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AN INTRODUCTION TO THE CHEMISTRY OF CELLULOSE

AN INTRODUCTION TO THE CHEMISTRY OF CELLULOSE

By

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With a Foreword by
SIR KENNETH LEE

SECOND EDITION



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To

THOSE WHO HAVE DONE THE WORK

DESCRIBED IN THESE PAGES

FOREWORD

CELLULOSE chemistry is a subject for the scientific expert, and hence I cannot attempt to add anything to the substance of this book. It has, however, been my experience that the close correlation of science to the textile industry has already had a profound effect on its development, and that a closer bond between the two is the surest way to promote future advances. The more science is applied, the greater the number of scientific workers engaged in probing the secrets of cellulose chemistry, the brighter will be the outlook for our industry.

A knowledge of the literature on the subject is of the greatest importance to the research worker; the scientific journals cover a wide range of subjects, whilst patent specifications are difficult to find and to read. Those concerned with industrial production and process control have not the time for such reading, whilst the young research worker now entering the industry finds an overwhelming mass of literature before him. This book should therefore present a very valuable introduction to the subject of cellulose chemistry, and should be of great assistance in these two cases.

To those who wish to obtain a wider general knowledge of the subject it should also prove most useful.

KENNETH LEE.

MANCHESTER,
May, 1938.

PREFACE

" Of making many books there is no end " but we trust that no excuse is needed for the present work.

The subject of cellulose chemistry is not among the simplest of studies, but the important advances of recent years have clarified it to such an extent that we feel the time is ripe for publishing a relatively simple book which may act as a guide to the younger chemists who are entering those branches of our great industries which are concerned with cellulose.

It is to the " ordinary " chemist that we hope this elementary account will appeal ; for this reason we have tried to maintain some sort of balance between the descriptions of the purely scientific aspect of the subject and the practical applications. The narrative, in many cases, has a slight historical flavour in order to emphasise the course of development, but we have not adhered to the chronological sequence of description.

We have given no bibliography, as the source-books and journals are mentioned as occasion arises. Our guide-book is not intended as a substitute for the original literature which should always be consulted by the student. Nevertheless, we feel that a good general knowledge should first be acquired rather than a detailed mastery of any particular section, for experience has shown that successful research need not necessarily depend on an initial deep knowledge of a subject, which is often only acquired during the actual course of research.

We wish to express our indebtedness for the loan of blocks to Sir Robert Pickard, F.R.S. of the B.C.I.R.A., Dr. Gibson of the L.I.R.A., Professor Haworth, F.R.S. of Birmingham University, Dr. Dorée of the Chelsea Polytechnic, Dr. Neale and Mr. Slattery of the Manchester College of Technology. Professor Kurt Meyer of the University of Geneva not only lent us a number of blocks but also his own model of cellulose, which is gratefully acknowledged.

A number of photographs were kindly given to us by Dr. Kling of Böhme-Fettchemie, Dr. Astbury of Leeds University,

and Miss Alexander of the Tootal Broadhurst Lee, Company, Limited ; we are grateful for this interest in our work.

We acknowledge with thanks, permission from editors and publishers to reproduce illustrations from the following: The Journal of the Textile Institute, the Journal of the Society of Dyers and Colourists, Helvetica Chimica Acta, The Chemistry of Sugars (Edward Arnold and Co.), Zeitschrift für physikalische Chemie, The Journal of Physical Chemistry, The American Naturalist, and the Colloid Symposium Monograph, Volume IV (The Chemical Catalog Co. Inc., Reinhold Publishing Corp., 1926).

We are obliged also to Professor Haworth, F.R.S., for kindly reading the final section of our work on the constitution and molecular structure of cellulose.

To those of our scientific and non-scientific colleagues with whom various aspects of cellulose have frequently been discussed, we express our thanks, especially to Mr. A. V. Midgley for reading the typescript and proofs.

MANCHESTER. 1938.

PREFACE TO THE SECOND EDITION

ALTHOUGH it is only three years since the first edition of this book was published, there have been many further developments in cellulose chemistry, and we have tried to incorporate these in the present volume. The constitution and structure of cellulose is now discussed earlier, and some short account is given of its relation to other textile materials.

We acknowledge with thanks the loan of blocks from the Silk Journal and Rayon World, and express our gratitude to those who helped in our work by their criticisms, suggestions or advice.

MANCHESTER. 1941.

CONTENTS

PART ONE

THE OCCURRENCE AND GENERAL PROPERTIES OF CELLULOSE

PAGE

CHAPTER 1. The definition, distribution and classification of cellulose—Cotton, flax and ramie—Purification of cotton cellulose 3

CHAPTER 2. The general chemical properties of cellulose—Colloidal nature — Sorption — Moisture relations. The general physical properties — Capillary structure and pore size—Optical properties—Electrical properties—Mechanical properties 23

PART TWO

THE CONSTITUTION AND STRUCTURE OF CELLULOSE

CHAPTER 3. Historical development of the constitution of cellulose as a molecular chain 51

CHAPTER 4. The molecular weight of cellulose, with special reference to the work of Staudinger . . . 61

CHAPTER 5. The chain molecule hypothesis and the evidence from other textile material 75

CHAPTER 6. The molecular structure—Development of the evidence from X-ray examination—Swelling—The models of Mark and Meyer—Orientation—Mercerising—Micelle or chain molecule ?—Network theory 100

PART THREE

DISPERSED CELLULOSE

CHAPTER 7. Dispersion with strong bases at low temperatures and in moderate concentrations — Mercerising with various alkalies and organic bases—Neale's theory . 135

CHAPTER 8. Dispersion with hygroscopic substances at high temperatures and in concentrated solution—Solutions of inorganic salts—Effect of inorganic acids . . . 162

PAGE

CHAPTER 9. Dispersion by means of specific reagents—Cuprammonium hydrate—The fluidity test—Preparation of rayon—Carbon bisulphide and sodium hydroxide—Chloral 171

CHAPTER 10. The properties of dispersed cellulose—Moisture relations—Increased absorption—Effect of drying conditions—Reactivity and activation—X-ray diagrams . 187

PART FOUR
MODIFIED CELLULOSE

CHAPTER 11. Modification by acid—Hydrocellulose—Introductory historical methods—More recent researches—Relation between copper number, viscosity and strength—Affinity for methylene blue—Effect of alkali—Solubility number—Reducing properties—The chain molecule . 207

CHAPTER 12. Modification by oxidation—Historical introduction—Recent work with characterisation of two types of oxycellulose—Copper number—Properties of two extreme types—Effect of alkali—Accelerated oxidation—The chain molecule—Alkali-sensitivity . . . 235

PART FIVE
THE DERIVATIVES OF CELLULOSE

CHAPTER 13. Esters of inorganic acids—Nitrate—Preparation and properties—Rayon manufacture—Sulphates, phosphates, etc. 289

CHAPTER 14. Esters of organic acids—Formate, acetate, etc.—Artificial silk manufacture—Other fatty esters—The higher fatty esters—Comparison of properties—Esters of hydroxy acids, dicarboxylic acids, unsaturated acids, aromatic acids—Sulphonic acids . . . 304

CHAPTER 15. Mixed esters—General methods of preparation and properties of mixed inorganic-organic esters and of mixed organic esters 349

CHAPTER 16. The ethers of cellulose—Methylene ether—Methyl, ethyl and other alkyl ethers—Comparison of properties — Benzyl cellulose — Hydroxyethers — unsaturated ethers—Halogenated ethers 364

CHAPTER 17. Mixed ethers of cellulose—General methods of preparation—Comparison of properties . . . 395

CHAPTER 18. The ether-esters of cellulose—General preparation and properties 401

PAGE

CHAPTER 19. Amino cellulose and other nitrogen-containing derivatives of cellulose—Nitriles and thiourethanes . 410

CHAPTER 20. Soda cellulose—Historical introduction—The work of Vieweg; Coward and Spencer; Neale; and Bancroft and Calkin 430

CHAPTER 21. Cellulose xanthate—The viscose reaction and its modern interpretation—Preparation and properties of viscose—Rayon manufacture 446

CHAPTER 22. General consideration of cellulose derivatives —Substitution and substituents—Solubility . . 469

APPENDIX

DENSITY TABLES 485

AUTHOR INDEX 487

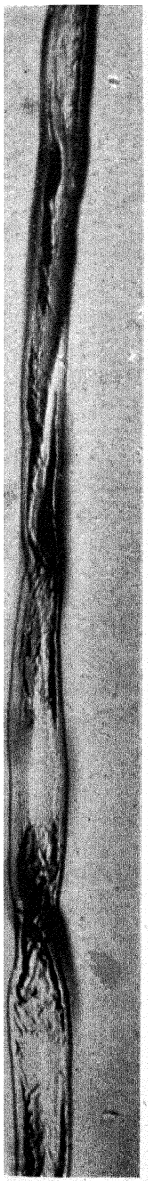
SUBJECT INDEX 495

LIST OF PATENT SPECIFICATIONS 506

ABBREVIATIONS FOR REFERENCE TO JOURNALS . . . 510

PART ONE

THE OCCURRENCE AND GENERAL PROPERTIES



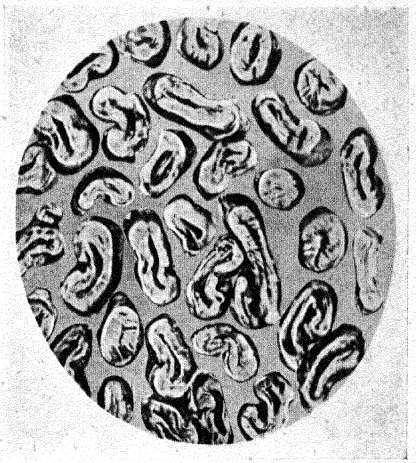
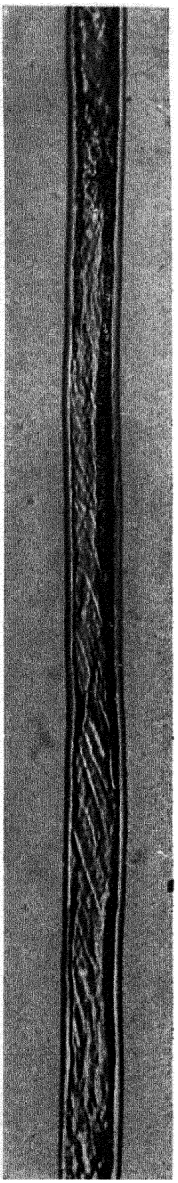


FIG. 3.



Figs. 1 and 2—cotton hairs mounted in the R-O-X medium, Fig. 2 showing the furrowed appearance in greater detail.

Fig. 3 represents typical cross sections.

Magnification × 400 diameters approx.

COTTON.

FIG. 1.

FIG. 2.

[*To face page* 2.

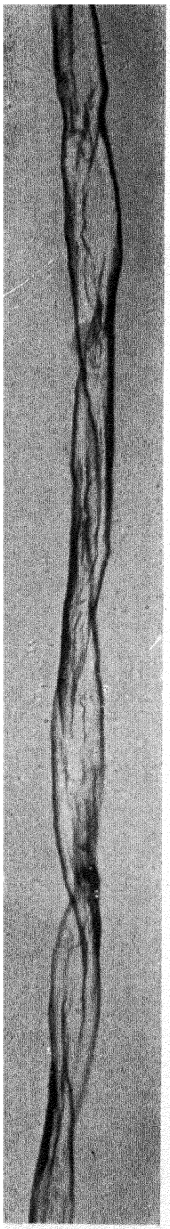


FIG. 4.

FIG. 6.

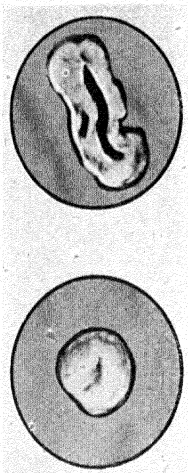


FIG. 7.

Figs. 4 and 5 are photographs of unmercerised and mercerised cotton hairs respectively, immersed in methylene iodide.

Magnification × 400 diameters approx.

Figs. 6 and 7 represent typical cross sections.

Magnification × 700 diameters approx.

COTTON.

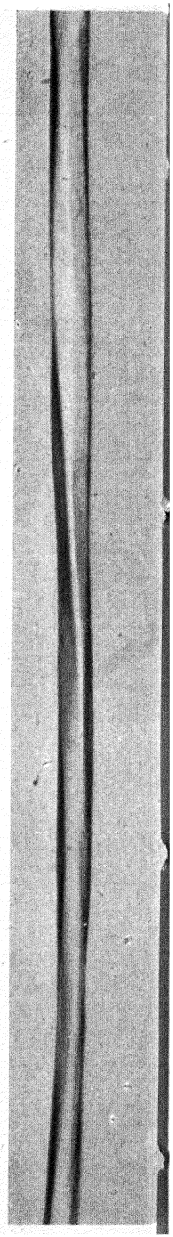


FIG. 5.

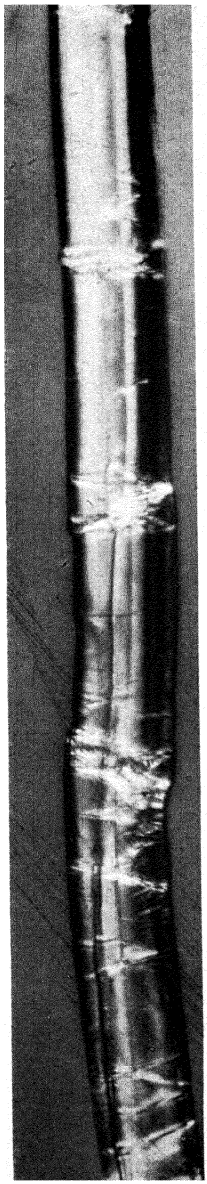


FIG. 8.

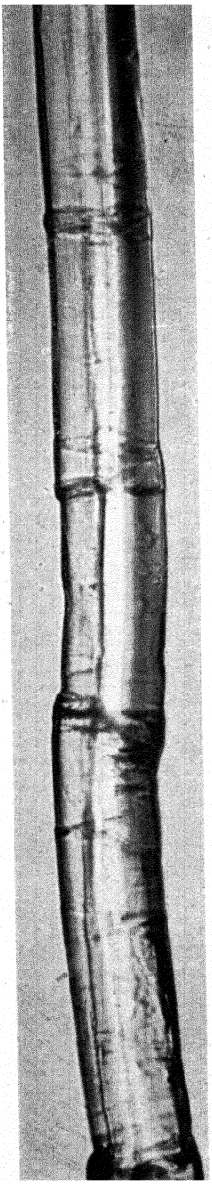


FIG. 9.

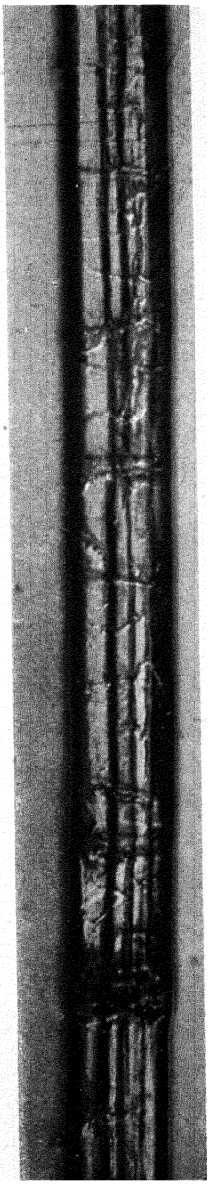


FIG. 10.

FLAX.

PLATE

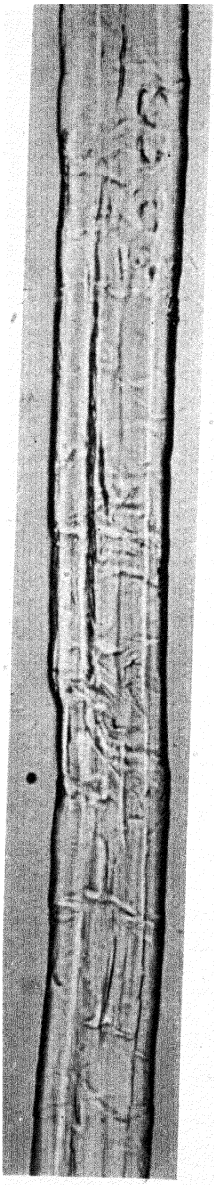


FIG. 11.

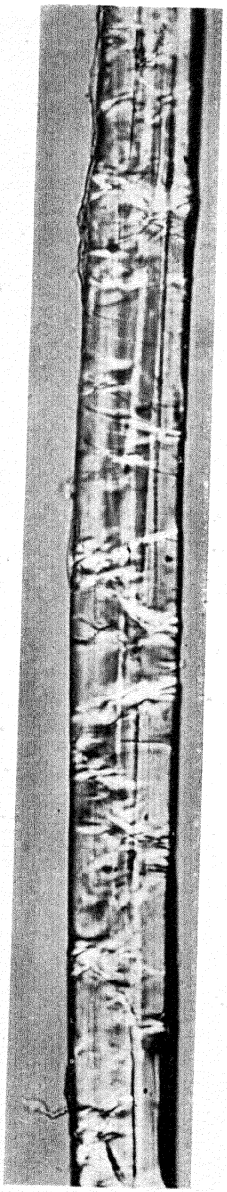


FIG. 12.

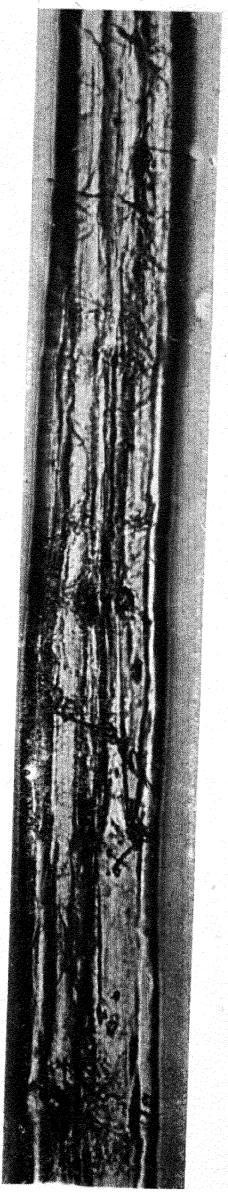


FIG. 13.

RAMIE.



FIG. 14.

Figs. 8 and 11 are from photomicrographs of flax and ramie fibres, when viewed in methylene iodide by normal light; Figs. 9 and 12 show the fibres when viewed by polarised light. Figs. 10 and 13 show flax and ramie fibres respectively in the R–O–X mountant.

Fig. 14 represents cross sections of ramie fibre.

Magnification × 400 diameters approx.

PLATE VI.

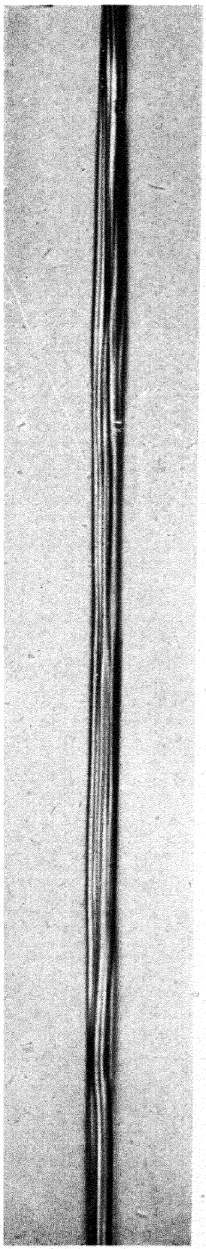


FIG. 15.

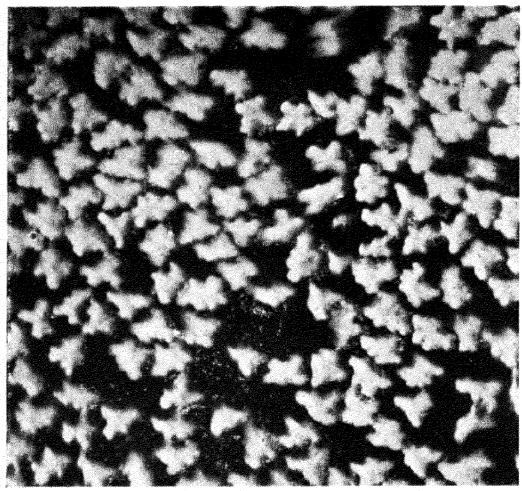


FIG. 16.

Figs. 15 and 16 are from photomicrographs of Courtaulds viscose mounted in the R–O–X medium. The denier of the filament is 1.2 and the magnification × 400 diameters approx.

VISCOSE RAYON.

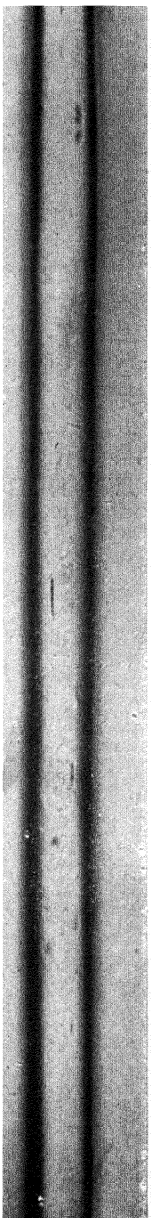


FIG. 17.

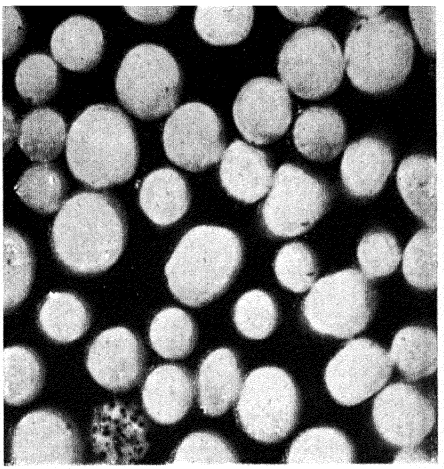


FIG. 18.

Figs. 17 and 18 are from photomicrographs of cuprammonium rayon, and Fig. 19 from cellulose acetate (British Celanese)—R–O–X mounting medium.

Magnification × 400 diameters approx.

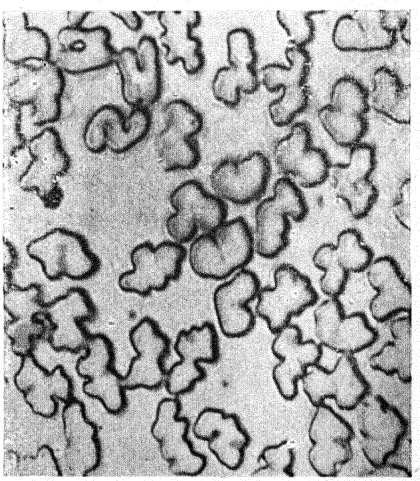


FIG. 20.

Photomicrograph of cross-section of cellulose acetate yarn.

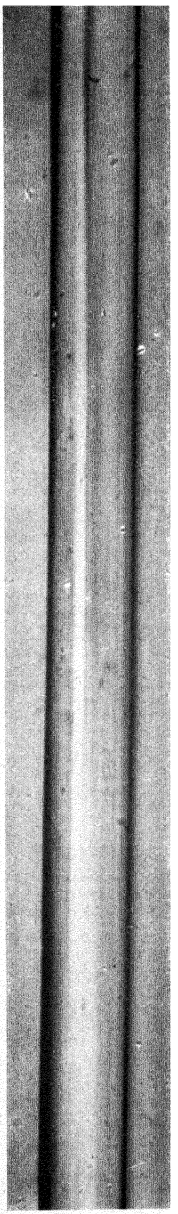


FIG. 19.

The foregoing illustrations, Figs. 1–20, are from photographs supplied by Dr. W. Kling of Bohme-Fettchemie Gesellschaft, m.b.H., Chemnitz.

The R–O–X method of mounting material for examination under the microscope has been described in a supplement to Kunstseide und Zellwolle, 1937, No. 7, and also in a supplement to Kleipzig's Textil-Zeitschrift, 1937, *31*, 509.

Fig. 20 is by courtesy of Miss Alexander.

[*To face page* 3.

CHAPTER ONE

DEFINITION, DISTRIBUTION AND PURIFICATION

THERE can be no better opening remark to any book on cellulose than the words of Cross and Bevan in their own book "Cellulose" (Longmans, Green & Co.; London, 1895).

"Cellulose is the predominating constituent of plant tissues, and may shortly be described as the structural basis of the vegetable world."

In view of the large number of varieties of cellulose, the term must be taken to indicate a chemical group rather than a chemical individual, and even in the case of cotton cellulose, which will, in general, be considered as the normal type of cellulose, its properties only reflect the average characteristics of the ultimate units of cellulose of which it is composed.

Occurrence

The highest proportion of cellulose is contained in the cotton hair and amounts to some 90%, but the bast fibres, such as flax, ramie, hemp, etc., also contain high proportions of cellulose. Wood and cereal straws contain a lower proportion of cellulose, amounting to 60% in the case of coniferous woods and about 30–40% for straw.

The most convenient classification of the types of cellulose for general purposes is on the fibre basis, but owing to the fact that cellulose does not occur naturally in the pure state it is necessary to deal briefly with the impure or native products from the chemical standpoint, that is to say, those products in which the impurities are in combination with the cellulose itself. The term applied to this class is "Compound Celluloses" and it owes its recognition to the fact that Fremy (Compt. rend., 1859, *48*, 862), found that vasculose or lignin was a constant constituent of woody tissue, so that the cellulose in certain plants was combined with secondary constituents of the cells. The original classification of vegetable tissue by

Fremy did not find much favour, but a somewhat broader differentiation into three main types appears to have been generally adopted.

The Lignocelluloses are the most important of the compound celluloses and are represented by two well-defined types, (*a*) the bast fibre, of which jute may be taken as the characteristic example, but the cereal straws, flax stems or shives, hemp and esparto grass are also included; (*b*) wood or the lignified tissues of perennial stems. The average constituents of the lignocelluloses appear to be some 60% cellulose, 20% lignin and 15–30% hemicellulose. The last mentioned substance is referred to below.

The Pecto- and Mucocelluloses form the class in which the non-cellulosic constituents are related to pectic acid and its derivatives. Examples are hemp, flax and ramie on the one hand and the algæ, fruits and tubers, which yield mucilaginous substances when extracted with water, on the other.

Adipo- and Cutocellulose contain fatty and waxy compounds as the typical non-cellulosic constituents. The chief example of adipo-cellulose is cork, which has been shown by Zetsche and Rosenthal (Helv. Chim. Acta, 1927, *10*, 346) to contain 2–3% of cellulose. Cutin is found in the epidermis of the leaves and stems of Phanerogams or flowering plants.

The above brief explanation of the classification is given for purposes of general reference in connection with a wider reading than that of the chemistry of normal cellulose. It is very doubtful whether the term "Compound" has any real justification except in the case of lignocellulose.

Whereas cellulose itself yields only glucose on hydrolysis, it was established by various investigators between 1840 and 1890 that the cellular constituents of plants also contained substances which gave other sugars on hydrolysis. Schulze (Zeit. physiol. Chem., 1892, *16*, 387) and Tollens (Ann., 1889, *254*, 304) showed that carbohydrates similar to cellulose were widely distributed in plant tissues. The proportion was found to vary with the growth of the plant and it was suggested that the function of the material was that of a "reserve" cellulose, as opposed to the normal cellulose which enters into the structure of the cell wall. The term "*Hemicellulose*" was applied to these reserve products from consideration of the chemical differences from cellulose itself. Hemicellulose may be regarded as a polysaccharide which, whilst insoluble in boiling water, is readily soluble in dilute aqueous solutions of

sodium hydroxide and is converted into pentoses and hexoses by warming with dilute acids at normal pressure.

Holocellulose comprises the largest amount of cellulosic material obtainable from wood and includes all the carbohydrate constituents after removal of the lignin.

Further information on the chemistry of both Hemicellulose and the Compound Celluloses may be found in Part III of Dorée's book, "The Methods of Cellulose Chemistry." (Chapman & Hall, London, 1933.)

The terms α, β, and γ-cellulose are also likely to be encountered and relate chiefly to the fractionation of the cellulose obtained from wood pulp. The classification is that adopted by Cross and Bevan on the basis of a treatment with 17·8% NaOH solution at 20° C. α-cellulose is the fraction which remains undissolved; β-cellulose dissolves but is precipitated on acidification, whilst γ-cellulose remains in solution. The α-cellulose is therefore of the same order as normal or cotton cellulose.

The fractionation is essentially based on the length of the molecular chain of various types of cellulose as described on page 228, although this was not known when this classification was suggested.

There is another term which is frequently encountered in cellulose chemistry and requires a few words of explanation. The word "degrade" is found to have two meanings, first that given to it by the textile technologist who is only concerned with degraded cellulose which still has fibre structure, and secondly the meaning which the organic chemist would attach to it, where the type of degradation is so severe from the textile standpoint as to be of theoretical interest only.

Native Cellulose

There are two main types of native cellulose, the seed hairs as represented by cotton, and the bast fibres of which flax, jute, hemp and ramie are examples. The seed hair of cotton is unicellular with a single solid apex, whereas bast fibres are multicellular and consist of completely enclosed tubes, pointed at each end.

Cotton

The cotton plant grows about four feet in height and takes some five to nine months for growth and maturing. The boll or fruit generally cracks about 48 days after the appearance

of the bud and is ready for picking two days later. It is necessary to separate the seeds from the hairs by a process called ginning, but after the removal of the hairs proper there is still a residue of short fibres and fuzzy undergrowth known as linters which are used for paper, guncotton, wadding and rayon manufacture. These linters are removed from the seed by a delinter machine.

The individual cotton hair whilst in growth consists of a long single tubular cell, with one end attached to the seed. It is roughly cylindrical with a lumen or central canal running through it. When the enclosing pod has burst, and the hair is removed from the seed, the cell collapses and becomes a flat ribbon-like structure which, on exposure to light and air, becomes twisted into an irregular spiral band, with from 150–300 twists per inch. The twist is not continuous in any one direction and these convolutions are largely responsible for the spinning properties of cotton.

The hair consists of the central canal or lumen, the secondary thickening and the primary wall. The lumen contains the remains of the protoplasm and near the apex is the nucleus, responsible for the growth of the hair. The lumen also contains the endochrome, which gives the cotton its natural colour. The secondary thickening is composed of cellulose, which has been shown by Balls to be laid down in successive layers corresponding to the annual rings in tree growth. The primary wall or cuticle appears to be a protective layer, which shows spiral fibrils in both quick and slow spirals. The fibrils are more easily seen in old or damaged cotton, and are sometimes reversed in the same hair. It has been suggested that these fibrils act as springs and impart elasticity and flexibility to the cotton hair. With bleached cotton the external cuticle may be absent. Some idea of the anatomical structure of the cotton hair may be seen from its behaviour in swelling agents, such as cuprammonium hydrate solution. When the swollen hair is examined under the microscope, the swelling is not uniform, but exhibits an appearance of a distended tube tied at intervals after the fashion of a string of beads. The annular constrictions are parts of the cuticle which has elsewhere been ruptured by the swelling forces allowing the cellulose in the swollen condition to protrude in the shape of globules. The walls of the central canal can also be seen as the cellulose begins to dissolve in the swelling agent. (See Figs. 21 and 22.)

The dimensions of cotton hairs vary considerably with the different types of cotton, a general average length being one inch, whilst the diameter varies from 0·001 to 0·0005 inches. The longest hairs—about 2·5 inches—have the least diameter. The hair is 3 to 4 times as broad as it is thick. Egyptian cotton is the most regular in length and diameter. The tensile strength of the hair lies between the figures for silk and wool and varies from 3·5 to 10 g., but is considerably below either of them in showing only some 4% extensibility. Some varieties of cotton have a fair lustre but in general cotton cannot be considered as a lustrous material. The following data give a broad general view of typical cottons:

CHARACTERISTICS OF TYPICAL COTTONS

	Sea Island	Egyptian	American	Indian
Length	1·8–2·5ins.	1·4–1·7ins.	1·08–1·2ins.	0·9–1·02ins.
Fineness	1/1600in.	1/1500in.	1/1300in.	1/1200in.
Feel	soft	soft	fairly soft	harsh
Lustre	silky	fairly silky	fair	poor
Colour	cream	light brown	white	cream
Convolutions per hair	300	228	192	150
Breaking strain in g.	8	7·6	9	3·2

The Fine Structure of Cotton

The most complete account of the growth of cotton has been given by Balls, whose work was mainly confined to Egyptian cotton. The details of his investigations are contained in two books—"The Development and Properties of Raw Cotton" (A. and C. Black, Ltd., London, 1915) and "Studies of Quality in Cotton" (Macmillan, London, 1928), together with a series of papers in the "Proceedings of the Royal Society," 1919, *B90*, 542; 1922, *B93*, 426; 1923, *B95*, 72. Anderson and Kerr of the United States Department of Agriculture have reviewed the growth and structure of cotton, utilising the Mexican variety of American Upland cotton (Ind. Eng. Chem., 1938, *30*, 48).

The cotton hair exists in the form of a single cell, about 1,200 times as long as it is wide, and is attached to the seed only at its base. Each hair originates as a growth from a single cell from the seed coat, and the first evidence of formation is the appearance on the day of flowering of a slight swelling which rapidly elongates on the following day. The diameter of the hair is established soon after it originates, but the elongation continues for some 15-20 days and then suddenly ceases.

The fibre origin is not limited to the day of flowering, but the swellings which appear after the second or third day only produce the linters, whereas the cotton hairs of commercial value all commence their growth within the first two or three days.

Primary Wall

During the period of elongation, the protoplasm is only enclosed by a thin primary wall, which is about 0·5 μ in thickness and forms the cuticle in the mature fibre. The primary wall of the young hair possesses a coherent skeleton of cellulose from the first day of its appearance, but it does not respond very clearly to the usual tests for cellulose in the early stages of development, and this has led a number of investigators to assume that the primary wall is free from cellulose, and others that the material of which the wall is composed is not actually cellulose, but some closely related substance.

According to Anderson and Kerr, these conflicting ideas are due to the fact that the cellulose in the very young fibres is associated with pectic substances, but they have found that if the young fibres are freed from pectic material a coherent skeleton of cellulose remains, which can be identified by the usual tests. This skeleton is doubly refractive, it is soluble in cuprammonium hydrate, gives the characteristic cellulose reactions with zinc chloride-iodine and with potassium tri-iodide and 70% sulphuric acid; it also shows the typical X-ray pattern of cellulose.

The fibre wall, when examined under the usual compound microscope, shows no evidence of structure, but by means of a special technique Anderson and Kerr have demonstrated that the cellulose in the primary wall forms an open mesh of very fine thread-like structures with anastomosis (i.e. they have a branching habit, like arteries). The primary wall was stained with Congo Red or zinc chloride-iodine and then examined between crossed nicols. The colouring matter is directionally adsorbed on the surface of the cellulose and the double refraction of the orientated colouring matter, in addition to the double refraction of the cellulose, makes the cellulose strands appear prominently. This method was first employed by Balls on young cotton fibres about ten days old; it was observed that there were present two opposing systems of fine, spirally wound, threads of cellulose at an angle of about 70° to the long axis of the fibre. Anderson and Kerr have confirmed

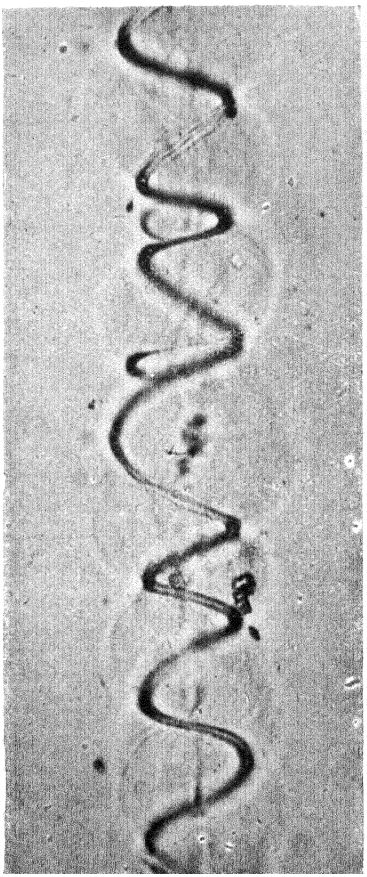


FIG. 21.

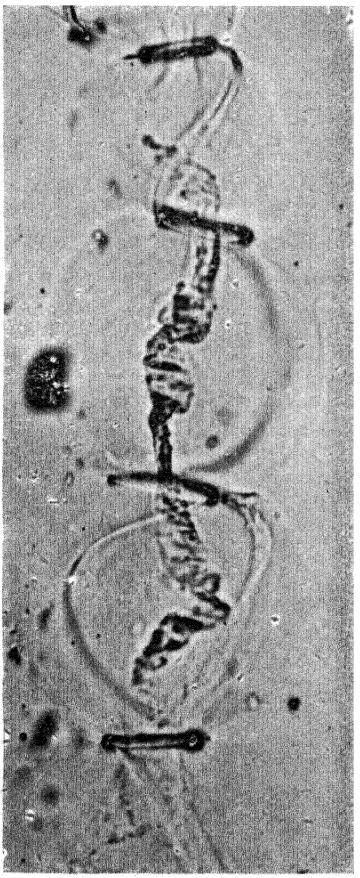


FIG. 22.

The cotton hair swollen with CS_2 and NaOH.

(Bright; B.C.I.R.A.)

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PLATE IX.

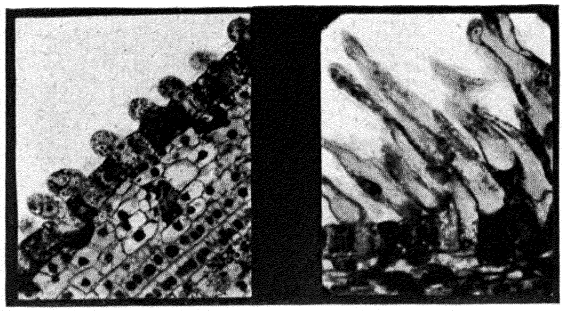
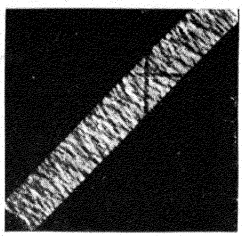


FIG. 23. FIG. 24.



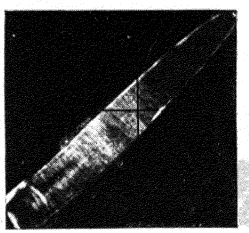


FIG. 25. FIG. 26.

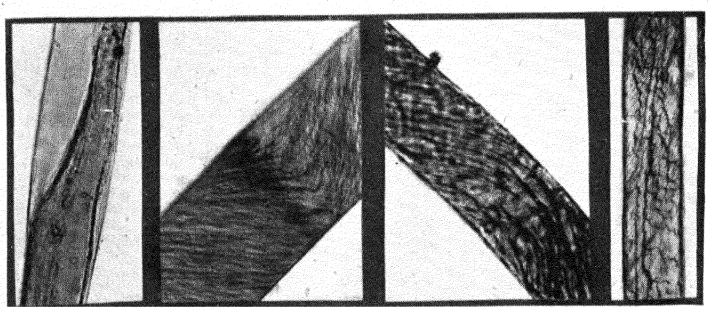


FIG. 27. FIG. 28. FIG. 29. FIG. 30.

Fig. 23 shows the cross-section of the epidermis of the cotton ovule on the day of flowering, and Fig. 24 two days later with elongation of young hairs. Fig. 25 shows orientation in the wall of a 15-day hair, and Fig. 26 transverse orientation in a 2-day hair. Fig. 27 shows the structureless primary wall of a 15-day hair. Fig. 28 shows spiral formation in secondary wall of a 16-day hair. Fig. 29 shows a reversal. Fig. 30 shows staining by zinc chloride-iodine.

(By courtesy of Ind. Eng. Chem.)

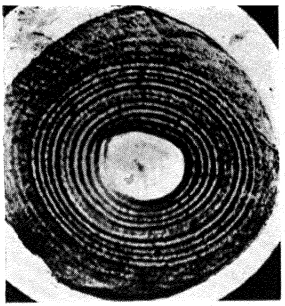


FIG. 31.

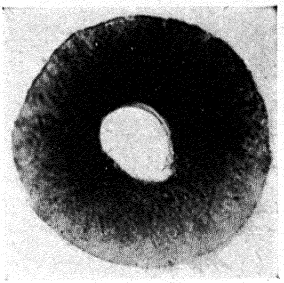


FIG. 32.

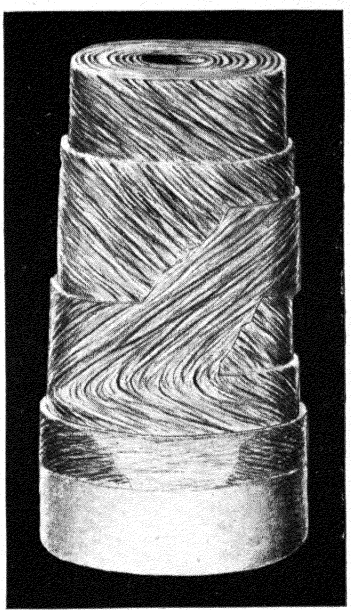


FIG. 33.

