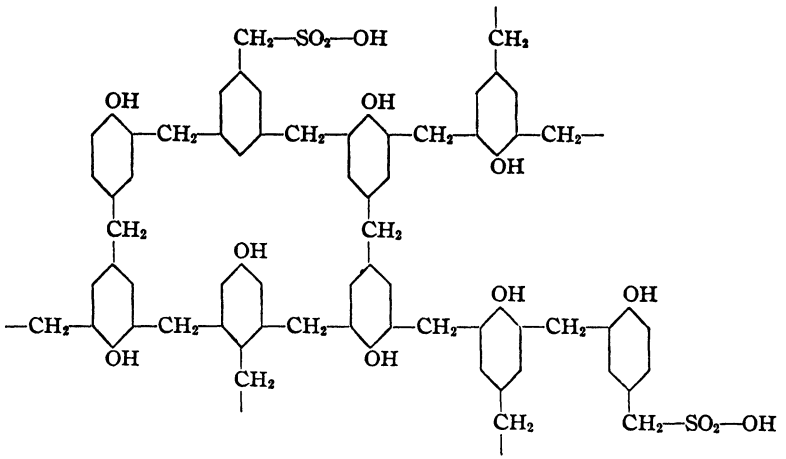
(30)

At the same time Adams and Holmes reasoned that acids would be removed from a fluid by basic resins such as are produced by amine–formaldehyde condensations. This was soon proved, for metaphenylenediamine–formaldehyde condensates were shown to remove acids and to be regenerated by alkaline solutions.

These simple resins represent initial stages in the development. Since that time considerable improvement has been made with both anion and cation types. The introduction of the sulfonic acid group by various means into the structure of the cation exchanger, as shown by the structure suggested by Beaton and Furnas[3] in Formula XXX, has greatly im-

[3] R. H. Beaton and C. C. Furnas, *Ind. Eng. Chem.*, **33**, 1500 (1941).

proved its exchange capacity; alternative techniques of preparation and the use of new raw materials have greatly improved the anion exchanger.



(XXX)

The ion-exchange resins may therefore be considered as porous gels which are prepared according to known principles of high-polymer chemistry and may be produced in almost any desired particle size, with high exchange capacity, offering efficient operation and rapid reaction velocity. Sulfur and nitrogen contents are frequently good indications of potential capacity for they are a measure of the sulfonic acid or basic nitrogen groups which are present in the exchanger. However, there are known exceptions where this correlation is rather poor due either to the inaccessibility of the groups or to their functioning as integral structural members of the exchanger.

B. APPLICATION OF ION EXCHANGE: THEORY

Much is still unknown concerning the actual mechanisms of ion exchange. Application has frequently outdistanced theory. Nonetheless, some progress has been made. Thomas[4] has recently presented a mathematical approach to describe heterogeneous ion exchange in a flowing system and has concluded that the kinetic rate is best described theoretically by a second-order law. Nachod and Wood[5] have presented experimental evidence which tends to substantiate this conclusion. Du

[4] H. C. Thomas, *J. Am. Chem. Soc.*, **66**, 1664 (1944).

[5] F. C. Nachod and O. A. Wood, *ibid.*, **66**, 1380 (1944).

Domaine, Swain, and Hougen,[6] introducing some mathematical approximations, have developed differential rate equations and performance charts for sodium–calcium exchange on one type of ion exchanger. Another form of mathematical treatment is given by the analogy between heat exchange and ion exchange. Beaton and Furnas[3] have used rather successfully the final equations derived by the latter method of analysis to characterize the concentration histories of certain copper and zinc solutions. A complete analysis of this analogy has been presented by Myers, Herr, and Atteberry[7] and is drawn from the mathematical treatment by Schumann,[8] expanded by Furnas,[9] of the unsteady state for heat transfer from a fluid stream to a bed of broken solids in terms of temperature distributions throughout the efflow. These temperature distributions are described in dimensionless terms so that they are independent of the dimensions of the system.

C. APPLICATION OF ION EXCHANGE: TYPES OF PROCESSES

The commercially feasible ion-exchange processes for resinous exchanges may be summarized as follows:

Those Involving Cation Exchange: (*1*) The use of a sodium cycle, as in water softening, where calcium and magnesium ions in the water are replaced by sodium ions. (*2*) The use of a hydrogen cycle, as in removal of cations from the solution, leaving only the acidic constituents in solution. (*3*) The use of a sodium cycle, as in the neutralization of dilute acid solutions.

Those Involving Anion Exchange: (*4*) The removal of acids from solutions.

Those Involving Both Cation and Anion Exchange: (*5*) Total deionization, involving the complete removal of salt by a combination of *2* and *4*.

Prior to the advent of resinous exchangers, only the first two processes were known. With the inception of the anion exchanger a two-step exchange process, deionizing or demineralizing, was feasible. This process permits the production of water free of all ionic impurities. The purity of de-ionized water, insofar as U.S.P. specifications are concerned, is discussed in detail by Harrisson, Myers, and Herr.[10] The value and position

[6] J. Du Domaine, R. L. Swain, and O. A. Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).

[7] R. J. Myers, D. Herr, and W. Atteberry. Paper presented at 105th meeting, American Chemical Society, to be published.

[8] T. E. W. Schumann, *J. Franklin Inst.*, **208**, 305 (1929).

[9] C. C. Furnas, *U. S. Bur. Mines Bull.*, No. 361 (1932).

[10] J. W. E. Harrisson, R. J. Myers, and D. Herr, *J. Am. Pharm. Assoc., Sci. Ed.*, **32**, 121 (1943).

of deionization is recognized universally and has been described heretofore by Myers, Eastes, and Myers[11] and by Tiger and Sussman.[12] The use of this two-step process to *de-ash* various sugar solutions has been related by Rawlings and Shafor,[13] Weitz,[14] and Englis and Fiess.[15]

In an excellent summary, Myers[16] has outlined in some detail many additional applications, such as formic acid removal from formaldehyde by an anion exchanger, the removal of copper from brass mill pickling liquor wastes, iron removal from alum solutions, fatty acids from mixed aqueous and nonaqueous solutions and a process for recovery of arginine, histidine, and lysine.

To these applications many others are being added, in ever-increasing numbers. A recent patent issued to Myers and Herr[17] described a means for specific fluorine removal from potable water by the use of an anion exchanger which has been treated with alum salts. The reaction is quite specific and the exchanger may be revivified for repeated use. By the combined use of cationic and anionic exchangers Ryznar[18] has prepared silica sols containing 99.3% SiO_2. The procedure is much simpler and more rapid than purification by dialysis. Matchett and co-workers[19] have shown by pilot plant scale experiments that the utilization of synthetic anion-exchange materials for the recovery of tartrates from grape wastes is a feasible procedure. The chloride–tartrate ion-interchange mechanism upon an anion exchanger was made use of in these studies.

As analytical tools for the research laboratory, ion-exchange resins are finding an ever-increasing usefulness. Cannan[20] has used a typical anion exchanger to estimate, quantitatively, the amount of dicarboxylic amino acids in a protein hydrolyzate. In a new approach to the determination of pectin, Williams and Johnson[21] have *de-ashed* solutions of pectin or pectates by the use of ion exchange resins and then electrolytically deposited the pectin or pectic acid at a platinum anode in a weighable amount. McCready and Hassid[22] have used ion-exchange materials to isolate and

[11] R. J. Myers, J. W. Eastes, and F. J. Myers, *Ind. Eng. Chem.*, **33**, 697 (1941).
[12] H. L. Tiger and S. Sussman, *ibid.*, **35**, 186 (1943).
[13] F. N. Rawlings and R. W. Shafor, *Sugar*, **37**, 26 (1942).
[14] F. W. Weitz, *ibid.*, **38**, 26 (1943).
[15] D. T. Englis and H. A. Fiess, *Ind. Eng. Chem.*, **34**, 864 (1942).
[16] R. J. Myers, *ibid.*, **35**, 858 (1943).
[17] R. J. Myers and D. Herr, U. S. Pat. 2,373,632 (1942).
[18] J. W. Ryznar, *Ind. Eng. Chem.*, **36**, 821 (1944).
[19] J. R. Matchett, C. K. Legault, C. C. Nimmo, and C. K. Notter, *ibid.*, **36**, 85 (1944).
[20] R. K. Cannan, *J. Biol. Chem.*, **152**, 401 (1944).
[21] K. T. Williams and C. M. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **16**, 23 (1944).
[22] R. M. McCready and W. Z. Hassid, *J. Am. Chem. Soc.*, **66**, 560 (1944).

purify a series of glucose phosphates. Frizzell[23] has applied the stoichiometric relations of ion exchange to the quantitative determination of various metal cations by passing the metal salt solution through a column of ion-exchange material, followed by direct titration of the acid effluent.

In the medical field, Steinberg[24] has reported that the coagulation of blood may be inhibited or prevented if certain ions, principally calcium, are removed from it by treatment with a cation exchanger. The determination of the total bases in blood serum by the direct titration of the mineral acidity liberated upon contact of the serum with an acid generated cation exchanger has been reported by Polis and Reinhold.[25] Englis and Fiess[26] have studied the adsorption of many amino acids by ion exchange materials. All the amino acids tested react with the hydrogen form of the cation exchanger. Since anion exchangers react with dicarboxylic but not monocarboxylic monoamino acids, a separation is to be expected. The basic amino acid hydrochlorides are not removed by an anion exchanger.

It is seen, therefore, that the application of ion exchange has developed rapidly and it is felt that only the beginning has been witnessed.

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[23] N. Frizzell, *Ind. Eng. Chem., Anal. Ed.*, **16**, 615 (1944).