Fig. 31 shows growth rings in the hair. Fig. 32 shows absence of growth rings. Fig. 33 is a diagram of a model of the cotton hair.

(By courtesy of Ind. Eng. Chem.)

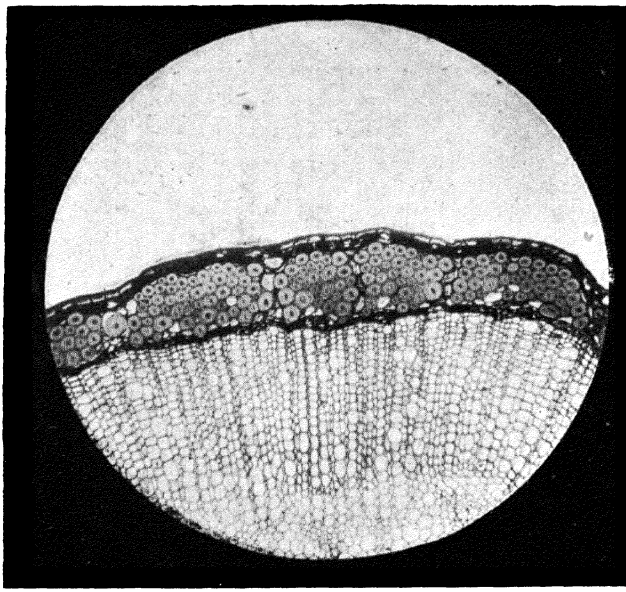


FIG. 34.—Photomicrograph of cross-section of flax stalk.

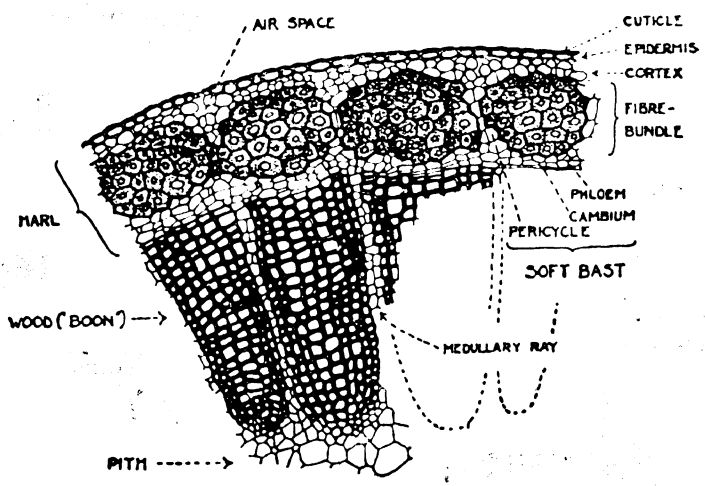


FIG. 35.—Diagram of the cross-section of flax stalk.

(By courtesy of L.I.R.A.)

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this observation and extended it to hairs only two days old. The cylindrical form of the young hair makes it possible to prove that the two systems of spiral threads exist in the same wall. Both right and left-hand spirals were seen when the microscope was focussed on the upper wall; they disappeared in the upper wall as the focal plane was lowered and appeared in the lower wall when the focus was established there.

A third arrangement of the cellulose in the primary wall appeared when the stage of the polarising microscope was rotated so that the long axis of the fibre made an angle of about 45° with the planes of the nicols; a system of transverse strands of cellulose became visible and these too anastomose. These three systems of strands which make the cellulose framework of the primary wall seem to be uniform over the entire surface and there is no evidence of the change of direction of the spiral which is so common in the secondary wall.

Secondary Layers

When viewed under the usual compound microscope, the second deposition of cellulose stands out in strong contrast to the structureless primary wall and even the first deposition of cellulose inside the primary wall is quite distinct when stained with zinc chloride-iodine. The branching and re-branching strands wind in a steep spiral round the inner surface of the primary wall. The spiral makes an angle of 20-30° with the long axis of the fibre as compared with 70° for the spirals of the primary cellulose. The first secondary depositions appear quite suddenly.

One of the characteristic features of the first layer of secondary cellulose is the reversal of the spirals; there are areas in the wall where the cellulose threads change from right-hand to left-hand spirals, or vice versa. The number of such reversals varies considerably, but it is quite common to find fifty or more on a single hair; close double reversals are not uncommon. One type of reversal is that in which one set of spiral strands ends and a second system running in the opposite direction begins; the ends of the strands overlap at the reversal. The commonest method of reversal is a simple change in direction by bending in the form of an arc.

The second layer of secondary thickening does not necessarily follow the pattern produced on the previous day. The points of reversals are at different places and the direction of the spiral is often exactly the reverse of that in the first layer of

the secondary wall. In many places, however, the pattern of the second layer conforms to that of the first layer.

It is difficult to follow the course of the subsequent deposition of cellulose, but in view of the behaviour of the hair on drying and also the result of swelling agents, some sort of pattern is established which is broadly followed by the later layers. The anastomosing character of the early depositions must be emphasised, for although the fibrils have a definite spiral path, they branch and rebranch with each other. The threads which form the spiral vary in length and also in diameter.

The deposition of cellulose continues for at least twenty-five days until a few days before the boll opens. When this takes place, the fibres dry and the walls become twisted ; the direction of these twists, or convolutions, conforms to that of the spiral in the greater part of the cell wall. Where a reversal takes place in the spirality, then a similar reversal or convolution occurs. There seems to be little doubt that the convolutions in the dry fibre are determined by the arrangement of the micelles in the cell wall.

Growth Rings

One of the characteristic features of the section of the cotton hair is that when it is swollen, growth rings appear much in the same way as the annual growth rings in trees. The presence of these lamellæ has been known for many years, but Balls was the first to correlate them with the actual number of days during which the wall of the hair increased in thickness. He observed that the cotton plant ceased to grow during the hot afternoon period and assumed that the deposition of cellulose also stopped at this time and resumed during the night and morning. The lamellæ were, therefore, regarded as a sign of discontinuous periodic growth.

These growth rings may be used to distinguish between cotton hairs which are produced early in the season and those which are produced later. Anderson and Kerr have observed that bolls developing from flowers that open in the early summer matured in about forty-five days, the fibre growing in length for sixteen days and thickening for about twenty-five days. Bolls that developed from flowers opening later in the summer required about seventy days for maturing ; the period of elongation of the cell was only a day or two longer than normal, but the period of secondary wall formation was enormously increased.

In the earlier fibres, the growth rings are relatively broad and may occasionally reach a diameter of 0·3 μ, but the rings formed in fibres which develop later in the season are much thinner and rarely exceed 0·14 μ in diameter. It may be remarked that there is considerable variation in the growth ring diameter, even in hairs from the same boll, but in general, the early fibres have fewer and wider rings in contrast to the larger number of narrow rings on the hairs appearing later in the season.

Kerr has confirmed the observation regarding correlation between the number of lamellæ and the number of days during which secondary thickening takes place, but, in contrast to Balls' hypothesis of intermittent growth, Kerr has suggested that the deposition of cellulose is a continuous process which varies in its rate according to temperature.

When cotton is grown under constant illumination and at a constant temperature of about 30° C., no growth rings appear. When the temperature is varied under conditions of constant lighting, then growth rings appear. Similarly, when the temperature is maintained constant and the artificial lighting is turned on and off at twelve hour intervals, then indistinct growth rings appear.

One important feature of this investigation is that although it is possible to control the growth ring pattern by the above means, yet it has not been found possible to control either the pattern of the spirals, or to influence the reversals.

Further work (*ibid.*, 1939, *9*, 325) showed that fibres produced under constant illumination are finer and of lower breaking load than normal cotton hairs ; the intrinsic strength, however, is the same.

Summary

The fine structure of the cotton fibre may be summarised as follows :

1. A primary wall contains cellulose and pectic substances. The cellulose micelles in this wall are grouped into delicate anastomosing threads which have at least two systems of orientation : (*a*) a flat right-hand spiral, (*b*) a flat left-hand spiral, and probably also (*c*) a transverse position. All three systems seem uniform over the entire surface of the fibre cell.

2. A secondary wall is composed of many lamellæ of cellulose. The lamellæ are not separated from one another by non-cellulosic substances but represent dense and less dense

areas of cellulose. The layers are formed of systems of spirally wound branching threads, and the direction of the spiral is reversed at frequent intervals.

3. Frequently the pattern of spirals first appearing in the secondary wall is not similar to that in subsequent layers of the wall. Most of the layers of the wall, however, follow a pattern that is established soon after secondary thickening has begun.

General

A number of important microscopical observations on the structure of plant fibres have been made during the last hundred years; the existence of fibrils in cell walls was reported by Meyen in 1838, whilst in 1852 Agardh was able to separate the spiral lines and demonstrate the fibrillar nature of the structure. Striations on the surface of the fibre and stratifications in the cross sections were observed by Nageli in 1877, whilst Wiesner in 1886, by means of a treatment with acids at fairly high temperatures, was able to obtain from fibres fine particles which he termed dermatosomes.

During recent years investigations have been directed more towards the isolation of the structural unit, as only a superficial observation is possible on the intact cell wall. Ritter (J. Forestry, 1930, *28*, 533) isolated a number of structural units from wood fibre, first, the fibrils and bundles of fibrils, and secondly, smaller spherical units.

Farr and Eckerson (Boyce Thompson Inst. Contrib., 1934, 6, 189 and 309), in their study of the development of the cotton hair demonstrated the presence of small particles of uniform size which were present in bead-like strands and considerably larger in size than Ritter's spherical units. These particles in chain formation appear to form a single fibril in the cell wall and they may be separated even from the mature cotton fibre. The question of these "particles" being the structural unit of cellulose is still under consideration as they are considerably larger than the micelles. Farr and Eckerson believe them to be the fundamental, biological, structural unit, but the question is one which must await further investigation. The chemical dissection of the cellulose wall of the cotton hair into fibrils, and the further dissection into dermatosomes, fusiform bodies, etc., is only accomplished as the result of severe chemical treatment so that some caution must attend the reconstruction of the hair from data of various investigators.

PLATE XII.

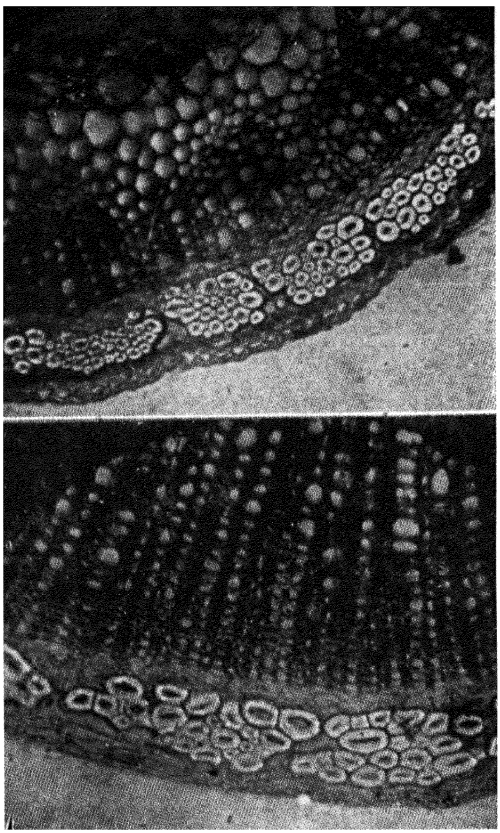


FIG. 36.—Sections from centre and root ends of flax stalk.
(Lower section is from the root end.)
Slattery (J.T.I.)

[*To face page* 13.

Flax

Flax appears to be the earliest vegetable fibre to be used industrially and the plant was grown in almost every country, but in modern times its production is confined chiefly to France, Ireland, Belgium, Holland, Russia and North America. The plant is an annual and grows from three to four feet in height. When it has reached its full growth the plant is pulled up or cut down and subjected to a process termed rippling whereby the leaves and seeds are removed by a series of upright forks. The flax stalk or straw is then tied in bundles for the purpose of retting, which involves the decomposition of the woody matter enclosing the cellulose fibres. The process is one of fermentation and may be carried out by stagnant water in pools, in slow moving streams, by exposing to sun and dew for about two weeks, or by various chemical methods. The older processes are still the most popular. The pectic matter which holds the fibres together must not be completely removed by retting as its presence in controlled amounts maintains the strength and elasticity of the flax—over-retted flax is brittle and weak.

The retted flax is dried and subjected to a process called scutching which involves passage through several pairs of fluted rollers, which break up the woody matter. The stalks are then placed in a machine with a rotating cylinder, on which are a number of wooden blades to remove the loosened woody matter. This procedure is known as heckling or hackling. The flax is then sorted according to quality, and is termed line whilst the waste is known as tow and used for the manufacture of twine and thin ropes.

The flax straw contains about 27 % of flax which is the inner bark or bast fibre. The flax fibre is multicellular with a tapering pointed end and a narrow lumen. It shows occasional longitudinal striations and peculiar cross-like dislocations termed nodes. The cell wall is uniform in thickness and the cross section is polygonal.

Flax varies in length from a few inches to three feet, but the average length of good flax is twenty inches. The individual cell, however, is from 0·25 to 2·5 inches in length and has a diameter of 0·005 to 0·001 inches.

The flax fibre is much stronger than the cotton hair, and the lustre is good except in the case of Egyptian flax which has a dull appearance. The colour is a pale yellowish white but some varieties are grey. The amount of moisture in the fibre varies,

but the accepted regain is 12 % compared with 8·5 % for cotton. Flax is a better conductor of heat than cotton, and it is this property which gives the much appreciated feel of coolness to linen and also makes it valuable for surgical bandages. Flax is more easily disintegrated by chemical means than cotton and the fibre is considerably weakened during the bleaching processes.

Ramie

Ramie and china-grass are really two distinct fibres obtained from sub-tropical and temperate regions respectively, but the fibres are so similar that it is customary to regard them as identical. The plant is from four to eight feet in height and belongs to the class of the stingless or dead nettle. The usual method of preparing the fibre is to soak the stalk in water and scrape off the bark. It is a very difficult matter to "de-gum" ramie fibres for satisfactory spinning. Ramie fibre is probably the strongest of the vegetable fibres and is also exceptionally white in colour, and possesses a high degree of lustre.

Ramie has thick cell walls with a wide lumen often containing granules or shreds of albuminous matter. The fibres taper but have pointed ends. Striations and cross markings are common, whilst joints and fissures are frequently visible. The fibres are broad and without twist and the diameter is uneven. The cross section is generally composed of one cell or a small group of cells with slight growth-ring formation. The section is large and elliptical. The strands of the ramie fibre are from 3 to 72 inches in length, but the chief characteristic is the size of the individual cells, which are 3 to 16 inches in length and 0·0008 to 0·003 inches in diameter. The fibre can be combed to a very fine state, but it lacks elasticity and flexibility. Osborne (Text. Res., 1934, *5*, 75) in an excellent account of the structure of ramie, indicates that its brittleness is due to trans-fibre fissures as well as to high orientation.

A good account of the vegetable (and other) fibres is given by Matthews in "The Textile Fibres" (Wiley, New York, 1924). Both cotton and flax contain some 5 to 10 % impurities, including the waxes, which are not removed until after the spinning operations, which they materially assist. Flax wax makes up about 2 % of the fibre and gives it a characteristic unpleasant smell.

Purification

As by far the greater part of normal cellulose is represented by cotton cellulose, it is proposed to take this as typical, but information on the purification of the other vegetable cellulosic material may be obtained from Huebner's book, " Bleaching and Dyeing of Vegetable Fibrous Materials " (Constable, London, 1912). The broad general procedure is to subject the impurities to a process of alkaline hydrolysis and emulsification, followed by an oxidising agent to remove the colouring matter.

Impurities

The natural impurities in the raw cotton consist chiefly of pectic matter, colouring matter, cotton wax, albuminous matter and inorganic salts. There is also a small amount of oil which appears to be identical with cotton seed oil, and is probably obtained from the seed to which the hair was attached. The albuminous or nitrogenous matter in cotton is very small and probably consists of protoplasmic residue. The nitrogen content has been investigated by many workers, some of the latest results being produced by Ridge (J.T.I., 1924, *15*, 94), the most noteworthy feature being that the actual amount is largely determined by the type of cotton and its origin. Raw Egyptian cotton has an average nitrogen content of 0·3% approximately, compared with 0·2% for American cotton. Purified and bleached cotton cellulose contains no nitrogen.

The amount of wax in native cotton is usually 0·5%, and varies according to the type of cotton. The wax appears to serve as a protective layer and resists wetting, hence in the purification of cotton it is necessary to remove the wax either by extraction with a solvent or more commonly by boiling with dilute alkali. The wax content of raw cotton was originally examined by Schunk (Mem. Manchester Lit. Phil. Soc., 1871, *24*, 95), but the most complete reports on the material removed by various solvents are those of Knecht and his collaborators (J.T.I., 1911, *2*, 22 ; J.S.D.C., 1911, *27*, 142 ; 1918, *34*, 220 ; 1920, *36*, 279 ; 1920, *36*, 43). More recent investigation by Fargher and Probert (J.T.I., 1923, *14*, 49) resulted in the isolation of Montanyl alcohol and the new Gossypyl alcohol from cotton wax, which mainly consists of the latter.

All vegetable tissues contain a certain proportion of mineral

constituents, and in the case of cotton this is usually of the order of 1% estimated as ash, but this will vary according to the degree of cleansing of the cotton. Raw cotton, direct from the bale, is often contaminated with earth and sand. The ash is naturally lower after purification, and in pure cotton amounts to 0·1 to 0·4%. When filter paper is required for quantitative work it is important to eliminate the ash constituent as far as possible, and this is generally effected by means of a treatment with hydrofluoric and other acids with the result that filter paper of good quality may contain 0·03 to 0·05% ash.

The ash content and its composition show certain relationships to the origin of the cotton cellulose. The work of Ure, as described in Bowman's "The Structure of the Cotton Fibre," shows that in the case of Sea Island cotton, which contained 1% ash, this was composed of 45% K_2CO_3 and approximately 10% of KCl, K_2SO_4, $Ca_3(PO_4)_2$, $CaCO_3$, $Mg_3(PO_4)_2$, with a trace of iron oxide and alumina. Geake (J.T.I., 1924, *15*, 81) has investigated the phosphorus content of various raw cottons and shown that it is possible to distinguish between certain types, particularly Egyptian and American, on the basis of the phosphorus content. The American cottons show figures of 0·04 to 0·06% P_2O_5, whilst Egyptian cottons vary from 0·08 to 0·13%.

The greater portion of the impurities present in raw cotton is represented by the pectin compounds, but when the cotton is boiled with dilute alkali these are decomposed from the complex organic combination in the hair to form sodium or calcium pectate. The gelatinous nature of the pectin may be observed in the brown masses, which are produced in the course of the kier boiling or alkaline treatment.

The colouring matter in cotton is supposed to consist of two organic pigments, one of which is readily soluble in alcohol, and the other is only dissolved by boiling alcohol. The pigment matter is found chiefly in the lumen, but is also in association with the cellulose itself. The pigment of cotton is most pronounced in the wild varieties and deepens as the cotton ripens. Egyptian cotton is much richer in pigment than the American varieties and may readily be distinguished by this property. There is also a peculiar variety of American cotton termed "blue bender," characterised by a bluish colour which cannot be removed by the usual bleaching processes. Experimental production of coloured cottons is being developed in the U.S.S.R.

The colouring matter of cotton is not immediately soluble in alkali, as air and light or chlorine are necessary for its complete removal. In the technical processes of bleaching a great part of the colouring matter is removed in the treatment with boiling alkali and completed in the bleaching process proper.

Some typical data on the constituents of raw cotton are 90% of cellulose, 8% of moisture, 1% of mineral matter, 0·5% of wax, etc., and 0·5% of pectic matter.

Standard Cellulose

In many of the earlier publications on cellulose it is customary to read that the starting product was well bleached cotton or surgical cotton wool or perhaps filter paper. Unfortunately, these do not necessarily represent the same cellulose, so that any results drawn from experiments with such materials are open to question ; for it is now well known that many varieties of, say cotton wool, are actually severely degraded in course of preparation. Indeed it seemed to have been realised with some surprise by the earlier investigators that the technical processes of bleaching cotton materials were designed to produce cellulose of a high order, not only of purity but also of minimum degradation. As it is now generally realised that native cellulose is *progressively* open to chemical attack which may not be particularly evident in its early stages, it is customary to characterise the starting product by various properties which are measures of any degradation of the material. These properties will be dealt with in some detail at a later stage, but for the present it is sufficient to state that they are based on the modern conception of cellulose as a chain of glucose residues. Any attack will, therefore, presumably affect the chain length, and may be measured by the viscosity or fluidity of the solution of cellulose, or alternatively by the increase in reducing power resulting from the formation of a larger number of shorter chains each possessing a reducing end group—this reducing power is measured as the " copper number." Alteration in viscosity or reducing power can each be measured to a degree of accuracy which enables one to detect degradation in the textile sense, long before it is apparent as diminution in tensile strength.

The following method has been suggested by the Cellulose Division of the American Chemical Society (Ind. Eng. Chem., 1923, *15*, 748) as a standard procedure for the preparation of " standard cotton cellulose."

100 g. of Wannamaker's Cleveland raw cotton is mechanically cleaned by removing the seeds and other visible impurities by hand picking. The cotton is then loosely placed in a nickel gauze container, to which a small nickel chain is attached passing through a hole in the centre of the cover of the surrounding glass vessel. A solution is prepared by raising 30 g. of sodium hydroxide and 15 g. of rosin in 3 l. of water to boiling point and into this solution is placed the nickel container containing the cotton. The boiling is continued for four hours, during which time the container is mechanically subjected to a continuous vertical up and down movement, avoiding exposure of the cotton to air. At the end of this time the brown alkaline solution is replaced with hot distilled water and washing continued until the wash water is only slightly alkaline. The cotton is again heated for 15 minutes with a solution containing 5 g. of NaOH in 3 l. of water, after which the liquor is removed by displacement with hot distilled water. The cotton is then immersed in cold water in a large glass beaker and allowed to cool to 18–20° C. It is then drained and bleached by immersion in 3 l. of sodium hypochlorite solution containing 0·1 % of available chlorine at 20° C. After treatment for one hour in this solution in diffused light, the cotton is rinsed by washing on a Buchner funnel with distilled water for 10 minutes and the operation repeated three times. During the final rinsing, a saturated solution of sodium bisulphite is added drop by drop until the filtrate does not colour starch-iodide paper. The cotton is again rinsed with distilled water and dried by folding in a linen cloth surrounded by filter paper and subjecting it to hand pressure, after which the material is left for several days in a room where no fumes can affect it.

The standard cellulose prepared in this manner is found to contain a slight trace of fat which is so small as to be considered negligible, but which may be removed by extraction with alcohol-benzene. Normal standard cellulose should contain no fats, mineral substances or nitrogen and its copper number (see page 239) should not be significantly different from zero. The following results show the effect of the above process :

ANALYSES OF RAW AND PURE COTTON

	Raw Cotton (Wannamaker's Cleveland)		
	I	II	III
Cellulose . .	89·55 %	90·45 %	89·35 %
Ash . . .	1·10 %	1·00 %	1·09 %
Cuticular matter .	0·71 %	0·69 %	0·72 %
Fat and Wax .	4·10 %	4·08 %	4·00 %
	Purified Cotton (Wannamaker's Cleveland)		
	I	II	III
Cellulose . .	99·56 %	99·61 %	99·62 %
Nitrogen . .	nil	nil	nil
Fat . . .	nil	nil	nil
Ash . . .	0·09 %	0·09 %	0·09 %
Copper number .	0·30 %	0·32 %	0·28 %

This method has been revised by Corey and Gray (Ind. Eng. Chem., 1924, *16*, 853; 1130), with the exclusion of the bleaching process. About 75 g. of hand cleaned raw cotton is extracted in a Soxhlet apparatus for six hours with 95 % alcohol and for a further six hours with ether. The cotton is then placed in the nickel basket and 3 l. of a 1 % aqueous solution of sodium hydroxide which has previously been boiled to expel air is added. The supply of NaOH solution is kept at boiling point, in a flask which is connected to the beaker containing the cotton in the nickel basket, so that fresh alkali syphons into the beaker. The alkaline solution enters at the bottom of the beaker and the old liquor is removed at the top by means of a constant level outflow. The whole system is so regulated that it takes about ten hours for the solution to enter. When practically all the alkali has been used, a supply of boiling distilled water is placed in the flask, and this procedure is repeated several times until the cotton has been thoroughly washed. The cotton is then transferred to a Buchner or other form of suction funnel where it is washed with three changes of water, after which it is allowed to remain for two hours in a 1 % aqueous solution of acetic acid. The material is finally washed with four changes of distilled water.

Commercial Purification

The former broad method is used for the technical purification of cotton goods. The losses in bleaching are generally higher than in the case of raw cotton on account of the sizing materials added preparatory to weaving. It is often customary

to give the goods a steep in dilute acid in order to assist in the removal of inorganic impurities, and it is usual to follow up the treatment with the hypochlorite solution by means of an " acid steep " or " sour." The treatment with hypochlorite solutions is frequently referred to as a " chemic."

The old " madder bleach " is often referred to as a method of producing a perfectly pure cotton fabric, but modern tendencies are towards shorter methods.

In most technical bleaching processes it is usual to start with a singeing process, which removes the loose hairs projecting from the surface of the fabric, after which it is steeped in water. In the classical madder bleach this steeping process continues for about 12 hours, after which the cloth, in rope form, is thoroughly impregnated with a 0·5 % suspension of milk of lime and carefully piled in a kier where it is boiled for several hours under pressure with a comparatively small amount of water. A steam injector or heater ensures continuous circulation of the liquor through the material. The fats and waxes in the cotton are converted into calcium soaps during this process and the nitrogenous matter is removed in the form of ammonium salts. The fabric is then removed from the kier and well washed in water, followed by a " sour " or treatment with cold dilute HCl or H_2SO_4 solution usually of 1° to 2° Tw. This removes the mineral salts and decomposes the calcium soaps into the free fatty acids. The cotton goods are then placed in a kier again, and given the first " lye boil," which consists in an operation similar to the lime boil, but in presence of sodium hydroxide or carbonate solution, together with a small amount of rosin. The process is followed by washing with water, which removes the sodium soaps which have been formed, and then a shorter " kierboil " in presence of sodium carbonate solution. The conclusion of the boiling operations is followed by a thorough washing process in cold water, which may also be succeeded by a steep in dilute acid solution and a washing process. The cotton is now free from all impurities except the natural colouring matter which is removed by a " chemic " or treatment for several hours in a solution of calcium or sodium hypochlorite containing 1·0 to 3·0 g. of available chlorine per litre. The goods are then well washed and treated with a solution of HCl (1–2° Tw), again washed, and finally dried.

The less drastic methods of modern bleachworks involve a steeping process, followed by a " soda boil " in which the cotton

goods are boiled under pressure in a kier containing a 2% solution of sodium hydrate or carbonate. The material is occasionally subjected to a second boil or scour before the bleaching process.

Methods of solvent extraction as an addition to or substitute for the kier boiling process appear to find little favour, and although the use of hydrogen peroxide as a bleaching agent for cotton is now arousing more attention than formerly, yet the use of hypochlorite solutions is still standard works' practice.

A good historical account of the development of bleaching has been given by Higgins (J.T.I., 1923, *14*, 209).

It is necessary to exercise strict control over the bleaching processes, for although cotton is not degraded by treatment with hot dilute alkali yet the presence of oxygen or air may cause severe damage (see page 260). Contact with acids or oxidising agents may also result in degradation with the formation of modified cellulose (see page 207).

The modern method of control is based on the viscosity tests (see page 174), whereas the older system of following the progress of purification contented itself with examination of mineral and organic impurities. The nitrogen content, for instance, has been followed through the bleaching processes (under which term scouring is included) by Knecht and Hall (J.S.D.C., 1918, *34*, 220). More recently Birtwell, Clibbens and Ridge (J.T.I., 1923, *14*, 227) have made use of the high absorptive capacity of native cotton for Methylene Blue. This is dependent on the alkalinity of the ash, the pectic impurities and origin of growth, but when allowance is made for origin and ash, the fall in absorption may be used as a measure of the efficiency of bleaching, provided there has been no oxidising attack on the cellulose itself (see page 244).

In addition to suffering attack by acids and oxidising agents, cellulose is also deteriorated under the influence of light with the formation of oxycellulose. The literature on this subject has been reviewed by Cunliffe (J.T.I., 1923, *14*, 314), whilst Cunliffe and Farrow (J.T.I., 1928, *19*, 169) have examined the loss of strength of fibres, yarns and fabrics on exposure to light.

Although cellulose is not attacked by moths and insects in general, yet it has long been recognised that it is susceptible to attack by fungi and mildew. This type of attack is usually associated with the presence of the starchy matter which is often present in the " finished " material and occurs in presence of excess of moisture and lack of fresh air. However, the pure

cellulose itself is decomposed by bacteria, and it is interesting to note that Dorée (Biochem. Journ., 1920, *14*, 709) considers that the disintegration of cellulose after three to five weeks' immersion in sea water is largely due to bacterial attack in presence of oxygen. Cellulose triacetate, however, was not attacked after six months' immersion.

Omeliansky (Chem. Zeit., 1902, *26* [13], 133) showed that cellulose is attacked by two types of anærobic bacteria, one being capable of producing hydrogen, and the other of producing methane, whilst both types of fermentation produced acetic and butyric acids. Cross and Dorée (Researches on Cellulose IV) showed that cellulose was completely destroyed by certain organisms with the production of alcohol, acetic acid, methane, carbon dioxide and hydrogen. Fleming and Thaysen (Biochem. Journ., 1920, *14*, 25; 1921, *15*, 407) and Thaysen (J.S.D.C., 1924, *40*, 101) have also investigated the action of various bacteria on cotton cellulose.

The literature on this subject has been reviewed by Armstead and Harland (J.T.I., 1923, *14*, 157), whilst Prindle (Textile Research, 1934, *4*, 413 and 463) has given a useful collection of abstracts from literature, concerning the destruction of cotton fibres at all stages of manufacture by bacteria and by moulds.

CHAPTER TWO

GENERAL PROPERTIES

Chemical Properties

The alcoholic nature of cellulose has been known for very many years and is shown by the following reactions which are common to the aliphatic alcohols: alcoholate formation, ester formation, ether formation, oxidation to aldehyde and acid, and the property of xanthation. The ethers are formed in the same manner as in the case of alcohols, i.e. by the action of alkyl or aryl halides on the alcoholate or by the action of an ester, such as dimethyl sulphate on the alcohol. Similarly, the esters may be formed by treating the alcohol—cellulose—with an acid, acid anhydride or acid chloride. Esterification may also be accomplished by the reaction between the acid chloride and the alcoholate.

The Colloidal Nature of Cellulose

Although there are references in the literature of the later part of the nineteenth century to the colloidal nature of cellulose, it is only comparatively recently that any attempt has been made to treat the matter methodically. Witt (Chem. Tech. d. Gespinstfasern, 1888, page 369) had classified all textile fibres as colloidal and Cross and Bevan made an attempt to deal systematically with the colloid properties of cellulose as a result of their investigations, not only of the dyeing properties but also of the formation of "colloidal double salts" in cuprammonium hydroxide and zinc chloride solution. Most of the later work appears to have been confined to the dyeing properties, possibly on account of the fact that the methods for investigating the properties of solid organic colloids had not been developed. However, even the solutions of cellulose and its derivatives appear to have escaped attention. The lack of data was commented upon by Schwalbe (Die Chemie d. Cellulose, Berlin, 1911), but during the next 15

years a number of publications were forthcoming which allowed the methodical treatment to be undertaken. Ostwald (Theoretical and Applied Colloid Chemistry, 1917) classified cellulose as an emulsoid on account of its ability to swell and the highly viscous nature of its solutions, but the first systematic treatment of the colloidal aspects of cellulose was made by Katz, who wrote the chapter entitled " Micellar Theory and Swelling of Cellulose " in Hess' book " Die Chemie der Zellulose und ihrer Begleiter."

Mark has also dealt with the problem from the standpoint of both physical and colloid chemistry in his book " Physik und Chemie der Cellulose."

Duclaux (Rapport sur les Hydrates de Carbone, 1ome conference, Union Internat. de Chimie, Leige, 1930) has also given an account of " the colloidal state of cellulose and its derivatives."

The admirable work of Stamm entitled " Colloid Chemistry of Cellulosic Materials " (U.S. Dept. of Agriculture, Misc. Publication No. 240) is a condensed modern (1936) account [and represents remarkable value for money (10 cents. !)], whilst the more recent publication by Valkó of " Kolloidchemische Grundlagen der Textilveredlung " (Berlin, Springer, 1937) represents a much more ambitious work, of which one half deals with the colloid chemistry of dyestuffs and dyeing processes.

This may be a suitable opportunity to mention the modern aspect of a colloid as merely a large molecule and not a peculiar class of substances whose properties are only revealed to the elect (see page 122, in this connection).

The colloidal structure of cellulose is shown most prominently in the four properties : *adsorption*, *swelling*, *dissolution*, and *coagulation*.

The absorption of water has an important bearing on many textile processes, but the main scientific investigations have been to determine whether the phenomenon of " hydration " was actually the same as when inorganic salts form hydrates with water. One of the chief workers in this field is Champetier, whose work will be considered in more detail later, but his most recent evidence (see page 40) points in the direction of chemical combination between cellulose and water.

The term *hydration* as applied in the paper-making industry was originally given a stoichiometric interpretation, but is now used in its physical sense and relates to the taking up of water

by absorption and imbibition. The effect of the beaters during paper making is to produce an enormous increase in the external surface of the fibres due to their disintegration into fibrillæ and to the pressure exerted by the beaters. Part of the hydrating capacity may be due to the pentosans, polyuronides, β- and γ-cellulose.

The connection between absorption and swelling is an intimate one, but the latter is the most obvious colloidal property of cellulose. For example, when sugar is placed in a solvent it gradually becomes smaller in bulk as it passes into solution, but cellulose swells as it absorbs the solvent and increases in bulk so that dissolution is merely an extension of the swelling process. The swelling properties of cellulose have been known from earliest times, for Katz (Trans. Farad. Soc., 1933, *29*, 279) has pointed out that the Egyptians " dynamited " rocks by filling a hole with carefully dried wood over which they poured water.

The absorption and swelling properties of cellulose have been examined in connection with sodium hydroxide solutions in some detail as will be seen in Chapter VII.

A more complete account of this subject may be seen in Mercerising by Marsh (Chapman and Hall, London, 1941).

The interminable arguments as to whether cellulose combines chemically with sodium hydroxide to form an alcoholate have not yet come to an end, but without some such hypothesis it is difficult to understand the viscose reaction, as carbon disulphide does not react with cellulose in absence of sodium hydroxide. The X-ray evidence is in favour of a chemical compound, whilst the last report of Bancroft (see page 444) shows a masterly reconciliation between the findings of various types of investigation of the problem.

The work on the dissolution of cellulose is described in the section entitled " Dispersed Cellulose," whilst the striking phenomenon of the viscous solution is discussed in the remarks on the molecular weight of cellulose under " Constitution " in addition.

The coagulation of cellulose is represented in the many processes for rayon manufacture, but that which has attracted most scientific attention is the viscose process which is described in Chapter XXI.

Absorptive Properties

It is a well known fact that purified cotton is remarkably

absorbent, and this property has been explained on the grounds that it forms a series of capillary surfaces which exert considerable force upon any liquid in which the cotton may be immersed. Cotton is extensively used for surgical purposes on account of this absorbency, which according to Matthews (Textile Fibres) is such that it will absorb 18 times its own weight of water. Dry cotton is also remarkably capable of absorbing gases, and it is similarly stated that it can absorb 115 times its volume of ammonia at atmospheric pressure.

Coward and Spencer (J.T.I., 1923, *14*, 28) showed that by means of a suitable centrifuge it was possible to remove the interfibrillar liquids from cotton hairs down to 10% of the weight of the cellulose. The centrifuge was described and will be mentioned again later, but for the moment it is sufficient to give the results on the water retention of cotton, without reference to the further work on preferential absorption and also the question of alkali cellulose formation. It was established that both scoured cotton hairs and well-bleached fabric retained about 50% of their weight of water after removal of the surface water by means of the centrifuge. The view was put forward that this water must be retained in the cellulose itself and not in the interstices of the cloth or the interspaces of the hairs. After swelling in caustic soda solutions (mercerising), thorough washing and centrifuging, anything up to 123% of water, varying with the concentration of the alkali, was retained.

The question of the moisture relations of cellulose is dealt with on page 29, but the above remarks are intended to give some indication of its general absorbency.

Although the earliest experiments on the powers of absorption possessed by cellulose must necessarily be regarded as dyeing phenomena, it is not necessary to discuss the various theories of dyeing, which are better followed in any good book on dyeing. Kolloidchemische Grundlagen der Textilveredlung by Valkó (Springer, Berlin, 1937) is useful in this connection, and a short, most interesting paper has been given by Boulton and Morton (J.S.D.C., 1940, *56*, 145). It is sufficient to state that the dyeing properties of cellulose may be regarded as evidence for its properties of absorption. Similarly it is well known that cellulose has the power of preferential absorption of alkali from moderately concentrated aqueous solutions, and this will be discussed further in the section on dispersed cellulose and the chapter on soda cellulose.

Some of the earliest recorded observations on the absorption of acid and alkali from dilute solutions were made by Mills and Takamine (J.C.S., 1883, *43*, 142), who showed that small but definite amounts of acids and basic oxides were absorbed from cold, highly dilute solutions by bleached cotton. In contrast to this somewhat feeble absorption of acids and bases of low molecular weight, there are a number of cases where a higher proportion is absorbed; for instance, tannic acid is conspicuous for its " affinity " for cellulose and is still used as a mordant. There are a number of metallic salts which are hydrolysed in aqueous solution, and in presence of cellulose, the hydrates are loosely fixed on the fibre. Many of the salts of lead, zinc, copper, tin, aluminium, iron, chromium, etc., have been used as mordants, the basic oxides being removed from solution. Certain of the acid oxides (e.g. stannic) are also removed from solutions of the salts by cellulose but generally in smaller proportions.

The various amounts of tannic acid absorbed by cotton cellulose in the form of raw cotton, bleached cotton, mercerised cotton and regenerated cellulose have been given by Knecht (J.S.D.C., 1892, *8*, 40) whilst Gardner and Carter (J.S.D.C., 1898, *14*, 143) have recorded the amounts of tannin and similar substances absorbed by cotton.

The action of mordants on cotton from the point of view of the absorptive capacity of cellulose has been examined by Haller (Chem. Zeit., 1918, *42*, 597), whilst earlier contributions have been made by Michælis (Pfluger's Arch. Ges. Physiol., Vol. 97, page 634) and Liechti and Suida (J.S.C.I., 1883, *2*, 537). The question is also dealt with in the standard textbooks on dyeing, and in such publications as " The Journal of the Society of Dyers and Colourists."

Coward, Spencer and Wood (J.T.I., 1923, *14*, 529) made use of their centrifuge method for further observations on the sorption by cotton of dilute solutions. Neutral salt solutions were absorbed to the same extent as water and there was no appreciable change in the concentration of the bath. In the case of dilute solutions of acid and alkali, however, the solution was again absorbed as a whole except for a small but measurable preferential absorption. The quantitative results with acid were not so regular as those obtained with sodium hydroxide solutions. A dilute solution of cuprammonium hydroxide was also preferentially absorbed.

Zanker and Schnabel (Farb. Zeit., 1913, *24*, 282) recorded

their observation that cotton retained adsorbed sulphuric acid with such tenacity as to introduce considerable errors into the method of estimating small amounts of acid, by titration of the aqueous extract. Higgins (J.S.D.C., 1918, *34*, 35) stated that it was practically impossible to wash small traces of acid from cloth by means of boiling water.

Observations of this type led to speculations as to the possible amphoteric nature of cellulose. Later work, however (see page 147), shows that cellulose behaves as a weak monobasic acid. Gavoret (Compt. rend., 1938, *206*, 1299) has determined the isoelectric point of cotton which occurs in the region of pH 2·4 to 2·8. This has been confirmed by Sookne and Harris (Text. Res., 1941, *11*, 307) in the course of electrophoretic studies of purified cotton when a reversal of charge below pH 2·5 indicates an isoelectric point.

Studies of the base-combining capacity of cotton by Sookne and Harris (Text. Res., 1940, *10*, 405) have shown that the pectic substances which only constitute 1% of the raw fibre, yet account for 85% of the total acidic groups in the material. The cotton was " de-waxed " by extraction with alcohol and ether, followed by boiling in 1% NaOH solution to produce a " de-pectinised " cotton.

The fact that even small amounts of acid, if left in cellulose materials, are apt to cause considerable textile damage on account of concentration and subsequent degradation of the material necessitates accurate methods of analysis. Coward and Wigley (J.T.I., 1922, *13*, 121), however, have shown that acidimetry and alkalimetry can be carried out by titrations with N/10 solutions, at the boil and in presence of the cloth, using phenol-phthalein as indicator.

In the case of dilute solutions of neutral salts, there is the interesting phenomenon that cotton exhibits a preferential attraction for the basic constituent and thus produces an acid reaction of that solution. This has been observed by Cameron (" The Soil Solution " ; 1911, page 66) and Truog (J. Phys. Chem., 1916, *20*, 457). Harrison (J.S.D.C., 1911, *27*, 279) showed that when solutions of sodium chloride were poured through a column of cellulose, the issuing solution showed an acid reaction. Similar observations have been recorded by Masters (J.C.S., 1922, *121*, 2026) whilst Willows (J.T.I., 1919, *10*, 161) pointed out that litmus paper was of no value for testing the neutrality of cotton goods as sodium ions are preferentially absorbed by neutral cellulose, thus allowing the

litmus to assume its characteristic red colour when no acid was present in the cellulose.

Practically all the data on the sorption of organic solutes refer to dyeing. Interpretation is difficult, for the solvent and solute are absorbed together and the process is complicated by the presence of salts. The basic dyes are absorbed to a higher degree than the acid dyestuffs. Neale and Stringfellow (Trans. Farad. Soc., 1933, *29*, 1167) showed that in the case of the direct dye Chlorazol Sky Blue FF the process is one of diffusion. The absorption from the pure aqueous solution was negligible, but it increased rapidly on the addition of salt.

There are comparatively few data on the sorption of gases. Davidson (J.T.I., 1927, *18*, 175) in his measurements of the specific volume of cellulose, showed that the absorption of helium was negligible. On this basis it was estimated that air was absorbed to the extent of 0·023 cc. per gramme of dry cellulose under standard conditions. Grace and Maass (J. Phys. Chem., 1932, *36*, 3046) examined the sorption of dry HCl, SO_2 and NH_3 on dry cotton. In the case of HCl, 0·8% was absorbed at 5·4 cm. of mercury and 2·0% at 70·2 cm.; the figures for SO_2 were 5% at 76 cm. and for NH_3, 4% at the same pressure. The time required to reach equilibrium was between 50 and 100 hours.

The sorption of non-aqueous vapours has been examined by Sheppard and Newsome (J. Phys. Chem., 1932, *36*, 2306). Normal aliphatic alcohols were investigated at saturation pressures. In proceeding from water to n-butyl alcohol there was a linear decrease in sorption from the saturated vapour by cotton linters. Figures at 30° C. show the sorption to be 15% for water, 11·2% for methyl alcohol, 8·6% for ethyl alcohol, 5% for propyl alcohol and 1·5% for butyl alcohol.

In connection with the sorption properties of cellulose it is interesting to note that it has been estimated that the internal surface of 1 g. of cellulose is between 1,000,000 and 10,000,000 sq. cm. (See also page 442.)

The Moisture Relations of Cellulose

It is a well-known fact that cellulose contains a certain amount of moisture even when it feels "dry." When, however, the cotton is dried by heating and then exposed to ordinary cold air, it quickly absorbs most of the moisture it has lost on drying. This property is common to all substances which have large surfaces and exist in the colloid state. The amount

of moisture in cellulose varies with the relative humidity of the surrounding atmosphere and with the temperature. It is obvious that the amount of moisture in the cotton is an important factor when buying and selling are considered, as raw cotton and yarns are sold by weight. The accepted regain is therefore fixed at 8·5%, the moisture being expressed as a percentage of the dry weight. The moisture contained in cotton is also referred to as the moisture of " condition," and the term moisture content strictly refers to the amount of moisture contained in conditioned cotton expressed as a percentage of the weight of the material in its conditioned state.

In addition to the commercial aspect of the moisture in cotton the physical properties of the material are also affected by the amount of moisture. The tensile strength of native cellulose, for instance, increases with increasing moisture content. An important physical property connected with manufacture is the electrification of dry cotton which causes a great deal of the " invisible waste " in spinning operations ; the moisture content is consequently of the utmost importance. Indeed the situation of the cotton industry in Lancashire is due to the high relative humidity of the atmosphere without which the cotton cannot be spun. Artificial humidification, however, has been universally developed to counter this natural advantage. Barwick (J.S.D.C., 1913, *29*, 13) and Urquhart (J.T.I., 1923, *14*, 183) published data on tensile strength and moisture content, and Collins (J.T.I., 1922, *13*, 206) has given an account of the available information on the influence of moisture on the electrification by friction.

Many " finishing " processes on cotton piece goods owe their success to a careful control of the moisture of condition ; the " beetling " of linen may also be quoted as a further example.

Whilst both relative humidity and temperature affect the moisture content, the former is the more important, for if it is kept constant the amount of water does not vary over a small range in temperature. On the other hand, there is considerable variation with a change in humidity. This variation has been studied by many observers, e.g. Lester (J.S.C.I., 1902, *21*, 388), Schloesing (Textile World Record, Boston, Nov. 1928), Hartshorne (Trans. Nat. Assoc. Cotton Manuf., 1905, *79*, 194 ; 1911, *90*, 81 ; 1915, 98, 254), Masson and Richards (Proc. Roy. Soc., 1906, *78a*, 412), Wilson and Fuwa (Ind. Eng. Chem., 1922, *14*, 913) and Scheurer (Bull.

Soc. Ind., Mulhouse, 1921, *87*, 129), but there can be no doubt that our present knowledge of the absorption of moisture by cellulose is largely due to the work of Urquhart and Williams, published in a series of papers in the " Journal of the Textile Institute " since 1924.

Moisture contents are usually determined by " oven-drying," but distillation with organic liquids has sometimes been employed in research work. Mitra and Venkataraman (J.S.C.I., 1938, *57*, 306) suggest a volumetric determination by heating with acetic anhydride in solvent naphtha, coverting the excess of anhydride to acetanilide and one molecular proportion of acetic acid and then titrating the total acetic acid.

In connection with the method of determining the amount of moisture in cellulose, Urquhart and Williams (J.T.I., 1924, *15*, 138) have shown that oven drying at 110° C. is as satisfactory as drying in a vacuum desiccator over phosphorus pentoxide at 15° C., much the same dry weight being obtained in each case, i.e. 5·66% loss by the vacuum method and 5·62% loss when dried at 110° C. The method of drying in an oven appears to produce no significant change in weight after a period of 24 hours, whilst with the vacuum desiccator weight continued to be lost during a week.

In the case of raw cottons, the desiccator method gave lower results, probably on account of some decomposition of the non-cellulosic constituents of the raw cotton. Lester (J.S.C.I., 1902, *21*, 388) has shown that the aqueous extract of raw cotton is more hygroscopic than the cotton itself; the extract amounted to 1·73% and took up about 29% of water compared with the 8% of the original raw cotton. Urquhart and Williams (loc. cit.) found the following average figures for loss of weight on drying.

DRYING OF COTTON

	Raw Cotton		Soda-boiled Cotton	
Dried at 15° C. . .	7·02	6·11	5·66	5·34
Dried at 110° C. . .	7·39	6·40	5·62	5·41

The figures show percentage loss in weight estimated on the dry weight of the cotton.

In their results of the examination of the moisture relations of cotton, Urquhart and Williams do not refer to the atmospheric conditions in terms of percentage relative humidity, but as relative vapour pressure or p/P, i.e. the pressure exerted

by the water in the cotton divided by the saturation pressure. As the pressure of the water in the cotton exactly balances the pressure of the water in the atmosphere when equilibrium has been attained, 100 p/P is equal to the percentage relative humidity. If the weight of water taken up by 1 g. of dry cotton is denoted by " a," then 100a is the percentage moisture regain. The results showed that there are two possible values of moisture regain, a lower value if the cotton was initially drier than the atmosphere and a higher value if it had been wetter. The difference between the two sets of observations had been noted by Masson and Richards (Proc. Roy. Soc., 1906, *78a*, 412), who attributed it to incomplete attainment of equilibrium.

This type of hysteresis or lag had been discovered by van Bemmelen (Z. anorg. Chem., 1896, *13*, 234) for silicic acid gels, and Urquhart and Williams (supra) showed that a real hysteresis existed in the case of cotton. The taking up of water was termed " absorption " and the giving up of water " desorption."

In considering the question of the moisture relations of cellulose, it must be realised that there is no very sharp line of demarcation between the " moisture of condition " and the water of constitution. On account of the constitution of cellulose and the structure of the fibre it is possible that the sorbed moisture may be held so firmly that even where vacuum methods are employed, high temperatures may be necessary for the complete removal of water and some decomposition may result. There appears to be quite a definite change in the affinity for moisture, for example, when the cellulose is dried for long periods at temperatures only slightly in excess of the usual 105° to 110° C. Some interesting results in this region have been recorded by Bateman and Beglinger (Wood Preservers' Assoc. Proc., 1929, *25*, 193), who examined the moisture content of wood by drying it in an oven under different conditions and also by distilling it with water-insoluble organic liquids. Drying for 24 hours over P_2O_5 at 105° C. removed 0·2 % more water than in absence of P_2O_5, but after a week the difference was only 0·02 %. Distilling in toluene and xylene (b.p. 111 and 140° C. respectively) for one to four hours gave practically the same figure as was obtained by oven drying over P_2O_5 for five to seven days. Distillation in eucalyptus oil (b.p. 171° C.) gave an increase of only 0·3 % in the moisture removed, but in the case of tetraline (b.p. 207° C.) the increase

in moisture evolved was 4·15%, which indicated destructive distillation. The efficient heat transfer of the distillation method with its more rapid removal of moisture, showed that an increase of only 0·3% in the moisture removed results from raising the temperature some 70° C. above normal drying practice. It appears, therefore, that the residual sorbed moisture in the ordinary estimation is less than 1%.

The moisture regain of cotton definitely depends on its previous heat treatment, heating to a high temperature reducing the capacity to absorb water. The hysteresis shown by soda-boiled cotton is greater than that for raw cotton.

The original method employed by Urquhart and Williams did not yield accurate results in the region of very high or very low humidities, and this was modified in a later paper (J.T.I., 1924, *15*, 433), which utilised a vacuum device. The cotton was placed in an evacuated bulb with a manometer, known amounts of water were admitted (or removed), and the resultant vapour pressure read directly. The hysteresis did not extend to zero humidity. It was found that the moisture content of soda-boiled cotton is 22·6% at 100% relative humidity. The measurements were made at 25° C.

An explanation of the phenomenon of hysteresis was put forward which depended on a theory of capillary structure, but this was superseded in a later publication by Urquhart (J.T.I., 1929, *20*, 125).

The effect of temperature on the absorption of water was also examined by Urquhart and Williams (J.T.I., 1924, *15*, 559), with the following results. When the relative humidity is constant at less than 80%, the moisture regain decreases as the temperature rises from 10° C. to 110° C. When, however, the relative humidity is constant at more than 80%, the regain falls between 10° C. and 50° C., but from 60° C. to 100° C. it increases. The maximum absorption of water therefore occurs at 100% relative humidity and 100° C., i.e. in saturated steam at atmospheric pressure. The view was put forward that the increase in moisture content under constant high humidities and which begins at 60° C. is due to the swelling of the material with consequent exposure of fresh surface. One of the practical bearings of such observations is on processes which depend for their success on the swollen state of the cotton, e.g. steaming in calico printing.

The absorption of water by cottons of various origins was also examined by Urquhart and Williams (J.T.I., 1926, *17*, 38),

who found that the difference noted by previous workers, e.g. Schloesing (Compt. rend., 1893, *116*, 808) were not significant. Any variations would not be sufficient to characterise the type of cotton. Such differences as were observed, almost disappeared when the cottons were boiled with water.

The effects of *mercerising* on the moisture relations was described in two papers—Urquhart and Williams (J.T.I., 1925, *16*, 155), and Urquhart (J.T.I., 1927, *18*, 55). The results are

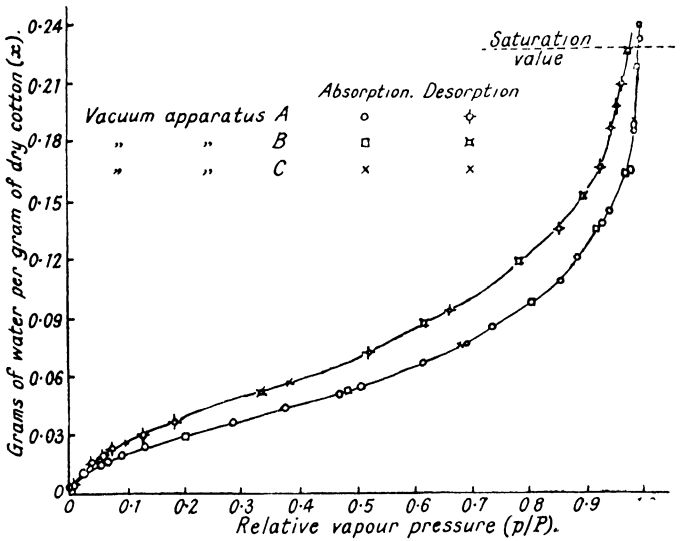


FIG. 37.—Absorption and Desorption by soda-boiled Cotton at 25° C.

also discussed in the chapter on Dispersed Cellulose (see page 187).

When the cotton was mercerised without tension, the variation in moisture absorption according to the strength of the mercerising solution was similar to the variation in the hair dimensions. Maximum swelling produces maximum hygroscopicity. The ratio between the moisture content of the mercerised and unmercerised cotton at the same relative humidity is independent of that humidity, being about 1·57 when absorbing moisture and 1·46 when losing it. The results indicate that mercerising increases the accessible surface of the cotton. The effects of tension were examined in the second paper, when it was found that the moisture regain of material mercerised under tension was less than when mercerised in the loose state.

An examination of the effects of processing on the moisture relations of cotton was made by Urquhart, Bostock and Eckersall (J.T.I., 1932, *23*, 135), but the results are mainly of interest for purposes of reference. However, it was established that hygroscopicity decreases slightly but steadily as the duration and temperature of drying are increased. The effect of air drying of mercerised material is greatly to reduce the very high absorptive capacity possessed immediately after the mercerising process (see page 191).

The adsorption of water by rayon has been investigated by a number of investigators Bitz (Textile Forschung, 1921, *3*, 89); Caille (Bull. Soc. Ind. Rouen, 1924, *52*, 422); Meunier and Guyot (Chim. et Ind., 1929, *21*, 585); Sheppard and Newsome (J. Phys. Chem., 1929, *33*, 1817) and Wilson and Fuwa (Ind. Eng. Chem., 1922, *14*, 913). Some of the results were over a sufficiently wide range to permit the construction of adsorption isotherms and it was shown that regenerated cellulose gives curves similar to those for cotton and with a similar hysteresis. The absolute values of the moisture regain are still higher than those for mercerised cotton, and the highest hygroscopicity appears in the case of cellulose regenerated from cellulose nitrate. Cellulose acetate has a lower regain (5·5% compared with 11% to 12%) than regenerated cellulose or even cotton (8·5%), but the difference also lies in the form of the curves as cellulose acetate does not give a sigmoid curve like cotton or regenerated cellulose.

The adsorption of water by *rayon* has also been examined by Urquhart and Eckersall (J.T.I., 1932, *23*, 163) on the lines of the methods previously adopted by Urquhart and Williams. The results are in agreement with those of the earlier workers and are of great interest for reference purposes.

These findings too, are discussed in the section dealing with dispersed cellulose—see page 189.

In addition to the interesting data on the moisture relations of dispersed forms of cellulose, there are some important observations recorded in connection with modified cellulose and also cellulose derivatives. Shepherd and Newsome have observed that the oxy- and hydrocelluloses, which they prepared (J. Phys. Chem., 1929, *33*, 1817), adsorbed less water than the original cellulose.

The most interesting data, however, are in connection with *cellulose derivatives*, showing very clearly the considerable effect of the hydroxyl groups, in that the substitution of the

hydroxyl groups of the original cellulose results in a decreased adsorption of water. Wilson and Fuwa (Ind. Eng. Chem., 1922, *14*, 913) have reported that cellulose nitrate and acetate absorb less moisture than viscose at the same relative humidity. Bancroft and Calkin (Textile Res., 1934, *4*, 371) determined the amount of water taken up by cellulose nitrate and cellulose acetate by immersing the samples in water from 24 hours and then blotting off the excess. The cellulose nitrate, of 12 % nitrogen content, retained 8 % of water, whilst the cellulose acetate of 40 % acetyl content, retained 14·5 % to 15 % of water. In the case of cellulose acetate, Sheppard (Trans. Farad. Soc., 1933, *29*, 77) showed that the degree of acetylation is important, for the water adsorbed progressively decreased with increasing esterification. The moisture content of the native cellulose was 16 % at saturation compared with 9 % for the cellulose triacetate (44·5 % acetyl content). Sheppard also reported that cellulose acetates of lower esterification have different water sorptions according to the lattice structure, that of the "hydrate" showing higher sorption than the native lattice structure (see X-ray analysis, page 117). The molecular weight of the ester group also affects the adsorption of water; if a series of esters of equivalent esterification but with increasing molecular weight of the acyl group from formyl to stearyl are prepared for sorption of water, it is found that this steadily falls with increase in molecular weight of the acyl group. Sheppard (supra) gives examples of triacetate—10 %, tripropionate—2 % to 3 %, tributyrate—1·8 %, trivalerate—1·6 %, tristearate—1 %.

The work of Coward and Spencer (J.T.I., 1923, *14*, 28) involved the use of a centrifuge exerting a force about 2,770 times that of gravity. Bancroft and Calkin (Textile Research, 1934, *4*, 371) made use of a high speed centrifuge with a force of 6,300 times that of gravity, and obtained a water retention of as low as 17·1 % in the case of cotton which adsorbed 27 % of moisture from saturated water vapour at 25° C. They point out that the new fact of the water adsorbed from saturated water vapour by cotton being partially removable by centrifuging requires a new technique before any physical significance can be attached to the amount of water retained after centrifuging.

The *hysteresis* effect has been discussed by Urquhart (J.T.I., 1929, *20*, 125) abandoning the original theory of capillary effects in favour of the view that the adsorption takes place

on the hydroxyl groups of the cellulose. The capillary explanation was held to be inapplicable on the grounds that cotton is an elastic gel steadily increasing in volume as it takes up moisture. The structure of the cotton prevents all of the hydroxyl groups from taking up water; only the available groups are capable of attracting moisture. When the cotton hair from the boll dries, there is a tendency for a rearrangement which results in the mutual satisfaction of some of the residual valencies of the hydroxyl groups, with a decrease in hygroscopicity. The absorption of water tends to restore the original orientation of the surface, so that during absorption the number of active groups will increase. (This is supported by the fact that there is a latent strain in dry hairs which is to a large extent removed by immersion in water.) This increase is not so great as the original decrease in the drying of the cotton from the boll, where the cellulose was originally formed in the presence of water. The adsorbing surface is in a less active condition during absorption than during desorption so that hysteresis results. Urquhart showed that the primary desorption curve of cotton straight from the boll was irreproducible and that the subsequent desorption curve showed reduced adsorptive power.

After this first drying, however, if the cellulose is capable of having its active groups removed from the surface during desorption and restored during absorption, the process should be capable of repetition. This was shown to be the case over three cycles. Hysteresis is due to the fact that the previous high moisture content of the material has increased the number of available active groups. As the molecular energy of vibration is greater at high temperatures, there is a decreased hygroscopicity for oven-dried cotton, but if the heating takes place in presence of water, then the hygroscopicity increases because the hydroxyl groups will be held by the attraction of adsorbed molecules of water, that is to say, the hydroxyl groups will be released from the effect of mutual influence.

Bancroft and Calkin (Textile Research, 1934, *4*, 371) have shown that the work of Davidson (J.T.I., 1927, *18*, 175) and others on the specific volume of cellulose is of interest in connection with *the manner in which water may be held* by cellulose. The specific volume when measured by displacement of helium is 0·640, but the apparent specific volume of a sample of the same material measured by displacement of water is 0·621, so that the disappearance in volume amounts to

12% of the water taken up. This contraction can only be accounted for by the fact that some part of the water is held on the surface of the cotton under the influence of attractive forces. They also referred to the work of Filby and Maass (Can. J. Res., 1932, *7*, 162), who reported that the volume of the system cellulose-water vapour is much smaller than that given by the component cellulose and condensed water as long as the amount of adsorbed water is below 4%, but with more than 8% of water, the density of the water subsequently taken up is the same as that of the normal liquid. The initial water taken up showed a greater apparent density than that up to 8%, after which the apparent density is the same as that for pure water.

The possibilities of capillary water and adsorbed water have been mentioned as separate views of the manner in which cellulose holds water, but suggestions have also been made that the water need not be held in one manner alone. Peirce (J.T.I., 1929, *20*, 133) suggested that the water is taken up in two phases, whilst Filby and Maass (loc. cit.) considered that the sorption of HCl on cellulose containing sorbed water, provides evidence for two states, i.e. chemically combined surface water and water held between micelles by capillary attraction.

Sheppard (Trans. Farad. Soc., 1933, *29*, 77) found that only some 5% of water is held by primary sorption in the case of native cellulose and about 7% in the dispersed celluloses. These amounts are retained at p/P of 0·5. The contention is advanced that the bulk of the water at higher vapour pressures is held by capillary condensation in the intermicellar spaces. The heats of adsorption are advanced in favour of this hypothesis.

Sheppard and Newsome (Ind. Eng. Chem., 1934, *26*, 285) also consider that the sorption of water vapour is determined by two phases, developing the views previously expressed. There is a primary surface or chemico-sorption dependent on the free hydroxyl groups; the water molecules are held by forces considerably stronger than for condensation. There is also a volume sorption or capillary condensation.

As the result of an examination of the relationship of insulation resistance to moisture content of cotton, Walker (J. Applied Phys., 1937, *8*, 261) has put forward the following theory. Moisture is first adsorbed on dry cotton on the outer hair surface, and it later penetrates by diffusion into the cracks

and pits that spiral round the hair. Less than 0·5% of moisture is estimated as being necessary to form a unimolecular layer on pit walls and growth ring surfaces, but about 1% of water is required to cover all internal surfaces with a unimolecular layer; hence only half of this may be significant as providing moisture paths along which current is carried. It is suggested that each adsorbed water molecule in the unimolecular layer is held at active points on the surface, i.e. the hydroxyl groups of the cellulose. A unimolecular layer of water does not necessarily provide a continuous film, as owing to the structure of cellulose there may be wider spaces between water molecules on certain hydroxyl groups than on others. Below 1% of moisture, the very rapid increase in resistivity of cotton with decreasing moisture content is due to discontinuities in the layer of water adsorbed on the fibril surfaces. In a further review of the moisture relations of cotton, Walker (Textile Research, 1937, *7*, 297) offers the opinion that whilst a monomolecular layer of water on all internal surface of the cotton hair necessitates about 1% of the hair weight, there appear to be at least two specific kinds of internal surface upon which moisture can be adsorbed. The fibril surface, which is less than half the internal surface, is involved in moisture adsorption which causes appreciable transverse swelling of the cotton hair. Multimolecular layers of water are assumed to condense on this surface, and the thickness of the layers increases up to saturation, with corresponding increases in hair diameter during the whole of the range. Each hydroxyl group in the cellulose surface is the base of a water chain, with separation between the chains corresponding to the arrangement of the hydroxyl groups on the cellulose surface.

The moisture adsorbed on the remaining internal surface is assumed not to be involved in transverse swelling, but may be responsible for the slight longitudinal swelling exhibited by cotton. In order to account for the amount of water necessary to form a monomolecular layer on this additional internal surface, it is assumed that the surface is within the body of the fibrils and is located on the ends of the crystallites. If only a monomolecular layer of water can be adsorbed on these surfaces, then the slight longitudinal swelling may be explained.

When cellulose takes up water it increase in volume, according to a number of publications—Neale (J.T.I., 1929, *20*, 373); Clayton and Peirce (*ibid.*, 315); Urquhart (*ibid.*, 125);

etc. In the case of cotton, the increase amounts to about one-third when the cotton has taken up about one-quarter of its weight of water. Peirce put forward the view that as regular systems of crevices can be made to appear in cotton under the microscope, it follows that the apparently continuous material must be built up so that water molecules can penetrate throughout. The water is strongly attracted to the cellulose and greatly modifies its properties. Small quantities of water are absorbed by cotton in the dry state very much more rapidly than the same amount added to cotton with a moderate moisture content. These small quantities have a much greater effect on the elastic properties, are more difficult to remove, and evolve more heat than when added to cotton already containing moisture. Peirce's suggestion is that in one phase, one water molecule attaches itself individually to one glucose residue, whereas in the other phase an indefinite number of molecules are absorbed in a looser fashion over the available surface.

There are two further possibilities in connection with the manner in which water may be held by cellulose—solid solution and in the form of stoichiometric hydrates. There appears to be no support for the first possibility, but the second was prevalent many years ago. The idea was then based on the assumption that mercerised cellulose existed in the form of a definite hydrate thus accounting for the greater moisture content compared with the unmercerised product. This was shown to be incorrect by the work of Ost and Westhoff (Chem. Zeit., 1909, *33*, 197), Miller (Ber., 1911, *44*, 728) and others; the matter is referred to later in the discussion of the work on dispersed cellulose—see page 187.

The idea of stoichiometric hydrates has recently been revived by Champetier in a series of papers (Compt. rend., 1931, *192*, 1593; 1932, *195*, 280 and 499). The method was based on a study of the ternary systems formed by cellulose, water and a substance such as sodium thiosulphate or pyridine which does not combine with the cellulose. The cellulose was immersed in the solution and then pressed, but at intervals during the pressing operation samples were withdrawn and analysed. The variation of the sodium thiosulphate or pyridine content expressed as a function of the water content gives a straight line, and when such lines were drawn for different concentrations of the original solutions, the composition of addition compounds could be detected from the

points of intersection. The results indicated the existence of two hydrates of cellulose corresponding to $2C_6H_{10}O_5.H_2O$ for ordinary cellulose and $C_6H_{10}O_5.H_2O$ for mercerised cellulose.

Tankard (J.T.I., 1937, *28*, 263) pointed out that the pressures used by Champetier were relatively small, so that by repeating the method, but with greater pressures, the extent of extrapolation was considerably smaller than in the case of Champetier's experiments. Tankard was able to reduce the amount of water associated with 100 g. of dry cotton to some 20 g. compared with some 106 g. of Champetier. Tankard's results indicate that cellulose does not form a limited number of hydrates, but that there is, for each substance examined, a maximum amount of water which may be regarded as chemically combined. This maximum value corresponds to 0·5 molecule of H_2O per $C_6H_{10}O_5$ for bleached cotton and linen cellulose, 0·75 molecule for mercerised cotton cellulose which has been dried, and 1·0 molecule for undried mercerised cotton cellulose, for mercerised linen cellulose and for regenerated (viscose) cellulose.

When cotton linters are treated with heavy water Champetier (Compt. rend., 1937, *205*, 1387) has shown that equilibrium is attained in 36 hours at 30° C. and three heavy hydrogen atoms (D) are associated with each glucose unit.

Degradation Products

The true chemical degradation products of cellulose, such as glucose were formerly given in great detail in considering the chemistry of cellulose. This was on account of divergent views on its structure. The most important products are mentioned in the section on "Constitution" (see page 51), whilst β-glucosan is referred to on page 42. According to Heuser and Schott (Cellulosechem, 1923, *4*, 85) a small amount of ω-hydroxy-methyl-furfuraldehyde is obtained by treating cellulose with dilute aqueous acids, but larger amounts are obtained from modified cellulose. A 5% solution of oxalic acid at 180° C. for 30 minutes on cotton gave 0·8% of the aldehyde, viscose rayon produced 5·2% and Knoevenagel's hydrocellulose (see page 208) gave 10·8%. Similar quantities may be formed by distillation with dilute hydrochloric acid. Treatment with anhydrous halogen acids gives ω-chlor- and ω-brom-methylfurfuraldehyde; chloroform or ether may be used as the solvent according to the methods of Fenton and Gostling

(J.C.S., 1898, *73*, 554; 1899, *75*, 423; 1901, *79*, 362). This was once considered important evidence for the existence of ketonic groups in cellulose, but the work of Hibbert and Hill (J.A.C.S., 1923, *45*, 176) exploded these theories.

Effect of Heat

It is often stated that cellulose suffers some decomposition if heated at 150° C., but in view of a number of technical processes which employ temperatures in excess of that stated, the matter must be regarded with caution. Knecht (J.S.D.C., 1920, *36*, 195) has shown that when cotton is heated for 336 hours at 80° C. it gains reducing powers. The time of heating is obviously of importance. A number of publications lead to the assumption that at temperatures of 150° C. and over, water is given off, increasing in amount with rise in temperature. This water is not regained on cooling the cotton and exposing to air. According to Dorée (The Methods of Cellulose Chemistry, page 209) cotton is not measurably affected up to a temperature of 140° C. after four hours. Above that temperature the copper number increases and the viscosity falls. The rate of change is reduced if the heating is done in an inert atmosphere, so that Dorée offers the opinion that the initial action is one of oxidation, and decomposition only arises in the later stages. Distillation of cellulose yields β-glucosan, in about 50% yield when heated in vacuum.

Physical Properties

A review of some of the physical properties of cotton cellulose has been compiled by Collins (J.T.I., 1922, *13*, 204).

There are many difficulties arising in the determination of the specific gravity of cellulose on account of its colloidal nature, but the generally accepted value lies between 1·50 and 1·53. Peirce (J.T.I., 1923, *14*, 1) has found that cotton hairs of all kinds have an approximately constant volume of cellulose.

It is sometimes stated that the amount of pore space in cotton is 30% to 40% of the structure, but a recent publication by Peirce and Lord (J.T.I., 1939, *30*, 173) indicates that the volume of the minute crevices in dry cotton is less than 1%, and increases to about 3·5% at a moisture content of 6%.

The capillary structure of cellulose results either from the tubular nature of hairs such as cotton or from the interstices between the micelles, of the partly unorientated fibres. Neale and Stringfellow (Trans. Farad. Soc., 1933, *29*, 1167) have

shown that the absorption of dyes by cellophane follows the diffusion law, e.g. a sheet of half-normal thickness dyed to a certain fraction of saturation in one-quarter of the time necessary for a sheet of normal thickness.

Pore Size

The actual size of the capillaries in cellulosic material has been examined by various methods, one of which is to overcome the surface tension of the liquid in the capillary system by applying sufficient air pressure to displace the liquid. This gives the size of the most permeable pores. Bartell and Carpenter (J. Phys. Chem., 1923, *27*, 252) found the pore radii of cellulose nitrate membranes to be 0·3 to 0·8μ,* whilst McBain and Whistler (Trans. Farad. Soc., 1930, *26*, 157) obtained values of 0·02 to 0·03μ for the pore radii of cellophane membranes. The air pressure is apt to cause distortion of the membranes and capillaries, but much lower pressures may be utilised by a method employing isobutyl alcohol and water instead of water and air. In this manner Bechhold (Kolloid Zeit., 1931, *55*, 172) obtained values of from 0·09 to 0·25μ for various cellulose nitrate membranes.

Instead of the maximum capillary radii, the average size may be determined by a combination of capillary cross section measurements and pressure-permeability measurements, but considerable variation in capillary sizes is obtained under different assumptions, e.g. capillaries at right angles to the surface, capillaries uniformly distributed in three dimensions with or without intersections, and equal distribution in all directions. The average pore radius of cellulose acetate membranes on the assumption of capillaries at right angles across the membrane was given as 13$\mu\mu$ by Duclaux and Errera (Rev. Gen. Colloides, 1924, *2*, 130; 1925, *3*, 97). On the basis of a three-dimensional distribution of capillaries Morton (Trans. Farad. Soc., 1935, *31*, 262) has determined the pore radius of viscose films before and after treatment with a 10% solution of sodium hydroxide; the values were 1·5$\mu\mu$ for the untreated film and 9·4$\mu\mu$ for the treated membrane. Hitchcock's electrical conductivity method (J. Gen. Physiol., 1926, *9*, 755) obviated assumptions concerning capillary distribution and gave results of from 3 to 20$\mu\mu$ for cellulose nitrate membranes.

Considerable work has been done on ultrafiltration as a

* The micron, written μ, is 10^{-4} cm.; $\mu\mu$ is 10^{-7} cm.

means of estimating the pore size of membranes. It is important to use particles or macromolecules whose charge with respect to water is the same as that of the membrane in order to minimise coagulation and adsorption effects. It is necessary that the particles should be smaller than the pore size—Bechhold (loc. cit.) states that the optimum ratio is 1 : 15 to 1 : 8, whilst Elford (Proc. Roy. Soc., 1933, *B112*, 384) gives 1 : 3 to 1 : 1. The permeability of viscose membranes to organic dyestuffs has been examined by Morton (loc. cit.), who found that membranes with average pore radii of $9\mu\mu$ allowed all the dyes tested to pass through to some extent.

Some further information on pore size is given on page 130.

Optical Properties

Cellulose does not dissolve in any solvent in the purely physical sense, but is modified in the course of solution. The solutions of cellulose rotate the plane of polarised light, but this appears to be due to the formation of degradation products. Hess and his co-workers (Die Chemie der Zellulose, Leipzig, 1927) attribute the rotation in cuprammonium hydroxide solution to the formation of a definite cuprammonium-cellulose complex. Murray, Staud and Gray (J.A.C.S., 1930, *52*, 1508) in their examination of modified cotton cellulose found that the hydrocelluloses formed by treatment with H_3PO_4, H_2SO_4 and HCl were dextro-rotatory whilst the alkaline extracts were lævo-rotatory. Alkaline solutions of the oxycelluloses prepared by treatment with potassium permanganate or dichromate were lævo-rotatory.

The *fluorescence* of cellulose in ultraviolet light was observed by Hartley (J.C.S., 1893, *66*, 243). A systematic examination was undertaken under the Research Scheme of the Society of Dyers and Colourists in conjunction with the Department of Scientific and Industrial Research by S. Judd Lewis. (J.S.D.C., 1918, *34*, 167–172; *ibid.* 1921, *37*, 201–4; 1922, *38*, 68–76; 99–108; 1924, *40*, 29–40). Whilst cellulose acetate was the most strongly fluorescent of the derivatives examined, the nitrate was almost devoid of these properties.

The *double refraction* of cellulosic materials was first shown by Ambronn (Kolloid Zeitschr., 1911, *9*, 147), and is due to a combination of three factors. The first is the result of an anisotropic arrangement of the atoms within the molecule as in the macrocrystals, the second to the anisotropic arrangement of the structural units, and the third to a special form of

the latter which only appears when the material is under stress.

Frey (Kolloid Chem. Beiheft, 1927, *23*, 40) examined the double refraction of fibres by the disappearance of the fibre in a liquid of equal refractive index in the directions parallel and perpendicular to the fibre axis, and found that it was higher the more nearly the micelles are orientated. Figures of 1·595 and 1·534 for axial and transverse refractions and 0·061 for the double refraction were obtained for ramie, which is the most perfectly orientated native fibre.

Preston (Trans. Farad. Soc., 1933, *29*, 65) obtained similar results. Cotton and other fibres with less perfect orientation gave lower axial refractions and higher transverse refractions resulting in lower double refractions. Frey's figures were 1·580, 1·534, and 0·046, whilst Preston's results were in good agreement.

Preston also calculated the angle of orientation from the axial refraction of cotton and found it to be 30°, which was in agreement with the assumption of Frey that the fibril structure was wrapped round the fibre axis of cotton at an angle of 30°, from which Frey had calculated the axial refraction for perfect alignment as 1·596 corresponding to the observed value for ramie.

The effect of tension was examined by Preston, who showed that mercerising under tension resulted in a smaller decrease in the double refraction than when the fibres were mercerised without tension. From the calculated angles of inclination of fibres mercerised with and without tension he calculated the contraction which should occur when no tension is applied, and the values compared favourably with observed contractions.

Herzog (Textile Forschung, 1921, *3*, 1) has given the refractive indices of certain artificial silks as under :

REFRACTIVE INDICES

Fibre.	Axial	Transverse	Double Refraction
Chardonnet .	1·548	1·515	0·033
Vivier . .	1·547	1·521	0·026
Lehner . .	1·549	1·515	0·034
Cuprammonium .	1·548	1·527	0·021
Viscose . .	1·548	1·524	0·024

The following data are taken from a table compiled by Stamm in " Colloid Chemistry of Cellulosic Materials " (U.S. Dept. of Agriculture, Miscellaneous Publications, No. 240).

REFRACTIVE INDICES

Fibre.	Axial Refraction	Transverse	Double Refraction
Ramie . .	1·595	1·534	0·061
Flax . . .	1·594	1·532	0·062
Cotton. . .	1·580	1·534	0·046
Cuprammonium rayon I	1·553	1·518	0·035
do. II	1·549	1·520	0·029
Viscose rayon I .	1·540	1·519	0·021
do. II .	1·539	1·519	0·020
do. III	1·534	1·518	0·016

Electrical Properties

The *electrical conductivity* of cotton has been examined by Walker (J.T.I., 1933, *24*, 123 and 145). It had previously been shown by Murphy and Walker (J. Phys. Chem., 1928, *32*, 1761) that the electrical properties of textile materials depend to a very large extent on their moisture contents and chemical composition. In the case of cotton, however, further investigation showed that these properties also depend on the water-soluble electrolytic impurities present in the native fibre, for the insulation resistance of untreated cotton was considerably improved by washing in water. This improvement was accompanied by a reduction in the inorganic ash content from about 1% of the weight of the dry cotton to less than 0·3%. The water soluble salts present in raw cotton constitute about 70% of the weight of the ash and are principally sodium and potassium salts. Their removal was accompanied by an improvement of from 50 to 100 fold in the insulation resistance. A further improvement, making a total of between 150 and 200 fold can be secured if the cotton is dried under certain conditions, but a large part of the further improvement due to the moisture relations of the cotton, is removed by subsequent exposure to high atmospheric humidities. Raw cotton gave an insulation resistance of 2·6 kilomegohms at 75% R.H. and 25° C. Washing with 5 litres of water caused a 40 fold improvement in the case of 200 g. of cotton, and further improvements were made by the use of greater volumes of water or dilute solutions of calcium or magnesium sulphate.

Walker's second paper showed that the D.C. insulation resistance of cotton is dependent, to a surprising extent, upon the previous treatment such as the manner of drying, the temperature of drying, and the atmospheric conditions to which it is exposed after drying. The higher the temperature at which the wet, water-boiled cotton was dried, the higher was

its insulation resistance. For example, cotton dried at 105°, 120° and 162° C. gave 139, 171 and 201 kilomegohms respectively when subsequently brought to equilibrium at 75% R.H. and 25° C.

It was also found that the insulation resistance of the material measured at 75% R.H. and 25° C. was less after an exposure to high humidities than before, even if the cotton was well dried before testing. The conclusion drawn was that exposure to high humidities causes a change in the colloid structure of the cotton due to absorption of moisture, and this change in structure affects the mechanism of current conduction. The changes in structure due to wetting and to drying have been investigated both practically and theoretically by various workers, but the small differences in structure are more clearly shown by the sensitive electrical tests, since very small changes in moisture content cause large changes in insulation resistance. These results support the theory that reversible swelling is a very difficult process in the case of cellulose. When cotton is dried the micelle surface contains a minimum of hydroxyl groups, for many of them are orientated into the interior of the micelle by the drying process, where their hygroscopicity is to some extent neutralised by the attraction of associated molecules. As the cotton is permitted to absorb moisture these hydroxyl groups are attracted to the surface to hold the adsorbed water, and on drying again they do not readily return to the interior so that a greater number of molecules of water are held at any relative humidity ; this accounts for the normal hysteresis effect. Rapid drying at high temperatures however, will give an internal surface containing a minimum of hydroxyl groups.

The *surface conductivity* of cellulose has been measured by Briggs (Colloid Symposium Monograph, 1928, *6*, 41), and when distilled water was used the surface conductivity was found to be ten times that of the bulk conductivity. The use of very dilute salt solutions showed an increase in surface conductivity with an increase in bulk conductivity. The ratio of surface conductivity to bulk conductivity decreases in more concentrated solutions and becomes negligible in approximately 0·1 N salt solutions.

The *electrokinetic phenomenon* has also received attention. When a solid is in contact with a liquid and there is a selective adsorption of ions, the solid assumes an electrical charge with respect to the liquid. The ions of opposite charge in close proximity to the adsorbed ions, become immobilised in the

bulk solution in order to maintain electrical neutrality. The electric potential set up between the adsorbed ions and the bulk of the solution is known as the ζ potential. Cellulose has a negative ζ potential with respect to water. Harrison (J.S.D.C., 1911, *27*, 279; Trans. Farad. Soc., 1921, *16*, 116) made the first estimation by the streaming potential method and obtained 0·0157 volts for the ζ potential of cellulose against distilled water. Briggs (J. Phys. Chem., 1928, *32*, 641) obtained values of 0·0214, 0·0161, and 0·0083 volts for two different filter papers and a sulphite pulp, measured against water. Briggs also (*ibid.*, 1646) showed that small concentrations of electrolytes affect the potential in a manner similar to that of other colloidal material which is negatively charged in respect to water.

Mechanical Properties

The methods of measuring the tensile strength of fibres and yarns have been described by Matthews (Textile Fibres, and by Dorée (The Methods of Cellulose Chemistry).

The mechanical testing of cotton materials has been reviewed by the investigators of the British Cotton Industry Research Association. Peirce (J.T.I., 1923, *14*, 161) has given an account of the measurement of the mechanical properties of cotton materials, and Midgley (*ibid.*, 189) of the machines commonly used for the testing of materials.

Peirce (J.T.I., 1923, *14*, 1) has examined the rigidity of the cotton hair.