[24] A. Steinberg, *J. Soc. Exptl. Biol. Med.*, **56**, 124–127 (1944).

[25] B. Polis and K. Reinhold, *private communication.*

[26] D. T. Englis and H. A. Fiess, *Ind. Eng. Chem.*, **36**, 604 (1944).

XV. TECHNICAL MANUFACTURE OF PHENOPLASTS

It is not the purpose of this book to discuss the design, construction, and operation of plants for the manufacture of phenoplasts; the emphasis has been entirely on the structure and properties of the resins and resin–filler combinations. However, this chapter covering the outlines of commercial phenoplast manufacture has been added in the belief that it will help the reader, who may be unfamiliar with the technology of the subject, to understand the steps involved in the manufacture of industrial resins, molding powders, and laminates.

The operations involved in the manufacture of phenoplasts on a large scale may be divided into several stages as the products approach the finished condition. The ultimate stage of a finished phenoplast may be regarded as either a molded product, a laminate, a surface coating, an adhesive, or any one of the many forms in which these versatile materials find application; however, many products intermediate between these and the finished resin are withdrawn for sale. The chart in Figure 67 illustrates the relationship among the various stages of phenoplast manufacture, and the order of the text in this chapter will follow this chart as closely as possible.

A. RESIN MANUFACTURE

The phenol (or cresol) is charged from a measuring tank into the resin kettle, followed by the formaldehyde and the catalyst. A *modifier*, such as aniline, is frequently added to the mixture before the reaction starts. The purpose of the modifier is to slow the curing reaction slightly, and to obtain a better flow in the molding compound so that the mold will be filled completely.

The resin kettle itself usually has a capacity of from 1000 to 3000 gallons, depending upon the production for which the plant is designed. The kettle must be supplied with good agitation; usually a scraper-type agitator is employed because the resin during dehydration becomes very viscous, and it is important to move the resin film from the sides of the kettle in order to maintain good heat transfer. The kettle is connected to a reflux

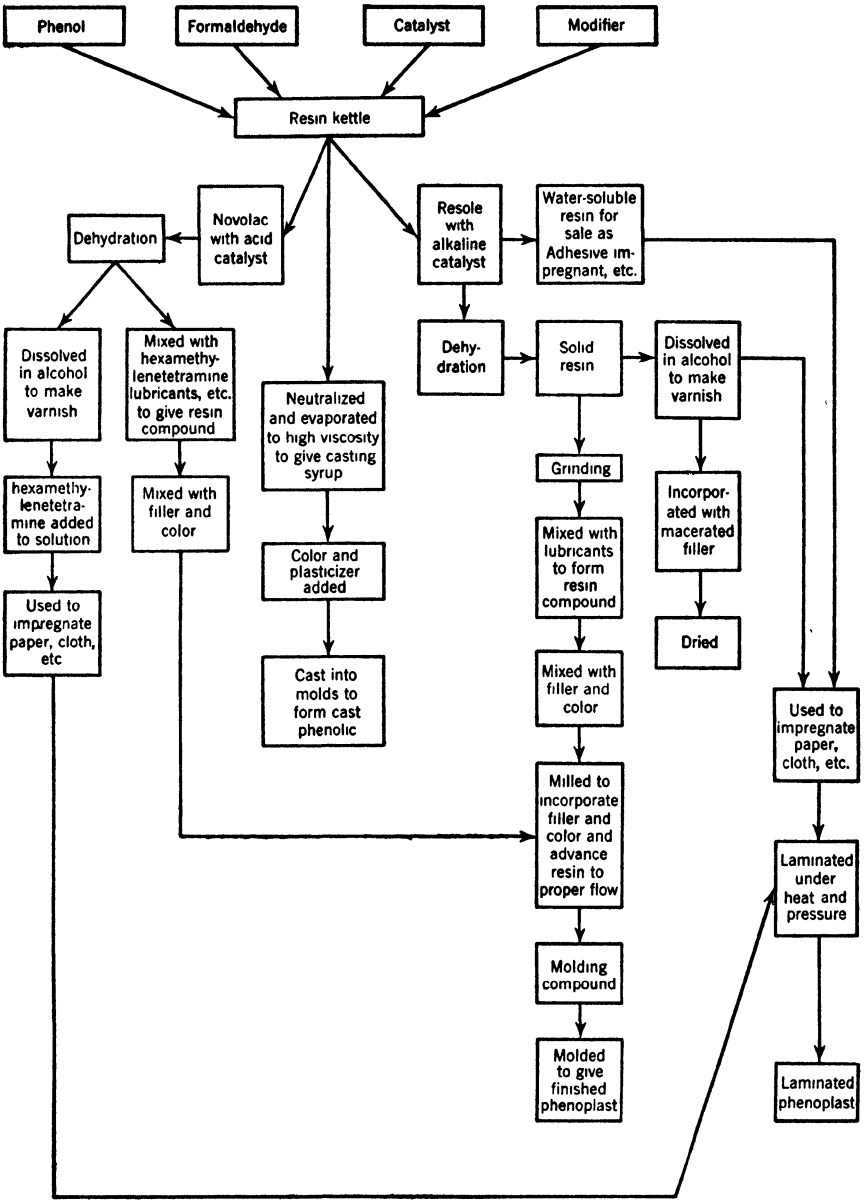


Fig. 67. Flow sheet of phenoplast manufacture.

condenser of ample capacity. The kettle and condenser are constructed so that they may be placed under vacuum, and the charge refluxed at reduced pressure. This is important when it is desired to conduct the reaction at less than 100°C.; the heat of reaction is usually so large, and the reaction velocity so rapid, that reflux rather than jacket cooling must be relied upon to remove the heat in the early stages of the reaction. The kettle is provided with a jacket, however; this is principally used for heating the charge to reaction temperature. The kettle and condenser are usually constructed of iron if the color of the finished resin is not important; if a light color is essential, as in casting resins, the equipment must be of nickel or nickel-clad steel.

When the entire charge has been placed in the kettle, steam is passed through the jacket and the charge is brought up to reflux temperature. If it is desired to conduct the reaction at approximately 100°C., the reflux is carried out at atmospheric pressure; if a lower temperature is to be employed, the pressure on the system is reduced to the proper level before refluxing starts. The steam is usually turned off some time before refluxing begins, since the heat of reaction is sufficient to maintain the refluxing temperature for a considerable time. The refluxing period may last from one to five hours, depending upon the nature and proportion ot the reactants. It may be necessary to pass more steam through the jacket of the kettle after the more violent stage of the reaction has passed.

If an alkaline catalyst has been used in sufficient proportion, the reaction mixture at this stage is all in solution. It may then be further processed, or drawn out of the kettle as a *water-soluble resin* which may either be used as is for adhesive purposes (bonding of plywood, etc.) or for the impregnation of paper, fabric, etc., in the manufacture of laminates. For certain uses, such as the manufacture of plywood adhesives, the aqueous resin solution may be spray-dried to yield a stable powder.

If an acid catalyst has been used to produce a novolac, the mixture in the kettle has by this time separated into two phases; the heavier phase is the resin, while the lighter phase is mostly the water which was present in the formaldehyde, plus the water of reaction. The water may be separated by decantation, after the agitation has been stopped, or it may be removed by distillation under vacuum. In either case, the resin is dehydrated by heating under vacuum.

When a solid, alkaline catalyzed resin (resole) is required, the dehydration is also carried out by careful heating under vacuum. When working with the resoles, great care must be taken to follow *exactly* the time and temperature schedule prescribed by experience. Heating for too long a

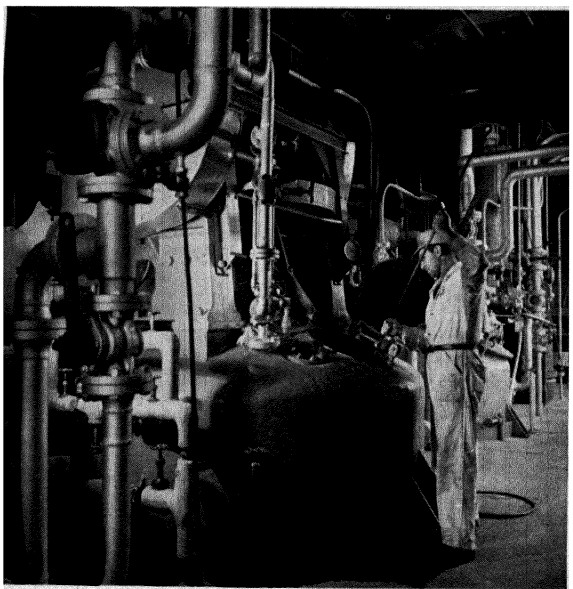


Fig. 68. Typical resin kettle installation.
(Courtesy Monsanto Chemical Co.)