Useful information on the mechanical properties of cellulose may also be found in " Mechanical Fabrics," by Haven (Wiley, New York, 1932), " Textile Testing," by Skinkle (Macmillan, London, 1940), " Textile Testing," by Lomax (Longmans, Green & Co., London, 1937), and the " Elasticity, Plasticity and Structure of Matter," by Houwink (Camb. Univ. Press, 1937).

Some comments on crease-resistance of fibres in general are made on page 98, but the time has not yet arrived for the publication of detailed information on the creasing properties of cotton ; the production of crease-resisting cotton and rayon by forming certain synthetic resins *in situ* is strictly outside the scope of Cellulose Chemistry.

An excellent description of the mechanism of fibre behaviour is given in Astbury's book " The Fundamentals of Fibre Structure " (Oxford University Press, 1933).

PART TWO

THE CONSTITUTION, MOLECULAR WEIGHT AND MOLECULAR STRUCTURE OF CELLULOSE

CHAPTER THREE

THE CONSTITUTION OF CELLULOSE

THE early attempts to establish the constitution of cellulose were necessarily based on very limited knowledge. It was generally recognised that the purified product had the following composition : C 44·4 % ; H 6·2 % ; O 49·4 %, and the simplest formula expressing this relationship is $C_6H_{10}O_5$. The formation of derivatives such as the tri-nitrate and the tri-acetate obviously lead to the conclusion that each $C_6H_{10}O_5$ unit contained three hydroxyl groups, but in view of the structure of native cellulose, its colloidal nature and inertness in the chemical sense, naturally the simple formula could not be accepted so that cellulose was generally regarded as $(C_6H_{10}O_5)n$.

Glucose

The relationship between cotton cellulose and glucose was accepted at least 50 years ago ; for instance, Flechsig (*Z. physiol. Chem.*, 1883, *7*, 523) claimed to have obtained 95–98 % of the theoretical amount of glucose from cellulose. In view of the relationship between glucose and cellulose, it was obviously of importance to examine the yield of the former by hydrolysing cotton with dilute mineral acids.

Ost and Wilkening (*Chem. Zeit.*, 1910, *34*, 461) hydrolysed cotton by means of dilute sulphuric acid and estimated the resulting glucose by means of optical rotation and reducing power. If cellulose is quantitatively hydrolysed to glucose $(C_6H_{10}O_5)n \longrightarrow n(C_6H_{12}O_6)$, then 100 parts of cellulose should yield 111·1 parts of glucose. The reduction of Fehling's solution and the polarimetric examination gave results in close agreement, as did the fermentation of the resulting glucose to alcohol followed by its estimation. In most of the experiments the yield of glucose from 100 parts of cellulose exceeded 100 parts.

Willstätter and Zechmeister (*Ber.* 1913, *46*, 2401) found that cellulose was soluble in 41 % aqueous solutions of HCl and hydrolysis took place on prolonged standing. They showed

that some 95 % of the theoretical yield of glucose was obtainable, estimated by reducing power and optical rotation. The conclusions reached by these methods were open to criticism as the glucose was not actually isolated, but doubts as to the cellulose-glucose relationship were settled by later investigators.

Monier-Williams (J.C.S., 1921, *119*, 803) hydrolysed cotton wool by means of sulphuric acid. The product was filtered, neutralised with barium carbonate, filtered and evaporated to dryness under reduced pressure. The product was extracted with methyl alcohol, decolorised with animal charcoal and evaporated, when a residue of crystalline and almost white glucose was obtained. On subsequent recrystallisation this was identified as glucose and no other product of hydrolysis was detected. The yield was about 91 % of the theoretical amount.

Irvine and Hirst (J.C.S., 1922, *121*, 1585) also produced a valuable piece of confirmatory evidence by making cellulose triacetate according to the method of Barnett (see page 312), which was then hydrolysed and methylated simultaneously by means of methyl alcohol containing 0·75 % of HCl, to produce methylglucosides in the pure crystalline form corresponding to a 95·1 % theoretical yield of glucose. This was an improvement on the results of Irvine and Soutar (J.C.S., 1920, *117*, 1489), who treated cotton with a mixture of acetic anhydride, acetic acid and sulphuric acid and then simultaneously hydrolysed and methylated the product by heating it with methyl alcohol containing 0·5 % of HCl. Cellulose was thus converted into methylglucoside, which was isolated in a crystalline condition and shown to be convertible into glucose. About 85 % of the theoretical amount of glucose was obtained in the form of pure crystalline methylglucoside.

Although the possibility of three hydroxyl groups in cellulose was recognised on account of the acetates and nitrates, the position of these groups was not determined until the work of Denham and Woodhouse (J.C.S., 1913, *103*, 1735; 1914, *105*, 2357; 1917, *111*, 244), who succeeded in methylating cotton by successive treatments with dimethyl sulphate and caustic soda until they obtained a fibrous product containing 25 % of methoxyl. This was hydrolysed by the methods of Willstätter and Zechmeister, when a crystalline trimethyl glucose was obtained which was shown to be identical with 2 : 3 : 6 trimethyl glucose. The methylation of cellulose was carried to the extent of a product containing 44·6 % of methoxyl, the theoretical amount being 45·6 %.

In a similar investigation with an almost completely methylated cellulose, Irvine and Hirst (J.C.S., 1923, *121*, 1585) confirmed the production of 2 : 3 : 6 trimethyl glucose. Their product containing 43·8 % of methoxyl was hydrolysed with methyl alcohol containing 1 % of HCl. The resulting methyl glucosides were carefully examined and 2 : 3 : 6 trimethyl glucose alone was found, no isomerides were present, and tetramethyl glucose, monomethyl glucose, glucose and other sugars were definitely shown to be absent. The yield of crystalline trimethyl glucose was 86 %.

Cellobiose

The combination of acetylation and hydrolysis of cotton, known as acetolysis, had also been examined and shown to give considerable yields of the octa-acetate of a disaccharide known as cellobiose. This substance was first isolated by Franchimont (Ber., 1879, *12*, 1941) and later examined by Maquenne and Goodwin (Bull. Soc. Chim., 1904, 3, *31*, 854), who made an extended study of the new disaccharide. Although cellobiose was first isolated in the form of its octa-acetate by Franchimont, it was Skraup who recognised the sugar as a disaccharide and the further work of Skraup and Koenig (Ber., 1910, *34*, 1115 ; Monatsh., 1901, *22*, 1011) produced important data on its preparation and properties.

Pringsheim (Zeit. physiol. Chem., 1912, *78*, 266) had observed that cellobiose was one of the degradation products when cellulose was acted upon by bacteria. Haworth and Hirst (J.C.S., 1921, *119*, 193) showed that this sugar consisted of two glucose residues united by a 1 : 5 or a 1 : 4 β-glucosidic linkage, and suggested that a similar linkage was represented in cellulose. The cellobiose octa-acetate was prepared by stirring 20 g. of dry filter paper in a water-cooled mixture of 80 cc. of commercial acetic acid (85–95 %) containing 11 cc. of conc. H_2SO_4 so that the temperature is maintained below 20° C. A paste formed in about five minutes, and was then heated in a $CaCl_2$ bath at 120° C., when it rapidly changed into a dark red mobile liquid which boiled at 112° C. and commenced to turn black, at which point it was poured into 1·5 litres of cold water, when a pale yellow precipitate of cellobiose octa-acetate was obtained. This is soluble in boiling alcohol, from which it was recrystallised in 25–35 % yield. The octa-acetate may be treated with alcoholic potash to yield the potassium cellobiosate. The free disaccharide may

be isolated by the addition of perchloric acid as described by Maquenne.

Haworth and Hirst, however, methylated potassium cellobiosate by means of dimethyl sulphate and sodium hydrate, and obtained the hexamethyl methyl cellobioside, which on further treatment with silver oxide and methyl iodide was further methylated to heptamethyl methylcellobioside. When this compound was hydrolysed with HCl, it was shown that about equal amounts of tetramethyl glucose and a trimethyl glucose were produced. The latter was shown to be identical with the 2 : 3 : 6 trimethyl glucose produced by Denham and Woodhouse (loc. cit.) from methylated cellulose and by Haworth and Leitch from methylated lactose (J.C.S., 1918, *113*, 188). By less drastic hydrolysis, only one methyl group may be removed—that protecting the reducing hydroxyl group. Haworth and Hirst considered that the cellobiose residue must be an essential part of cellulose and that the linkage of glucose residues to cellobiose is probably largely represented in the structure of the cellulose molecule.

The acetolysis process was also examined by Freudenberg (Ber., 1921, *54*, 767) and by Karrer and Widmer (Helv. Chim. Acta., 1921, *4*, 174), when it was shown that cellobiose itself is not stable under the conditions of acetolysis and that when corrections are made for the amount destroyed in the process, it was estimated that cellulose is composed of cellobiose to the extent of at least 60%. Freudenberg also suggested that cellulose consisted of long chains of glucose residues linked together as in cellobiose.

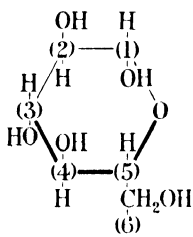
The idea of cellulose as a chain structure had been advanced by Tollens about 1895 (Handbuch der Kohlenhydrate, Leipzig ; 1914, page 564).

Prior to 1926, cellulose was regarded as a small structural unit forming large aggregates by means of forces of association. Its inertness in the chemical sense pointed to some form of polymer, using the term in a wide manner. There were also advanced possible structures based on the linkage of glucose units by primary valencies to form closed rings. The " early " constitutional formulæ have been reviewed by Hibbert (Ind. Eng. Chem., 1921, *13*, 256 and 334) and are of interest as showing the prevailing views of the period. During the next five years the tendency to regard cellulose as a small structural unit was strengthened by the evidence from X-ray analysis and structures were proposed in which the unit consisted of

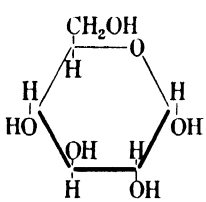
from one to three glucose residues. One of the most acceptable was that put forward by Irvine and Hirst (J.C.S., 1923, *123*, 518), who advanced the possible structure of cellulose as a ring of three glucose residues united by glucosidic linkages as in cellobiose.

Six-membered Ring Structure

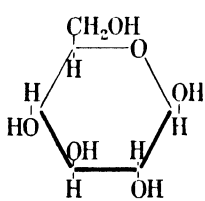
None of the early formulæ is given here because up to 1925 glucose was represented as a five-membered ring, but its formulation as a six-membered ring by Haworth (Nature, 1925, *116*, 430; J.C.S., 1926, 89) completely altered the situation. On this modern basis glucose is represented as follows:



The use of atom models is really essential to the full understanding of the position, for the problems are mainly stereochemical and not structural; indeed there is no other group of organic compounds in which stereoisomerism has such an important place as with the sugars. When an attempt is made to picture the formulæ on flat paper, differences of configuration may be represented by distribution of hydroxyl groups above and below the plane of the paper and thus show the α and β forms of glucose which differ only in stereochemical arrangement.

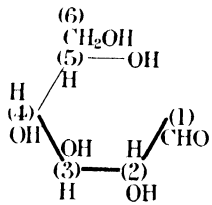


α-glucose.



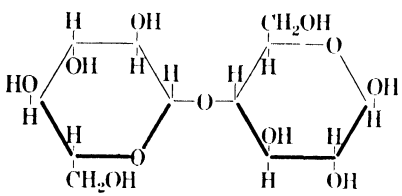
β-glucose.

The aldose form of glucose may be represented by



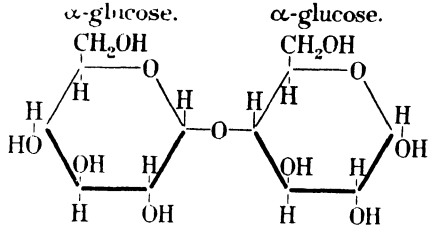
The most symmetrical of all possible modes of linking two glucose units is between the carbon atoms in the 1 and 4 positions. Structurally, but not in configuration, this linkage also occurs in maltose and, therefore, in starch, but in this case α-glucose is involved. Comparison of actual models, of which a representation is given later, shows that in maltose, the hydroxyl group in the 4 position is below the plane of the ring and in a position to combine with the hydroxyl of the other glucose residue, this also being below the plane; the two rings are then in alignment. A similar condition can only be obtained in the case of cellobiose by turning one of the glucose units through 180° so as to bring the hydroxyl at the 1 position of glucose below the plane in order to unite with the hydroxyl in the 4 position of the other glucose residue.

This new conception was confirmed by Haworth, Long and Plant (J.C.S., 1927, 2809), so that the glucosidic linkage is formulated as 1 : 4 instead of 1 : 5.

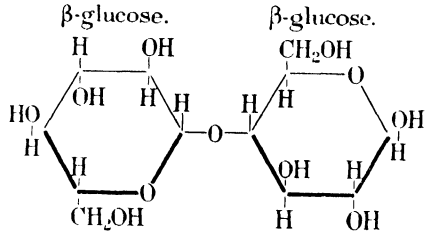


Cellobiose.

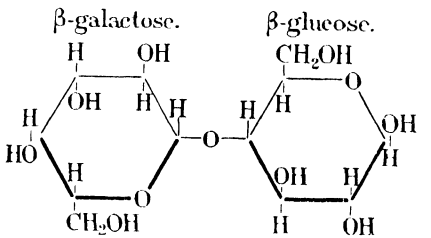
This new development in the chemistry of cellulose was not examined in that connection but as part of a comprehensive survey which is well described in " The Constitution of Sugars " (Haworth, London, Edward Arnold & Co., 1929). For example, the three reducing disaccharides are represented as follows :



Maltose (α - form).



Cellobiose (β - form).



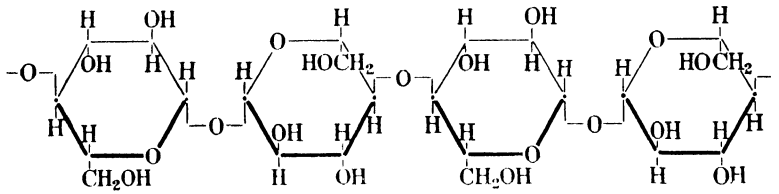
Lactose (β - form).

The free reducing group is that on the right.

Sponsler and Dore

Sponsler and Dore (Colloid Symposium Monograph, 1926, *4*, 174—New York) examined the X-ray diagram of ramie fibres on the basis of comparison with various suggested formulæ for cellulose and found that the six atom ring structure for glucose provided the most satisfactory explanation of the X-ray spacings. The axes were calculated to be $a = 10{\cdot}8$, $b = 12{\cdot}2$, $c = 10{\cdot}25$ Å. This unit cell accommodates eight glucose residues. The dimension along the fibre axis, indicated by $c = 10{\cdot}25$, represents the length of two glucose units in a chain and linked by the intermediary oxygen atom. The length of the single unit of glucose was, therefore, in agreement with that of the atom model constructed of spheres having a diameter of 1·5 Å the value determined from other X-ray data on the diamond, fatty acids and the hydrocarbons. Three-dimensional models were constructed and the final model

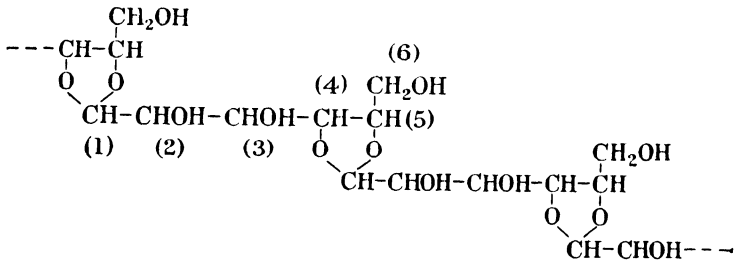
consisted of long parallel chains of glucose residues linked by primary valencies and held together by secondary valencies. Sponsler and Dore could not reconcile their data with a 1 : 4 linkage throughout and claimed that the spacings were best explained by alternate 1 : 1 and 4 : 4 linkages, as shown below.



Glucosidic Ether Glucosidic

Although the general conclusion offered a remarkable confirmation of Haworth's thesis, yet the idea of alternating glucosidic and ether linkages presented difficulties, for the 4 : 4 linkage is not encountered in the sugar series whilst the ether grouping which it represents should offer resistance to hydrolysis and was hardly likely to have escaped detection in the many examinations of the products of hydrolysis of cellulose. Another stumbling block was the fact that on the 1 : 1 and 4 : 4 linkage cellobiose could only be regarded as a reversion product and not as pre-formed in cellulose.

Nevertheless, the work of Sponsler and Dore explained many of the properties of cellulose, such as the fibrous form which could be converted into esters and ethers without any loss of this structure, the swelling powers and tensile strength. Although this work may be regarded to mark the beginnings of evidence for the idea of cellulose as a molecular chain, the new conception was not immediately acceptable and was only gradually approved as more evidence was forthcoming from other sources. The evidence from X-ray data alone is limited to the calculation of the dimensions and size of the unit cell of the lattice and the above advance was only made possible by use of the chemical evidence of Haworth. On the other hand, as Haworth states (The Constitution of Sugars, page 87) there was a lack of direct chemical evidence for the existence of the six-atom ring in cellulose ; it had been proved to exist in the disaccharides and the unproven hypothesis advanced for the polysaccharides by analogy, but much of the chemical evidence could also be explained by Tollens' formula.



Haworth

The proposed structure of Sponsler and Dore was criticised by Haworth at the Annual Meeting of the Society of Chemical Industry at Edinburgh in 1927, and also in a lecture before the University of Basle and again to the Swiss Chemical Society at Neuchatel (Helv. Chim. Acta, 1928, *11*, 547). At Edinburgh, Haworth acquainted Meyer with the work of Sponsler and Dore suggesting at the same time that the 1 : 1 ; 4 : 4 linkage must be replaced by the 1 : 4 ; 1 : 4 linkings. A note to this effect is also given by Freudenberg (J.S.C.I., 1931, *50*, 287. cf. Annalen, 1928, *461*, 130).

The work was taken up again in conjunction with Mark, and in 1928 Meyer and Mark confirmed in detail the structural formula applied to cellulose by the organic chemist.

Meyer and Mark (Ber., 1928, *61*, 593) used the dimensions established by Polanyi (Naturwiss., 1921, *9*, 288), as they claimed that the lattice adopted by Sponsler and Dore could not account for all the details of the X-ray diagram. Agreement was maintained, however, on the length of the fibre period accommodating two glucose residues, but in addition they were able to reconcile the X-ray data with the chemical evidence for the pre-formation of cellobiose in cellulose.

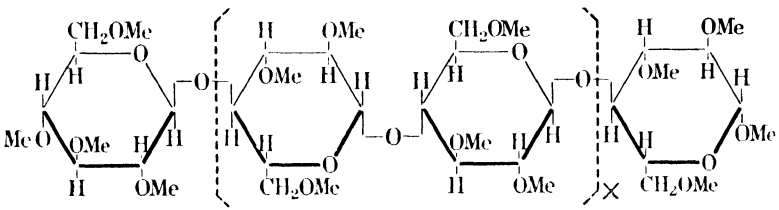
The conclusions of Meyer and Mark were later confirmed by Andress (Z. physik. Chem., 1929, *B4*, 380) ; and also by Hengstenberg (Zeitschr. Kryst., 1928, *69*, 271).

If the hypothesis of the molecular chain is correct, it follows that there should be in each of the terminal glucose residues, one more group open to methylation than in the other glucose residues making up the chain. In the reducing residue it is the reducing group which is open to methylation but the methoxyl group is split off again on hydrolysis, whereas, in the case of the non-reducing residue the terminal hydroxyl when methylated will withstand hydrolysis. In this manner hydro-

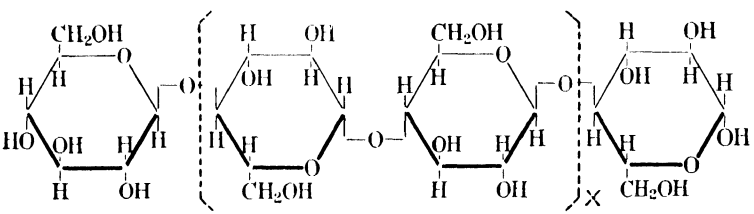
lysis should yield a certain proportion of tetramethyl glucose ; this had not been found previously and its absence had been regarded as evidence for some of the earlier ring structures.

Denham and Woodhouse (J.C.S., 1914, *105*, 2357) had found in their hydrolysis products a trace of crystalline material resembling tetramethyl glucose and recognised the possibility of long open chains of glucose residues condensed to form cellulose but their observation was not confirmed in later work on methylated cellulose. Irvine and Hirst (J.C.S., 1923, *123*, 518) based their ring structure on the fact that they were unable to find any trace of tetramethyl glucose in the products of hydrolysis of methylated cellulose whilst Freudenberg and Braun (Annalen, 1928, *460*, 288) assumed from a similar negative result that the molecular chain must be very long. It was left to Haworth and Machemer (J.C.S., 1932, *134*, 2372) to supply the final chemical proof of the molecular chain theory for cellulose by the isolation of tetramethyl glucose from the hydrolysis of tri-methyl cellulose (see page 64).

This may be illustrated by the following formula :



The modern constitution of cellulose is represented by



and the number of glucose residues making up the chain will be considered in describing the work done on the molecular weight of cellulose.

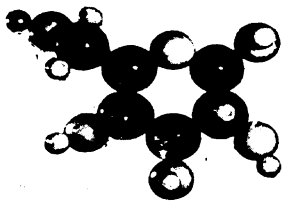


FIG. 38.
β—glucose
(Strainless model).

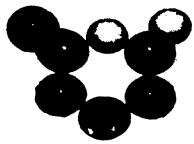


FIG. 39.
β—glucose
(Skeleton model).

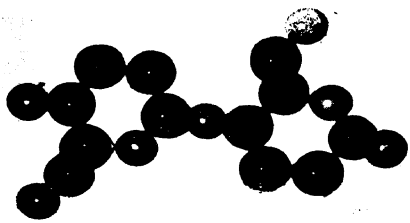


FIG. 40.
Cellobiose
(Skeleton model).

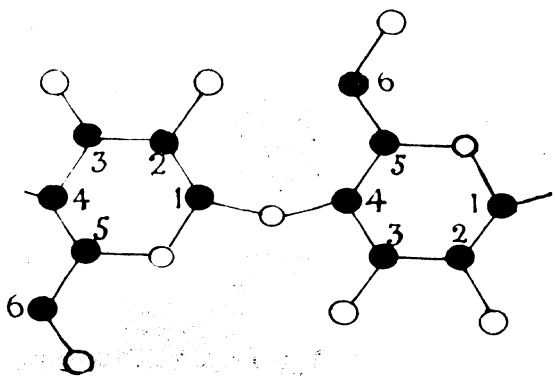


FIG. 41.—Diagram of cellobiose residue.

From " The Constitution of Sugars," by W. N. Haworth.
(London : Edward Arnold & Co.)

[*To face page* 60.

PLATE XIV.

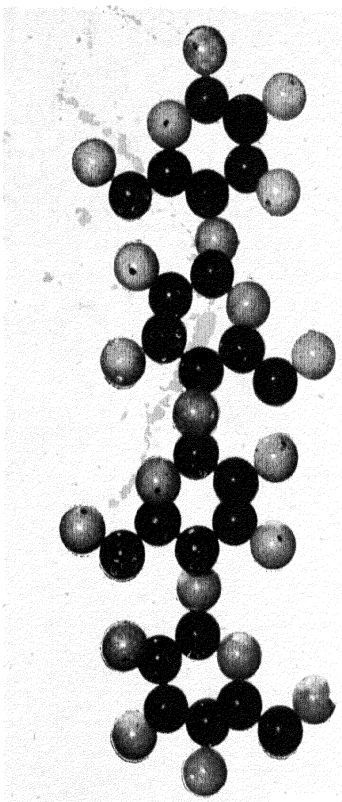


FIG. 42.—Haworth's model for cellulose showing four units.

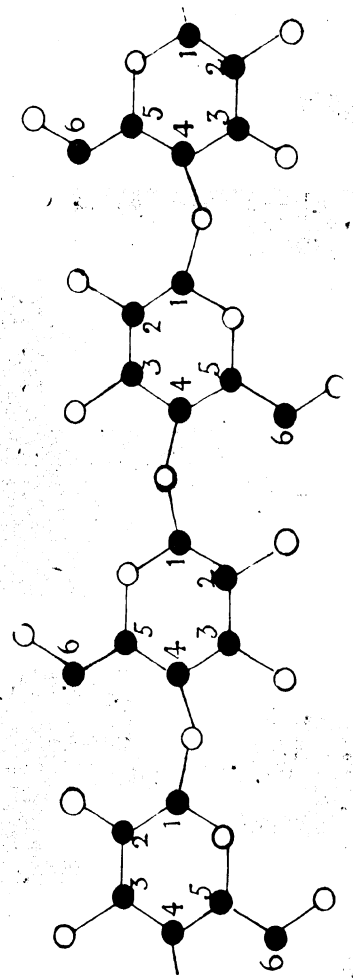


FIG. 43.—Diagram corresponding to Fig. 42.

From "The Constitution of Sugars," by W. N. Haworth.
(London: Edward Arnold & Co.)

[*To face page* 61.

CHAPTER FOUR

THE MOLECULAR WEIGHT OF CELLULOSE

Freezing Point Method

The cryoscopic or freezing point method has been frequently used for the determination of the molecular weight of cellulose derivatives. The results were generally explained on the basis of cellulose as an aggregate of small molecules; indeed, they were often brought forward in support of this hypothesis, but it is now generally recognised that the materials used were highly degraded products. Pringsheim (Ann., 1926, *448*, 136) examined the "anhydro-glucose acetates," as did Hess (*ibid.*, page 99); the latter also dealt with "biosan acetates" (*ibid.*, *450*, 40), but according to Freudenberg (Ber., 1929, *62*, 3078) the cryoscopic method is not reliable even for such substances.

The Ultra-Centrifuge Method

The sedimentation velocity method for studying the nature of protein solutions and involving the use of the ultra-centrifuge was developed by Svedberg (J.A.C.S., 1927, *49*, 2920).

Stamm (*ibid.*, 1930, *52*, 3047) applied this method to the study of cellulose dispersions in cuprammonium solutions. Using cotton linters as the source of cellulose, it was found that cellulose must be made up of from 200–260 glucose residues. A similar experiment on a viscose solution gave approximately the same molecular weight, i.e. 40,000 ± 5,000.

Kraemer and Lansing (Nature, 1934, *133*, 870) continued Stamm's work and obtained values ranging from 60,000 to 180,000. They estimated the molecular weight of native cellulose to be in the neighbourhood of 300,000. They suspect that degradation inadvertently occurred during Stamm's determinations, but also point out that Stamm assumed that one Cu atom combined with each glucose residue, corresponding to a correction factor of 72% in the calculation, whereas their own results on combined copper lead to a correction factor of 60%.

X-Ray Diagrams

Herzog (J. Phys. Chem., 1926, *30*, 457) and Hengstenberg and Mark (Z. Kryst., 1928, *69*, 271) have estimated the approximate size of the micelle from the breadth of the X-ray spots and the latter has calculated that in ramie fibre the dimensions were 600 × 55 × 55 Å, indicating that the micelle was a bundle of about 100 chain molecules. The degree of polmerisation (i.e. the number of glucose residues) of ramie and of viscose rayon were calculated to be 120 and 60 respectively, corresponding to approximate molecular weights of 20,000 and 10,000. Peirce (Trans. Farad. Soc., 1930, *26*, 809; 1933, *29*, 50) has pointed out, however, that the interpretation of the broadening of the spots as an indication of micellar size is open to question.

Osmotic Pressure Method

This is the commonest of all the methods for the determination of the molecular weight of cellulose derivatives. It is not applicable to cellulose itself, which is only soluble in aqueous solutions of electrolytes. In most cases the ratio of pressure to concentration increases with the concentration; i.e. the molecular weight apparently decreases with increasing concentration. This difficulty can be obviated by extrapolation to infinite dilution and by utilising the ratio of osmotic pressure to concentration. The molecular weight determined in this manner is independent of the solvent used, which is not otherwise the case according to Dobry (J. Chim. Phys., 1935, *32*, 50, and Bull. Soc. Chim., 1935 (v) *2*, 1882).

Some recent results are shown in the table on page 63 of degrees of polymerisation according to different investigators.

(The molecular weight is obtained by multiplying the " degree of polymerisation " by 162 in the case of cellulose, and by a varying corresponding figure for each derivative.)

Determination of End-Groups

According to the idea of the molecular chain, such a structure has two types of end group—a reducing group at one end and a tetrahydroxy glucose residue at the other. Both of these can be determined by suitable analytical means and the methods are independent of the laws of solutions which apply to other means of molecular weight determination.

In making use of the determination of reducing power, it is assumed not only that all reducing power is due to the

OSMOTIC PRESSURE METHOD.

Compound.	*D.P.*	*Investigator.*
Cellulose nitrate	200	Duclaux and Woolmân (Compt. rend., 1911, *152*, 1580).
,, ,,	80–270	Duclaux and Woolman (Bull. Soc. Chim., 1920, *27*, 414).
,, ,,	50–200	Duclaux and Nodzu (Rev. gen. coll., 1929, *7*, 385).
,, ,,	25–190	Grard (Compt. rend., 1933, *196*, 773).
,, ,,	70–770	Buchner and Stentel (Proc. Acad. Sci Amsterdam, 1933, *36*, 671).
,, ,,	100–280	Medvedev (Kunstoffe, 1933, *23*, 249).
,, ,,	430	Dobry (J. Chim. Phys., 1935, *32*, 50).
,, ,,	1600	Staudinger and Schulz (Ber., 1935, *68*, 2320).
Cellulose acetate	80–250	Herzog and Deripasko (Cellulosechem., 1932, *13*, 25).
,, ,,	110–600	Herzog and Herz (Trans. Farad. Soc., 1933, *29*, 57).
,, ,,	90–130	Grard (J. Chim. Phys., 1932, *29*, 287).
,, ,,	130–180	Buchner and Samwell (Trans. Farad. Soc., 1933, *29*, 57).
,, ,,	310	Herz (Cellulosechem., 1934, *15*, 95).
,, ,,	380	Obogi and Broda (Kolloid Z., 1934, *69*, 172).
,, ,,	260	Dobry (Bull. Soc. Chim., 1935, V*2*, 1882).
Benzyl cellulose	84	Herzog and Spurlin (Z. physik. Chem. Bodenstein Festband, 1931, pp. 239–46).
Ethyl cellulose	60–270	Okamura (Cellulosechem., 1933, *14*, 135).
Methyl cellulose	450	Staudinger and Schulz (Ber., 1935, *68*, 2320).

terminal group, but also that every chain molecule terminates in a reducing group ; both of these assumptions are open to doubt.

The reducing power is measured either by the copper number method or by the iodine number method of Bergmann and Machemer (Ber., 1930, *63*, 316). On the basis of considerable experience, Mark (Physik und Chemie der Cellulose—Springer, Berlin, 1932—page 196) considered the results to be of questionable reliability as absolute values. Davidson (J.T.I., 1936, *27*, P144) pointed out that Mark's figures were probably too low, for he assumed that oxidation of the reducing group required one atom of oxygen, whereas the copper number of glucose (300 approx.) corresponds to the consumption of 2·5 to 4 atoms of oxygen according to the composition of the alkaline copper solution.

The end group determination in the above sense was not applied by Schmidt (Cellulosechem., 1932, *13*, 129) but analogous principles were involved in the calculation of molecular weight from the determination of acidity, i.e. free carboxyl groups of various celluloses.

Haworth and Machemer (J.C.S., 1932, 2270 and 2372) have based their calculation of molecular weight on the non-reducing end group. Cellulose acetate was converted to a completely methylated cellulose, which was then completely hydrolysed and the yield of tetramethyl glucose determined. It was assumed that these processes involved little or no reduction in the length of the chain molecule so that a minimum chain length of about 200 glucose residues found or the methylated cellulose also applied to the native product, which might contain even 1,000 glucose units.

The " end-group " determination as a means of estimating the size of the cellulose molecule has been confirmed by Hess, Grigorescu, Steurer and Frahm (Ber., 1940, *73*, 505). Oxygen must be excluded from the methylation stage of the estimation. True cellulose does not lead to any tetramethyl glucose so that the assay gives some measure of degradation.

Haworth and his co-workers (J.C.S., 1939, p. 1901) have applied the end-group assay of Haworth and Machemer to hydrocellulose and oxy-cellulose.

The difficulties in comparing the results of various workers along any one line are often due to inadequate definition of the material on which the experiments were done and these same difficulties are increased when investigations have been made

on the derivatives of cellulose, for it is sometimes assumed, that the formation of derivatives has little effect on chain length—a point which is open to dispute.

There is good reason to believe that the various methods of molecular weight determination apply to different products, so that comparative data must be regarded with caution.

The results of the various methods are shown in the following table :

COMPARISON OF MOLECULAR WEIGHTS

Reducing group.	*D.P.*	
Cellodextrin acetates	8–11	Bergmann and Machemer (Ber., 1930, *63*, 316).
Native cellulose	70–175	Mark (Physik und Chemie der Cellulose).
Regenerated cellulose	75–155	Mark (Physik und Chemie der Cellulose).
Cellulose acetate	105	Mark (Physik und Chemie der Cellulose).
Native cellulose	50	Freudenberg (Ber., 1930, *63*, 1510).
Carboxyl group.		
Purified cellulose	96	Schmidt (Cellulosechem., 1932, *13*, 129).
Tetramethyl glucose.		
Biosan acetate	12–25	Haworth and Machemer (J.S.C., 1932, *134*, 2270 and 2372).
Cellulose acetate	100–120 (minimum)	

Viscosity Determination

Staudinger's contribution to the problem of the constitution of cellulose is based on the fact that one of the most striking properties of natural substances of high molecular weight is the high viscosity of their solutions in relatively low concentration.

A series of solutions of substances of low molecular weight and with approximately spherical molecules was examined (e.g. lower sugars, malonic, succinic and glutaric acid) and in dilute solution it was found that the specific viscosity of equally concentrated solutions is independent of the molecular weight and depends only on the concentration (Ber. 1930, *63*, 230).

The behaviour of substances with long chain molecules was found to be different (normal paraffins, fatty acids, and fatty acid esters) and the viscosity of equally concentrated solutions was found to be proportional to the molecular weight of the substance. In order to connect viscosity and molecular weight, the relative viscosities of solutions were not compared, but rather the specific viscosity, i.e. the increase in viscosity which is produced in a solvent by the dissolved substance. The specific viscosity is then $\eta_r - 1$ and between the specific viscosity, η_{sp} of equally concentrated solutions and the molecular weight of substances with long chain molecules, there is a simple relation $\eta_{sp}/c = K_m M$ where c is the concentration of a primary molar solution (Ber., 1930, *63*, 222). The primary molecule of a long chain molecule is the structural unit, i.e. CH_2 group in the paraffin series which would have a primary molar solution concentration of 1·4%. As M (mol. wt.) is proportional to the length of the chain and as the specific viscosity increases with chain length, the formula can be written

$$\frac{\eta_{sp}}{c} = K_C L \text{ where } L \text{ is the chain length in Å.}$$

(K_m or Kc is a constant for the particular series under consideration.)

The relationship between viscosity and molecular weight was investigated in the case of highly polymeric hydrocarbons, such as the polystyrenes, esters, polyvinyl acetates, polyoxymethylenes and ethers whose molecular weight could be determined by the cryoscopic method and had values lying between 1,000 and 10,000. The degree of polymerisation varied between 10 and 300 according to the size of the primary molecule. Substances with these relatively low molecular weights do not, when in solution, exhibit the properties of such natural products as rubber or cellulose, but form a transitional group between them and substances with small discrete molecules, and are termed hemi-colloids (Ber., 1926, *59*, 3031).

Viscosity measurements cannot always be made in a concentration range where the specific viscosity is proportional to the concentration so that the value of η_{sp}/c was obtained by extrapolation to zero concentration.

The viscosities of cellulose in cuprammonium or of triacetyl cellulose in m-cresol are higher than those calculated on the basis of the viscosity laws. (Staudinger—Die hoch moleku-

laren organischen Verbindungen—Berlin, 1932, page 446). This abnormal behaviour is due to the fact that it is not a question of simple long chain molecules with a chain arrangement of the atoms, but one of six membered rings being the fundamental molecules acting as chain members. The six membered ring requires increase in viscosity as can be shown by examination of six membered rings attached to long chains, e.g. stearic acid ester of phenol or piperidides of acids. When this definite increment is taken into account values are obtained from the viscosity laws which agree with those found experimentally. The values of the constant K_m for cellulose acetate, cellulose and cellulose nitrate were determined from viscosity measurements of highly degraded cellulose acetates and on the cellulose and cellulose nitrate derived from them. The molecular weights of the acetates were measured and it was assumed that the hydrolysis of the acetate and the nitration of the cellulose were accomplished without further reduction of chain length. Utilising the constants obtained in this manner, Staudinger calculated the molecular weights of the more highly polymerised materials and gave the following degrees of polymerisation. (Naturwiss., 1934, *22*, 797 and 813.)

DEGREE OF POLYMERISATION.

Cellulose acetates .	150–250
Regenerated cellulose .	100–250
Sulphite pulp . .	230–310
Ramie . . .	1000
Cotton . . .	750

Hence the average molecular weight of cotton cellulose should be 120,000 and cellulose acetate 103,000.

Kraemer and Lansing (J. Phys. Chem., 1935, *39*, 153) pointed out that the osmotic pressure and end group methods give a " number-average molecular weight," whilst the viscosity and ultra-centrifuge methods correspond to a " weight-average molecular weight," and that as Staudinger's factors were determined by molecular weight methods giving " number averages " the figures calculated from his viscosity data are, therefore, too small. Correlation of the specific viscosity-concentration ratio with molecular weight determined by means of the ultra-centrifuge showed that the specific viscosity-concentration ratio was proportional to the degree of poly-

merisation, but as the results from the ultra-centrifuge data gave degrees of polymerisation 2·5 to 3·5 times as great as predicted by Staudinger, Kraemer and Lancing suggest the use of their own constants in place of Staudinger's.

A comparison of some of the results obtained by the above methods as discussed at the Faraday Society Symposium (Trans. Farad. Soc., 1933, *29*) show a wide range of values.

COMPARISON OF MOLECULAR WEIGHTS.

Material.	*Molecular weight.*	*Method.*
Cellulose from linters	20,000–40,000 (minimum)	Chemical-tetramethyl glucose—Haworth and Machemer.
Cellulose acetate .	120,000	Viscosity—Staudinger.
Cellulose acetate .	35,000 (average)	Osmotic pressure—Buchner and Samvel.
Cellulose linters .	40,000	Ultra - centrifuge—Stamm.
Cellulose . .	16,000 (minimum)	Chemical—Schmidt.
Ramie or cotton .	24,000–32,000	X-ray—Mark.

Many of the various methods have been applied to different products so that no comparison is really satisfactory—in addition, it must be taken into acccount that there is no reason to assume the same molecular weight for the different natural celluloses.

Staudinger's recent work, however, gives higher results for the degree of polymerisation than those previously obtained.

Staudinger and Feuerstein (Annalen, 1936, *526*, 72) have determined the degree of polymerisation of various celluloses from measurements of the viscosity of their dilute solutions in cuprammonium hydrate according to the equation

$$\eta_{sp}/c_{gm} = 0{\cdot}81 \times \text{“ degree of polymerisation.”}$$

In the previous work where the equation $\eta_{sp}/c = K_m.M$ was utilised the value of the constant K_m was taken to be 10×10^{-4}, whereas in the paper under consideration this value has been altered to 5×10^{-4}. In round figures the degree of polymerisation of native cellulose appears to be 2,000, but actual figures for various types of raw cellulose are given on page 69.

In many of the experiments the material was dissolved in cuprammonium hydrate and reprecipitated in Rochelle salt solution in order to remove the non-cellulose impurities; this was effected in absence of white light and air and according to the data produced, there is little degradation under these conditions. The degree of polymerisation of native cellulose originally 2020 falls to 1890 with one such treatment and to 1760 on a second solution and precipitation. The measurements on viscose rayon gave degrees of polymerisation varying between 320 and 360, whilst in the case of "Cellophane" values of 270–280 are recorded.

CELLULOSE.

Cotton	2020
Cotton linters	1440
Ramie	2660
Belgian flax	2390
Italian hemp	2300
Manila	1990
Jute	1920
Papyrus	2000
Synthetic β-cellulose	1890

An interesting table which follows the degree of polymerisation through the various manufacturing processes in the production of rayon shows the following figures:

DEPOLYMERISATION IN RAYON MANUFACTURE.

	Cuprammonium rayon.	Viscose rayon.	Nitrate rayon.	Cellulose acetate.
Raw linters	1400	—	—	1400–700
Bleached linters	700	—	—	700
Wood pulp	—	700–900	—	—
Spinning solution	—	—	—	—
	400–500	—	~500	250–350
Rayon	400–500	300–450	~200	250–350

A comparison of the degree of polymerisation with some of the physical properties of the celluloses and related oligosaccharides (see page 73) is also of interest.

(In all the cases where figures are given for the degree of polymerisation of cellulose, the corresponding molecular weight may be obtained by multiplying by 162.)