Fig. 69. Resin discharging to cooling floor.
(Courtesy Monsanto Chemical Co.)

time, or at too high a temperature, will advance the resin to such a point that cross linking, with violent exothermal reaction, will take place within the kettle. The resin then "sets up" or becomes solid within the kettle, and the only course is to chip it out. The novolacs do not pass into an insoluble stage, and there is not much danger of overheating. In any case,

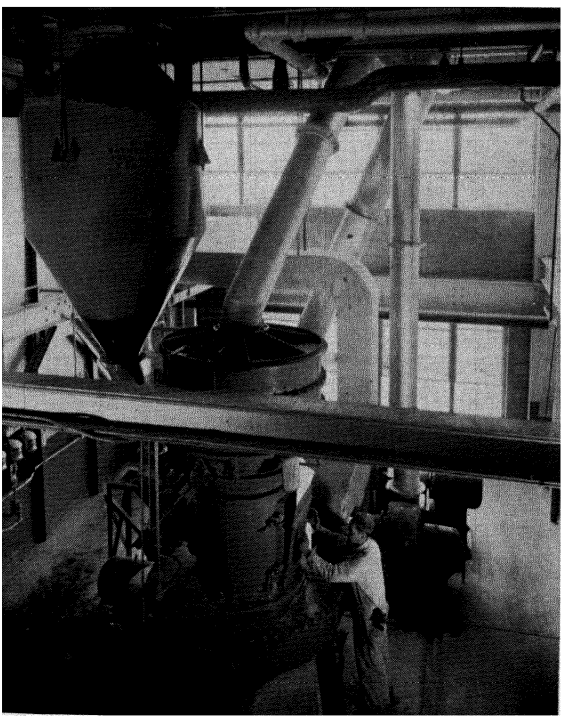


Fig. 70. Grinding phenoplast resin.
(Courtesy Monsanto Chemical Co.)

careful control of quality of the finished resin is obtained by the examination of samples taken from the kettle at frequent intervals. Figure 68 shows a typical resin kettle, with the operator taking samples during the reaction.

As soon as the resin is dehydrated, it is run out of the kettle by means of a bottom discharge valve, onto the cooling floor. The cooling floor is usually constructed of sheet iron plates welded together to form a smooth surface; the lower side of the floor may be cooled by water or air. In the

case of the resoles, it is important that the contents of the kettle be emptied within a few minutes and cooled rapidly; the resin is very reactive at this point and will set up unless handled quickly. Figure 69 shows resin running out of the kettle onto the cooling floor.

When the resin has cooled to a brittle solid, it is broken up with sledges into pieces three or four inches square. These are ground to a coarse powder, and then pulverized to a fine powder in an impact mill that is equipped with an air separator. Figure 70 illustrates this stage of the grinding operation.

Attempts have been made to produce phenoplast resins by a continuous process. Turkington has covered such a system in U. S. Pat. 1,660,403 (Feb. 28, 1928). Popandopulo[1] has described a pilot plant apparatus of very similar design for the preparation of novolac resins. The phenol, formaldehyde, and catalyst are mixed together cold and pumped through coils which are heated in a bath of mineral oil. The temperature of the oil bath must be about 160°C., and the reaction mixture is kept under a pressure of four atmospheres. The reaction products pass into a copper container which is evacuated to remove the water. The principal problem in operating the equipment seems to be the prevention of clogging of the coils by the resin; accurate temperature control at this point is necessary.

B. CAST RESINS

The cast phenolic resins are manufactured principally for two reasons: (*1*) When a small quantity of a wide variety of shapes is required, casting into simple molds followed by hand fabrication is frequently more economical than the more costly and elaborate procedure of preparing steel molds for hot pressing. (*2*) The resins have great clarity and brilliance, and can be supplied in a wide variety of colors. For the latter reason, great care is exercised in their manufacture in order to preserve as light a color as possible. Pure nickel or nickel-clad apparatus is used, and the raw materials are carefully selected for purity and freedom from color. More recently, the casting types of resins have found use as dies for shaping light metals, oil well tools, and in similar applications,[2,3] where freedom from color is not so important.

The first step in the manufacture of a casting resin is similar to that of a resole. The reaction is catalyzed with alkali (usually sodium hydroxide).

[1] U. G. Popandopulo, *J. Chem. Ind.* (*U.S.S.R*), **8**, No. 12, 16–18 (March, 1941).

[2] D. Dreher, *Plastics* (*Chicago*), **1**, 26–8 (1944).

[3] J. J. Pyle, L. E. Fiedler, and T. V. Ferris, *Modern Plastics*, **22**, 132–133, 190–192 (Feb., 1945).

A high ratio of formaldehyde to phenol—from 2.5 to 3.0—is used so that the resin may be as hydrophylic as possible, with a large proportion of methylol groups. After the alkaline condensation has reached a certain stage, the reaction mixture is neutralized with a weak organic acid such as lactic acid, or an easily decomposed ester, such as ethyl phthalylethyl glycollate. The water is then removed at reduced pressure, and heating is continued until the resin has reached the required viscosity. Color and pigments are then added, together with a reagent such as glycerol which will serve as a common solvent for the resin and the water of reaction; the resin is poured or "cast" into thin lead molds which have the shape of the desired piece. The molds are placed in an oven at a temperature of 85° to 100°C. for three to five days until the resin has cross-linked to a hard, infusible mass. The lead molds are then stripped off, and the casting trimmed by machine to remove the mold flash or other undesirable portions.

C. RESIN VARNISHES

The phenoplast industry applies the term *varnish* to a solution of resin in a nonaqueous solvent, usually alcohol. Varnishes are very easily prepared by dissolving the correct amount of resin in solvent. If a resole is used, it is not necessary to use anything else to promote curing of the resin; when a novolac varnish is prepared, sufficient hexamethylenetetramine must be added to cause cross linking when the dry resin is heated. Small quantities of other ingredients, such as waxes, lubricants, or color may be added to the varnish, depending on the exact use for which it is designed.

Resin varnishes are used in impregnating paper or fabric for the preparation of laminates and high strength molding compositions. Varnishes are more stable on storage than aqueous solutions of resoles; the presence of alcohol inhibits advancement of the resin.

D. RESIN COMPOUND

In the manufacture of molding powders the finely ground solid resin is usually not mixed directly with the filler. It is first mixed with small amounts of lubricants, such as carnauba wax or zinc stearate, which aid in causing flow during molding, in separating the piece from the mold, and in improving the finish of the molded piece. If a novolac type of resin is used, hexamethylenetetramine is mixed in at this stage. Sometimes, to obtain special types of flow or cure, two or more grades of resin are used in the mixture.

The mixing is usually accomplished in a simple type of ribbon mixer. The finished mixture is known as resin compound.

E. MOLDING POWDER

When a finely divided filler, such as wood flour, cotton flock or mica, is to be used, the resin compound and filler are intimately mixed in a ribbon-type mixer. Color is also added at this stage. Some molding powders



Fig. 71. Rolling operation for phenoplast molding compound. (Courtesy Monsanto Chemical Co.)

are sold as "natural" color—that is, with a rather dark brown shade due to the color of the resin itself. The greater proportion of phenoplast molding powders are colored black by the addition of from 1 to 2% of carbon black or black dye. A small proportion of molding powders are produced in rather heavy shades of red, brown, or green; a heavy shade must be used in order to hide the color of the resin and minimize the darkening which inevitably takes place on aging or exposure to light. When the mixing is complete, the charge is dropped in portions onto milling rolls, where the resin and filler are brought into intimate contact. The front roll usually revolves at about 60 r.p.m., while the back roll is geared at a slightly higher speed. Both rolls are heated with steam, with individual valves for each

roll so that the temperature may be varied on each. The temperature of the rolls, combined with their squeezing and grinding action, causes the resin to soften and coat every particle of the filler. At the same time, the relatively high temperature (120–150°C.) causes the resin to advance, or cure partly. The time of rolling, and the temperature employed, must be carefully regulated so that the right degree of resin advancement is obtained. In order to control this, frequent samples are taken from the rolling operation and subjected to molding and flow tests. Figure 71 illus-

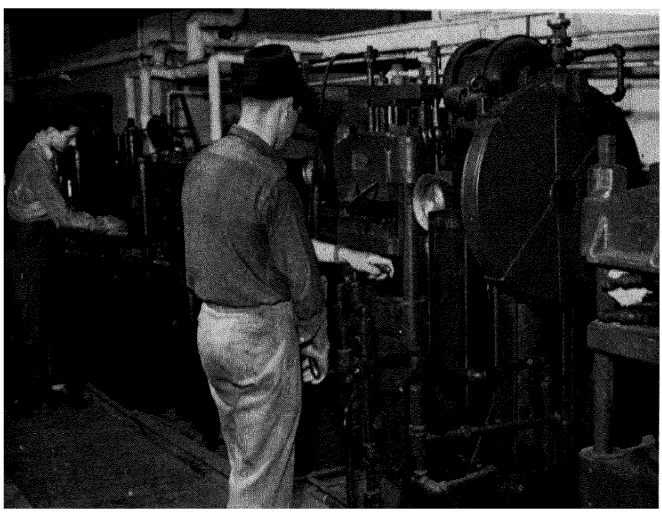


Fig. 72. Testing the molding quality of phenoplasts. (Courtesy Monsanto Chemical Co.)

trates a typical rolling operation, while Figures 72 and 73 show control tests for molding and flow, respectively.

When the charge on the rolls has been properly mixed and advanced, it is cut from the rolls by the customary knife arrangement in the form of a sheet or "blanket." The sheet is cooled and passed to a grinder, where it is ground to the proper fineness. The ground powder then goes to sifting screens, where the very fine or very coarse portions are removed. The intermediate portion goes to a blender, which usually has a capacity of 30,000 to 50,000 lb. The powder is thoroughly mixed in this equipment in order to insure absolute uniformity of an entire carload.

In place of rolls, some factories use a Banbury-type mixer to bring the resin and filler into intimate contact. The principle of the operation is

much the same as that of the mill rolls, except that the Banbury contains a larger charge of resin than can be held on the rolls.

Milling cannot be used to mix resin with filler when the latter is a coarse fiber such as fabric or cord. The action of the rolls tears the fibers, and reduces the impact strength of the molded article. Fillers of this type are usually incorporated with resin by soaking them in a varnish, followed by drying to remove the solvent.