The reasons which led to the change in the value of the constant K_m are given by Staudinger and Daumiller (Ann., 1937, *529*, 219), who studied the relationship between viscosity and molecular weight in a series of purified tri-acetates of cellulose with degrees of polymerisation varying from 83 to 825, by making measurements of osmotic pressure and viscosity. The constant K_m was estimated from the equation $\eta_{sp}/c_{gm} = K_m M$. and the same relationship between specific viscosity and molecular weight was found to exist, K_m being evalued as $6{\cdot}3 \times 10^{-4}$, whereas previous measurements on hemi-colloidal acetates gave a value of 10×10^{-4}. An explanation of the discrepancy is put forward and on this basis the value for the cellulose regenerated from the acetate without depolymerisation is 5×10^{-4}, which was verified by experimental results. The old figures based on the value of 10×10^{-4} must be doubled and this gives better agreement with the results from the work on cellulose nitrates. Different values of K_m indicate differences in solution and it would appear that the viscosity values are always to be corrected by osmotic pressure measurements. A table is given showing the changes in physical properties of cellulose triacetates with rising degree of polymerisation.

Staudinger (Papier Fabrikant, 1938, *36*, 381) has given a list of the constants to be used in viscosity calculations for the various solvents for cellulose and its derivatives. There is now reasonably good agreement for the degree of polymerisation according to the osmotic pressure, viscosity and ultracentrifuge methods of determining molecular weight.

DEGREE OF POLYMERISATION.

	Viscosity Staudinger	Ultracentrifuge Kraemer.
Native Cellulose . .	2,000 to 3,000	3,500
Purified Cotton Linters .		1,000 to 3,000
Wood Pulp . . .	900 to 1,500	600 to 1,000
Commercial Rayons .	250 to 500	200 to 600
Cellulose Nitrate Lacquers	300 to 600	500 to 600
Commercial Cellulose Acetate . . .	200 to 350	175 to 360

These data are taken from the work of Staudinger (Papier Fabrikant, 1938, *36*, 474) and Kraemer (Ind. Eng. Chem., 1938, *30*, 1200).

Two interesting further papers by Staudinger and his co-workers deal with the effect of the degree of polymerisation

on the physical properties of modified cellulose (Ber., 1937, *70*, 1565 and Textilber., 1937, *18*, 681). The starting material was purified cotton with a degree of polymerisation of 1,650, which was treated for times varying from 1 to 1,226 hours with water, sodium bisulphite and bisulphate, and N-solutions of hydrochloric, boric, acetic, formic, phosphoric, sulphuric and nitric acids at 53° C.

Depolymerisation plotted against time shows rapid degradation, which then slows down and almost comes to a standstill.

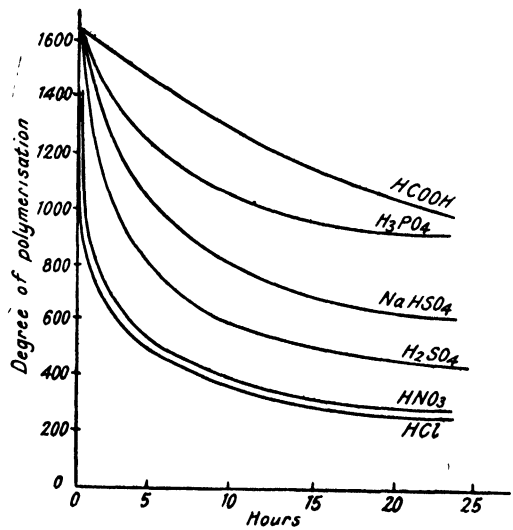


FIG. 44.—Degradation of cellulose with acid reagents.

Strong acids effect the greatest changes, but the number of broken bonds is not greatly increased by the length of the treatment. The effect of N.HCl or N.HNO_3 at 53° C. comes to a standstill after 120 hours with a degree of polymerisation of 150 to 200. Only some ten bonds in the long cellulose chain have been broken (this refers to the residual material for some of the degraded cellulose dissolves in the acid).

Changes in breaking strength, bending strength and extensibility have been measured and plotted against degree of polymerisation giving similar curves. There is very little change in mechanical properties until the degree of polymerisation falls to 700 or 800, but severe damage is evident at 600 and less. The bending strength (Franz-Textilber., 1936, *17*, 121) is the most sensitive physical property in respect of the

degree of polymerisation ; this was clearly shown in the examination of a number of different rayons. In the case of polymers of about 100 units, it is not possible to make strong threads or films, but the experience of rayon manufacture has shown that the strength of a filament does not depend solely on the degree of polymerisation or chain length, but also upon the molecular arrangement. Staudinger's results, however, show that the bending strength of rayon is more strongly influenced by chain length or polymer size than is the tensile strength or extension. (Different types of rayon give degrees of polymerisation lying between the limits of 170 to 560.)

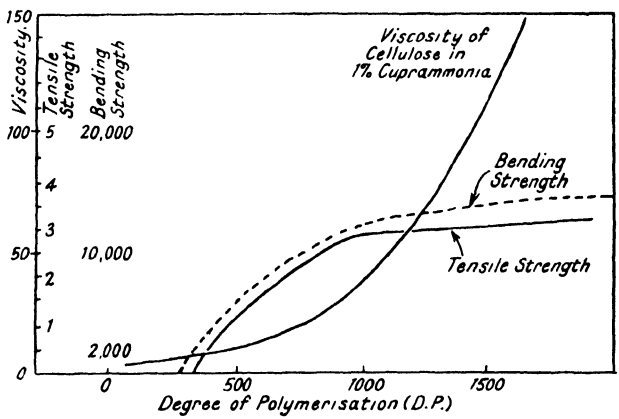


FIG. 45.—Physical properties and degree of polymerisation of cellulose.

This is probably due to the fact that there are a greater number of breaks in the individual chains making up the macro-molecule and these gaps provide a means of finding the weak places in the filament, which are not revealed by tensile strength or extension unless the number of breaks is large. The " gap number " is inversely proportional to the degree of polymerisation and is a good guide to the mechanical soundness of the material, probably reflecting its durability.

Strict comparison of the properties of rayon and degraded native cellulose of the same degree of polymerisation is not possible on account of the different molecular arrangement, but it would appear that pronounced improvements could be made in rayon manufacture by increasing the degree of polymerisation from 500, its present maximum, to 700 or 800, which represents degraded native cellulose of good strength.

Extent of Polymerisation and Properties.

	Degree of polymerisation.	Length of molecule.	Appearance.	Strength of material.	Solubility in cuprammonium.	Film forming properties.	Viscosity of 1% solution in cuprammonium.	Type of flow.
Low molecular oligosaccharides γ cellulose	1–10	50 Å	Crystal and powder.	Friable	No swelling; easily soluble.	None	Low viscosity —sol.	Normal—no deviationfrom Hagen-Poiseuille rule.
Hemi colloidal β cellulose	10–50	50–250 Å	Powder.	Friable.	No swelling; soluble.	Very slight; brittle films.	Somewhat viscous—sol.	Normal—no deviation.
Meso colloidal α & β cellulose	50–500	250–2500 Å	Short fibres.	Strong.	Slight swelling and slow solution.	Good; strong films.	Viscous.	Slight deviation.
Eu colloidal α cellulose	500–2000	>2500 Å	Long fibres & fibrillar micro-structure.	Very strong.	Severe swelling and very slow solution.	Very good; very strong films.	Very highly viscous—gel.	Strong deviation.

This might be accomplished by using the highest quality of starting material, but the spinning solution would be highly viscous and perhaps be difficult to " spin."

An interesting minor point is that the extrapolation of Staudinger's curves for native cellulose shows that an unending chain length instead of the usual 2,000 units would produce little improvement in physical properties.

Staudinger and Jurisch (Kunstseide, 1939, *21*, 6) have shown that regenerated cellulose with degrees of polymerisation up to 1,500 are soluble in alkaline solutions, in which cotton cellulose degraded to a degree of polymerisation of 400 to 500 is insoluble, namely, 11% NaOH at -10 to -15° C., and 7% LiOH solution. The difference in alkali-solubility of native cellulose and regenerated cellulose is only observed where the degree of polymerisation is 400 or over, and persists in the fully dried materials and appears also in the solubility of the tri-acetates in organic solvents. The explanation of this difference is not yet clear.

CHAPTER FIVE

CHAIN MOLECULES

THE idea that cellulose fibres are constructed of chain molecules is now commonly accepted, but it must be remembered that at the same time as the researches on the constitution and construction of cellulose were prosecuted, similar researches were being carried out on other fibres both natural and artificial.

It is generally believed that all textile fibres are composed of chain molecules and that the fibre itself in its macro-structure is a reflection of its own micro-structure; in both cases the length is several hundred or several thousand times the breadth.

A certain amount of evidence in support of the idea of chain molecules influencing fibre structure can be produced from the regenerated fibres, but this evidence, which will be mentioned later, is necessarily restricted in its scope because all the regenerated fibres have as starting material, some naturally occurring product the structure of which has not been fully proved.

Work on polymerisation has advanced enormously during the last five or six years, and very many polymeric substances are now available commercially; the idea of cellulose as a polymer of β-glucose is in the same line of thought as the term polysaccharide shows. One of the difficulties of considering the naturally occurring polymers is that there are several gaps in our knowledge of the complete polymerisation process from the monomer. It has not yet been possible to utilise chemical synthetic processes to produce cotton, wool or silk.

On the other hand, the work on polymerisation, from the standpoint of synthetic resins and synthetic rubbers, is of great importance in considering fibrous structure, because the complete synthetic process has been established and studied. Now some of these polymerisation processes have been adapted to the production of textile fibres which may rightly be termed

truly synthetic fibres, as against the regenerated products such as viscose, Lanital, etc. These truly synthetic fibres may be regarded, therefore, as presenting collateral evidence for the existence of molecular chains in textile fibres generally.

Vinyon

It has been known for some years that vinyl chloride, $CH_2 : CHCl$, was capable of being polymerised to form a plastic material and considerable work was done on drawing the polymer into fibrous form, particularly in Germany, where what is believed to be the earliest synthetic fibre, PC, was produced. Unfortunately, the polymeric vinyl chloride suffers from certain defects which restrict its commercial exploitation.

There are, of course, a large number of substances which exist in the monomeric state and which are capable of polymerisation, and some of these are capable of admixture in various proportions. In the work on polymerisation in general, as distinct from its application to synthetic fibres, it was found that a mixture of two polymers gave a result, which might be predicted from consideration of each of the component parts. On the other hand, in certain circumstances, it was possible to mix two different monomeric substances and polymerise them together; this is called copolymerisation. These copolymers often have properties which are quite different from those of a mere mixture of polymers. A very interesting application of this principle has been used in textile production in order to form a truly synthetic fibre which is called Vinyon. This material has been developed to a certain commercial extent in the U.S.A. because the two monomers vinyl chloride $CH_2 : CHCl$ and vinyl acetate $CH_2 : CH.O.CO.CH_3$ are fairly cheap products arising from modern developments in the American petroleum industry.

Vinyon is a copolymer of 89% of vinyl chloride and 11% of vinyl acetate and the mixture is polymerised up to a molecular weight of about 20,000. The copolymer may be dissolved in acetone and spun into fibres by the "dry spinning system," similar to that used for cellulose acetate filaments. Moderately coarse filaments of the copolymer are spun and these are later stretched several hundred per cent, when they acquire very high tensile strength and can also be drawn out finer than real silk.

The following table gives comparative data for Vinyon, two rayons and real silk :

VINYON AND OTHER FIBRES.

Fibre.	Tensile strength wet g. denier.	Extensibility wet per cent.
Vinyon, not stretched	1·0	120·0
Vinyon, medium stretched	2·3	25·0
Vinyon, highly stretched	4·0	18·0
Acetate rayon	0·85	36·0
Viscose rayon	1·0	25·0
Degummed silk	3·4	26·3

Vinyon suffers from certain disadvantages as a textile fibre; it is thermoplastic and melts below the boiling point of water which makes certain hot finishing processes difficult to execute. The softening on heating is accompanied by shrinkage in length. Vinyon will not burn but only melts. It is also soluble in certain chlorinated hydrocarbons and certain organic esters. It is very highly water repellent and absorbs practically no moisture from the atmosphere. One of its most important properties is the resistance to chemical reagents, both concentrated acid and concentrated alkali.

The copolymerisation of vinyl acetate and vinyl chloride presumably takes place in the following manner:

$$\begin{matrix} CH_2:CH \\ O.COCH_3 \end{matrix} + \begin{matrix} CH_2:CH \\ Cl \end{matrix} \longrightarrow -CH_2-\underset{\displaystyle O.COCH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$

Nylon

Some interesting work which bears upon the question of chain length and molecular weight has been published by Carothers and Hill (J.A.C.S., 1932, *54*, 1579). They have prepared linear condensation superpolymers by means of self esterification of substances such as ω-hydroxy decanoic acid. The poly-esters are not highly viscous in solution and show no signs of colloidal behaviour. The molecular weights vary from 800 to 5,000. The term "superpolymer" refers to linear polymers having molecular weights above 10,000, and these exhibit colloidal behaviour and show some of the properties associated with naturally occurring high polymers. The designation α-esters is also used for polyesters having molecular weights from 800 to 5,000 and ω-ester for the superpolymers. Owing to the type of condensation and product, the molecular weight can be determined by direct chemical means, as the terminal groups are still present. Whereas the

α-polyesters dissolve readily in cold chloroform, the ω-esters dissolve much more slowly, first imbibing the solvent and swelling, to form a highly viscous solution.

Carothers and Hill have shown that these linear condensation superpolymers may be drawn into strong pliable transparent fibres. Filaments of the superpolyesters from hexadecamethylene dicarboxylic acid and trimethylene glycol have been made by " spinning " a chloroform solution by extruding the viscous solution through an ordinary rayon spinneret into a warm chamber to evaporate the chloroform, and if sufficient tension is applied the filaments formed without tension exhibit the phenomenon of " cold drawing," i.e. when stress is gently applied a transparent lustrous orientated fibre is formed with a sharp boundary at the junction of the transparent and opaque sections of the filament. The breaking strength of transparent filaments is about six times that of the opaque. The tensile strength of 16–24 kg./sq. mm. compares favourably with that of cotton (about 28 kg.) and natural silk (35 kg.). The wet tenacity is fully equal to the dry. The filaments also showed remarkable springiness and elastic properties.

Filaments have also been made from superpolyesters of ω-hydroxy decanoic acid, ω-hydroxypentadecanoic acid, ethylene glycol and sebacic acid, trimethylene glycol and adipic acid and ethylene glycol and succinic acid.

Van Natta, in the same laboratories (Du Pont de Nemours & Co.), has shown that it is not possible to spin continuous filaments from the polyester of hydroxydecanoic acid until the molecular weight reaches about 7,000 and that the phenomenon of cold drawing does not appear until the molecular weight reaches 9,000. Carothers and Hill conclude that a useful degree of strength and pliability in a fibre requires a molecular weight of 12,000 and a molecular length of 1,000 Å.

In addition to the polyesters described above, it has also been found possible to produce giant molecules by condensing amino acids with themselves. During the course of this research it was found that the molten material could be drawn out in the form of a long fibre, somewhat resembling silk; even after the fibre was cool, it could be drawn out still further to several times its original length. Such a phenomenon had not been previously observed in the case of any crystalline organic compound.

In a similar manner, therefore, to the production of polyesters, it is possible to form polyamides and this is the basis

of the production of nylon. The term nylon is a generic name chosen by the Du Pont Company for the long chain synthetic polyamides whose structure broadly resembles that of the proteins, although there is no exact chemical counterpart occurring in nature. The term nylon does not refer to the fibres or yarns made from the polyamides but rather to the superpolymer itself; further, the word nylon is not limited to any particular form of polyamide, any more than the words glass or steel refer to any particular glass or steel. In view of the fact that there are numerous amino acids which might be used, it follows that a number of different types of nylon are possible and the physical properties of these different types may vary.

One of the simplest methods of nylon production is the reaction of the amino acid with itself, as previously stated, and this has been described in B.P. 461,236 where one or more amino monocarboxylic acids are subjected to a fairly extensive heat treatment. It is necessary to choose the amino acid so that the NH_2 group is as far removed as possible from the COOH group. In the case of the general formula for amino acids, $NH_2(CH_2)_n$ COOH, the value for n must not be less than 5, otherwise cyclisation of the amino acid occurs, producing imides.

These superpolymers are formed by the tail of one molecule reacting with the head of its neighbour.

$$NH_2(CH_2)_9COOH + NH_2(CH_2)_9COOH + NH_2(CH_2)_9COOH$$
$$\downarrow$$
$$-NH(CH_2)_9CO.NH(CH_2)_9CO.NH(CH_2)_9CO.NH(CH_2)_9CO-$$

Filaments produced by these methods are cold drawn to give some 300% elongation and have been found to be exceptionally strong, tough and pliable; the tenacity is from 3-4 grammes per denier, which is higher than that of any rayon. The superpolyamide fibres are not sensitive to temperature or humidity and possess remarkable recovery from elastic stretching.

Consideration of the polyamides from amino acids shows that the reacting groups are two amino groups and two carboxyl groups, but it has been shown in B.P. 461,237 that the same type of condensation may be brought about if the two amino groups are on one molecule and the two carboxyl groups are on the other, i.e. superpolyamides are produced from diamines and dicarboxylic acids.

It is believed that this method is utilised in the production of nylon on a commercial scale.

The general scheme is to condense together compounds of the following types. $NH_2(CH_2)_x\ NH_2$, where x is at least 4 and $COOH(CH_2)_y\ COOH$ where y is at least 3. The radical of dibasic carboxylic acid is that fragment remaining after the two acidic hydroxyls have been removed from its formula. Thus the radical of carbonic acid is $-CO-$; that of adipic acid is $-CO-CH_2-CH_2-CH_2-CH_2-CO-$. The radical length is the number of atoms in the chain of the radical. Thus the radical length of carbonic acid is 1 and that of adipic is 6.

Similarly the radical of a diamine is the fragment remaining after one hydrogen has been removed from each amino group and the radical length is the number of atoms in the chain of the radical. Thus the radical of ethylene diamine is $-NH-CH_2-CH_2-NH-$ and its length is 4, while similarly the radical length of pentamethylene diamine is 7.

Obviously the unit length of a polyamide is the sum of the radical lengths of the diamine and acid used in its synthesis. In order to obtain a suitable superpolymer the total length of reacting radicles must be at least 9. From this type of product, which is formed from two different molecular species, it is possible to produce exceedingly fine filaments with a denier of 0·2. The density of the fibres or filaments is a little greater than unity, 1·14, and the melting points range from 167-278°C., the highest being obtained from tetramethylenediamine, $NH_2(CH_2)_4NH_2$ and adipic acid, $COOH(CH_2)_4COOH$. Hexamethylenediamine, and adipic acid may also be used, similarly pentamethylenediamine and sebacic acid.

$$\underset{\text{adipic acid}}{HOOC.(CH_2)_4COOH} + \underset{\text{hexamethylene diamine}}{H_2N(CH_2)_6NH_2}$$

$$\downarrow$$

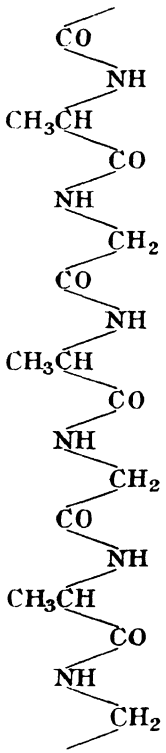
$$-OC(CH_2)_4CO\left[NH(CH_2)_6\ NH.CO(CH_2)_4CO\right]_x NH(CH_2)_6NH-$$

polyamide.

This gives a superpolyamide whose unit length is 14.

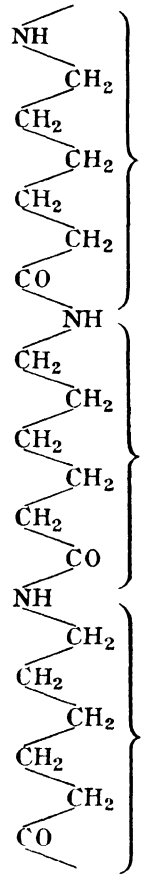
An improvement in the method of manufacture was described in B.P. 474,999, it being found beneficial first to isolate the salts from the base and the acid as a separate operation and then to heat them. The salts are much more stable than the

SILK.

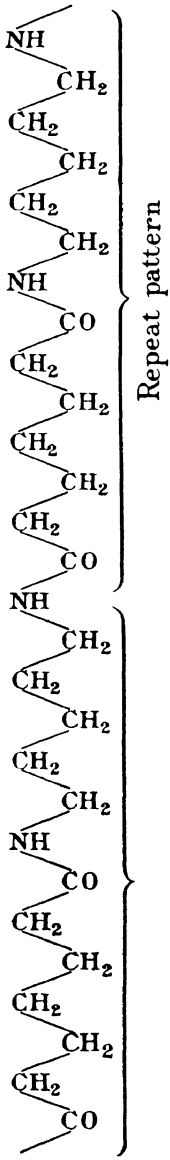


POLYAMIDES.

B.P. 431, 236
B.P. 461, 237



B.P. 474, 999
B.P. 487, 734



diamines and can be stored until ready for the polymerisation process. Further, it is possible to purify the salts by recrystallisation and thus facilitate the standardisation of the end product.

The salts are subjected to heat treatment, e.g., hexamethylenediamine adipic acid salt is heated with an equal weight of mixed xylenols (B.P. 218-220° C.) for three hours in an atmosphere of nitrogen, utilising a vessel provided with some means of returning the solvent as it distils. The warm mixture is poured into a large volume of alcohol where the superpolyamide separates as a white powder (M.P. 248° C.) and the fibres may be spun either from the molten mass or from the solvent.

In a further specification (B.P. 487,734) the polyamides produced by heating together diamines and dibasic acids with a total radical length of not less than 7 and at least one of which contains oxygen or sulphur in the chain of atoms separating the reactive groups are condensed with decamethylenediamine; for instance, salicyl acetic acid could be utilised.

As previously stated, one of the most interesting properties of nylon is that it can be cold drawn to three or four times its original length, depending upon the particular polyamide.

The molecules are originally arranged in random fashion, but during the drawing they become orientated, that is, they are parallelised and brought much closer together.

This orientation is not only an interesting scientific point but is largely responsible for the great industrial value of nylon, because after this drawing process, it becomes exceedingly strong, probably owing to the fact that decreased intermolecular distances produce increased molecular attraction.

Not only has nylon high tensile strength, but it also shows almost 100% recovery from elastic extension. Its water-absorption is quite low, amounting to 3·5% at 60% R.H., under which conditions viscose rayon takes up about 12% moisture.

It is interesting to note that the research took approximately ten years and cost more than a million dollars.

This most important synthesis of fibres demonstrates the correctness of the idea that long-chain molecules must be put together in order to obtain strong organised fibrous material; the molecular weight of nylon is approximately 20,000-40,000.

The similarity between silk and the nylons with regard to molecular structure is quite interesting. In the case of silk,

the groups of NH and CO occur very frequently and are only separated by a group such as CH_2 or $CH.CH_3$. This is in agreement with the analysis of silk which gives simple amino acids by hydrolysis. In the case of the polyamides produced according to B.P. 461,236 and 7, the groups of CO-NH occur much less frequently along the molecular chain, and the neighbouring CO—NH arrangement is separated by five CH_2 groups. The repeat pattern of the fibre consists of at least seven atoms excluding hydrogen.

In the case of polyamides produced according to B.P. 474,999 the CO—NH grouping is reversed in alternate repeats, and appears as NH—CO, so that the actual repeat pattern here is about twice as long as in the first example.

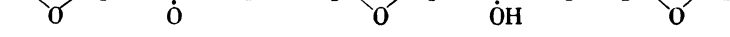
Nylon filaments do not swell in water and are not affected by boiling in 5% NaOH solution. The general resistance to swelling of the chemical reagents with the exception of phenols may be due to the large number of CH_2 groups in the structure causing the NH—CO groupings to be widely separated.

The American specifications dealing with nylon production and the preliminary work are U.S.P. 2,071,250 to 2,071,253 inclusive; 2,130,947 and 8.

Polymers

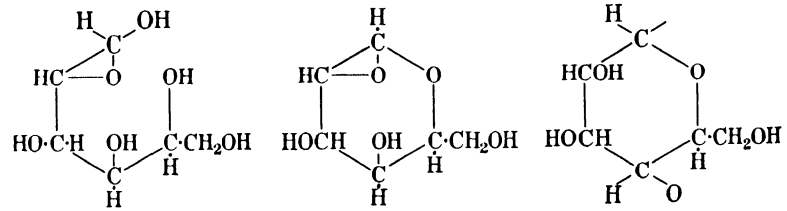
The bearing of this work on that of Staudinger is that whilst both use synthetic polymerisation as an approach to the problem of the molecular weight of the naturally occurring polymer cellulose, the products studied by Staudinger (polyoxy methylene, polystyrene, polyacrylic acid, etc.) are produced by reactions of unknown mechanism and their behaviour is generally not sufficiently simple to furnish proof of their structure. The condensation polymerisation methods of Carothers and Hill, however, provide simple methods for the synthesis of chain molecules whose structure follows directly from the method of preparation.

Hibbert (Can. J. Res., 1933, *8*, 103; 192; 199) has followed somewhat similar lines and succeeded in building up long chains of ethylene glycol units by the methods of polymerisation first established by Nef for glycidol and by Levene and Walti for other ethylene oxide derivative, e.g.



Hibbert also put forward a working hypothesis for plant

synthesis of sugars and polysaccharides, by assuming that glucose reacts in its ethylene oxide equilibrium form, loses H_2O to form the anhydride, and undergoes polymerisation



In this connection it is interesting to note that cellulose has been synthesised by bacterium xylinum and acetylo-bacter according to Hibbert (Can. J. Res., 1931, *5*, 580). This biochemical synthesis produces cellulose which is chemically the same as plant cellulose and also gives the same X-ray diagram as observed by Clark (Applied X-ray, New York, 1932, page 445), Champetier (Ann. de Chimie, 1933, *20*, 5), and Khouvine (Compt. rend., 1933, *196*, 1144 ; 1934, *198*, 1544).

The relationship between molecular weight and colloidal properties has been shown by Emil Fischer in his synthesis of the polypeptides, when colloidal properties were not encountered until a molecular weight of about 1200 was reached. The most important work of this nature which throws light on the constitution of cellulose is that of Staudinger on the long chains of polyoxymethylenes, which are comparable with cellulose in their physical properties to a great extent. The basic principle of the structure of these polymers was taken from the study of the action of acetic anhydride on polymerised formaldehyde. The product was separated into fractions whose solubility and vapour pressure decreased with increase in the ratio of formaldehyde to acetic acid (Helv. Chim. Acta, 1925, *8*, 41 and 67). This is in agreement with the conception of chains of CH_2O units terminating in acetyl groups and containing different numbers of units in the chain. The acetic acid content of the various fractions gave a measure of the chain length and hence of molecular weight which was in agreement with that determined cryoscopically (Ber., 1926, *59*, 3019 ; Annalen, 1929, *474*, 145). It was also shown by means of X-ray diagrams that the polyoxymethylenes have a long chain and a small unit cell (Z. physik. Chem., 1927, *126*, 425), thus confirming the point that a small unit does not necessitate a small molecule.

From the study of many other polymers, Staudinger (Ber., 1926, *59*, 3019) formulated the theory that the structure of all polymerised products was a combination of small units by means of primary valencies. The polymerisation products of styrene, vinyl acetate, acrylic acid, etc., have also been described by Staudinger in " Die hochmolekularen organischen Verbindungen-Kautschuk und Cellulose " (Berlin, 1932). One of the most interesting features of this work is the variation of properties with increasing chain length—substances with a low degree of polymerisation usually being powders which dissolve without swelling to give low viscosity solutions, whilst the higher polymers are strong elastic products which exhibit swelling and give viscous solutions if they dissolve.

The work of Carothers and his collaborators which has already been mentioned (see page 77) confirms that of Staudinger on the polymerisation of the unsaturated compounds.

Investigations of these types show extraordinary resemblances between the properties of the synthetic chain polymers and those of cellulose and provide very strong additional evidence for the molecular chain theory of the constitution of cellulose.

Saccharides

Still further evidence for the chain theory may be obtained from the chemistry of the sugars themselves, particularly from the oligosaccharides, which are sugars containing a small number of glucose residues linked together as in cellobiose. Bertrand and Benoist (Bull. Soc. Chim., 1923, *33*, 1451) had described a trisaccharide isolated from the products of acetolysis of cellulose. Similar work by Irvine and Robertson (J.C.S., 1926, *128*, 1488) also resulted in the isolation of the trisaccharide by interrupting the acetolysis immediately before the formation of the octa-acetate of cellobiose. Ost (Zeit. angew. Chem., 1926, *39*, 1117) recorded similar results also.

Willstätter and Zechmeister (Ber., 1913, *46*, 722) had isolated what are now known to be a triose and a tetrose from the mixture which results from the hydrolysis of wood by strong hydrochloric acid. This work was repeated (Ber., 1929, *62*, 722) and confirmed, but in addition cellobiose was also found among the products of hydrolysis. Further work by Zechmeister and Toth (Ber., 1931, *64*, 854) again confirmed these observations and added a cello-hexose to the triose and tetrose already found, but the cello-hexose was not isolated

in crystallised form. The cellotriose on acetolysis produced octa-acetyl-cellobiose and was therefore shown to be a cellobiosido-glucose.

The constitutions of the cellotriose and cellotetraose were established by Haworth, Hirst and Thomas (J.C.S., 1931, page 824) and by Freudenberg, Friedrich and Bumann (Annalen, 1932, *494*, 41) by means of complete methylation of these sugars followed by hydrolysis, which gave the necessary mixtures of 2 : 3 : 6 trimethyl and 2 : 3 : 4 : 6 tetramethyl-glucose in proportions agreeing with three and four unit chains of glucose residues united by 1 : 4 linkages.

Freudenberg and Nagai (Annalen, 1932, *494*, 63) succeeded in synthesising cellobiose and triose in the form of the methylated derivatives, by allowing trimethyl-methylglucoside to react on the chlorhydrins of methylated glucose and methylated cellobiose.

The work of Freudenberg, Friedrich and Bumann (loc. cit.) on the optical rotation of the oligosaccharides and their methylated derivatives has shown that the same configuration and structure linkages persist throughout. The molecular rotation changes by a constant amount for each additional glucose unit as the oligosaccharide series is examined in order commencing with the biose and ascending to the hexose. Hence it appears very probable from this evidence alone that cellulose itself only contains linkages of the β configuration, for only one α-linking as in maltose to 100 β linkages would show itself by a distinct change of molecular rotation. The oligosaccharides may, therefore, be regarded as the early members of a series of condensation products of β glucose which series extends to the high molecular weight product—cellulose itself.

Additional evidence that there was only one method of linking between the individual glucose units in cellulose has been supplied by a study of the rate of hydrolysis and acetolysis of cellulose and the oligosaccharides. The kinetics of the chain scissions were investigated by Meyer, Hopff and Mark (Ber., 1929, *62*, 1103; 1930, *63*, 1531) and by Kuhn (Ber., 1930, *63*, 1503) and when the fundamentals were established the results were applied to the experimental data of Freudenberg and his co-workers. The hypothesis that all the linkings undergo cleavage with the same ease is complicated by the fact that the oligosaccharides hydrolyse more easily than the longer chain products, but the results were in agreement with the idea of the same linkage persisting throughout.

Although the molecular chain theory for the constitution of cellulose is now generally accepted, yet Hess and his school still regard cellulose as essentially a substance of low molecular weight and the properties which are advanced as evidence of a polymeric structure are explained by him on a morphological basis, known as his " Membrane Theory."

A recent summary of his theory states that the cellulose fibres contain a system of membranes which permeate the structure and enclose the true cellulose in small cells. (Naturwiss., 1934, *22*, 469.)

These membranes fulfil the most important rôles in the behaviour of cellulose being responsible for the swelling phenomena, the elastic properties, and the fact that it is possible to form many derivatives of cellulose without loss of the fibrous structure. The fall in viscosity as a result of the modification of cellulose, attributed to a reduction in chain length on the molecular chain theory, is due to partial destruction of these membranes according to Hess. Two of the main objections to this view are that it cannot be generalised to account for the striking similarities between cellulose and the synthetic polymers which obviously have no biological structure, and it is incapable of explaining the chemical evidence of the hydrolysis and acetolysis of cellulose.

A summary and criticism of the " membrane theory " has been given by Davidson (J.T.I., 1936, *27*, P152).

Alginates

It is well known that alginic acid is contained in substantial amounts in many seaweeds and may be extracted from them fairly easily. The production of films and filaments from alginic acid and alginates has been suggested on several occasions and attracted some attention in Japan many years ago. Within more recent times, however, the production of alginate films and filaments has taken on a renewed interest, particularly in view of the fact that developments in the elucidation of the constitution of alginic acid have shown that it stands in a midway position to homopolar cellulose on the one hand and heteropolar proteins on the other.

Hirst, Jones and Jones (J.C.S. 1939, 1880) have shown that alginic acid is probably composed of mannuronic acid residues having a pyranose ring structure similar to cellulose, neighbouring units being linked through the *1* and *4* carbon atoms via oxygen. The carboxyl group of alginic acid replaces the

primary alcohol group of cellulose as shown in the formulæ. Lunde, Heen and Oy (Kolloid Zeit. 1938, *83*, 196) showed that the molecular arrangement and orientation fitted in with a structure somewhat similar to that of cellulose, but that the degree of polymerisation was only 80.

Bonniksen, B.P. 415,042, has produced films and filaments by preparing an aqueous solution of an alkali-metal alginate which, after extrusion, is rendered insoluble by treatment with a solution of a calcium salt. A later specification, B.P. 492,264, discloses the manufacture of films and filaments by extruding a 7% solution of a soluble alginate, whose viscosity is not less than 10 centipoises in a 1% solution, into a precipitation bath containing calcium chloride (approximately 10%).

B.P. 502,482, by the Nihon Kaisan Kogyo Kabushiki-Kaisha, Japan, discloses the production of filaments by preparing a 3% solution of ammonium alginate, and this viscous solution is spun into a coagulating bath containing a 10% aqueous solution of sulphuric acid. The resulting fibres are immersed in 10% aluminium sulphate solution and finally in 1% solution of lead acetate.

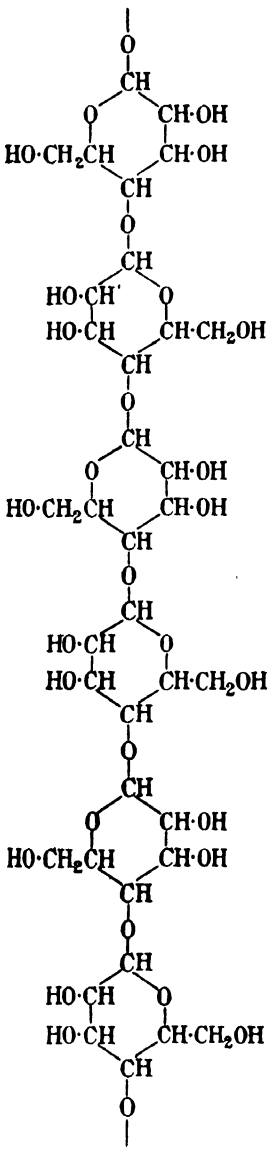
Gohda, B.P. 417,222 has produced rayon from seaweed by dissolving in cuprammonia and spinning into a suitable bath.

More recent work by Speakman (Textile Mfr. 1940, *66*, 464) results in the production of beryllium alginate which is stated to be highly resistant to soap and soda and therefore a great improvement over the calcium and aluminium alginates.

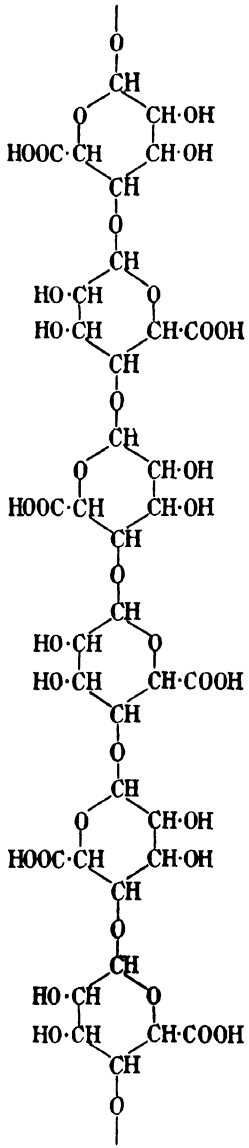
A typical method is to extrude the sodium salt solution into a sulphuric acid/olive oil emulsion bath, and then convert the alginic acid filaments into the beryllium filament by leading into a bath of beryllium basic acetate made by adding one mol of beryllium carbonate to one mol of sodium acetate in solution. During the treatment with the beryllium acetate the temperature of the solution is raised to 100° C. The calcium alginate filaments treated with the beryllium acetate in a similar way still contain 5·2% calcium, but in spite of this are highly resistant to soap and soda.

The alginates are readily depolymerised by alkali and attempted preparation of esters and ethers results in considerable decomposition.

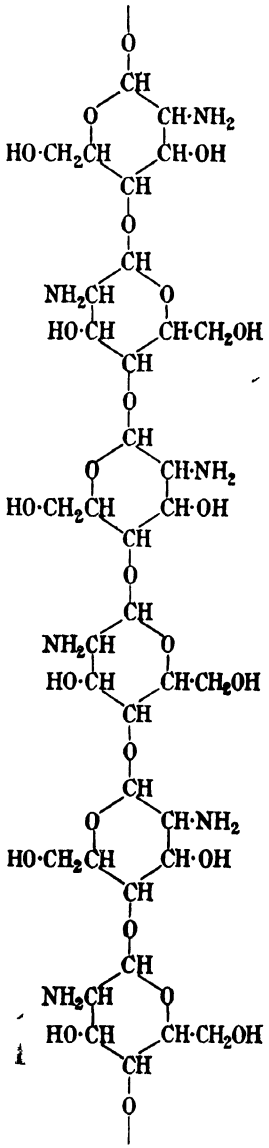
Alginate rayon has not yet reached any commercial importance but is nevertheless of considerable interest in considering



Cellulose.



Alginic acid.



Deacetylated chitin.

the general question of the chain molecule in relation to fibre structure.

Chitin

Interesting information has recently appeared about chitin, which largely composes the shell of many shellfish such as lobsters, crayfish, crabs and shrimps. The Du Pont Company (B.P. 458,839) showed that in certain circumstances it was possible to purify and hydrolyse the chitin and produce a deacetylated chitin of practical value.

The deacetylated chitin exists as a molecular chain made up of glucoseamine residues and bears a strong resemblance to cellulose, but the OH group in the 2 position of cellulose is replaced by NH_2. The deacetylated chitins, according to B.P. 458,839 contain about 100-1,000 glucoseamine units in the chain molecule. Meyer and Wehrli (Helv. Chim. Acta, 1937, *20*, 353) found that deacetylating chitin with caustic soda gave a deacetylated chitin with a chain length of only 20-30 aminoglucose units, whereas the viscosity measurements of the original chitin showed the chain length to be of the order of that obtained for wood pulp.

Kunike (Kunstseide, 1926, *8*, 182) also succeeded in producing artificial silk from deacetylated chitin, the strength of which was higher than that of rayon. Thor and Henderson of the Viking Corporation of Chicago (U.S.P. 2, 217, 823) found that deacetylated chitin could be xanthated and regenerated in a similar manner to cellulose. They confirmed that the dry strength is better than that of rayon, but they found that the wet strength was lower. (See also Am. Dyes. Rep., 1940, *29*, 461.)

Apparently insufficient commercial supplies of chitin hinder its commercial development ; nevertheless, the similarity between deacetylated chitin and cellulose is of interest in considering the chain molecules.

Animal Fibres

Silk

The structure of completely degummed silk or fibroin has not yet been fully elucidated ; it has not attracted the same amount of intensive research as other native fibres. On hydrolysis it gives three amino acids, glycine, alanine and tyrosine, but the two former predominate.

Glycine and alanine are two of the simplest amino acids—NH_2CH_2COOH (Glycine) and $NH_2CH(CH_3)COOH$ (Alanine); there are no reactive side groups so that the polypeptide chains of fibroin must be made up of alternating glycine and alanine residues, held together in the direction of length by peptide linkages, as shown on page 81, the chains being held by partial valency forces. The only approach to the side chain is the methyl group in alanine.

The X-ray examination of natural silk indicates that the long thin crystallites of fibroin which lie roughly parallel to the long axis of the fibre are composed of bundles of fully extended polypeptide chains. Although the chemical constitution of fibroin is quite different from that of cellulose, yet they are both assembled on a similar molecular plan, and because of the extended state of the molecular chains they have comparatively little elasticity as compared with wool for instance.

The chain length of cellulose has been estimated by its viscosity in cuprammonia and as silk is also composed of chain molecules, attempts have been made to measure the chain length by means of its viscosity in appropriate solvents and also to estimate any damage which may be due to such factors as light, oxidation, acid, alkali, etc. The original method of Trotman and Bell (J.S.C.I., 1935, *54*, 141) has been modified by Tweedie (Can. J. Res., 1938, *16B*, 134), utilising a solution of zinc chloride of specific gravity 1·67; undamaged silk gave viscosities of 19-24 cps., damaged silk gave values of less than 19 cps. until the figure of 10-12 cps. indicated complete disintegration of the silk.