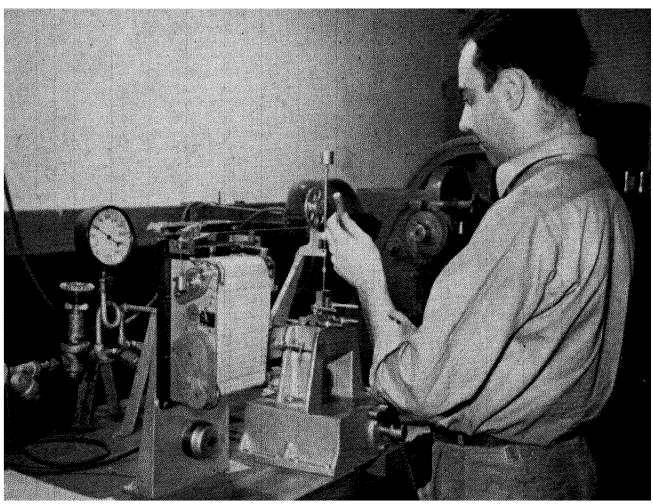


Fig. 73. Control test for flow of molding powder.
(Courtesy Monsanto Chemical Co.)

F. PHENOPLAST MOLDING

The molding of phenoplasts is an art and science by itself. For this reason, an outline of the essentials of phenoplast molding is given as a separate chapter (XVI) of this book.

G. LAMINATES

Laminates differ from molding powders in that the filler consists of a continuous web of paper or fabric. It is obvious that mill rolls or a Banbury mixer cannot be used to incorporate a dry resin, and the web must be impregnated with either a varnish or a water solution of resin. Alcohol solutions are usually employed for the heavier cotton fabrics, and frequently for papers. Some papers, however, are impregnated with a water-

soluble resin. The impregnated web is then passed through a drying system, cooled, and wound on rolls.

In the manufacture of flat laminates, sheets of the impregnated filler are cut to the proper size, and laid up between polished steel plates. A sufficient number of layers must be used to give the desired thickness to the finished laminate. The lay-up is then charged to a steam-heated, hydraulic press, where the laminate is pressed at from 1000 to 3000 p.s.i. and at a temperature of 120° to 150°C. until the entire lay-up has been thoroughly cured. When certain special properties are desired, the type of filler used for the surface of the laminate may be different from that used in the core. This is particularly true when decorative effects are needed on the surface.

Laminated phenoplast tubes are made by winding the laminate on a steel core. A special machine is used which gives the right degree of tension during winding, and supplies enough heat to tack the layers of the laminate together. The tube and core are then placed in an oven, where the final cure of the resin is accomplished. The assembly is cooled, the core is removed mechanically, and the rough ends of the tube are trimmed by machine.

The paragraphs above refer to the use of high pressure for the production of laminates. The shortage of critical metals during World War II created a demand for shaped laminates of rather large area—for example, pilots' seats, airplane wing tabs, and helmet liners.[4,5] To manufacture such articles by conventional high pressure laminating would have required large hardened steel dies and heavy presses, none of which were readily available. Successful methods were developed for laminating such articles under pressures ranging from a few pounds up to 200. In processes involving extremely low pressures—contact to 25 p.s.i.—phenoplasts or other condensation-type resins have not been as successful as resins which polymerize from a monomeric form without the elimination of water or other by-product. Phenoplasts have been very successfully used in the intermediate pressure range—75 to 200 p.s.i. The articles produced compare favorably with high pressure laminates in strength and other mechanical properties. The properties of low pressure laminates have been discussed in some detail in Chapter IX.

[4] Anon., *Modern Plastics*, **20**, 70 (Aug., 1943).

[5] H. C. Guhl, *Plastics Resins Ind.*, **3**, 7 (Aug., 1944).

XVI. MOLDING TECHNIQUE FOR PHENOPLASTS

CARL H. WHITLOCK, *Monsanto Chemical Co., Detroit, Michigan*

A. INTRODUCTION

The statistics given in the introductory chapter showed that the largest single application for the phenoplasts is in the production of molded articles. Because molding is such a large part of phenoplast application, and because the development of optimum physical properties is often associated with the molding technique, this chapter is included to explain the elements of molding technique as practiced with the phenoplasts. There are three molding methods in common use today for the phenol–formaldehyde molding compounds: (*1*) compression molding, (*2*) transfer molding, and (*3*) injection molding.

B. COMPRESSION MOLDING

The compression-molding method was the first method used for the phenoplasts and is still the most commonly used today, though the details of the technique have changed considerably in the past twenty-five years. When phenol–formaldehyde molding compounds were first introduced, the molding equipment consisted of hand molds and presses which were either manually, mechanically, or hydraulically operated. The heat needed to cure the molding compound was obtained from heating platens in the press itself. Since the molds were of the hand type, they were removed from the press for ejection of the part and for reloading. The fact that the molds had to be removed manually from the press limited the size of the mold and consequently restricted the production as compared to that from the semiautomatic molds which are in general use today. The hand-mold operation has given way to the modern semiautomatic press which does not require the mold to be removed from the press. In these machines, the mold is opened by hydraulic pressure or by mechanical means and the molded parts are ejected by self-contained knock-out arrangements within the mold.

Compression molding with a semiautomatic mold comprises the following cycle of operations. (*1*) The press opens and the previously formed part is ejected by means of self-contained knock-outs. (*2*) The mold is cleaned and recharged with molding compound. (*3*) The press is closed and is held in a closed position under carefully controlled temperatures for a period of several minutes, during which time the molding compound cures to the C stage, and becomes a hard, infusible mass which duplicates exactly the contour of the cavity within the mold.

In addition to the hand mold and the semiautomatic mold, two other types are in use. the semihand mold and the fully automatic mold. The semihand mold was developed to enable the use of larger molds than could be employed manually. These semihand molds are identical to the hand molds in design, but one-half of the mold is fastened to the platens of the

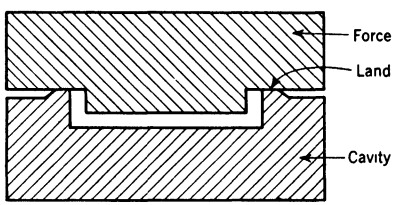


Fig. 74. General construction of a flash-type mold.

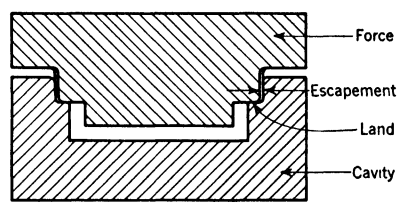


Fig. 75. General construction of a semipositive type.

press and the mold is broken within the press. Only half of the mold is removed for the ejection of the part and recharging with the molding compound. The use of the semihand mold almost doubles the mold capacity, especially when multiple-cavity molds were used.

The fully automatic molds are dependent on a fully automatic press which has been developed during the last few years. These molds are similar in design to the semiautomatic mold. The difference lies in the fact that the molded part is removed from the cavity by an air blast after the knock-out pins have raised the molded part out of the cavity; the mold is then cleaned by a series of air blasts. After cleaning, the mold is automatically recharged with molding compound. To safeguard against closing the mold on a molded part which might stick in the cavity, a safety device is incorporated directly behind the cavity. This safety device receives the molded part as it is ejected, and the weight of the molded part is needed to trip the machine for a continuance of the operation. If the part is not ejected properly, the press stops and a bell rings. Because of these automatic features, the parts molded in a fully automatic mold must

be rather simple in design, as an intricate part will not lend itself to a continuous uninterrupted operation. Up to the present, fully automatic presses are limited in size and the size of the moldings is therefore restricted.

The general types of molds used in compression molding can be subdivided into flash, semipositive, and fully positive types. Figures 74 to 76 illustrate the general construction of these types, and designate the more important parts. The flash-type mold is one which does not restrict the material within the cavity during the operation until the mold is completely closed. The semipositive mold restricts the material in that the force-plug of the cavity enters the cavity for a short distance before coming into contact with the land of the mold. Usually escapements are incorporated in the semipositive arrangement to allow any excess material to escape.

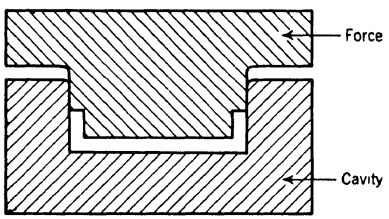


Fig 76. General construction of a fully positive type mold.

The fully positive mold is similar to the semipositive, except that there are no lands on the cavity; the entire pressure is applied upon the molded article. The most popular type is the semiautomatic, semipositive type used in simple compression molding. Molds used in automatic presses are generally of the flash-type due to the ease in which this type of mold can be freed of flash around the land area and the freedom with which the part separates from the cavity.

The type of phenoplast to be molded determines, in great measure, the type of mold which must be selected. Flash-type molds cannot be used very successfully with anything but low bulk materials, such as those containing wood flour or mineral fillers. As the bulk factor of the molding compound increases, it is usually necessary to add loading wells above the cavity to retain the loose powder. This loading well forms the semipositive section of the mold. When high bulk materials are used, it is sometimes necessary that the space above the cavity be ten times the volume of the molded article.

The semipositive mold forms the loading well and also tends to hold the force and cavity in alignment; it is not necessary to rely fully on the guide pins for this alignment. The flash mold relies entirely on the guide pins for alignment and frequently gets out of alignment due to the great pressures used. For this reason, the flash mold can be used only when accuracy of dimensions in the finished part is not too important.

The fully positive mold is gradually losing its position, as it is most diffi-

cult to maintain any exact height of the molded part, because the height depends entirely on the accuracy with which the charge of molding compound was measured before putting it into the cavity. An overcharge results in an oversize piece, whereas an undercharge results in an undersize piece. The semipositive mold corrects all these difficulties. A slightly excessive charge of molding powder is put into the cavity. Escapements are provided along the semipositive section of the force, and through these escapements the molding powder will equalize itself and the mold will come together on the lands; the only variation is the thickness of the flash around the lands. It is possible to design molds with sufficient escapement to maintain a proper density of the molded part and yet cut the flash on the lands down to 0.002 or 0.003 in. thickness. It is important, however, that the size of the escapement be carefully controlled as the pressure within the cavity is dependent to a great extent on the friction created by the material overflowing through the escapement.

C. TRANSFER MOLDING

As moldings became more complex, the simple compression molding method became inadequate and the need for improvement resulted in the development of transfer molding. Transfer molding is accomplished by transferring the molding material from a transfer pot into the die cavity while the latter is in a closed position. The transfer pot is separate from the cavity, usually just above it, and is connected to the cavity by an orifice and gate.

The projected area of the transfer pot is slightly larger than the projected area of the cavity. The pressure applied to the transfer pot is transmitted to the force of the cavity, holding it in a closed position during the transfer of the material. The essentials of a transfer molding system are illustrated in Figure 77. The transfer molding method has several advantages: (*1*) more intricate shapes may be molded; (*2*) inserts may be included and held in position by a closed cavity; the inserts are held more securely than in the case of compression molding; (*3*) the moldings are dense and uniform.

The fact that the material, when injected into the cavity, is in a plastic state enables the inclusion of fragile mold sections and core pins which would be impractical in compression molding. This is because the molding material, when injected into the cavity, takes the path of least resistance and does not build up any high pressure within the cavity until the latter is completely filled. The closed cavity makes it possible to support inserts on the top and bottom of the cavity.

It is possible to manufacture more dense moldings using transfer technique because there is no escape of material from the cavity and full pressure is therefore applied to the material within the cavity. It is generally conceded that this greater density increases the strength characteristics of the material, but this is only true when the filler does not consist of fibers which would be broken in passing through the somewhat restricted orifices and gates to the cavity. It has been pointed out in earlier chapters that the impact strength of fabric- or cord-filled phenoplasts is dependent upon the size and properties of the filler. Any disintegration of these fillers will reduce the impact strength. Another possibility for loss of impact strength in transfer molding exists when the molding composition is

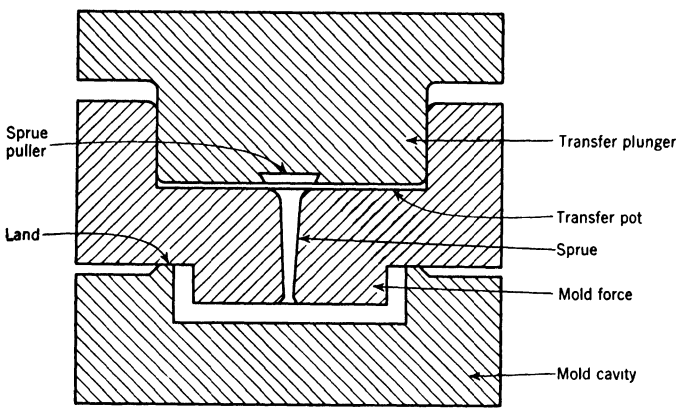


Fig. 77. Essentials of a transfer molding system.

injected into the cavity in streams. When the mold is completely filled, the streams lie against one another in a parallel fashion, with a decrease in the number of interlocking fibers. Although the high impact molding compounds suffer some loss of strength when transfer molded, this method offers much greater ease of handling than the compression technique. High impact materials are usually bulky and in compression molding require additional loading space above the cavity, which in turn increases mold cost. In transfer molding, the high bulk is taken care of by the height of the transfer pot. Where extremely bulky materials are used, the bulk may be reduced by the use of preforms.

When transfer molds are used in the standard compression molding press, the transfer pot must be incorporated in the mold itself. During the last few years, transfer molding presses have been developed so that

the transfer pot is part of the press and, being of a universal design, can be used for almost all transfer molds. This construction simplifies the mold design.

Transfer molding requires pressures which are five to ten times those needed in compression molding. The greater pressure is used primarily to inject the material into the cavity. The friction developed in moving the material from the transfer pot to the cavity accounts for about 75% of the pressure required. Therefore, the actual pressure on the material within the cavity is not much more than that which would be used in compression molding. It is generally conceded that the upkeep of a transfer mold is lower than that of a compression mold in spite of the higher pressure used.

D. INJECTION MOLDING

Injection molding of phenoplasts differs from that of transfer molding in that it is a semicontinuous operation similar to the injection molding of thermoplastic materials. The development is very recent and has not yet been thoroughly proved in practice. In operation, the molding compound is fed into a cylinder and carried by an injection ram into a section of the cylinder where the temperature is sufficient to cause the material to flow, but not sufficient to cause rapid cure. The temperature is controlled so that the material will flow at a pressure of about 20,000 p.s.i. The material is injected into a heated mold, where the condensation or polymerization is completed. The frictional heat developed when the material is forced through the sprue into the cavity raises the temperature of the material to such an extent that the curing time is reduced considerably over that which would be possible in either transfer or compression molding. A simple diagram of the injection molding arrangement for phenoplasts is given in Figure 78.

The jet process is a special form of injection molding for thermosetting material. The material when injected into the mold passes through a special heating arrangement on the nozzle attached to the heating cylinder. This heating arrangement contains electrodes through which a low voltage, high amperage current is passed; the temperature of the nozzle is raised to 500° or 600°F. The temperature on the nozzle is controlled by the forward motion of the ram in such a way that the heat is applied only when the material is in motion through the nozzle. To safeguard against overheating of the material in the nozzle when the ram has completed its forward travel, a cooling device immediately lowers the nozzle to such a temperature that the material will not cure. The operation of the jet proc-

ess requires careful attention, and is successful only when the timing of the ram travel is closely coordinated with the superheating of the nozzle.

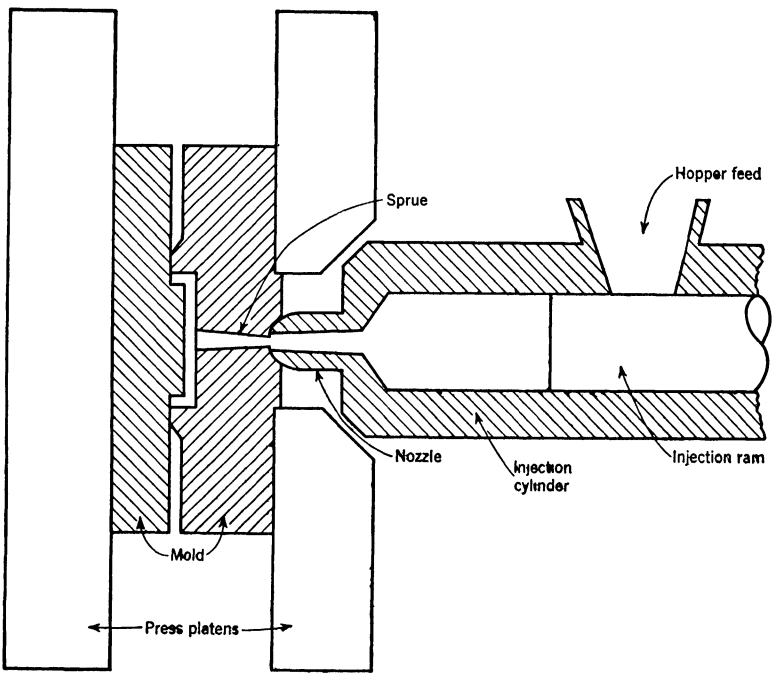


Fig. 78. Essentials of an injection molding system for phenoplasts.

E. MOLDING PRACTICE

Too much emphasis cannot be placed on the necessity for well-designed molds and tools in the fabrication of molded articles from phenoplasts. The most experienced application of molding technique will not produce satisfactory moldings if the tools with which the operator has to work are not correct. The molding will be as good as the mold from which the molding is made. Too often, jobs which should be simple are nonprofitable because the molds are inferior either in design or workmanship.

All molds have to be "broken in" before they are used for production. The trouble encountered in breaking in a mold depends largely on the polish of the mold cavities. Usually, the better the polish, the easier it is to condition a mold. Newly machined steel surfaces have minute ridges and crevices which are leveled off during polishing. Wax is usually applied for the first few heats or moldings, and this tends to fill up any

crevices or undercuts. Once the mold is working smoothly, further application of wax is unnecessary.

The breaking-in of a mold is a task for one who is well versed in the art of molding plastics. The operator must have some basic knowledge of the material used and of the working of the mold and of the press. Usually, there is one individual who does this work. It is considered an important function in every molding plant. The objective is to get the mold working and to establish a molding cycle, after which the job is given to a routine operator who follows the established molding technique. In the case of compression molding, great care must be exercised in placing the first charge of material in the mold cavities. The required weight of the charge is predetermined by calculation. The molder invariably will put in a smaller amount to be sure that the cavity is not overcharged. When the cavity is not completely filled, the resulting imperfectly molded part will give an excellent indication of the flow of the molding compound as it fills the cavity. This knowledge of the flow characteristics of the material in the cavity is extremely important, especially if the part is of complicated design. It is often necessary to load the powder or preforms—whichever is used—into certain locations in the cavity to equalize the flow of the material around bosses, pins, barriers, etc. Under the high pressures used to mold the phenoplasts, there is danger of breaking a pin or even a section of the cavity if care and study are not given to the flow of the material.

Part of the function of breaking in the mold and establishing the molding cycle is the choice of the proper flow of the material to be used. The grade of phenoplast to be used—wood flour-filled, cord-filled, mineral-filled—has been pre-established by the properties desired in the finished part. The only variation which the molder has is in the flow, or plasticity, of the material. It is not too difficult to judge the proper flow. The usual choice is the material of lowest plasticity which will fill the cavity without excessive pressure. Low plasticity is chosen so that the time of cure is reduced to a minimum, as in most cases a viscous material will cure faster than one with high plasticity.