More recent work on the fluidity of silk solutions has been carried out by Garrett and Howitt (J.T.I., 1941, *32*, 1), who made use of cupri-ethylene diamine solution which is neutralised directly after dissolution of the silk. Measurements of a 5% solution of silk gave a range of fluidities from 4 for the untendered material, down to 50 for the chemical tendering, corresponding with almost complete loss of strength.

Wool

In the same way as the long chains of cellulose are built up of glucose residues, and the molecular chain of fibroin in silk is composed of amino acid residues, so, in the case of wool, we have the keratin which is built up from a large number of amino acids and on this account the elucidation of its structure

has been a much more difficult problem than in the case of other textile fibres.

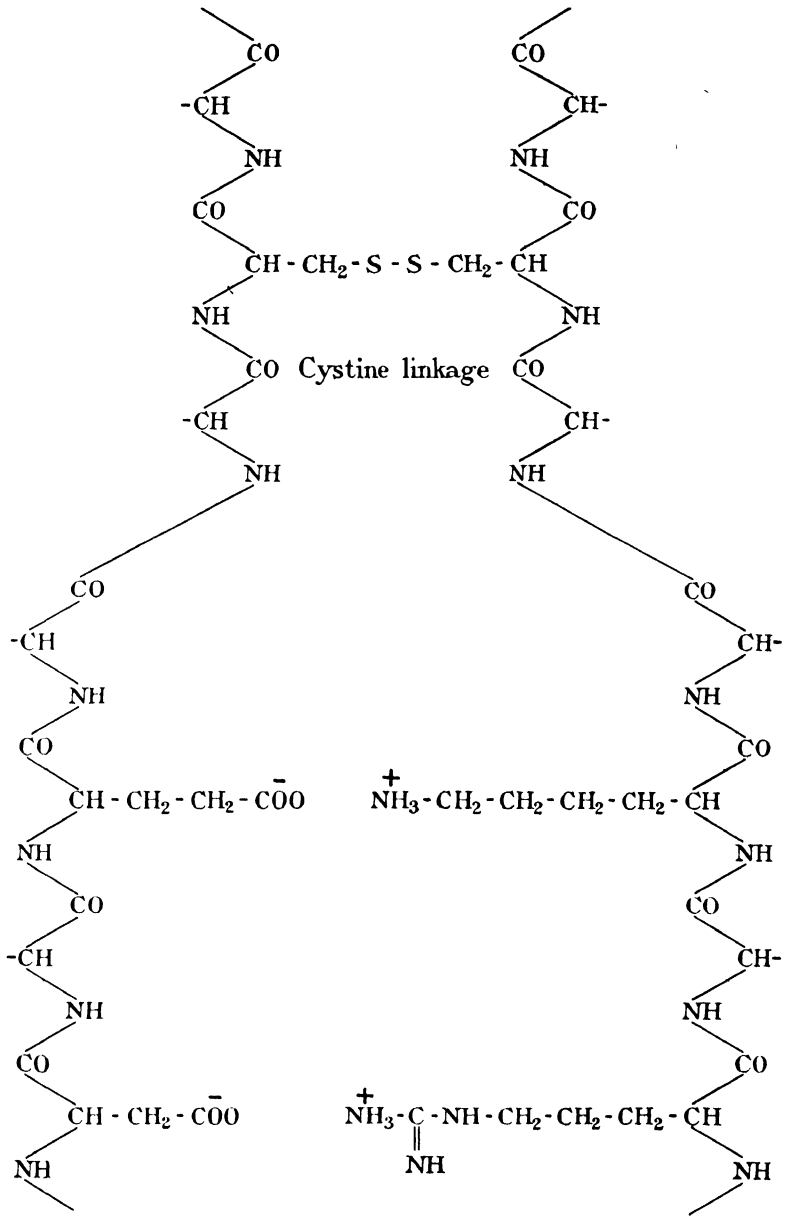
As previously stated, the method of linking amino acid molecules by means of the peptide linkage, $-CO-NH-$, can produce long chain compounds of high molecular weight, as shown by Emil Fischer; these compounds are classified as polypeptides and most of the proteins fall into this class.

The case of silk is comparatively simple because hydrolysis produces mainly glycine and alanine, but wool keratin is made up of a large number of amino acids, as follows:

Glycine	0·6%
Alanine	4·4%
Valine	2·8%
Leucine	11·5%
Serine	2·9%
Proline	4·4%
Aspartic acid	2·3%
Glutamic acid	12·9%
Cystine	13·1%
Tyrosine	4·8%
Tryptophan	1·8%
Arginine	10·2%
Histidine	6·9%
Lysine	2·8%

The fact that the long peptide chains are built up by condensation of these amino acids, is based on X-ray analysis and chemical investigation, from which it appears that the chains are regular repeats of the $-CO-CH-NH-$ unit. Now the peptide chains will carry side chains which vary in their nature according to the particular amino acid from which they come and whereas many of these side chains are non-reactive, yet a number of them are of fundamental importance in considering the structure of wool.

In the textile fibres previously considered, the main chains are held together by general cohesive forces and also by residual valencies, but in the case of wool keratin there is a more complex attraction between the main chains which, in certain cases, exists as the ordinary bonds of chemical combination. Two important examples of side chains are those which come from the residues of glutamic acid and lysine and these together may form a salt-like linkage; similarly with aspartic acid and arginine. The case of cystine is somewhat



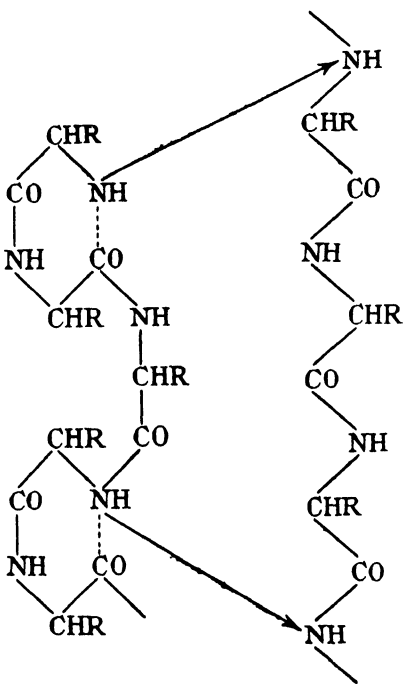
Salt linkage

different as it is a di-amino dicarboxylic acid and therefore capable of supplying a side chain residue to each of the two neighbouring main chains.

With main chain and side chain formations, as outlined above, it is possible to picture the molecular structure of wool as shown by the generally accepted formula (page 93).

From the results of Astbury's work on stretched and unstretched wool, it appears that the main polypeptide chains are not fully extended but are crumpled; when wool is stretched 100% there is a transformation from α-keratin to β-keratin and the X-ray photograph of the latter is similar to that of real silk.

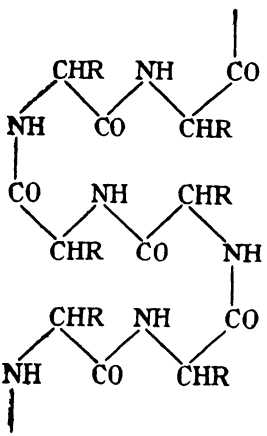
The molecular transformation which takes place on stretching is shown below.



It is believed that some of the characteristic elastic properties of wool are due to the folded or crumpled state of the main chains, but that a great deal of the elasticity is due to the contractile powers of the cross linkages. In just the same way as cellulose contains some chain molecules which are not in

orderly array, so natural silk contains a certain proportion of polypeptide chains in a crumpled state.

Considerable work by Speakman on the nature and properties of the cross linkages has led to great advances in our understanding of the physical and chemical properties of wool. It is possible to break and reform many of the cross linkages, and when both the salt linkages and the cystine linkages are broken, the main peptide chains fold into a still more compact form and the fibre contracts 30 % in length, as compared with its normal unstretched state.



The molecular architecture of wool, therefore, appears to be a grid or ladder arrangement which is folded or crumpled along its length.

The side chains or cross linkages of wool are much more susceptible to chemical attack than the main polypeptide chains, and it is for this reason that viscosity methods of estimating damage in wool cannot be applied.

The combination of the folded main chains and the cross linkages preserves its structure during mechanical distortion and may account for the high elasticity of wool compared with other fibres ; the contractile power is probably due to the stress generated in the cross linkages when the crumpled form is extended. [The pseudo-hexagon type of fold appears to be in course of revision by Astbury (Nature, 1941, *147*, 696, and Chem. and Ind., 1941, *60*, 491.)]

The mechanistic interpretation of the behaviour of chain molecules is not the only explanation ; Meyer (J.S.C.I., 1938,

57, 439) has provided a thermodynamical basis for the tendency of stretched main-valency chains to shorten, i.e., for elasticity.

Regenerated Proteins

It has not been possible to regenerate fibres from wool which has been dissolved in an appropriate solvent, although wool treated with chlorine peroxide dissolves in lithium thiocyanate solution with little degradation according to Nilssen (Thesis; Leeds; 1937), but silk, on the other hand, has been regenerated in filament form.

Artificial fibres from other proteins have attracted considerable attention during recent years, and if they have not had the same commercial success as rayons, it must be remembered that this may not be entirely due to technical considerations. Rayons compete with real silk which is expensive, and are made from a cheap material—wood.

The commonest artificial protein fibre is prepared from casein which is not particularly cheap and must compete with wool which is relatively cheap.

Casein-wool has been known for some time, the first suggested use of casein for textile fibres having been disclosed by Todtenhaupt in B.P. 25,296 of 1904. Within more recent times, however, the production of Lanital, according to the processes of Ferretti, has attracted great attention; the chief specifications are B.P. 483,731; 483,807; 483,808; 483,809; 483,810.

The casein is produced by the acid treatment of milk under certain definite conditions, following which the casein is dissolved in sodium hydroxide solution and allowed to mature, when it becomes more viscous, given certain definite temperature conditions. When the required volume and viscosity have been obtained, the temperature is lowered slightly and the viscous solution is spun into filaments by coagulation in an acid bath containing aluminium salts and formaldehyde.

The treatment with formaldehyde and with aluminium salts is of great importance from the standpoints of tensile strength and resistance to swelling. It appears that the formaldehyde will form links with the amino-groups in adjacent chains; similarly, the aluminium is capable of bridging the chains through the carboxyl groups.

Another interesting method of making artificial protein fibres is given in B.P. 467,704 by Astbury, Bailey and Chibnall. Globular proteins, such as ground-nut globulin or soya bean

globulin, may be dissolved in an aqueous solution of urea and allowed to degenerate or de-nature, during which process the solution gradually becomes more viscous. Filaments may be produced from this viscous solution by spinning into a suitable bath which usually contains inorganic salts, together with acid and sometimes formaldehyde solution.

These processes are of particular interest because the globular proteins are now known to consist of large round molecules which are formed of coiled polypeptide chains. During the degeneration or de-naturation, the globular configuration breaks down and the polypeptide chains unfold and then agglomerate into parallel bundles, similar to those found in β-keratin.

General

Chain molecules may be grouped into three classes, (*a*) coiled chains, (*b*) straight chains, (*c*) branch chains.

In the case of the coiled chains it is sometimes possible to uncoil these chains and prepare fibres of more or less straight chain structure from them. On the other hand, some of the coiled chains, such as starch, have not yet apparently been uncoiled and although they give solutions of high viscosity, yet they do not form flexible films or filaments ; the derivatives of starch are not miscible with similar derivatives of cellulose. Work by Hirst and Young (J.C.S., 1939, p. 1471) on the methylation and degradation of starch, appears to favour a highly branched system, in which the average length of the branches corresponds to a molecular weight of some 4,500.

Straight chains composed of long thread-like molecules generally are capable of forming fibres which, in certain circumstances, are sufficiently tough and elastic to possess some technical interest. A long chain molecule, however, is not the sole requirement for textile fibres as the extent of mutual attraction between the neighbouring chains must play a large part in determining textile value.

If there is no interaction between the neighbouring chains, then the fibre would be unstable to swelling agents. The commonest type of interaction is by means of secondary valencies through polar groups in the macro-molecules which interact and keep the structure together. This is the case in cellulose, for instance, and a very useful picture of the method of interaction may be seen in Rideal's analogy of a zip fastener.

A stronger force may hold the neighbouring chains together as, for instance, in the salt linkages and cystine bridge of keratin. Synthetic resins from phenol formaldehyde and from urea formaldehyde also are presumed to possess a grid form of molecular architecture. It has been suggested that sulphur bridges are formed in vulcanised rubber between the hydrocarbon chains of unvulcanised rubber, and within the series of synthetic polymers the effect of very small bridges of divinylbenzene between the polystyrene chains has been demonstrated by Staudinger. The effect of main valency linkages between long chains has been discussed by Mark (Nature, 1938, *142*, 937) from which it appears that numerous cross linkages tend to produce a brittle product. On this account it would appear that urea formaldehyde and phenol formaldehyde resins of sufficiently high chain length would nevertheless be too brittle for use as textile fibres.

In the case of wool the effect of the cross linkages is offset by the crinkled nature of the main polypeptide chains.

During recent years, considerable interest has been shown in the resistance to creasing of various textile fibres. General experience has shown that the common textile fibres may be placed in the following order of creaseability: wool, natural silk, acetate silk, viscose, cotton, linen, and there is also good evidence to show that within the cellulose series the creasing power increases with the orientation of the micelles. Attempts have been made to relate creaseability with absorption of moisture or swelling in water, but these attempts will not withstand critical examination—similarly, with attempts to explain creaseability on the basis of pore size.

Until such time as information is available for publication, there appears to be a reasonable explanation of crease-resistance on the basis of the entanglement of the chain molecules, irrespective of whether these chain molecules are main chains or the regularly arranged bridges, as in wool, the latter offering an orderly system of entangled chain molecules. It must be remembered that synthetic resins which are capable of imparting crease-resisting properties to cellulose, themselves possess a branched or grid structure so that a system of entangled molecular chains may be established with the cellulose. Straight chain polymers, such as the acrylate series do not impart resistance to creasing. It is also known that formaldehyde, which is one of the best bridge forming compounds, can produce crease-resisting cellulosic material, although at some

cost to the strength, extension and durability of the product. It also appears that filaments from alginates of polyvalent metals, too, possess some degree of resistance to creasing. Resistance to creasing may be defined as three-dimensional elasticity.

June, 1912 ; see also Naturwiss., April, 1922), which established recognition of the fact that a crystal behaves as a three-dimensional diffraction grating to X-radiation and this indicated a regularity of interatomic distances and, therefore, a regularity of internal structure.

The method of analysis of colloids developed by Debye and Scherrer (Phys. Zeitschr., 1916, *17*, 277) was applied by the latter (Goettinger Nachrichten, 1918, page 98) to cellulose and starch. In the previous year, however, Ambronn (Kolloid Zeit., 1916, *18*, 273) predicted that if cellulose was a crystalline material as shown by double refraction, it should, when exposed to monochromatic X-rays, give the spectrum characteristics of crystalline substances. Although Ambronn was not himself in a position to make the necessary experiments he supplied the ramie fibre preparation. Scherrer's first report was that cellulose gave an amorphous pattern, but the work was repeated and a definite crystalline pattern obtained from which it was concluded that the micelles must be parallel to the fibre axis. About the same time Hull (Physic. Review, 1917, *10*, 661) obtained independently his first X-ray diagrams of cellulose fibres. The method followed in these experiments of either Debye-Scherrer or Hull was to press the material into the form of a small rod, which was then surrounded by a film on which the effect of the X-radiation was then observed.

In the meantime Herzog and Jancke at the Kaiser-Wilhelm Institut fur Faserstoffchemie, considering that Scherrer's first reports on the amorphous nature of cellulose were not correct, commenced a long and important series of investigations. Their first paper was published in 1920 (Z. Physik., 1920, *3*, 196) and showed that cellulose has a definite crystalline structure which is the same regardless of the material from which it comes. In a later paper (Ber., 1920, *53B*, 2162) they stated that if a parallel bundle of ramie fibres was used instead of a powder, then a fibre pattern was obtained resembling that for a cold drawn wire. Rayon fibres gave a similar pattern to that for natural cellulose, but differed in that the parallel fibres gave concentric circles. Herzog (Cellulosechemie, 1921, *2*, 101) contributed further data and suggested that the $C_6H_{10}O_5$ groups must be repeated regularly in cellulose. Three possible types of structure were propounded, (*a*) internal anhydrides, (*b*) closed rings of glucose residues linked by oxygen bonds and (*c*) open chains of glucose residues linked together in groups of four in series by oxygen bonds.

Polanyi (Naturwiss., 1921, *9*, 288) made the first observations on the size of the unit cell, i.e. the smallest unit which still possesses the geometrical properties of the whole crystal lattice. He assumed that the lattice on which the cellulose crystal is built was of the rhombic-quadratic system and the dimensions were

a = 8·65–8·75 Å Horizontal.
b = 10·25–10·35 Å The vertical period along the fibre axis.
c = 7·8 –7·9 Å Forming an angle with "*a*."
The Angström unit Å is 10^{-8} cm.

From these dimensions the volume of the unit cell was calculated, and from the volume and mass of the anhydroglucose unit together with the density of cellulose it was found that four glucose residues could be accommodated in the unit cell. The insistence on the figure four is of interest, for at this time the prevalent idea was that cellulose may be represented by an association of monomeric glucose or cellobiose anhydrides. It was, therefore, assumed that the cellulose molecule and the unit cell were identical. The fact that the same values were found for celluloses of different origins supported the hypothesis of chemical identity which had been drawn from chemical evidence many years previously.

Herzog (Papierfabr., 1923, *21*, 388), in reviewing some of his previous work, also brought forward the important idea that the crystals in rayon lie in all possible directions, and that the tensile strength and swelling properties of cellulose fibres depend on the crystal arrangement. As the effect of mercerisation is slightly to increase the lattice constant but not the density, Herzog (Naturwiss., 1924, *12*, 955) offered the opinion that there must be a rearrangement in the cellulose without an increase in molecular size. One of the most important of Herzog's contributions at this time was that in which he showed that in the molecule $(C_6H_{10}O_5)n$, the value of "n" may be very large or that it may be 1, 2 or 4—the values 3 and 5 were definitely excluded. (Cellulosechem., 1925, *6*, 39.)

Swelling

The application of the X-ray technique to the phenomena of swelling by Katz (Z. Physik., 1924, *25*, 659) brought forward the important view that the spacings obtained are smaller than the distance between the centres of the molecules themselves, probably on account of the atomic groupings in the

molecule ; hence it was doubtful whether the swelling processes could be followed by means of X-rays since the liquid enters between the molecules themselves instead of penetrating them. Another valuable contribution from Katz (Cellulosechem., 1925, *6*, 37) suggested that the cellulose molecule may be larger than the units indicated by the X-ray data. The residual valency of these elementary cells may determine the degree of association of the cellulose particles and the strength with which they are bound together. The enlargement of the cellulose lattice as the result of treatment with various swelling agents of mercerising concentrations was observed by Katz and Mark (Z. Elektrochem., 1925, *31*, 105) ; Katz and Viewig (*ibid.*, 157) and Katz (Cellulosechem., 1925, *6*, 35).

A summary of Katz' views is outlined (Trans. Farad. Soc., 1933, *29*, 279), in which he states that the question at issue is to determine whether the liquid penetrates into the interior of the micelles or is only adsorbed at the surface. The problem was examined (Physik. Z., 1924, *25*, 351—see also Katz' section in " Die Chemie der Zellulose und ihrer Begleiter " by Hess) by means of X-ray spectrography.

If the X-ray diagram is different after swelling then it can reasonably be assumed that the liquid is taken up into the interior of the micelle, but if the liquid is only absorbed at the micelle surface then there should be no change in the diagram. An unchanged diagram, however, does not necessarily imply that the liquid does not penetrate into the interior of the micelle, for if only one or two layers of molecules are affected then the diagram would not be changed. It is also possible that the intermicellar substance (see page 104) might be changed without influencing the X-ray diagram.

The various types of swelling may, therefore, be classified.

(*a*) Where the diagram is changed the dimensions of the elementary cell of the crystals may be enlarged continuously with the swelling. This is termed intra-micellar swelling. When the change in dimensions of the cell is so large as to explain the change in the swelling body then the intra-micellar swelling has much the same character as a solid solution of water in the solid (cf. gelatine).

(*b*) The diagram may also be changed in a manner which is not a continuous function of the swelling, i.e. a new diagram is formed whilst the old changes in intensity. In this case it is assumed that the liquid forms a chemical compound with the solid. The swelling is not explained by the change of

X-ray diagram but by the adsorption of liquid on the surface of the cells.

The change of crystal structure is a phenomenon accessory to the mechanism of swelling. In this case the term permutoid swelling is used—examples of which occur in the swelling of cellulose nitrate in its solvents. It is often found that the number of crystals changed in the inner structure changes with the concentration of the swelling agent ; the system reaches an equilibrium and the force governing this equilibrium may be given by the arrangement and interaction of the micelles. This may explain the fact that when cellulose swells in solutions of sodium hydroxide, the amount of cellulose converted to soda-cellulose is greater the more concentrated the solution of sodium hydroxide. It may also be assumed that this force is different in strength for each set of micelles in the cellulose fibre.

(*c*) Where the X-ray diagram is not changed, it may be concluded that there is no change in the interior of the micelle, but only at the surface where the layers of liquid are absorbed according to the laws of surface adsorption. This is termed inter-micellar swelling.

If the cellulose structure is inexactly co-ordinated there may be no sharp distinction between in tra-and inter-micellar swelling.

Katz also points out that when cellulose is precipitated from solution a swelling substance is formed which has strong cohesion between the micelles and when dried it is impossible to pulverise it. This is in sharp distinction to the case say $BaSO_4$, and may be due to the long form of the micelle or to the existence of a binding substance. The latter recalls the membrane theory of Hess (see page 87), for which there is insufficient support. It is an exaggeration to assume that no swelling is possible without a binding agent, and even if the theory explains the swelling of native fibres, it would not imply that the pure precipitated swelling substance should also contain these membranes. Such a condition is not impossible, but there is inadequate supporting evidence.

Sponsler and Dore

The general advance in the technique of X-ray analysis due to the work of W. H. and W. L. Bragg (X-rays and Crystal Structure, London, 1912, see The Crystalline State, London, 1933) led to a great deal of knowledge concerning the structures of not only inorganic compounds but also organic substances.

In the case of the diamond, the carbon atoms were found to be 1·54 Å apart and the distance between lines joining opposite pairs of atoms was 2·51 Å ; in graphite the carbon atoms were closer together (1·42 Å).

Examination of naphthalene and anthracene showed the carbon-carbon distance to be 1·42 Å in the ring and the distance between a carbon in the ring and in the methine group was 1·54 Å. The diameter of the oxygen atom is nearly the same as that of carbon and in the grouping –C O the value is given as 1·35 Å.

Data of this type allowed the construction of models which could be used to demonstrate properties of compounds which were rather obscure unless a three dimensional picture was available ; this also enabled the correct tetrahedral angle of 109° 28′ to replace the angle of 120° as used in the flat projections of hexagonal rings.

For several years Sponsler had been collecting data on the structure of cellulose, and in 1926 two papers of great importance were published. In the first of these Sponsler (J. Gen. Physiol., 1926, *9*, 677) put forward the opinion that the cellulose building unit consisted of parallel chains running in the length of the fibre. The chains were stated to be 6·10 × 5·40 Å apart, thus giving two $C_6H_{10}O_5$ units within the 10·25 dimension and four $C_6H_{10}O_5$ units within the unit cell 6·10 × 5·40 × 10·25 Å. The view was also advanced that the chains are arranged in concentric cylinders or layers in the cell walls. This was the first insistence on the differentiation between the cellulose molecule and the unit cell recognising that the latter was only part of the former. Emphasis must also be placed on the equally important conception that the cellulose units were arranged in long chains. A longer paper was presented by Sponsler and Dore (Fourth National Symposium on Colloid Chemistry Monograph, 1926, Massachusetts Institute of Technology) in which use was made not only of X-ray data on cellulose but also of the work of Bragg and his collaborators on atomic radii and interatomic distances and the chemical evidence on the constitution of cellulose and the sugars. Models were constructed and compared with the X-ray diagram for ramie fibres. The structure for glucose was selected for arrangement within the unit cell on a three dimensional model carefully made to a scale based on the atomic radii of carbon and oxygen and the distances between carbon-carbon and carbon-oxygen as published by W. H. Bragg. It was found

that the ring structure recently advanced by Haworth for glucose best fitted into the lattice spacing from X-ray data, but for reasons of symmetry the beta-structure was preferred to the alpha-structure.

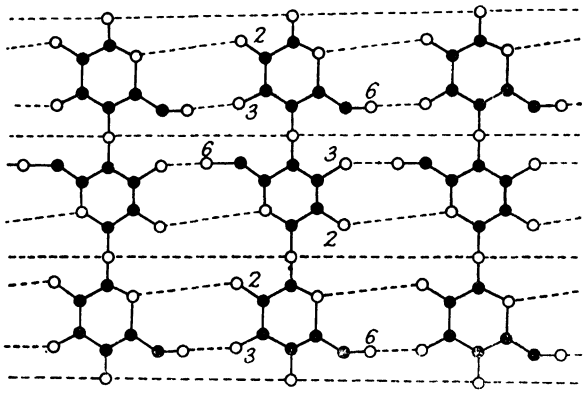


FIG. 46.—Tangential section of Ramie, according to Sponsler and Dore.

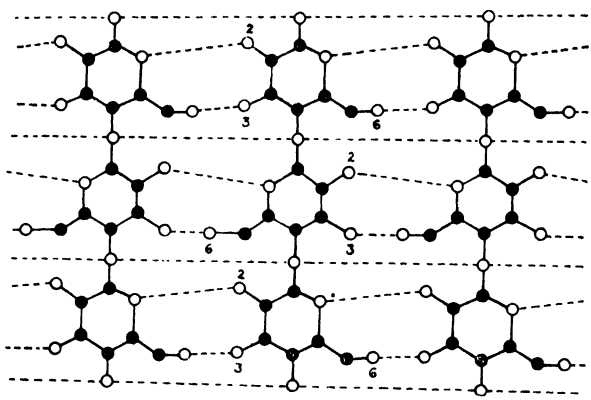


FIG. 46A.—Corrected version of Fig. 46 (in accordance with chemical requirements).

As previously mentioned Sponsler and Dore did not think that the exclusive 1 : 4 linkage of cellobiose was in agreement with their X-ray data and adopted the system of alternating 1 : 1 ; 4 : 4 linkages. The most important result was the recognition of the fact that the repeat period of 10·25 Å along the fibre axis was dependent on the glucose unit of Haworth, which

was calculated to have a diameter of 5·13 Å, i.e. one half of the repeat period. This suggested that the constituent units are arranged in continuous chains which are arranged parallel to the fibre axis and run through the unit cell which contains a certain number of them in parallel formation according to the dimensions of the unit cell. A quadratic cell would accommodate eight glucose residues. The cellulose units were bound longitudinally by primary valency forces and laterally by secondary valencies. The primary valencies would account for the chemical and mechanical stability of cellulose as they must be broken before the great tensile strength of the fibre would suffer. The secondary valencies, however, are easier to rupture, thus explaining the fact that fibres possess relatively low strength in the direction perpendicular to the fibre length.

This structure also accounted for the difference in thermal expansion in the two directions of the fibre, that in the lateral direction being much greater than in the length, on the basis that there is more freedom of molecular movement laterally. Katz' interpretation of the phenomenon of swelling is also in agreement with this structure which allows swelling by liquids which do not attack the cellulose molecule but which may enter between the chains, and thus widen the space between them. The chemical reactions of cellulose are also in agreement with this picture of its structure, for esterification and etherification are possible without loss of fibre form if the assumption is made that the new groups will accommodate themselves in the spaces between the chains. The breakdown of the fibre structure under more vigorous chemical treatment would begin with the separation of the chains from one another, i.e. the breaking of the secondary valencies before attack on the actual chain length or primary valencies as in hydrolysis.

Meyer and Mark

Haworth's criticisms of this structure have been dealt with on page 58. The subsequent work of Meyer and Mark (Ber., 1928, *61B*, 593) showed that a model could be produced which was in strict agreement both with the chemical considerations involved and the X-ray data. The unit cell dimensions used to accommodate the glucose residues were those established by Polanyi in 1921. The length of cellobiose on the Haworth model was 10·3 Å, that is the length of the repeat along the fibre axis, but crystallographic considerations showed that a diagonal screw axis runs along the fibre axis and X-ray evidence

showed that the screw component equals half of the repeat pattern in this direction, i.e. 5·12 Å. The lower part of Haworth's cellobiose formula also shows this arrangement.

In an actual model it is possible to turn the lower half through 180° and move it upwards when it will exactly cover the upper half of the formula. The structural arrangements will, therefore, allow for the cellobiose or 1 : 4 linkage throughout in agreement with the chemical evidence.

The model of Meyer and Mark was that of a unit crystal cell having the dimensions $a = 8{\cdot}7$ Å, $b = 10{\cdot}3$ Å and $c = 7{\cdot}8$ Å, with "b" as the edge of the cell parallel to the fibre axis.

The usual diffraction pattern enables small periodicities and simpler constitution to be directly measured on account of the spiral character of the long molecules. One turn in the screw axis is sufficient for a diffraction periodicity, since all the other turns are exactly the same. Hence, within the unit cell, only a small number of molecules are found instead of one or more of the actual long macromolecules.

The unit cell accommodates four glucose residues, but these are not separate as in a molecular crystal but joined together in the direction of the fibre axis—"b"—so as to form long chain molecules held together by ordinary molecular forces.

The linkage of the glucose residues is 1 : 4 as on the Haworth model. The carbon-carbon distance is 1·5 Å and the carbon-oxygen distance is 1·2 Å, whilst the length of the two joined rings is 10·3 Å. The cellobiose residues are thus joined by an oxygen bridge from unit cell to unit cell, the axis of the chain thus formed being the fibre axis. This structure also is not essentially affected by mercerisation or the formation of cellulose derivatives, which only change the cell size as the substituent groups attach themselves to the sides of the chains without necessarily breaking them. Hence cellulose is not composed of molecules in the usual sense but particles or micelles made up of cellobiose chains arranged in parallel formation and held together by secondary valencies. The chains are not necessarily all of the same length, and from the breadth of the X-ray interference lines and diffusion coefficients Meyer and Mark estimated that there are about 1500–2000 glucose residues per micelle corresponding to 40 to 60 chains each having 30 to 50 glucose residues. No definite conclusions were reached concerning the form of the crystallite, but it was shown that they are easily orientated and must be rectangular. Many of the features of Meyer and Mark's cellulose structure

are similar to those advanced by Sponsler and Dore, particularly the main conception of long chains of glucose residues united by primary valencies. The new view of the micellar structure according to Meyer and Mark was capable of explaining many physical and chemical properties such as viscosity and other properties of cellulose in solution.

It is important to realise that this crystal unit must not be confused with the chemical entity—cellulose, or with the micelle. The crystal unit is merely the pattern which repeats itself in all directions and the long chains run through it along the "*b*" axis.

The suggestions of Meyer and Mark were later supported by the work of Andress (Zeitschr. phys. Chem., 1929, page 380), Astbury (Nature, 1931, *127*, 12) and Hengstenberg (Zeitschr. Kryst., 1928, *69*, 118).

Attention was then turned to the study of the size and position of the micelle or crystallite in the various fibres. Hengstenberg and Mark (Zeitschr. Kryst., 1928, *69*, 271) showed that in the ramie fibre the micelle is present as a rhombus measuring 500 to 600 Å along the fibre axis and 50 by 55 Å across the axis. From photographs taken at the temperature of liquid air it was found that the coefficient of expansion for the direction parallel to the fibre axis is considerably smaller than at right angles to the axis. The estimate of micelle size was in good agreement with that previously advanced by Herzog (J. Phys. Chem., 1926, *30*, 457) and was verified by Clark (Ind. Eng. Chem., 1930, *22*, 474) by the use of X-rays of relatively long wave lengths.

The model shown on page 110 was put forward by Meyer and Mark (Z. phys. Chem., 1929, *B2*, 115) after reviewing all the evidence. The dimensions are $a = 8{\cdot}35$ Å, $b = 10{\cdot}3$ Å, and $c = 7{\cdot}9$ Å. It may be regarded now as generally accepted, subject to Meyer's revision (page 115).

The model shows the planes of the ring lying mainly in the *ab* and parallel planes. The strong reflection from this set of planes is an important guide to the actual model and the distance of 3·95 Å from plane to plane is in agreement with the work of W. H. and W. L. Bragg on other compounds, e.g. the closest approach of carbon atoms in different molecules in the diamond is 3·5 Å, the layers of graphite are 3·41 Å apart and in naphthalene and the fatty acids the distance is about 3·5 Å.

A further opinion of Mark (J.S.D.C., 1932, *49*, 54) on the

micelle and the model of the unit cell was that the former consisted of 40 or 50 main valency chains held together by secondary valencies, each chain containing 100–200 glucose residues.

Meyer and Mark (Z. physik. Chem., 1929, *B2*, 695) in considering the reactions to which the new structure would lead classified them in two types: micellary surface reactions in which the reagent penetrates between the micelles without attacking the internal structure, and molecular or permutoid

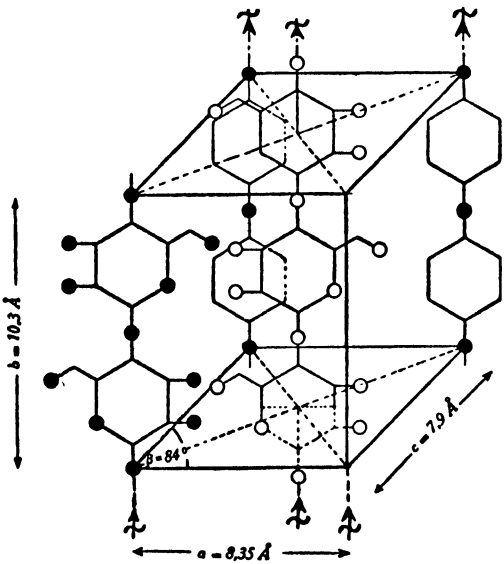


FIG. 47.—The cellulose crystal unit of Mark and Meyer.

reactions in which the reagent penetrates the entire structure and attacks specific groups at various points of the lattice.

An examination of Valonia ventricosa by Sponsler (Nature, 1930, *125*, 633) proved to be an important contribution to the knowledge of the manner in which the chains are arranged in the cell wall, for in this case the cellulose is deposited in relatively large sheets instead of small cylinders. The material gives a clear separation of some of the important reflections which are close together in the diagram of the ordinary fibre so that the unit cell of cellulose could be described with some certainty.

Sponsler and Mark had arrived at different dimensions for the cell as shown below:

	a	*b*	*c*
Sponsler .	10·7	12·2	10·3
Mark . .	8·35	10·3	7·9

Bragg (Nature, 1930, *125*, 634) commented on the importance of Sponsler's paper and was able to show the correlation between the two sets of dimensions for Mark and his co-workers had deduced a monoclinic structure, whereas Sponsler and Dore assumed an orthorhombic cell—there is very little difference between the two.

The unit cells are closely related and are merely differently orientated in the lattice.

Now as the result of the probable structure of the cellulose in the cell wall, the plane of the glucose units lies at an angle of some 45° to the wall surface, which is, therefore, studded with the hydroxyl groups. The influence of this reactive surface on the cell activity was discussed by Sponsler (Trans. Farad. Soc., 1930, *26*, 813).

Micellar Arrangement

Mark (Physik und Chemie der Cellulose, Springer, Berlin, 1932) pointed out that the primary valency structure does not exist in an ideal state in native cellulose, but is occasionally interrupted by disturbances of the lattice, which may be accidental or may be due to conditions of growth. Herzog (Naturwiss., 1921, *9*, 320) had pointed out that in ramie and other fibres the micelles are orientated parallel to the fibre axis, whilst in cotton they are turned spirally round the axis, but that in rayons and films of regenerated cellulose this orientation is missing; it may, however, be produced to some extent by stretching. In wood pulp fibres the direction varies from an arrangement which is almost parallel to the fibre axis in the inner part of the fibre to a direction which is almost at right angles to it on the surface. These views were confirmed by the work of Clark and Farr (Contrib. Boyce Thompson Inst., 1932, *4*, 273) and by Steinberger (Textile Research, 1934, *4*, 495 and 531) in his researches into the plastic and elastic properties of textile fibres.

Atsuki and Ishiwara (J.S.C.I., Japan, 1933, *36*, 517) examined hemp, cotton and rayon fibres and suggested that in hemp the crystal axes are parallel to the fibre axis, whilst in cotton they

are arranged around and inclined to the fibre axis. In viscose rayon part of the crystals are parallel to the fibre axis but others have an irregular arrangement. A further investigation of the minute structure of cotton (J.S.C.I., Japan, 1933, *36*, 221B) by means of X-ray and microscopic analysis showed that the fibrils were wound spirally in the direction of the fibre axis with the main axes of the micelles parallel to the axis of the fibril.

The high degree of orientation in the ramie fibre was the reason for its almost exclusive use in most of the X-ray examination of cellulose, particularly in the early days.

A comparison between the micellar size of native cellulose and viscose rayon by Hengstenberg and Mark (Z. Krist., 1928, *69*, 271) resulted in the following data :

SIZE OF MICELLE.

	Perpendicular to fibre axis.	Parallel to fibre axis.
Ramie . .	55 Å	600 Å
Viscose rayon .	41 Å	305 Å

This decrease in micellar size supports the view that the cellulose chains have been broken in the processes of manufacturing rayon. It is also in agreement with the lower tensile strength of rayon, particularly in the wet state. The tensile strength properties of cellulose may be attributed to the force necessary to cause the micelles to glide over each other, and the fibre thus breaks with a reduced diameter and a jagged edge.

When the micelles are reduced in size and orientated at random the tensile strength must fall, and in the case of random orientation there is a better and more rapid penetration by water, which is absorbed on the hydroxyl studded surface of the micelles and so covers the active hydroxyl groups which normally provide the forces holding the micelles together. The structure swells, and as the tertiary forces are inoperative for purposes of mechanical strength on a smaller area than in native cellulose the tensile strength in the wet state is very poor.

Morey (Textile Research, 1934, *4*, 491) produced important contributions on the micellar orientation and spiral structure of fibres by means of measurements of the polarisation of the fluorescence from fibres dyed with strongly fluorescent dyes and found that the highest orientation occurred in the flax

CELLIBIOSE.

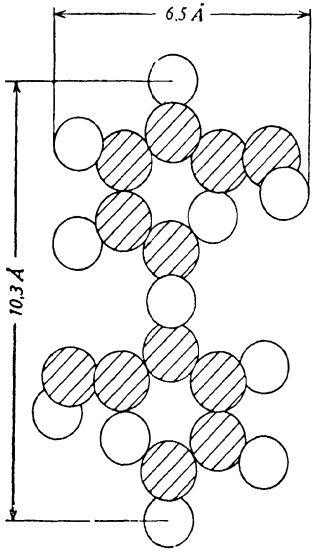


FIG. 48.—Meyer and Mark

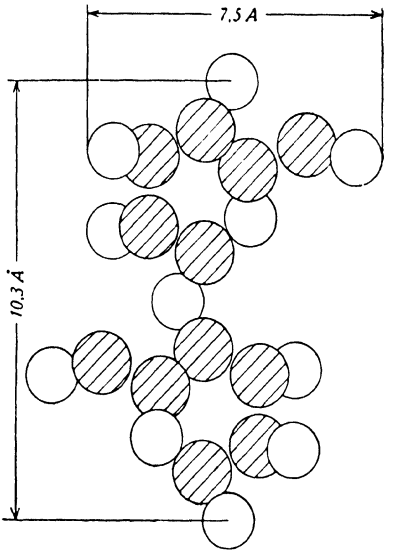


FIG. 49.—Andress

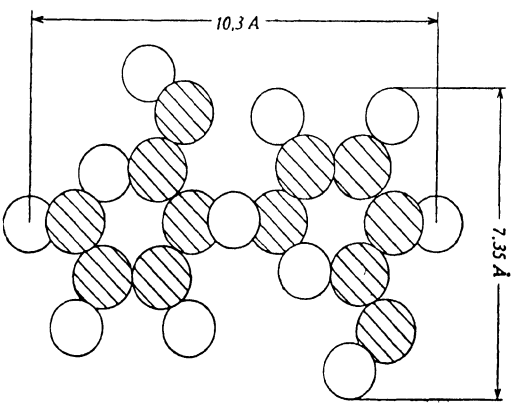


FIG. 50.—Meyer

Meyer Helv. Chim. Acta.