Mold temperatures are important and are varied to some extent with the plasticity of the molding powder. A molded piece that is flat or has a shallow draw can be made from a resin composition that has fast cure and stiff flow; a molded piece of complicated shape or long draw will require a slower cure to assure filling out of the cavity. Low mold temperatures will permit sufficient time for flow even when a fast curing material is used. The molding pressure must also be coordinated with the mold temperature and the flow of the material. In all, there are many combinations of the

variables, and a condition must be found which will produce the most satisfactory molded part in the most economical cycle.

In transfer molding, entirely different factors establish the molding cycle. The softening of the molding powder by heat takes place in the transfer pot, which is separate from the cavity and is connected to the cavity by an orifice and gate. The initial flow of the material is not into the cavity—it has to flow through the orifice and gate before reaching the cavity. Due to the speed with which the material travels through the gate, a great deal of frictional heat is developed, and the temperature of the phenoplast is raised. Consequently, when the material reaches the cavity, the cure takes place rapidly. A much more plastic material is usually required in transfer molding than for compression molding. The proper molding pressure is established by the speed at which the material is transferred from the pot. In transfer molding too much pressure, within reason, does not endanger the cavity to the same extent as in compression molding. However, in some cases excessive pressure tends to compress the molded part beyond its normal density; as a result, the plastic part may expand or "grow" on removal from the cavity. There have been cases where this growth has resulted in moldings which were 2% oversize.

In transfer molding, mold temperatures are much more important than the flow characteristics of the molding material. The temperature of the transfer pot is usually kept below that of the mold. It is not the function of the transfer pot to cure the phenoplast. Its function is to heat the material to a point such that the latter will flow and can be delivered under pressure to the cavity. Too high a temperature on the transfer pot will shorten the curing cycle of the phenoplast so much that the molded piece will have low strength characteristics.

Invariably, the mold temperature of the transfer mold is lower than that used in compression molding. As has been pointed out, the friction of flow through the orifice raises the temperature of the phenoplast. The temperature is uniform throughout the mass of the molded part. The relatively low mold temperature gives the material a chance to flow and prevents premature cure on a hot mold surface. As an indication of the temperatures used in transfer molding, an actual case may be cited in which the temperature of the plunger in the pot was held at 250°F.; the pot and the force plug of the cavity, which were both mounted on a common plate, were held at 280°F.; the cavity itself was held at 305°F. In comparison, normal mold temperatures in compression molding are from 300° to 340°F.

The injection molding of phenoplasts requires advanced technique, because many factors have to be considered in establishing a successful mold-

ing cycle. Temperature control is required at two points on the heating cylinder, on the nozzle and on each half of the mold. A slight variation in any of these controlled temperatures can put the mold out of operation. In addition, the ram travel and the ram pressure have to be established. It is very difficult to obtain just the correct combination.

In general, most types of phenoplast molding compounds are suitable for molding by the injection process. There is one exception which has not been successfully molded. This is the type containing mica or quartz as a filler. It is assumed that the abrasive nature of these fillers does not permit the material to flow properly through the heating cylinder and nozzle. In general, phenoplasts for injection molding have to be lubricated to a greater extent than those normally used for compression and transfer molding.

F. PREHEATING

The preheating of molding compounds just before loading the mold has been practiced for many years. The preheating may be carried out either on the loose powder or on a preformed block. Such preheating helps the flow of the material within the cavity. Phenolic molding compounds have poor heat conductivity. When cold materials are loaded into the cavity and pressure is applied, the heat transfer from the heated cavity to the material is slow. As a result, the material next to the cavity walls starts to flow first, much in the same way that butter melts in a hot pan. High pressure is required to cause the unheated portion to flow. When the phenoplast is preheated, the flow takes place much more rapidly and with less pressure. In the older conventional types of preheaters, such as hot plates and ovens, there was limitation on the amount of heat which could be applied without causing premature cure. Recently, high frequency heating by electronic means has been used with astonishing success. This success is based on the fact that the phenoplast can be preheated throughout more rapidly and to a higher temperature than was possible by thermal conduction. The molding compound outside of the mold can be heated by high frequency up to molding temperature. When the preheated material is loaded into the cavity and pressure is applied, flow begins immediately. Under these conditions, molding pressures can be reduced from 25 to 50%, and the strain on the mold cavity is minimized. The time of cure of preheated material can be reduced substantially, especially when large sections are molded. The scarcity of high frequency equipment during the war has retarded this type of heating; now that equipment is available, many new techniques will, no doubt, be developed.

XVII. MISCELLANEOUS TECHNICAL APPLICATIONS OF PHENOPLASTS

The phenoplasts have always been the work horses of the plastics industry. With the exception of the cast phenolics, which are widely employed for decorative purposes, the dark color of the phenoplasts has limited their use to utilitarian fields. Fortunately, the excellent mechanical and electrical properties of the phenoplasts, combined with their stability and chemical resistance, have extended their usefulness into nearly all branches of modern manufacture. As was pointed out in an earlier chapter, the most important uses for the phenoplasts, in order of decreasing volume, are in molding powders, laminating varnishes, and protective coatings. The properties and uses of the phenoplasts when employed in these fields have been covered in the previous discussion. Individual applications of the molded or laminated phenoplasts are so numerous that it would be outside the scope of this volume to enumerate even the more important ones.

There are, however, miscellaneous uses for the phenoplasts which are quite important; these represented about 30% of the total phenoplast resin production in 1944. The miscellaneous uses largely depend upon the adhesive quality of the cured resins, although some of the newer uses depend upon the ability of the phenol alcohols to cross link with some thermoplastic resins, and thereby improve the heat resistance of the latter.

A. WOOD ADHESIVES

The largest single miscellaneous use is in the wood-adhesive field, and particularly in the production of plywood adhesives. This application accounted for about 8% of the total phenoplast resin production in 1944.

Plywood has been known for a long time, and its advantages have been widely recognized. The early glues for wood lamination were based on animal or fish protein; these were later followed by less expensive adhesives from starch. None of these glues was resistant to moisture or high humidity, and plywood which was made with them tended to delaminate under severe conditions. Considerable improvement was obtained by the use of

casein or blood, and much improvement, particularly in the case of Douglas fir plywood, was effected after the introduction of soybean glues. Wood laminated with properly formulated soybean glues is reasonably moisture resistant. However, the maximum advantages of plywood are realized through the use of synthetic thermosetting adhesives, which are unaffected by immersion in water for long periods, even up to several years. Phenol–aldehyde resins are the most widely used of all the synthetics, and are specified for the production of the exterior grade of Douglas fir plywood.

Baekeland mentioned the possible use of the phenoplasts in bonding wood in his early papers. In 1919, John R. McClain obtained U. S. Pat. 1,299,747 (assigned to Westinghouse Electric and Manufacturing Co.); this patent covered the impregnation of a fibrous sheet with a solution of phenoplast resin. The process, in the form described by McClain, does not seem to have been widely used in the United States. Between 1920 and 1930, attempts were made to use either dispersions (i.e., emulsions) of phenoplasts, or to spread dry adhesive on the plies; alcoholic solutions of resins were also used. None of these processes was successful, partly because of the lack of satisfactory machinery to obtain a uniform glue spread. The early part of the next decade—that is, the period about 1935—witnessed the development of phenoplast adhesives for plywood in the practical and economical forms which are in use today.

Phenoplast resin for the plywood industry today is supplied in three forms:

(*1*) *An aqueous solution*, which is simply spread on the core. The plywood assembly is then pressed under heat to cure the resin. The phenoplast resin employed for this use is generally a rather well-advanced water-soluble alkaline condensation product. Water solubility is maintained by the presence of a rather large amount of sodium hydroxide or other alkaline catalyst. The adhesive solution which is spread on the wood contains about 40% solids, and usually contains from 10 to 20% (on the dry resin content) of a filler such as wood flour or walnut-shell flour. These fillers aid the spreading of the resin solution on the wood, and prevent too rapid absorption by the wood fibers.

(*2*) *A spray-dried powder*, which is dissolved in water to produce an aqueous solution similar to that described above. Before the solution is spread on the wood, filler is added. The spray-dried powder is somewhat more expensive than the solution, but it has the merit of keeping for long periods, and is particularly useful when shipments of the adhesive have to be made over long distances.

(*3*) *A film adhesive*, similar in nature to that originally described by

McClain, but improved with respect to curing time and ease of handling. The most widely used film adhesive is known as Tego film. The film adhesive is particularly useful when thin veneers are to be bonded together, as in the case of aircraft plywood. These thin veneers tend to warp badly when treated with an aqueous solution of adhesive.

All of the above adhesives require pressing for about five and one-half minutes at temperatures around 270°F. to set the resin (for a five-ply, $^{9}/_{16}$ in. panel). For many purposes, an adhesive which sets at a lower temperature is required. To meet these requirements, phenoplast adhesives setting at low temperatures have been developed which will cure in a few hours at temperatures in the neighborhood of 100–120°F. Rapid cure is obtained by the use of resorcinol–formaldehyde products, either alone or in combination with other phenoplasts. Such adhesives have water resistance comparable to the high temperature setting resins. Klein[1] has given a rather complete description of the development of phenolic resin adhesives, with a bibliography.

B. BONDING OF INSULATING MATS

Another important adhesive application of the phenoplasts is in bonding of glass- or mineral-wool fibers to make insulating mats. The insulating qualities of these mats depend upon the entrapment of air between loosely woven and rather fragile filaments of glass or mineral wool. In order to give strength and stability to the mat, the fibers must be cemented together at their points of contact. A water-soluble resole, mixed with modifying agents, is usually employed. The resin solution is sprayed upon the fibers, and subsequently cured by passage through a heated chamber.

C. RESINS FOR BONDING GRINDING WHEELS

Grinding wheels are made by bonding abrasive grits together with a cement or adhesive. Until about ten years ago, nearly all grinding wheels were bonded with vitrified ceramic. The ceramic required firing in a kiln at high temperatures for a long time in order to fuse the cement to the abrasive grains. Due to the very brittle nature of the bond, the vitrified or ceramic-bonded wheels can only be operated at a relatively low peripheral speed. The introduction of phenoplast resins as bonding agents for the abrasive grit has permitted operation up to a peripheral speed of 9000 to 9500 ft. per min. for snagging wheels, and up to 16,000 ft. per min. for thin cut-off wheels, and has resulted in much faster cutting wheels. Because of

[1] L. Klein, *Ind. Eng. Chem.*, **33**, 975–980 (1941).

this, phenoplasts are now used to bond nearly all snagging and cut-off wheels, where high cutting speed is important.

An acid-catalyzed phenoplast is usually employed for bonding grinding wheels, and the finely powdered resin is mixed with enough hexamethylenetetramine to insure proper cure. In the manufacture of the wheel, the abrasive grits are usually wet first with a small amount of liquid resin, which insures contact of the grit with the resin binder. The powdered resin is then added and mixed thoroughly with the grit. The quantity of resin employed is from 7 to 15% of the wheel, depending upon the grade or hardness desired. Frequently a filler, such as Greenland cryolite, is added in quantities up to 12% by weight of the wheel. The mixture is then densified in a mold under pressure, removed from the mold, and baked at a carefully controlled time–temperature cycle in order to cure the resin.

A recent refinement in phenoplast-bonded grinding wheels has been the so-called "lens generator ring," used for the fine polishing of optical lenses. The body or hub is preformed of high impact phenoplast molding powder, and the grinding rim of diamond dust, filler, and phenolic resin. The two preforms are then molded together.[2]

D. WOOD IMPREGNATION

Phenoplast resin can be used to impregnate wood and thereby increase the strength of the wood, decrease the swelling due to moisture, and improve the resistance to decay and weathering. The term *impreg* has been coined to denote wood which has been simply impregnated with a resin solution and then heated to cure the resin; the term *compreg* denotes a laminated structure consisting of an assembly of wood veneers impregnated with a synthetic resin and converted under heat and pressure to cure the resin and yield a solid mass.

Various types of phenoplast resin may be used for the impregnation. The earliest workers employed an alcoholic solution of a resin which had been advanced beyond the water-soluble stage. In 1936, Stamm and Seborg[3] showed that the maximum efficiency of a phenoplast resin as an antishrink agent is obtained from a low degree of polymerization—that is, while the phenoplast is still in essentially the phenol alcohol stage. There are three reasons why the best results in impregnation are obtained from aqueous solutions of the phenoplasts in an early stage of condensation: (*1*) The water present causes greater swelling of the wood cells and consequently

[2] Anon., *Modern Plastics*, **22**, 114 (June, 1945).

[3] A. J. Stamm and R. M. Seborg, *Ind. Eng. Chem.*, **28**, 1164–1169 (1936).

opens the structure and gives a better bond. (*2*) The smaller, uncondensed phenol alcohol molecules diffuse into the structure much faster and more completely. (*3*) The uncondensed phenol alcohol molecules can orient themselves in the structure so that their polar groups can satisfy a large proportion of the hydroxy groups in the wood cellulose. It is these hydroxy groups in the wood which are responsible for moisture absorption, and they must be blocked in order to prevent swelling. Only a few of the remaining polar groups of an advanced phenoplast molecule could fit themselves into the lattice of the hydroxy groups in the wood.

As it is rather difficult to obtain deep penetration of any resin solution into thick sections of wood, the best impregnation results are obtained by the use of plywood veneer. The veneer may be treated either while green or after drying. In the latter case, pressure treatment has been recommended in order to secure thorough impregnation.[4] However, MacKinney and Repsher[5] have shown that thin veneers, up to a maximum of $^1/_{16}$ in., may be impregnated by simply applying the resin with a glue spreader.

Perry[6] has shown that high density plywood may be obtained by compressing thin layers of veneer (less than $^1/_{30}$ in.) with alternate layers of Tego film. Under pressures of about 1000 p.s.i., sufficient flow of resin is obtained to give a resin content of the wood up to 20%.

The antishrink efficiency of the resin treatment increases with increasing resin content of the wood up to a resin content of 30 to 40%, above which additional resin content has but little effect. The explanation for this lies in the fact that at concentrations around 30%, the cell walls are saturated with synthetic resin and any excess resin is deposited in the coarse capillary structure where it can show very little antishrink effect.[7]

The physical properties of either impreg or compreg depend on the resin content, the wood species, and the applied pressure during lamination. For example, birch with no resin has an apparent density of 0.65; when impregnated with 15% resin and compressed at 2000 p.s.i., the density rose to 1.38; when impregnated with 25% resin and compressed at 900 p.s.i., the density was 0.99. The impact strength decreases with increasing resin content. Birch compreg made with a water-soluble phenoplast will show a notched Izod impact value of 5 to 7 ft. lb. per in. of notch.[8]

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[4] A. J. Stamm and R. M. Seborg, *Trans. Am. Inst. Chem. Engrs.*, **37**, 385–395 (1941).

[5] H. W. MacKinney and L. Repsher, *Modern Plastics*, **21**, 103–105, 166–168 (March, 1944).

[6] T. D. Perry, *ibid.*, **19**, 61–63, 110–114 (May, 1942).

[7] A. J. Stamm and R. M. Seborg, *Ind. Eng. Chem.*, **31**, 897–902 (1939).

[8] A. J. Stamm, *Modern Plastics*, **21**, 97–99 (Dec., 1943).

E. MISCELLANEOUS ADHESIVE APPLICATIONS

Other adhesive uses for the phenoplasts are in the bonding of cork, the manufacture of sandpaper, in foundry sand binders, and in vacuum tube and light bulb adhesives.

F. BRAKE-LINING RESINS

An interesting and important use for the phenoplasts is in the impregnation of friction material for brake linings. The impregnation with the resin greatly reduces the rate of wear of the friction material, and at the same time improves the resistance to deformation, particularly in respect to "mushrooming" or spreading of the lining under load, and increases the structural strength of the composition, thereby giving more resistance to the pulling out of rivets. The data of Bruce and Halstead,[9] which indicate the manner in which the rate of wear at high operating temperatures is decreased by impregnation, are given in Table LXXIV.

TABLE LXXIV

EFFECT OF RESIN IMPREGNATION ON WEAR OF BRAKE LINING

Average operating temperature, °F.	Rate of wear, in.³/h p hr.	
	No synthetic plastic	Impregnated with thermosetting resin
160	0.0018	0.0012
350	0.0046	0.0029
400	0.0073	0.0066
800	0.384	0.124
1000	....	0.290

For this type of service, a rather flexible resin is required; at the same time, it must be stable enough to exhibit very little breakdown under severe friction against the brake drum. These requirements are met by combining a phenoplast resin with a drying oil, such as tung oil. The combination is then diluted with a suitable solvent, and employed to impregnate the fabric of the brake lining. The resulting composition is then baked to cure the resin.

G. CROSS LINKING OF THERMOPLASTS

An interesting recent application of the phenoplasts has been in cross linking or curing of thermoplast resins. This application is similar to the use of

[9] D. S. Bruce and R. T. Halstead, *Modern Plastics*, **19**, 40–41, 94–96 (Jan., 1942).

sulfur in the vulcanization of rubber—in fact, the phenoplasts themselves may be used to vulcanize rubber, as has been discussed in Chapter XIII. The use of thermosetting resins for cross linking of thermoplasts is still too new to permit many generalizations. However, it appears that for successful cross linking, the thermoplast must have either unsaturated double bonds, as in the case of rubber, or reactive hydroxy groups, as in the case of polyvinyl alcohol or its partially acetalized derivatives.

The cross-linked thermoplasts possess properties which are superior to either of the base resins, in that the toughness, flexibility, or elasticity of the thermoplast is retained, while the cross linking agent reduces the susceptibility of the composition to heat or solvent action. A large amount of the formal of polyvinyl alcohol, cross-linked with a phenoplast, has been used for magnet-wire coating; the cross-linked butyral derivative of polyvinyl alcohol has found considerable application in fabric coatings where flexibility is required.

H. WAR USES OF PHENOPLASTS

The plastics industry in general has reason to be proud of its contribution to the war effort. Before Pearl Harbor, a large fraction of plastics production went into novelty and decorative articles, nearly all of which became unessential after the outbreak of war. Within one to two years, virtually all of this plastics production was converted to the manufacture either of military articles, or items essential for the civilian economy. In many cases, plastics were used as substitutes for scarce light metals. There were a few cases where new applications for plastics led to failure, largely because the mechanical and thermal service requirements were not fully considered in relation to the properties of the plastics. However, such cases were rare in contrast to the many successful new uses developed; the military applications have been particularly satisfactory, largely because of the careful study which various branches of the armed forces have made of the service requirements, and the careful specifications which have been set up for plastic parts.

It would be impossible to list all the military applications which have been found for the phenolic resins—many applications are still on the secret or confidential list, and cannot be discussed. However, the following list gives some idea of the many useful parts which have been fabricated from these resins. The development of war-time uses has led to a significant increase in our knowledge of the mechanical properties of the phenoplasts, and has also resulted in new techniques for their processing. It is certain that

this new information will be applied to the expansion of peace-time uses for this type of resin.