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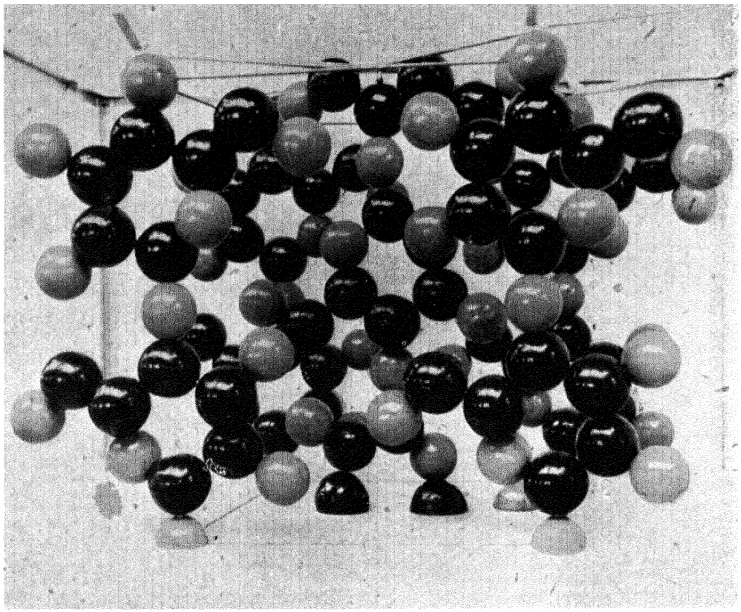


FIG. 51.

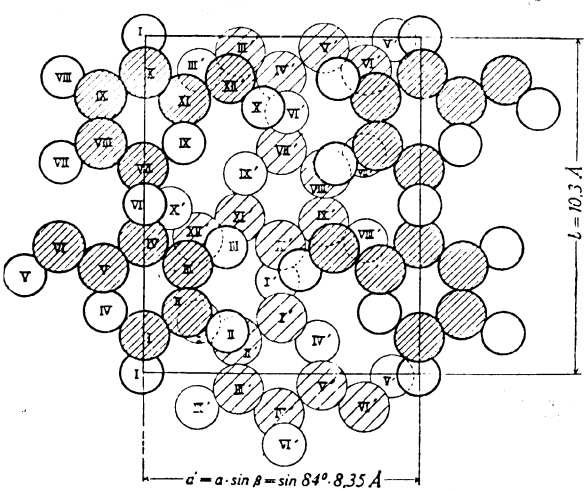


FIG. 52.

Meyer's Model of Cellulose.

Model by courtesy of Kurt Meyer. *Diagram from Helv. Chim. Acta.*

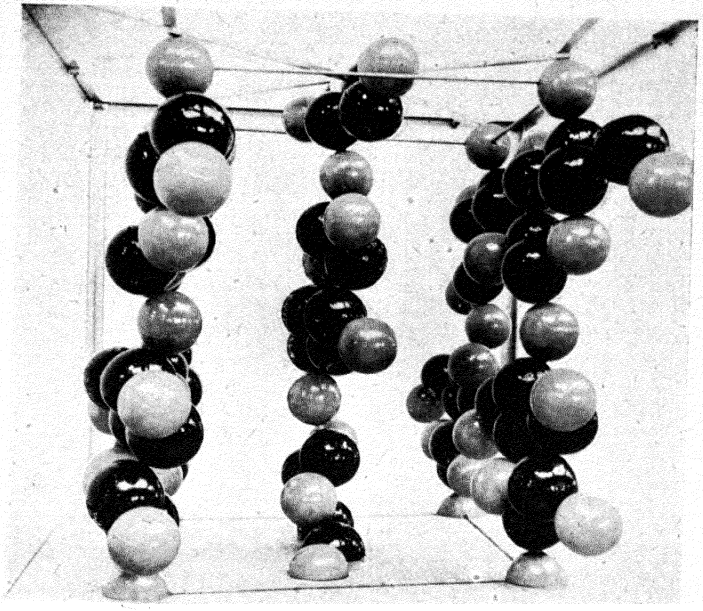


FIG. 53.

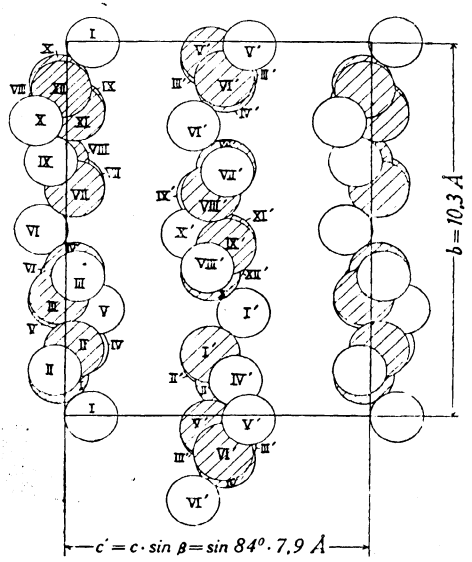


FIG. 54.

Meyer's Model of Cellulose.

Model by courtesy of Kurt Meyer. *Diagram from Helv. Chim. Acta.*

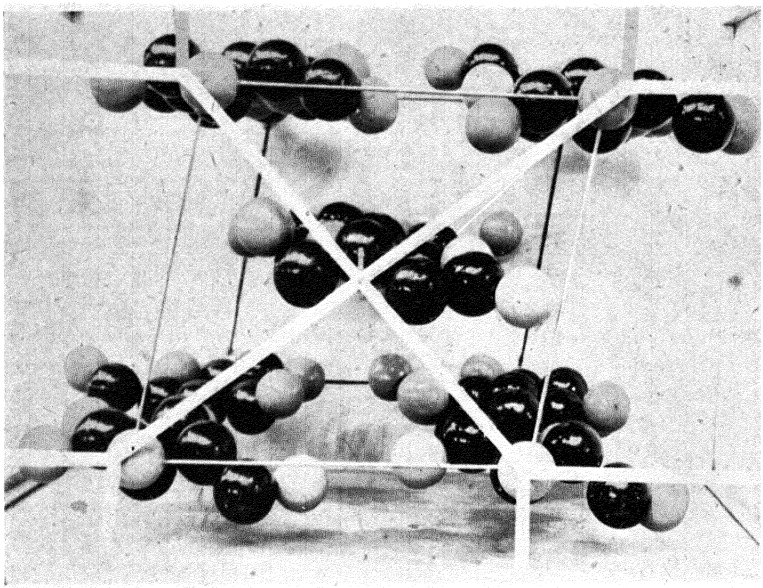


FIG. 55.

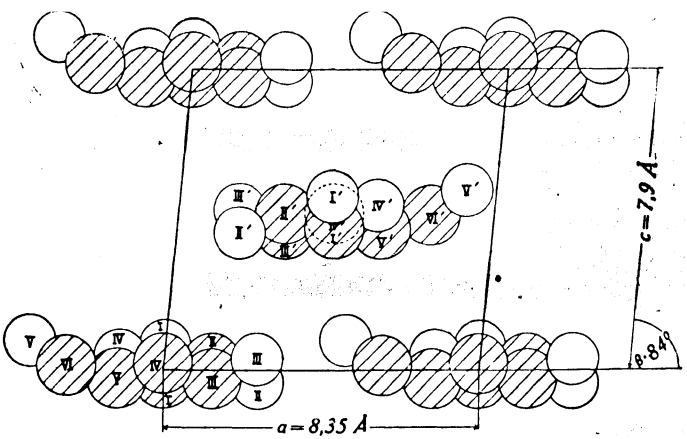


FIG. 56.

Meyer's Model of Cellulose.

Model by courtesy of Kurt Meyer. *Diagram from Helv. Chim. Acta.*

[*To face page* 113.

fibre, whereas, hitherto, it was thought that ramie was the best orientated cellulose fibre. The method also showed the degree of spiral arrangement in the fibres to be higher in flax than in ramie. The orientation of fibres by stretching has been examined by Herzog and Gonell (Kolloid Z., 1924, *35*, 201), Herzog and Jancke (Zeitschr. Phys., 1929, *52*, 755), Susich (Zeitschr. phys. Chem., 1929, *4*, 431) and Sponsler (Nature, 1930, *125*, 633) and described by Mark in his book (Physik und Chemie der Cellulose). The work was mainly concerned with artificial fibres and films as a means of confirming the X-ray data found for native fibres and for examining the relation between orientation of the micelles and the physical properties of the fibres. By stretching a viscose fibre in the swollen state a high degree of orientation may be obtained accompanied by a three- or four-fold increase in tensile strength but the extensibility decreases accordingly to about one-fifth of the original value. The tensile strength of the fibre perpendicular to the axis is also decreased; although it cannot be demonstrated on fibres, yet measurements may be made on stretched films. Mark (J.S.D.C., 1932, *48*, 51) showed that there is also a definite connection between the orientation of the micelles and the tendency of the fibre to crease. Natural silk has a core of orientated micelles and an outer shell in which the micelles are distributed at random. When, however, a silk worm was caused to spin faster by means of a rotating glass rod, threads were produced of greater orientation in the outer layers and these showed similar creasing properties to the artificial fibres. The dyeing properties also suffered. The stretched rayon thread, in contrast to natural silk, is strongly orientated on the surface but less orientated towards the centre, but by precipitating cellulose on to a highly orientated thin filament good resistance to creasing may be obtained because the surface is not highly orientated and, therefore, possesses elasticity. (See also page 98.)

Preston (Trans. Farad. Soc., 1933, *29*, 65) has brought forward some interesting evidence to show that the refractive indices of celluloses are quantitatively related to the orientation of the micelles.

An interesting observation on the velocity of acetylation has been recorded by Elöd and Schmid-Bielenberg (Zeitschr. phys. Chem., 1934, *B25*, 27), who found that in the case of dry fibres the velocity increased in the order of decreasing orientation of the structural units, i.e. flax, hemp, ramie and cotton.

Mark (Textilber., 1929, *10*, 695) has made some calculations of great interest which are based on the cellulose model. The tensile strength of various materials is given as follows:

STRENGTH OF MATERIALS.

	Kg./sq. mm.
Cast iron	20
Steel	170
Copper	40
Wood (in fibre direction)	8–15
Silk	35
Cotton	28
Flax	100
Viscose	25
Cellulose acetate	18–20
Orientated viscose	80
Orientated acetate	60

Hence cellulose in the form of the highest orientated natural fibre has a strength comparable to steel. The calculations were made on the assumption that the fibre is made up of endlessly long chains of glucose residues so that the tensile strength represents the work done in breaking the primary valency bonds. The work required to break C — C and other bonds in organic compounds is known, so that a value of 800 Kg./sq. mm. could be calculated. This is much too high as compared with actual values, but as it was known that the chains are not endlessly long but only contain about 100 glucose residues, it follows that part of the break is due to slipping of the micelles and chains. The secondary valency forces due to hydroxyl and other groups are fairly accurately known in organic compounds and calculations of about 200 kg./sq. mm. were made for the textile fibre.

A further calculation may be utilised from the known value of breaking strength for a sugar crystal, together with a correction for the difference in cross section due to the jagged surface of the fibre compared with the plane surface of the crystal; this calculation results in a value of 180 kg./sq. mm., which represents the ideal state of orientation which is never actually realised in fibres.

Meyer's Model

The cellulose model of Mark and Meyer has recently been revised by Meyer and Misch (Ber., 1937, *70*, 266; Helv. Chim.

Acta, 1937, *20*, 232). The main hypothesis was that there is no good ground for assuming that all the chains should lie in the same direction in regenerated cellulose and, therefore, in the mercerised native fibres which give the same diagram as the regenerated celluloses. Indeed work on chitin, a somewhat analagous compound, has shown that the chains alternate in the direction of their orientation (Helv. Chim. Acta, 1935, *18*, 589). In a solution of cellulose, the crystalline network is destroyed so that subsequent coagulation of the cellulose

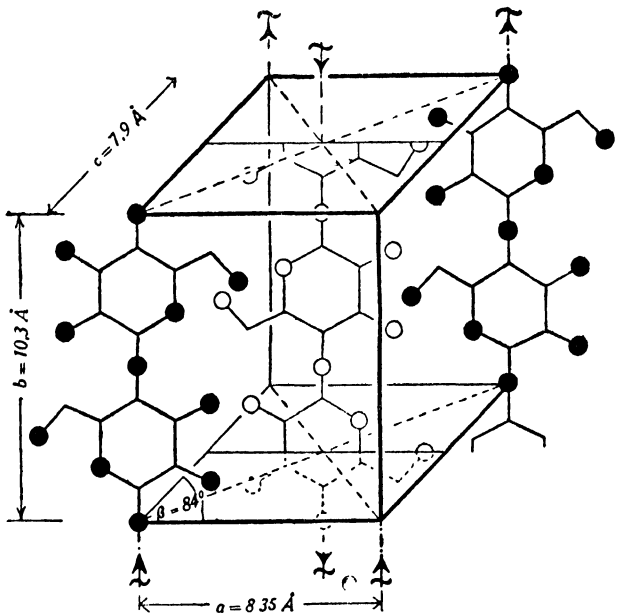


FIG. 57.—The revised crystal unit of cellulose. (Meyer.)

should produce chains lying in all directions and the stretching of the filament in " spinning " should produce the same number of chains orientated in each direction. The original model of Meyer and Mark was based on the X-ray data of Polanyi and it was later (1929) studied by Andress, who gave certain interatomic distances which do not satisfy the state of knowledge of nine years later.

Meyer, therefore, reinvestigated the structure of the unit cell by means of the X-ray technique, on the basis of alternating orientation of chains. It was found that the calculated intensities required by the new model were in good agreement

with the observations. Both fibre diagrams and powder diagrams were used and considerable support obtained for the new spacial model. With a system of chains forming networks with alternating orientation, it was found that the distance from oxygen atom 5 of the chain was 2·6 Å to that of oxygen atom 3 of the neighbouring chain—a figure in perfect agreement with the work of Bernal (Proc. Roy. Soc., 1936, *151*, 384) on other compounds containing hydroxyl groups.

The same reasoning was applied to the case of native cellulose, for it is not likely that the mercerising process would cause the inversion of a set of chains.

The new model is based on the following data :

(*a*) the first element of structure is the cellobiose chain in which the principal valency distances are C : C = 1·54 Å ± 0·01 Å and C : O = 1·45 Å ± 0·03 Å.

(*b*) In the direction of the " *a* " axis, these chains are associated by " hydrogen bonds " between the hydroxyl groups to form a network parallel to the plane " *ab* " and consisting of identical chains. The distances between the hydroxyl groups of the two chains is 2·6 Å, which is much smaller than the 3·0 Å found for many crystal structures where only van der Waal's forces operate.

(*c*) The nets are united into a spacial system by secondary valency forces, but the orientation of the networks in the direction of the " *b* " axis of neighbouring networks is always in opposite directions. The smallest distance between the networks is found between 0/5 of the first net and C′/1 and C′/10 of the second net ; it is 3·1 Å. The smallest distance between two hydroxyl groups 0/5 and 0′/1 is 3.8 Å. The carbon atoms are at greater distances than 3·5 Å in the spacial model. The carbon valency angle lies at the correct tetrahedric angle of 109° 40′.

The cellulose lattice, therefore, comprises a chain-lattice and a layer-lattice ; the strongest forces act along the *b* axis, but those along the *a* axis are comparatively strong. Main-valency chains hold the structure together along the *b* axis and hydrogen bond nets in the *ab* plane. Normal to this plane there are weaker forces and greater spacings (see Figs. 54 and 56) which permit penetration of reagents into the lattice where they may react with the hydroxyl groups. This lattice system also explains the observations of orientation by purely mechanical means.

In connection with the revised model by Meyer, it is interest-

ing to recall that Haworth (Helv. Chim. Acta, 1928, *11*, 534) has given an illustration of two parallel chain molecules lying in opposite directions.

Mercerising

The X-ray examination of the effect of mercerising has been recorded by numerous workers and the following results are typical:

CHANGES ON MERCERISING.

	Native cotton.	Mercerised cotton.	
a .	8·35 Å	8·1 Å	
b .	10·3 Å	10·3 Å	Andress
c .	7·9 Å	9·1 Å	(Z. physik. Chem.
β .	84°	62°	1929, *B4*, 190).

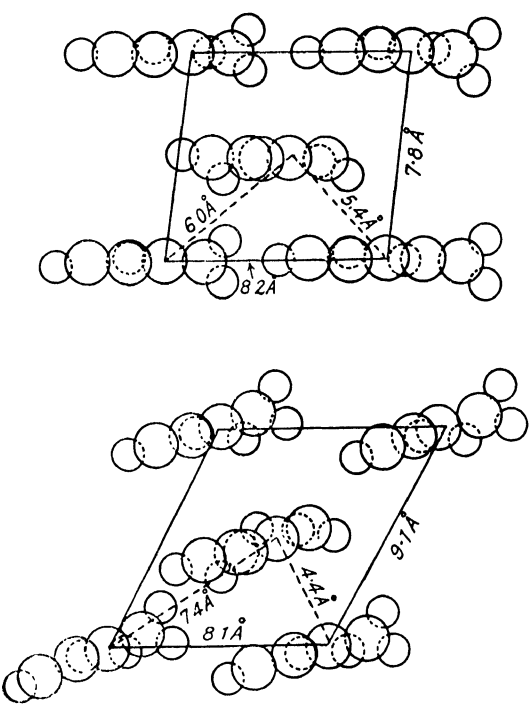


FIG. 58.—Comparison of unmercerised and mercerised cellulose.

The longitudinal period (*b*) is unchanged, and the first transverse period (*a*) is almost unchanged but the other transverse period (*c*) is much larger. The long chain of glucose residues remains unbroken, but the planes of the molecular chains have been moved apart. This is in accordance with the modern view of dispersed cellulose and agrees with the increased moisture content and affinity for dyestuffs in the case of mercerised cellulose; the fact that the hydroxyl groups are thus more accessible is in agreement with observed increased reactivity to chemical reagents.

Sisson (J. Phys. Chem., 1936, *40*, 343) in commenting on the work of Andress (loc. cit.) pointed out that some of the planes of the mercerised lattice have about 25% more available hydroxyl groups per unit of surface than in the case of unmercerised cellulose and this may partly account for the greater absorption and reactivity.

The lattice of mercerised cellulose is regarded by Herzog and Jancke (Z. physik. Chem., 1928, *A139*, 235) as the more stable arrangement on the grounds that it is the form which is assumed by cellulose not only after swelling but also after regeneration from solution or from a derivative which has been highly swollen or dissolved during its preparation.

Whilst Katz (Physikal Z., 1924, *25*, 321) showed that the X-ray diagram of cellulose is not altered by swelling with water, and therefore concluded that the water does not penetrate into the micelles but merely goes between them, he also produced instances of swelling in which the X-ray picture showed an expansion of the lattice with increased swelling, and in such cases he assumed (Trans. Farad. Soc., 1933, *29*, 279) that the swelling agent penetrates into the interior of the micelle. A full account of his views is given in the "Micellartheorie und Quellung der Zellulose" in Hess' book, "Die Chemie der Zellulose und ihrer Begleiter" (Leipzig, 1928).

Derivatives

The X-ray examination of a number of chemical reactions of cellulose has brought forward a certain kind of evidence for the existence of compounds about which there was only theoretical support from the standpoint of the organic chemist.

Trogus and Hess (Z. physik. Chem., 1929, *B4*, 321) examined the product resulting from the treatment of cellulose with cuprammonium hydrate and reported that fibre diagrams for

two compounds were obtained, but on washing with water the diagram of mercerised cellulose was found.

The question of the possible formation of a compound between cellulose and sodium hydroxide has also received attention. Mark and Susich (Naturwiss., 1929, *17*, 803), who used very intense X-rays, reported that two intermediate compounds are formed in the course of five minutes mercerisation. Further work by Hess and Trogus (Z. physik. Chem., 1931, *B12*, 381) showed that two new fibre diagrams are obtained by treating cellulose with aqueous solutions of sodium hydroxide. Sodium cellulose I was formed in solutions containing up to 19% NaOH, whilst sodium cellulose II resulted from treatment with solutions containing over 21% NaOH. The action of potassium and lithium hydroxides was also investigated. Katz and Dirksen (Rec. Trav. Chim., 1931, *50*, 736 ; 746 ; 149) carried out an X-ray analysis of cellulose fibres swollen with lithium thiocyanate solutions, from which they concluded that for dilute solutions the salt is adsorbed on the surface of the micelle, whilst for higher concentrations addition products are formed. A quantitative relation between the X-ray diagram and the degree of mercerisation was pointed out by Schramek and Schubert (Z. physik. Chem., 1931, *B13*, 462), who also suggested the use of X-rays as a measure for the degree of mercerisation. (See also the chapter on Soda Cellulose.)

Hess and his co-workers showed that X-rays may be used to follow the methylation of soda-cellulose which consists of two simultaneous reactions (Annalen, 1933, *506*, 260). The same investigators showed (Z. physik. Chem., 1931, *B14*, 387) that hydrazine, ethylenediamine, and tetramethylenediamine form addition compounds with cellulose and these are decomposed on treatment with water.

The existence of addition compounds between cellulose nitrate and its solvents was shown by Trillat (Compt. rend., 1932, *194*, 1922) using the X-ray methods. Similar examples of addition compounds for cellulose acetate were demonstrated by Katz and Weidinger (Rev. Trav. Chim., 1932, *51*, 847).

X-ray diffraction diagrams were used by Champetier (Ann. Chim., 1933, *20*, 5) to study the addition compounds formed by alkali, acid and water with cellulose. Several addition compounds were formed and it was concluded that the rate of formation depends on the origin and nature of the cellulose.

An excellent summary of the literature has been provided by Sisson (Textile Research, 1932–3 and 1933–4).

A great deal of work has been done on the X-ray diagrams of cellulose derivatives by Hess and his co-workers, and from the views developed in the foregoing pages there is no reason to expect any change in the fibre period, but only in the side spacings. Whilst many derivatives are known in which the fibre period of 10·3 Å is unaltered, yet examples have been recorded in which the period is 1·5, 2·0, or 2·5 times this length. Hess and Trogus (Z. physik. Chem., 1931, Bodenstein Festband, 885) have shown that for cellulose and its derivatives the fibre periods are integral multiples of 5·15 Å, which corresponds to the length of the glucose group, from which they conclude that the value of 5·15 Å has a closer relationship to the constitution of cellulose than the accepted value of 10·3 Å. This is in agreement with the theory of growth structures that the identity period along the direction of growth should be the shortest side of the unit cell.

Micelle and Chain Molecule

The simplest form of the micelle structure implies an arrangement in which the micelles may be likened to the bricks in a wall, overlapping each other in much the same manner. They are held together by tertiary forces sometimes known as micellar forces, to form the fibrils, which are the most elementary constituents of the natural fibre which may be detected under the microscope. From the fact that the X-ray diagram only accounts for some 75 % of the cellulose existing in the crystalline state, it has been concluded by Herzog (Kolloid Z., 1926, *39*, 98), that the remainder consists of a cementing material or " Kittsubstanz " which it deposited between the micelles or crystallites.

Peirce (Trans. Farad. Soc., 1930, *26*, 809) pointed out that whereas the diffuse nature of the interference spots shows that the regular repetition of the crystal planes is interrupted at small intervals and is usually interpreted as a measure of the size of the crystallites in a supposedly amorphous matrix, it is more in conformity with the evidence to suppose that the molecular order only approximates to crystalline perfection. The order is interspersed with partial local discontinuities, which have the same effect on diffraction as have the continuous boundaries of crystallites. A continuous and coherent structure can be built in a regular but imperfect molecular

order from the large " loose " molecules. Consideration of the strong swelling, and even solution under suitable conditions, by means of strong bases shows that the size of the dispersed particles depends on the balance between the osmotic dispersing force and the strength of the flaws randomly distributed throughout the structure. There is, therefore, according to Peirce, no need to suppose pre-existence boundaries in the cell wall; the conception of micelles as structural units is, on this basis, an unnecessary complication. Neale (J.T.I., 1929, *20*, 373) has explained many of the features of swelling on the conception of one acidic hydroxyl group in each glucose residue.

Astbury and Woods (J.T.I., 1932, *23*, 17) also state that the X-ray photographs show that there is no very marked success

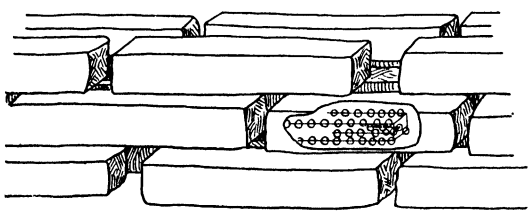


FIG. 59.—Diagram of the arrangement of micelles and the chain-molecule in the micelle.

in the grouping together of the molecular chains to form crystalline bundles. Miles (Trans. Farad. Soc., 1933, *29*, 110) put forward the opinion that the micellar theory of nitration, by which a cellulose nitrate consists of micelles of cellulose each esterified to the trinitrate in a peripheral layer is not in agreement with the evidence which points to all the chain molecules being esterified to approximately the same extent and not to any one being completely esterified before the rest.

Neale (Trans. Farad. Soc., 1933, *29*, 228) has also criticised the micelle theory on several grounds. It does not explain the axial shrinkage and lateral swelling without dissolution in swelling agents and the great restraining influence of axial tension on such swelling, and it necessitates an arbitrary distinction between inter- and intra-micellar reaction. As examples of this distinction he quotes the work of Craik and Miles (Trans. Farad. Soc., 1931, *27*, 756), who showed that in the fractionation of cellulose nitrate from aqueous acetone solutions, fractions are obtained which differ in chain length but not in degree of esterification; similarly Birtwell, Clibbens

and Geake (J.T.I., 1928, *19*, 349) showed with oxycellulose that fractions may be obtained which differ in degree of oxidation. These difficulties do not arise if it be supposed that the reactions occur more or less at random in a structure which, though imperfectly crystalline, is continuous except for random breaks in the primary valency chain. In the fractionation by solvents the longer chains aggregate and come out of solution most easily so that the separation is by chain length or viscosity, and chains of different lengths having been esterified in random fashion show the same average nitrogen content. In the case of oxidation the frequency of oxidation and chain length are interdependent. Neale's support of the assumption that the structure is continuous but slightly imperfect is based on the explanation that degradation consists in the irreversible cleavage of the primary valence bonds, whilst " activation " is the partially reversible separation of hydroxyl groups normally bound together by secondary valencies. The X-ray evidence precludes purely random variations from the perfectly crystalline structure, but it is possible to assume a rhythmic variation from the perfectly crystalline state without sharp discontinuities.

The work of Staudinger naturally implies the conception of cellulose as a long fibre molecule and he accounts (Cellulosechem., 1934, *15*, 66) for the very high viscosity of solutions of cellulose nitrate as compared with other derivatives on the hypothesis that the high concentration of HNO_3 and H_2SO_4 used for esterification may prevent dissociation of the acids and degradation of the cellulose. In solutions of cellulose nitrate, therefore, the long chain molecules correspond most closely to those of native cellulose.

Staudinger has also suggested a new classification for the colloid systems (Ber., 1926, *59*, 3029 ; 1929, *62*, 2893).

(*a*) Suspensoids and emulsoids. Any solid or liquid substance may be colloidally distributed in a suitable dispersing agent. The particles generally possess a spherical shape and show low viscosities.

(*b*) Molecule colloids. In this group the colloid particles are the molecules themselves and macromolecules of a molecular weight of 100,000 and more may occur. Most of these macromolecules have a fibre shape and their solutions show a particularly high viscosity. If the molecules of high molecular substances possess an approximately spherical shape, then their solutions have a relatively low viscosity.

(*c*) Micelle colloids. In this group the colloid particles arise through the association of relatively small molecules. The formation of micelles takes place in the salts of the higher molecular acids or bases, e.g. soaps. The micelles are stretched in length on account of a one-sided growth, but the internal composition of the micelle is quite different from that of the macromolecule. The micelle colloids also exhibit high viscosities.

The strength of the micellar theory lies in its explanation of the X-ray data, but it is weak when explanations are required of the difference between the physical and chemical properties of the natural fibres and rayons and also for certain other properties of the native fibres. On the other hand, the weakness of the continuous structure theory is its inability to account for all the X-ray data in a simple manner.

The physical properties of the native fibres are better explained on the basis of a continuous structure—for example, the fact that the tensile strength of cotton is high and increases with increasing moisture is accounted for on the assumption that the molecular chains themselves are broken when a cotton fibre is ruptured. Moisture would tend to loosen the lateral adhesion between the chains and so equalise the distribution of the stress with consequent increase in tensile strength. The observations on the dry and wet tensile strengths of rayons, however, are better interpreted on the micellar hypothesis.

These two theories, together with a cellulose particle theory, have been discussed in some detail by Sisson (Textile Res., 1935, *5*, 119).

The essential conception in the micelle theory is the existence of discrete rod-like sub-microscopic crystalline particles which are orientated with respect to the fibre axis and separated by amorphous material which, nevertheless, allows the micelles to move as a unit during intermicellar swelling and also to be dispersed during the early stages of dissolution.

The continuous structure theory is based on the conception of long cellulose chains which have crystallised in such a manner that the crystalline regularity is intercepted by warped or irregular regions which behave as amorphous matter towards X-rays and also towards the penetration of swelling and dispersing agents.

The *particle theory* of Farr (Textile Research, 1926, *7*, 65) is based on the existence of small uniform ellipsoid particles

with a major axis of about 0·00006 ins. in length. In the development of the fibre, the particles are formed in an "end-to-end" arrangement in a single strand and their identity becomes less distinct in the formation of the fibril. The fibrils are held together by a cementing material of pectic character and this material, which only constitutes 3 to 4% of the fibre mass, may be extracted with weak alkali or weak acid. Prolonged treatment brings about breakdown of the fibril into its constituent particles, but more rapid disintegration may be brought about by HCl (sp. gr. 1·19) or HCl gas, assisted by slight mechanical treatment. The membrane is disintegrated without degradation of the cellulose. The particles give the typical chemical analyses of cellulose, the same X-ray diffraction pattern and the same refractive indices. The separate particles do not give a viscous solution in cuprammonium hydroxide solution, and it is postulated that the usual high viscosity is due to a reaction between the cementing material and the cuprammonium hydrate, the particles themselves being in a state of suspension. Farr suggests that the particles account for the crystalline behaviour of cellulose and the cementing material for the colloidal behaviour. This new theory is not yet established as a great amount of experimental work has to be done.

The particle theory contains certain points of resemblance to the membrane theory of Hess; it is also interesting to consider the similarities of the pectic cement, the amorphous cellulose, the regions of non-crystallinity and the "Kittsubstanz" as postulated by various investigators.

An attempt has been made by Sisson (Textile Res., 1936, *6*, 143) to compromise between the conception of discrete micelles on the one hand and the existence of a continuous structure on the other. As it is impossible to explain the physical properties of any crystal on the classical hypothesis of a continuous lattice work of ions or molecules, typical of the unit cell arrangement but extending in all directions within the external crystal form, Zwicky (Phys. Rev., 1931, *38*, 1772; 1932, *40*, 63; 1933, *43*, 765) has postulated that superimposed on the lattice, as revealed from X-ray diffraction data, there is another lattice on a much larger scale consisting of crevices or cracks which give the crystal its secondary structure. A single crystal is, therefore, a latticework of points occupied by ions or molecules on which is superimposed a coarser structure separated by crevices. This view has been shown to be

consistent with the theories of crystal growth, the low tensile strength of crystals, intensity data of diffracted X-rays, diffusion through single crystals, etc. Astbury (Trans. Farad. Soc., *1933*, *29*, 193) has pointed out the possible analogy between the micellar structure of protein fibres and the secondary structure of single crystals, and Sisson (supra) suggests that the imperfect crystalline structure of cellulose might also be explained on the basis of Zwicky's theories.

The chemical properties, density, X-ray diffraction lines, etc., are practically the same for all the purified cellulose fibres, and they depend on the chemical structure of the cellulose molecule and the lattice structure of the unit cell. This chemical and crystalline structure may be termed the " primary structure of cellulose."

However, most of the practically important physical properties of cellulose fibres such as tensile strength, elasticity, swelling, shrinkage, etc., vary widely among the different fibres. These properties depend on the configuration of the cellulose crystallites, their orientation and association with amorphous or non-cellulosic material in the fibre. This structure, arrangement and association of crystallites is termed the " *secondary structure* of cellulose." The crystalline surface of the secondary structure may be roughly compared with the surface of a dried pond, covered with cracks and crevices, with the exception that the principal crevices run parallel to the cellulose chains and are partly occupied by amorphous material.

Although little is known regarding the mechanism of crystalline growth in cellulose fibres, yet it must take place in presence of impurities so that the views of Davey (A Study of Crystal Structure and its Applications ; New York, 1934) and Buckley (Z. Krist., 1932, *82*, 31 ; 1934, *88*, 381) on this matter, which agree with Sisson's suggestion, are of value when considering long fibrous crystals of native cellulose. The nature of the cellulose molecule is conducive to the formation of long fibrous crystals and this tendency should be reinforced by the impurities which are held by the hydroxyl groups retarding crystal growth in the direction perpendicular to the cellulose chains.

The secondary structure includes the more or less continuous structure, but at the same time the regularity is interrupted by crevices occupied by non-crystalline material. There is nothing in the X-ray data which conflicts with this conception. It is also in agreement with the known data on the

dispersion and modification of cellulose which are difficult to explain on the rigid basis of a micellar theory. For instance, the existence of discrete and uniform micelles should give a uniform micellar size on dispersion, which is not supported by experimental evidence; modification and degradation is known to proceed gradually and not in uniform steps, so that the final micellar size appears more as a function of the chemical process than of the previous micellar size in the native cellulose.

Sisson also comments on the dyeing properties of the various cellulose fibres which are essentially similar chemically but must be dissimilar in physical structure. This is difficult to explain on a purely micellar or continuous structure theory. Harmony may be obtained by the assumption of secondary structure, which is also related to the history of the fibre. Sisson, however, emphasises the fact that there is no direct proof for the existence of a secondary structure.

Kratky and Mark (Z. physik. Chem., 1937, *B36*, 129) have also reviewed the different ideas of the molecular structure of cellulose and pointed out that the theory of individual micelles has recently been giving place to that of long principal valency chains extending through many of the crystal units or micelles determined by X-ray methods.

It is not possible to decide by X-ray examination which theory is correct, but the production of higher orientation by suitable mechanical means points to some sort of micellar structure with a certain individuality, and this form may possibly lie between the two extremes of micelle and fibre-molecule.

Network Theory

The simple micellar hypothesis is no longer rigidly upheld, for it is now clear that the molecular order only approximates to crystalline perfection, and further, it is difficult to account for the high tensile strength and other mechanical properties of native cellulose by postulating a simple brick-like structure. The recent views developed by Astbury, Gerngross, Hermann, Frey-Wyssling, Krakty, Mark and others embrace the possibility of some of the chain molecules persisting through the micelles, or the distribution of chain-endings giving the effect of regularly arranged units. Some of these speculations have been represented diagrammatically by Frey-Wyssling (Die Stoffausscheidung der hoheren Pflanzen; Springer; Berlin). Fig. 60. The possibility of individual chain molecules per-

sisting through the micelles reconciles the conflicting deductions derived from X-ray and viscosity data, and is in agreement with the mechanical properties of cellulose fibres.

Further developments are illustrated in Fig. 61, the chain molecules being shown as lines which are not always parallel

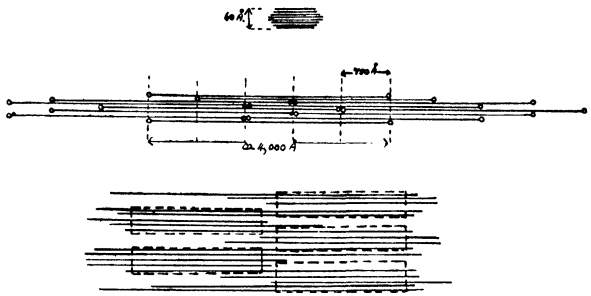
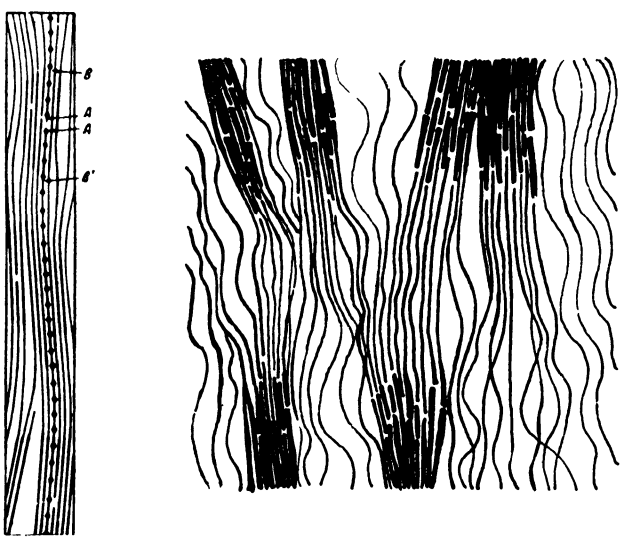


FIG. 60.—Micelle and chain-molecule.



FIGS. 61–62.—Micelle and chain molecule.

but occasionally come together in orderly manner (as indicated by the darker lines) to give the effect of discrete crystalline particles. Nevertheless, these aggregates or chain bundles are linked together by chains which extend from one region of regular arrangement to another, protruding from the ends of the crystallites as amorphous fringes. In the diagram, chain

endings are shown by A and A', which come within the crystalline region, which extends from B to B'.

More recent developments in the structure of cellulose have come from consideration of regenerated cellulose. The chain molecules of cellulose are not necessarily straight; indeed, since free rotation is possible at every glucosidic linkage, there is a tendency to agglomeration where the chains are sufficiently free. On the other hand, the secondary valency forces of the hydroxyl groups tends to bring about an alignment of adjacent chain molecules, producing an orderly arrangement; the secondary valencies cause a crystalline arrangement.

The agglomerated state predominates when the cellulose exists in dilute solution, and the crystalline state predominates in the solid form, but even here there are some agglomerated molecules whose presence becomes more prominent on swelling. Individual micelles are no longer held to exist as fundamental structural elements but, as in other aspects of cellulose chemistry, the old term is still employed with a different meaning. Micelles are regions where the crystalline tendency predominates but they have fringes of chain molecules in which the disorderly array accounts for the presence of "amorphous" material. (See Fig. 62). The persistence of some of the chain molecules through the micelles explains the high tensile strength of a system of small units and reconciles the requirements of X-ray and viscosity measurements.

One of the difficulties of the older conceptions of the structure of cellulose was to explain the cohesion of highly swollen regenerated cellulose on the basis of non-swelling crystallites, for the X-ray pictures of dry and wet cellulose show no difference. The modern view assumes that water penetrates between the micelles and into the fringes or clusters of molecular chains which open and close, umbrella fashion, on wetting and drying.

Boulton, Delph, Fothergill and Morton (J.T.I., 1933, *24*, 113P) pictured cellulose as a three-dimensional network of more or less parallel chain molecules which occasionally produce regions of crystalline regularity. Between the crystallites, the molecular chains form, in the swollen condition, an open network through which small molecules easily pass. The network basis has been extended further in recent years, and the micellar system of cellulose is now pictured as a porous structure in which regions of crystalline arrangement are suspended by fringes or regions predominated by the tendency to agglomeration.

Further developments are being made by Hermans and Krakty (Kolloid Z., 1939, *86*, 245), who are attempting to bring the mechanical properties of viscose filaments with different amounts of orientation into some sort of scientific system. Krakty's publications (ibid., 1938, *84*, 149; 1939, *88*, 78) envisage a network of long chains of micelles held together by cross-linkages of micelles. This is represented in Fig. 63, where micelles are shown as lines and the amorphous intermediate areas as ellipses. Two types of structure were postulated (*a*) the ideal loose network which on deformation behaves as separate chains, and (*b*) the ideal close network; a

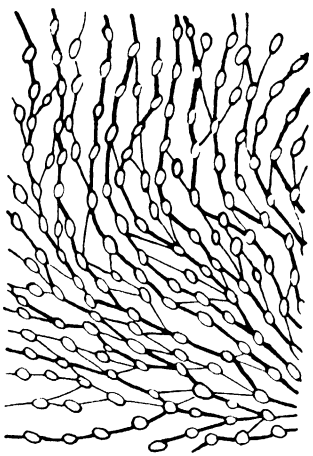


FIG. 63 — The network basis of the micellar system of cellulose.

number of equations were developed on this basis. In the loose network, the micelles are suspended in the swelling medium without any mutual interaction, but in the close network, the swelling is such that owing to the expansion of the pores a considerable extensibility is established, but there is always some interlocking of the whole porous system which prevents a slipping of the chain bundles over one another.

Deformation of the close network produces a volume contraction due to a tightening up of the net.

Highly extensible, swollen, isotropic filaments of regenerated cellulose have been examined by Hermans and Krakty, and during extension it was found that increase in orientation accompanied extension up to 80%, but in the further extension from 80 to 120% no further orientation took place. The cluster of chain molecules protruding from the micelles and acting as hinges must, therefore, be regarded as elastic and

not as inextensible. During extension, when the point is reached where the transverse connections of the micelles offer appreciable resistance to stretching, then an extension of the molecular fringe takes place without any improvement in micellar orientation.

The stretching of swollen isotropic filaments produced orientation with the crystallites in the direction of extension, but there was much less orientation with air-dry filaments of equal extensibility.

Measurements have been made of length, diameter, breaking load, extension, degree of swelling, refractive index and orientation according to X-ray diagrams, in the case of isotropic filaments and films in which orientation is progressively produced by stretching. The form of the load-extension curves varied with the degree of orientation and the fully isotropic viscose filaments, gave curves closely resembling those for wool and rubber; they were equally strong in both dry and wet states. These measurements were compared with the calculated values based on the two limiting cases of the ideal loose network and the ideal close network, and the results for swollen filaments showed good agreement with the theory; the greatest deviations occurred with the least swollen filaments, which represent a state between that of free micelles and a rigid network. The researches are continuing.