One very successful application of the phenoplasts has been the *Army helmet liner*. The standard U. S. Army helmet developed for use in this war consisted of two pieces: a steel helmet that weighed about three pounds, and a plastic liner that weighed only seven and three-quarter ounces. When not in an active combat area, the soldier wore only the liner, which was



Fig. 79. Molded helmet liner and helmet.
(Courtesy Monsanto Chemical Co.)

light and comfortable. The liner was designed to have considerable shock resistance, so that it would protect the solder from minor blows such as falling objects or flying stones. The type of construction chosen was of molded laminated fabric; the laminating stock consisted of four-ounce cotton sheeting impregnated with a quick-drying, fast-curing resin to such an extent that the stock contained 54% cotton and 46% resin. The impregnated sheet was then dried and the resin heated to advance it to a point where it had the proper flow characteristics. The laminating stock was then cut to a

shape such that it could be laid up in the mold to give the proper shape. In one interesting method of fabrication, the dried, impregnated sheet was cut into ribbons of $^3/_4$ and 2 in. width. These ribbons were wound on an egg-shaped mandrel. The ellipoidal shape so obtained was cut in half to give two "preforms" which were then molded into the exact shape by the bag method under a pressure of about 250 p.s.i.[10,11] A typical helmet liner is illustrated in Figure 79.

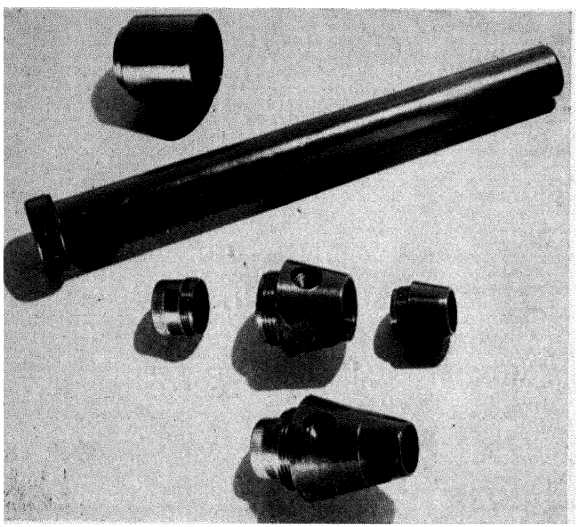


Fig. 80. Booster tube (top) and M-52 fuze.
(Courtesy Monsanto Chemical Co.)

Another important development was the *M-52 trench mortar fuze.*[12,13] This fuze, molded of a medium impact black phenoplast molding powder, replaced an earlier design made from aluminum, which required extensive machining. The production of this fuze was a difficult molding job because of the shape of the part and the close tolerances required, and called for extreme precision in design, mold making, molding, and finishing. These problems were solved by the industry, in some cases by the use of new techniques such as high frequency heating of the preform, and many millions of these fuzes were successfully produced and used.

[10] Anon., *Modern Plastics* **20,** 49–52, 152 (April, 1943).
[11] Anon, *ibid.*, **20,** 53–55 (Nov., 1942).
[12] Anon., *ibid.*, **21,** 101–114, 162–164 (April, 1944).
[13] W. S. Larson, *ibid.*, **20,** 71–73, 146 (Jan., 1943).

Tubes for holding the bursting charge for white phosphorus bombs were made of paper-laminated phenoplast, and successfully replaced metal tubes. In this case, the relatively low impact resistance of the paper laminate was an advantage, because the plastic tube burst in its entirety when detonated, while the metal tube tore or ruptured at only one point and therefore did not disperse the bomb contents over as large an area as was desired.[14]

The auxiliary booster tube for high explosive bombs was made of standard wood flour-filled composition. This tube held the detonating charge out of contact with the prime explosive; the plastic proved better than metal because the latter was corroded by contact with amatol, which was used as the prime explosive.[15] The construction of the booster tube and the M-52 fuze is shown in Figure 80.

Ammunition boxes for the storage of machine gun bullets, with mechanical devices for the proper feed to the gun, were made of cloth-base laminates.[16] The original box was made of stainless steel. The substitution with plastic resulted in a reduction in weight and a lowering of cost, without any serious deterioration of function or ability to fulfil the purpose.

A particularly interesting development, which required a new type of plastic, was the T-44 *frangible bullet.* This bullet is used in gun practice with a towed target such as a captive plane, and is so designed that it disintegrates on contact with the target, leaving a black smudge but not otherwise damaging the plane. A special lead-filled phenoplast was developed for this purpose.[17] The low flow and high specific gravity of this powder required the solution of many molding problems.

A macerated fabric-filled phenoplast was used to mold, by the transfer process, *gun butts for the Browning semiautomatic rifle.*[18] These gun butts had to withstand salt-water immersion during landing operations, the steaming atmosphere of the jungle, and the subzero temperatures encountered on northern battlefronts. In addition, the material had to be impervious to combat gases, resist the action of slime and fungus growth, meet high impact strength requirements, withstand extreme variations in temperature, and meet exacting requirements of weight and balance.

Tank periscope parts, previously machined from aluminum castings, were molded from phenoplasts.[19] The *No. 69 hand grenade,* together with the

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[14] Anon., *Modern Plastics,* **21,** 119-123 (Feb., 1944).
[15] Anon., *ibid.,* **20,** 65–66, 142 (Oct., 1942).
[16] C. G. Trunbach, *ibid.,* **20,** 59–61 (May, 1943).
[17] Anon., *ibid.,* **22,** 131-135, 198–200 (May, 1945).
[18] Anon., *ibid.,* **21,** 86–87, 174 (July, 1944).
[19] H. McCann, *ibid.,* **20,** 76–77, 154 (March, 1943).

247 fuze, was molded of medium impact cotton flock- and wood flour-filled phenoplast.[20] *Parts for the Sherrill compass* for mobile tanks were molded of various types ot phenoplasts.[21] Many parts of a portable *x-ray field unit* were molded of phenoplasts, and a wide variety of types were required to fill the varied electrical and mechanical requirements for these different parts.[22]

The above is only a partial list of phenoplast moldings which were developed for use by the Army, and does not cover the many uses which were standard before the war—electrical parts, plywood panels, gears, buttons, and similar articles. The Air Forces have likewise made a wide and varied use of phenoplasts, both for plane parts and for items used by the Ground Forces. The use of phenoplasts for many component parts of aircraft has been particularly desirable, since their use has in most cases resulted in a saving of weight.

An outstanding example of weight saving combined with a high degree of utility is shown in the low pressure molding and postforming of relatively large parts such as *pilot seats, bomb racks, trim tab fairings, map and data cases, gun-turret seats, glider control tabs, carburetor air scoops,* and *instrument panels.*[23] *Rocket launching tubes* were developed from laminated paper tubes. These were lighter than steel, and in case of premature bursting of the rocket there was less danger to the plane, since the plastic tube was designed to fracture more readily.[24]

Ammunition truck rollers, molded of graphite-filled phenoplast, were light in weight and provided self-lubrication. Other molded parts included *rotor units* for power transmission to gun turrets, *antenna masts* for transport planes, streamlined *antenna housing,* parts for the *pitch-changing mechanism* of propellers, the *propeller brush holder,*[25] poppet valves, check valves, packing rings, and other parts in the hydraulic system of planes,[26] *gasoline tank fittings,* parts for the *handpump* to inflate emergency rubber boats, *cockpit light* parts, the *firing block* and *fuze-setting ring* of parachute flares, *oxygen mask parts, signal flare grips,* and *control pulleys. Jettison gasoline tanks* for planes were molded of sisal-filled phenoplasts.

The use of phenoplasts has not been new to the Navy. Since 1922 phenol-

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[20] L. J. Falkenhagen, *Modern Plastics,* **20,** 66–67 (June, 1943).
[21] C. Lichtenberg, *ibid.,* **21,** 87–89, 170 (March, 1944).
[22] Anon., *ibid.,* **21,** 91–92, 180 (Aug., 1944).
[23] E. F. Lougee, *ibid* , **20,** 69–70, 148 (June, 1943).
[24] Anon., *ibid.,* **22,** 127–129, 204–206 (Nov., 1944).
[25] M. E Cushman, *ibid.,* **22,** 140–142, 192–194 (Apr., 1945)
[26] E. F. Lougee, *ibid.,* **22,** 103–105 (March, 1945).

ics have been used by the Navy for electrical purposes.[27] Light weight is not so essential aboard ship, but sturdiness and durability are of great importance. In addition to numerous electrical parts, many instrument components have been developed from the phenoplasts. A good example is the *chassis cover for Navy gun directors*.[28] This is a large molding, weighing four and one-quarter pounds, made from shock-resistant, cord-filled phenoplast. This part replaced one previously made of aluminum, and not only conserved this critical metal but reduced the machining operations necessary on the metal part. Another example was the *binocular adapter eyepiece and eyemount*, which saved about 6000 lb. of aluminum and 78,000 man hours of labor when redesigned to be molded of phenoplasts. The *clinometer*, which is used to indicate list on a ship, was molded of high strength phenoplast. The *Mark Validade*, which is used to determine the distance of surface objects, made use of various plastics, including a body and main gears of high impact phenoplast. *Handwheels* for valves on Navy vessels were pulp-molded, using phenoplast resin to impregnate the pulp preform. The *Navy training bayonet* was compression molded of phenolic resin board. *Tompions* are stoppers for the muzzles of ships' guns while they are not in action. A molded phenoplast was a logical choice because these parts called for resistance to salt water and grease.

[27] J. B. Lunsford, *Modern Plastics*, **20**, 45–49, 126 (Oct., 1942).

[28] Anon., *ibid.*, **22**, 136–137, 194 (March, 1945).

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