The *intermicellar system* of cellulose has been examined by Frey-Wyssling (Protoplasma, 1937, *27*, 372). Cellulose was impregnated with solutions of gold and silver salts and crystals of the metals precipitated by reduction; these produce both dichroic and X-ray effects. It was estimated that the particles of gold and silver deposited in the cellulose fibres have diameters of about 100 Å, which is about twice the width of the micelles. Hence the fibres must contain coarse capillaries, which accommodate the colloidal dyestuffs, but fine capillaries of the order of 10 Å are also postulated, water and molecular solutions being presumed to penetrate into these. The two capillary systems possess branching habits (anastomosis) and merge into one another forming a hetero-capillary system.

The cross section of the intermicellar system is shown diagrammatically in Fig. 64. The micelles (small white areas *G*) are grouped together to form "micro-fibrils" shown as indefinite ellipses *F*— between which runs the coarse capillary system (*K*) of diameter from 50 to 130 Å. The fine hetero-

capillary system between the micelles is indicated in black (S).

The data of Frey-Wyssling are perhaps open to criticism on account of the swelling process during impregnation with the salt solutions; 100 Å must be regarded as a maximum value. The theory of dyeing has also contributed to our knowledge of pore size and the present position has been reviewed by Boulton and Morton (J.S.D.C., 1940, *56*, 145). Dry viscose sheet is impermeable to alcohol, benzene and picric acid, which pass easily through the swollen material. Hence the capillary canals may be estimated to be about 5 Å or less in the dry material and 20 to 30 Å in the water-swollen state.

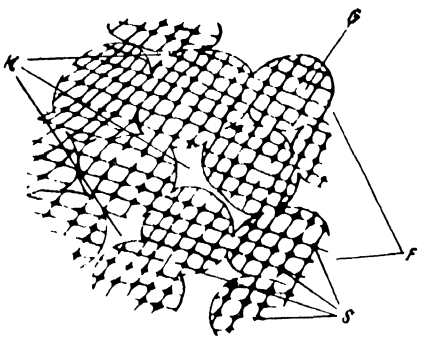


FIG. 64.
The intermicellar system.

In the swollen state all fibres take up dyestuffs, but in the unswollen condition viscose rayon and cotton mercerised under tension are almost unstained, whereas cuprammonium rayon and the native fibres absorb dyes almost as easily as in the swollen state. Presumably the capillary system of the latter class contains comparatively large canals.

The micro-fibrils of Frey-Wyssling, mentioned above, must not be confused with the fibrils seen in native cellulose under the microscope, for the micro-fibrils are submicroscopic and consist of chains of micelles. Fibrils, on the other hand, may actually be obtained from native cellulose by a combination of chemical and mechanical treatment and may even be dissected further to smaller particles known as fusiform bodies, dermatasomes, etc. (See page 12.)

The dimensions of some of the components which go to make up cotton cellulose have been tabulated by Frey-Wyssling, as shown on page 132.

From Frey-Wyssling (Die Stoffausscheidung der höheren Pflanzen : Springer ; Berlin).

The figures refer to the number of times the smaller structure is contained in the larger ; the value for the chain molecule is arbitrary.

The Angström unit, Å, is 10^{-8} cm.

							AMICROSCOPIC.	
								Glucose residue. $7{\cdot}5 \times 5{\cdot}2$ Å
					SUBMICROSCOPIC.		Cellobiose. residue $7{\cdot}5 \times 10{\cdot}3$Å	2
						Chain molecule $7{\cdot}5 \times 750$ Å	about 75	about 150
			MICROSCOPIC		Micelle. $60 \times 60 \times 750$ Å	about 100	$7{\cdot}5 \times 10^{3}$	$1{\cdot}5 \times 10^{4}$
				Dermatasome. $0{\cdot}4 \times 0{\cdot}4 \times 0{\cdot}5$ μ	3×10^{4}	3×10^{6}	$2{\cdot}2 \times 10^{6}$	$9{\cdot}5 \times 10^{8}$
			Fibril. $0{\cdot}4 \times 0{\cdot}4 \times 100$ μ	200	6×10^{7}	6×10^{8}	$4{\cdot}4 \times 10^{10}$	9×10^{10}
MACROSCOPIC.		Lamella $0{\cdot}4 \times 10\pi \times 5 \times 10^{4}\mu$	4×10^{4}	8×10^{6}	$2{\cdot}4 \times 10^{11}$	$2{\cdot}4 \times 10^{13}$	$1{\cdot}8 \times 10^{15}$	$3{\cdot}6 \times 10^{15}$
	Section. $(0{\cdot}01)^{2}\pi \times 50$ mm.	25	1×10^{5}	2×10^{8}	6×10^{12}	6×10^{14}	$4{\cdot}5 \times 10^{16}$	9×10^{16}
Hair. $(0{\cdot}01)^{2}\pi \times 50$ mm.	1	25	about 1 million	about 1/10 milliard	order of 1 billion	order of 1 billiard	order of 1/20 trillion	order of 1/10 trillion

PART THREE

DISPERSED CELLULOSE

CHAPTER SEVEN

TREATMENT WITH BASIC SUBSTANCES

Alkaline Hydroxides

INTRODUCTORY.

IN 1844 John Mercer observed that if cotton, in the form of yarn or fabric, was treated with a sufficiently concentrated solution of sodium hydroxide and then washed free from alkali with water, it underwent certain changes ; it suffered considerable shrinkage, its tensile strength increased and its capacity for dyestuffs also increased. The concentration of alkali found most suitable for his purpose lay between 20 % and 25 % at 15° C., lower concentrations giving the effect to a lesser degree or requiring more than the few minutes otherwise necessary. Mercer patented the production of these effects (B.P. 13,296/1850). Modern mercerising, however, is associated with increased lustre, which was discovered by Lowe in 1889 (B.P. 20,314/1889 and 4,452/1890), who observed the result of mercerising under tension in order to maintain the full length in the case of yarn.

A number of Mercer's observations are not fully appreciated, probably on account of the large amount of work done by subsequent investigators, but he was well aware of the fact that a greater shrinkage is produced by 27 % NaOH than by 32 % NaOH, and also that the solution of 8·5 % NaOH which was too dilute for technical shrinkage could be rendered effective by the addition of zinc hydroxide, the best molecular proportions being $Zn(OH)_2$: 4NaOH. The increased tensile strength was noted when it was necessary to separate pieces of mercerised cloth by tearing. Mercer recorded the fact that when cotton is passed through a bath of caustic soda, a diminution in alkali concentration took place, it being necessary to supply liquor of 60° Tw. in order to maintain a strength of 45° Tw. Mercer also observed the effect of other swelling agents. The absorption of caustic soda by cotton was explained

by early investigators on the grounds of chemical combination between cellulose and sodium hydroxide followed by decomposition of the compound by the action of water on the same lines as sodium ethoxide or other alcoholates. The evidence for " soda cellulose " will be considered in the chapter on this complex reaction (page 430) but it is interesting to note that this view gave rise to the terms " cellulose hydrate " and " hydrated cellulose," it being assumed that the mercerised product differed from the original cotton by the presence of water in hydrate combination, which accounted for the alteration in properties. The name still persists but its meaning has been modified, and dispersed cellulose is becoming more general.

The cotton hair which has been mercerised without tension has lost its flat ribbon-like form and has become rounder, smoother and more uniform. The characteristic convolutions have disappeared, whilst in cross section the lumen, or central canal is greatly contracted, appearing as a slit in an oval or circular section quite distinct from the wide lumen in an irregular oval. In the case of cotton mercerised under tension, the hairs appear very smooth and almost perfectly cylindrical, whilst the cross-section reveals an almost perfect circle in which the lumen often appears as a point. (See Figs. 4 to 7.)

The addition of $Zn(OH)_2$ to solutions of NaOH by Mercer has already been mentioned, but Lewis (J.T.I., 1933, *24*, 122) has described the use of sodium zincate solution as a means of swelling cotton hairs in order to test for chemical or mechanical damage. The zincate solution is prepared by saturating hot 60° Tw. NaOH with $Zn(OH)_2$, cooling and filtering.

The increased lustre of cotton which has been mercerised under tension is generally attributed to the increased surface smoothness. There is also evidence to show that the effect of lowering the temperature is to improve the lustre—the patents of Heberlein (B.P. 108,671 ; 191,203 ; 192,227) claiming that treatment with concentrations from 14% to 20% at temperatures below 0° C. gives an effect different from ordinary mercerisation, making fine material transparent, and producing a permanent linen-like character.

Sodium Hydroxide

Huebner and Pope (J.S.C.I., 1904, *23*, 404) examined the action of caustic soda solution on loose hairs and found that concentrations up to 6·5% exerted no effect, but that solutions between 7% and 11·5% of NaOH caused a rapid uncoiling of

the hair, i.e. de-convolution, but only with solutions of 15·5 % was any swelling noticed and this swelling took place after de-convolution whereas with concentrations of 17·5 % swelling and de-convolution were simultaneous. At higher strengths the swelling preceded untwisting. As 17·5 % NaOH is the lowest concentration for producing lustre the investigators concluded that the production of lustre is connected with the uncoiling taking place either during or after swelling. They also showed that at a temperature of 90° C. a solution of 22·5 % NaOH produces a much inferior lustre, and that the processes of uncoiling and swelling are reversed from the order at lower temperatures and the hairs uncoil before swelling.

QUANTITATIVE EXAMINATION.

Willows, Barratt and Parker (J.T.I., 1922, *13*, 229) investigated the effect of various concentrations of caustic soda solution on the length of single cotton hairs using lightly "scoured" material. The hairs were maintained under a constant tension of 50 milligrams during the experiment, and the change in length was considered complete after three minutes contact, after which the changes in length were very slow. The maximum contraction was observed in solutions containing 13·5 % NaOH; with increasing concentration the contraction diminished up to 17·5 % NaOH and then rose to 25 % NaOH above which there was a further slow diminution in shrinkage. [See Fig. 65.]

The full curve shows the changes produced by the alkali alone and the dotted curve the effect of mercerising followed by washing. For concentrations of 23·5 % and over there is a contraction additional to that caused by the alkali alone, produced by dilution during washing resulting in a shrinkage characteristic of the lower concentration. Reducing the temperature was observed to cause greater contraction above 22° Tw. (9·5 %) and the maximum effect was produced with weaker solutions, e.g. at 0° C. the maximum contraction is produced by 25° Tw. (11 %) solutions. Willows and Alexander (J.T.I., 1922, *13*, 237) measured the change in sectional area of cotton hairs on mercerising, and by combining the results with those obtained above for change of length were able to estimate the change in volume. [See Fig. 70.]

A further interesting feature of this work was the observation that with sodium hydroxide solutions of 30–40° Tw. (13–18 %) sections of cotton hairs assumed a dumb-bell forma-

tion due to the inner part of the hair bulging at the ends over the cuticle. This may be regarded as evidence of the strength of the cuticle, for in stronger solutions the cuticle is more extensible as the diameter of the swollen hair is greater and there is no bulging. When the cuticle has been damaged as

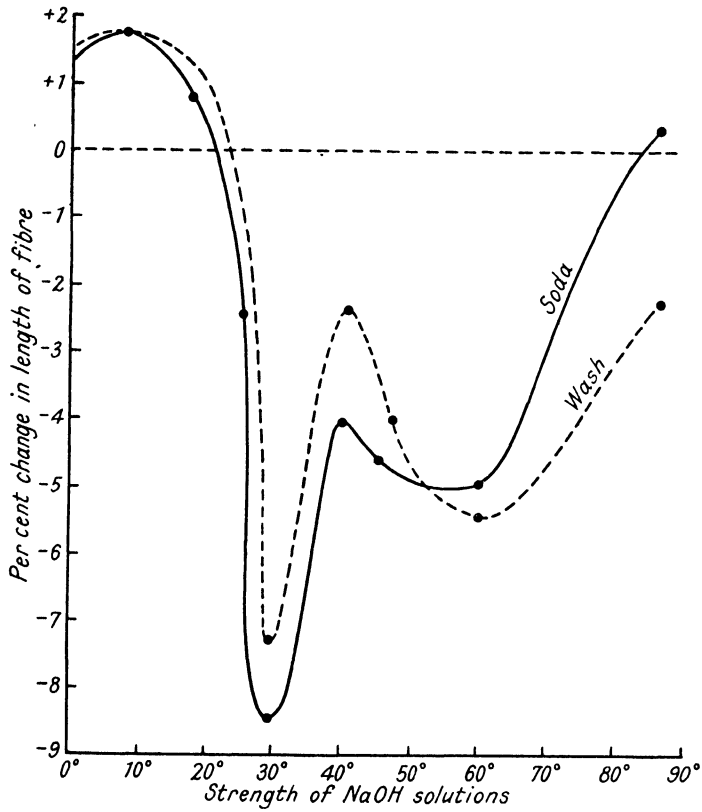


FIG. 65.—Changes in length of single cotton hairs (scoured) placed in single solutions of NaOH. (50 mg. tension.)

with chemical tendering, the dumb-bell formation does not appear. [See Figs. 66 and 67.]

Collins and Williams (J.T.I., 1923, *14*, 287) also investigated the effect of sodium hydrate solutions on cotton hairs which had been well boiled in water and soda. They observed that the initial increase in length on immersion in water and dilute solutions is due to removal of the convolutions, so that with

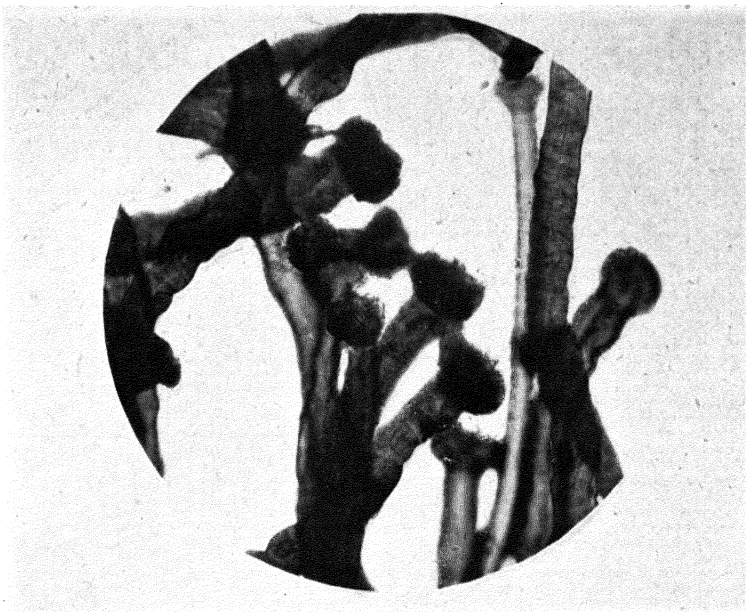


FIG. 66.

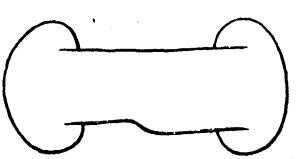


FIG. 67.

Photomicrograph and diagram of the dumb-bell effect due to the restrictive action of the cuticle, when cotton hairs are swollen with sodium zincate solution.

(*By courtesy of Miss Alexander.*)

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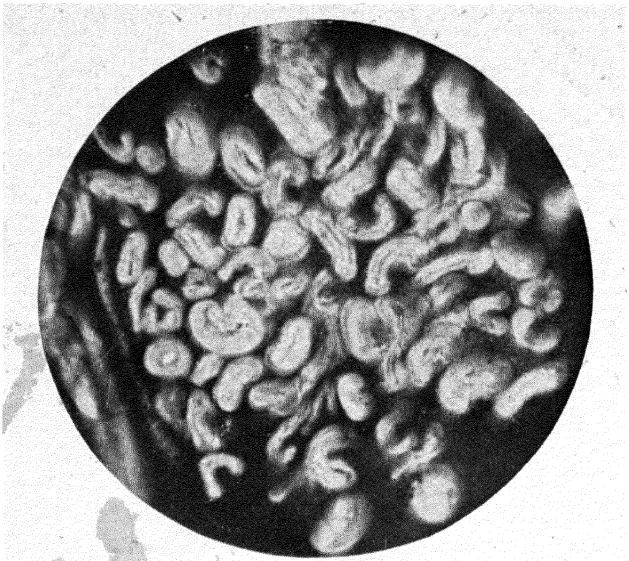


FIG. 68.—Cross-section of unmercerised yarn.

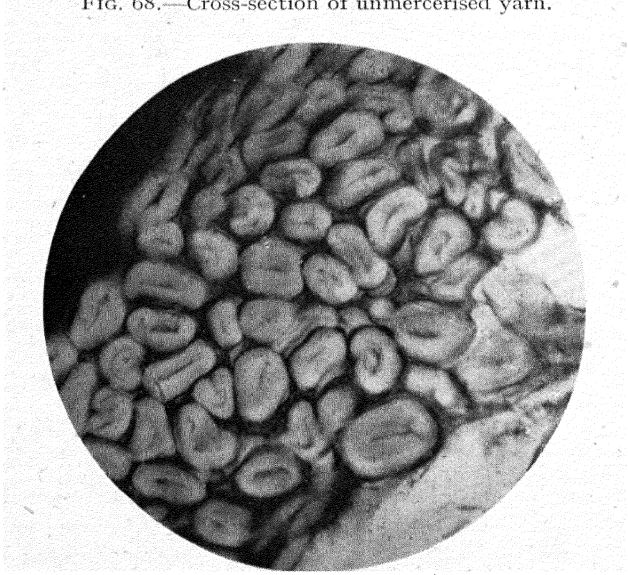


FIG. 69.—Cross-section of well-mercerised cotton yarn showing effect of good penetration and tension during treatment.

(*By courtesy of Miss Alexander.*)

[*To face page* 139.

yarns, the more completely the convolutions are removed by the preliminary processes such as boiling in water or soda, the greater will be the contraction of the individual hair when completely mercerised. Measurement of change in length and diameter confirmed the observation of Willows and his collaborators, i.e. the maximum shrinkage concentration of 30° Tw. (13·1 %) NaOH, but showed that the hairs continued to contract up to 102° Tw. (48·2 %) instead of extending after 30° Tw.

The method adopted by Collins and Williams was to treat the single cotton hair with a *series* of solutions of sodium

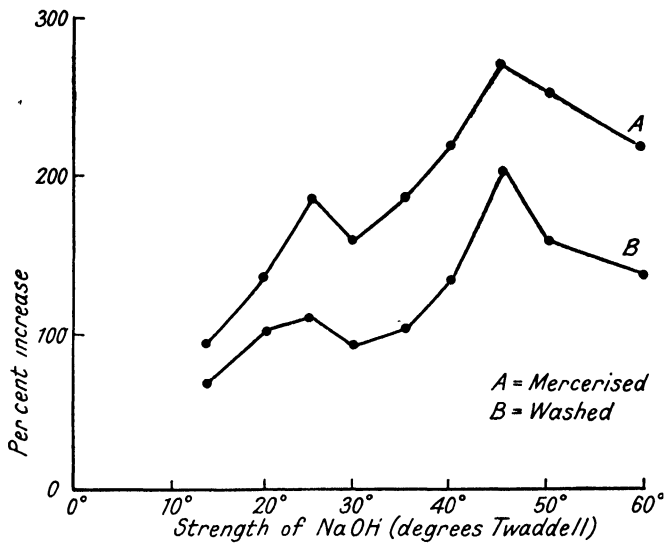


FIG. 70.—Changes in volume of cotton hairs on mercerising.

hydroxide, of ascending (or descending) concentration; Willows, Barrett and Parker, on the other hand, worked on the basis of one hair in one solution.

Figure 71 shows the results obtained by Collins and Williams.

Quantitative examination of the action of solutions of sodium hydroxide on cotton hairs also received attention from Calvert and Summers (J.T.I., 1925, *16*, 233). In a wider survey of the different types of cotton, than that attempted by previous investigators, they confirmed that the maximum increase in width took place in a solution of caustic soda of 35° Tw. concentration and the use of higher concentra-

tions failed to reveal any significant difference. An interesting observation concerning the restrictive action of the cuticle was made by taking cotton hairs direct from the boll, placing them under the microscope and making a slight cut in the cuticle both before and after irrigation with 40° Tw. NaOH. In both cases extrusion of the cellulose took place, demonstrating the existence of tension within the cuticle.

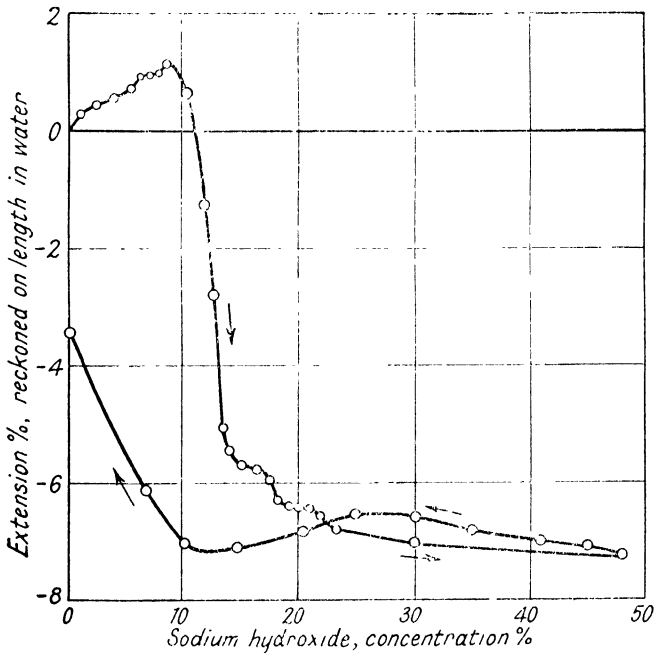


FIG. 71.—Changes in length of cotton hairs on treatment with a series of solutions of sodium hydroxide.

Returning to the work of Collins and Williams (loc. cit.), from changes in diameter, combined with those of length it appears that the maximum swelling occurs in a 15% (34° Tw.) solution of sodium hydroxide. It was also noticed that hairs which were immersed in the complete range of solutions up to 48% NaOH, on subsequent immersion in more dilute solutions also exhibited a maximum swelling in 15% NaOH. The changes in length were measured by means of an apparatus designed on the lines of Justin-Mueller's turgometer and under a constant load of 10 mg.

The relationship between the changes in length and diameter of cotton hairs during mercerisation with increasing strengths of caustic soda, shows that maximum swelling occurs in caustic soda of 14·5%, but that with an increase in strength of solution contraction of the hair is not accompanied by an increase in diameter—see Figure 72.

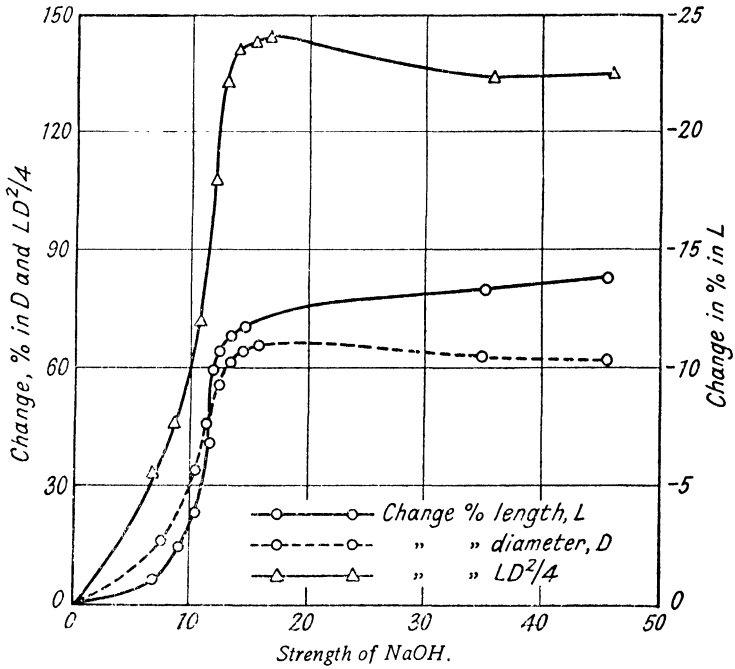


FIG 72.—Dimensional changes in the cotton hair on treatment with solutions of sodium hydroxide

Coward and Spencer (J.T.I., 1923, *14*, 32) observed maximum swelling of cotton in all solutions of caustic soda containing more than 14·3%, but their method was to immerse the material in various strengths of alkali and then remove the interfibrillar liquid by means of a centrifuge. The liquor removed was estimated from weighings of the dry cotton and the centrifuged mass together with its content of alkali (see soda cellulose—page 430).

Ordinary cotton retains about 50% of its weight of water after treatment in the centrifuge, but if mercerised with sodium hydroxide and thoroughly washed it retains up to 123% of

its weight, the amount varying according to the concentration of alkali. From a concentration of 14·3 % NaOH up to 48·8 %, an almost saturated solution, the increase in volume of 100 g. of cotton was almost constant, this again suggesting that the swelling is in some manner limited by the cuticle.

With sodium hydroxide solutions of concentrations ranging from 4 to 50 %, the preferential absorption of NaOH amounted to as much as 35 % of the weight of the cotton and was roughly

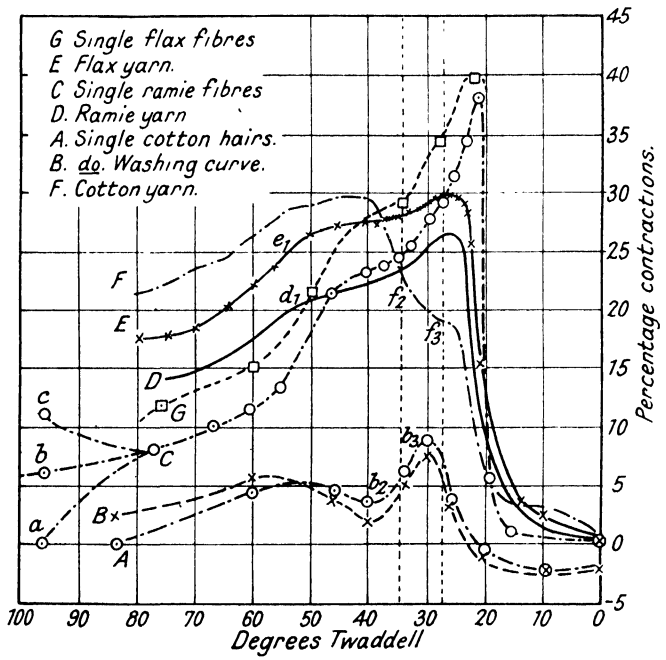


FIG. 73.—Shrinkage of flax, ramie and cotton.

proportional to the concentration of the solution. This preferential absorption was noted by Mercer in his original work and is the reason for the use, in works' mercerising, of concentrations of sodium hydroxide solution above that necessary for the maximum swelling action, to allow for the fall in the alkali concentration of the external solution.

Nodder and Kinkead (J.T.I., 1923, *14*, 142) have compared the effect of caustic soda solutions on cotton hairs and yarn with that of flax and ramie fibres and yarn. The changes in length are shown above.

Other Alkaline Hydroxides

The action of potassium hydroxide on cotton hairs has been examined by Collins and Williams (J.T.I., 1924, *15*, 149), who found that whilst the contraction of length is of the same order of magnitude as with sodium hydroxide yet the increase in diameter is less than attained in solutions of the latter, so that changes in length alone cannot be used as a measure of swelling in different solutions. Maximum swelling was found

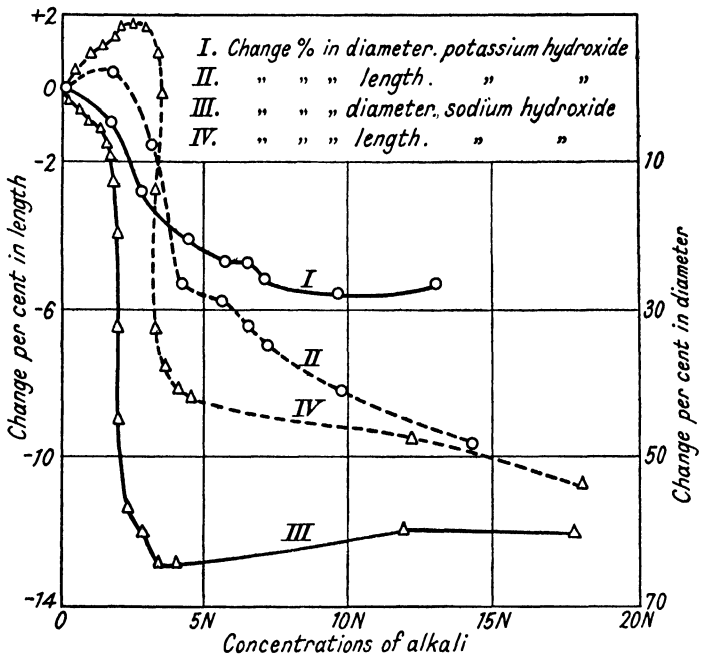


FIG. 74.—Comparison of KOH and NaOH.

to occur in 28% KOH solution—close agreement with the observation of Haller (Kolloid Z., 1917, *20*, 127), who found an increase of 23% in diameter of bleached cotton hairs in 18·6% KOH solution.

The concentrations of 28% KOH and 15% NaOH for maximum swelling confirmed the estimation of Ristenpart (Textilber., 1921, *2*, 130) that the mercerising action of 1 mol. of NaOH is equivalent to that of 1·5 mols. of KOH.

Comparisons of the action of NaOH and KOH are shown above.

With solutions of lithium, rubidium and caesium hydroxides, Collins observed (J.T.I., 1925, *16*, 123) that the contraction of the cotton hairs is much less than with potassium hydroxide, and in concentrated solutions of caesium hydroxide they only extend. The change in diameter is less than 30 % in the maximum swelling concentrations of 49 % for rubidium hydroxide and 6·6 and 10 % for lithium hydroxide. Heuser and Bartunek (Cellulosechem., 1925, *6*, 19) published data on the swelling of cotton hairs in alkali hydroxide solutions which mainly agree with the above observations except in the case of lithium hydroxide, showing increase in hair diameter of 97 % with 9·5 % LiOH, 78 % with 18 % NaOH, 64 % with 32 % KOH, 53 % with 40 % RbOH and 47 % with 40 % CsOH the alkali concentration being in volume percentages. [The order is that of the supposed hydration of the ions.] These authors, unlike Collins, worked on the basis of one hair-one solution.

The most striking feature of the comparisons is the emphasis on the swelling power of sodium hydroxide and the evidence for maximum swelling to correspond to the solutions in which the metallic ions are fully hydrated.

Tensile Strength

The effect of mercerisation without tension on the breaking load of single cotton hairs has been studied by many investigators, and some of the early work showed a decrease in breaking load.

The results of Clegg, however (J.T.I. 1924, *15*, 6), were obtained by mercerisation without tension in 40° Tw. NaOH, the measurements being made on a modified O'Neill apparatus. An increase in the mean breaking load of from 11·8 to 49·2 % was obtained with a decreased coefficient of variability in each case, that is the hairs not only become stronger but more uniform in strength.

Langer (Textilber., 1935, *16*, 507) gives an increase in breaking load of from 32 to 35 % and Schubert (Dissertation ; Dresden, 1932) an average increase of 25 %.

The position is still more difficult in estimating the effect of mercerising on the breaking load of the yarns as the effect of tension must be taken into account ; but Lindemann (Dissertation, Dresden, 1909) mentions an increase in breaking load of 16 % ; Greenwood (loc. cit.) about 20 % ; Huebner and Pope (J.S.C.I., 1903, *22*, 70) give an increase of 26 % whilst Ristenpart (Textilber., 1921, *2*, 130) states that yarn mercerised

without tension by means of KOH or NaOH has an increased breaking load of nearly 40%.

When linen is mercerised without tension it suffers a decrease in tensile strength according to Victoroff (Textilber., 1925, *6*, 169) varying from 6 to 8%; overstretching increased the breaking load and it seems probable that correct tension should enable linen to be mercerised without loss of strength. When crease-resisting linen is mercerised without tension there is an improvement in strength according to B.P. 437,361.

General

The change in length of yarn, as a consequence of mercerisation, is the resultant of changes both in length and section of the cotton hairs and is complicated by the slipping, rearrangement and accommodation of the hairs in the yarn so that measurements of shrinkage are of little scientific value in examining the mercerising phenomenon. Most of the measurements, however, show that a maximum contraction is produced by solutions in the region of 20% sodium hydroxide.

However, the progressive nature of the relation between shrinkage and concentration was first clearly demonstrated by measurements of yarn by Huebner and Pope (J.S.C.I., 1904, *23*, 404), showing maximum contraction at 45° Tw., whilst the original work by Lowe on the application of tension during mercerisation with the resultant lustre was also carried out on yarn. Another interesting observation which came from large scale mercerisation of yarn, was that the force required to prevent the material from contracting during mercerising is considerably less than that required to restore it to the original length if shrinkage is permitted. Willows, Barratt and Parker (loc. cit.) observed a similar result with cotton hairs—no contraction occurred under a load of 0·16 g. but if the hair was allowed to contract then a load of 0·32 g. was required to restore it to the original length.

The effect of varied tension applied to cotton hairs treated with varying concentrations of alkali has been recorded by Calvert (J.T.I., 1930, *21*, 293), who also found that scouring with boiling alkali or rubbing with very fine emery paper affects the surface of the hair so that greater swelling in diameter and hence greater shrinkage in length takes place.

These observations are of some importance in confirming the restrictive action of the cuticle on the swelling of cotton.

Neale's Theory

The swelling of regenerated cellulose has been examined by Beadle and Stevens (8th International Congress Applied Chemistry, 1912, *13*, 25), who immersed hanks of "cuprammonium rayon" in alkali of varying concentrations and temperatures, removed the surface liquor and weighed the material. The total alkali absorbed was measured by titration and the water absorbed calculated from the data obtained. Their results were recorded graphically by Neale (J.T.I., 1929, *20*, 373), and it will be seen that the maximum swelling took place in 9 % NaOH at 5° C. (See Fig. 78.)

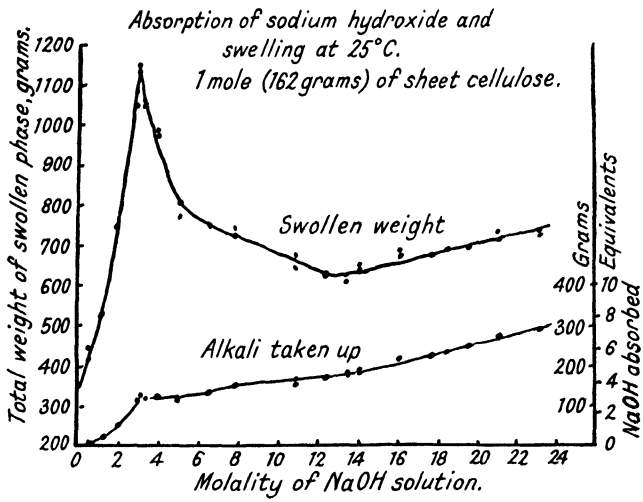


FIG. 75.—Swelling and absorption of NaOH by cellulose.

Neale's own experiments were made with Cellophane sheets about 0·004 cm. thick, taking pieces about 5 cm. square and weighing about 0·2 g. These were washed in distilled water overnight and dried between filter papers to prevent crinkling and finally dried for several hours at 80° C. and for 30 mins. at 110° C.

The weighed samples were transferred to rubber-stoppered bottles containing 75 cc. of NaOH solution and kept at 25° C. for two days. The swollen sheets were then rapidly dried with filter paper and weighed in stoppered bottles to obtain the total weight. The alkali absorbed was determined by titration with standard HCl, and the cellulose was then washed for

several days in distilled water to remove the sodium chloride, dried and weighed as before.

The experimental results are shown in Fig. 75.

The heat of reaction of various forms of cellulose with sodium hydroxide solutions was also examined. Neale then put forward the following theory of mercerising basing the swelling ultimately on osmotic forces.

Swelling

It is assumed that cellulose behaves as a weak monobasic acid, and forms a sodium salt to an extent which increases with

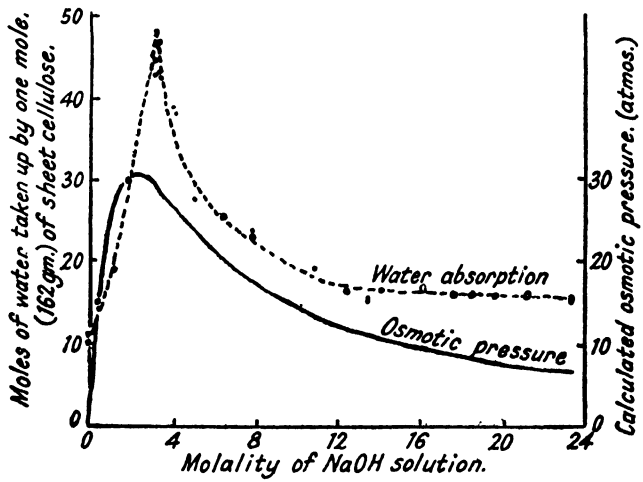


FIG. 76.—Swelling of cellulose in NaOH solution.

the concentration of the alkali. Additional alkali diffuses into the cellulose phase in amount determinable by Donnan's thermodynamic equation of membrane equilibrium. The resulting unequal distribution of ions causes an osmosis or movement of water which distends the cellulose until the osmotic pressure is balanced by the forces arising from the cohesion of the gel. If the alkali solution is then replaced by a large excess of water, the sodium salt of cellulose is hydrolysed, the osmotic pressure falls, and the cellulose is recovered unchanged chemically, but is permanently distorted if the osmotic pressure has been sufficiently high.

Equations deduced from this hypothesis were employed to calculate the absorption of sodium hydroxide from the absorp-

tion of water by cotton as determined by Coward and Spencer (loc. cit.). The results show good agreement. The calculated osmotic pressure was also in fair agreement with observed swelling of sheet cellulose as shown in Fig. 76.

The effect of the change of temperature on the conditions of equilibrium was also calculated, and the theoretical curves show that as the temperature falls, the maximum osmotic pressure rises and the maximum occurs at a lower concentra-

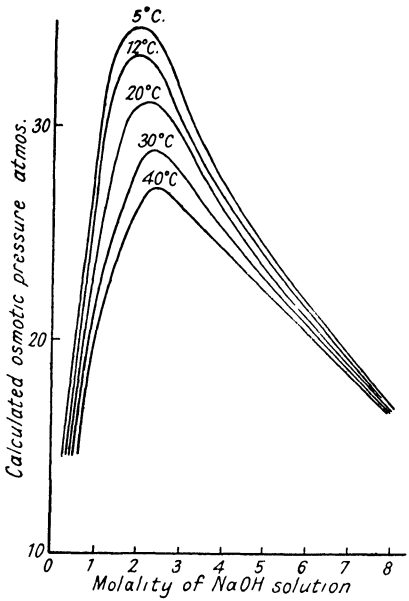


FIG. 77.—Theoretical data by Neale.

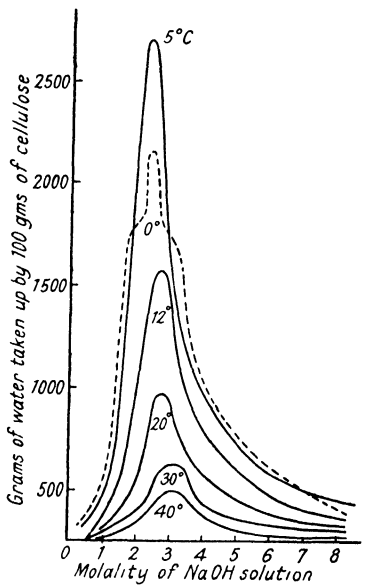


FIG 78.—Curves by Neale from the data of Beadle and Stevens. (Cuprammonium rayon)

tion of alkali. These theoretical curves shown above, figure 77, when compared with the data of Beadle and Stevens (loc. cit.) figure 78, lead to the conclusion that the swelling increases much more rapidly than the pressure, which is the relation commonly observed between strain and stress in solid bodies.

The observed curve at 0° C. of Beadle and Stevens shows an abnormally low water absorption in the region of maximum swelling probably due to partial solution of the cellulose.

Transient Swelling

Neale has also examined the transient swelling of cellulose, i.e. that still greater swelling which takes place during the mercerising process when the alkali is removed by washing with water. From observations of the dimensional changes of

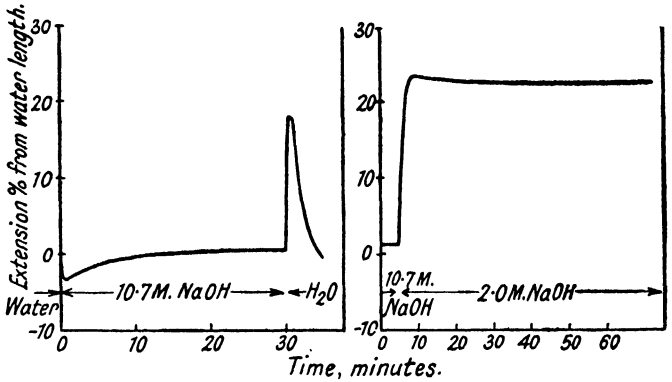


FIG. 79. FIG. 80.

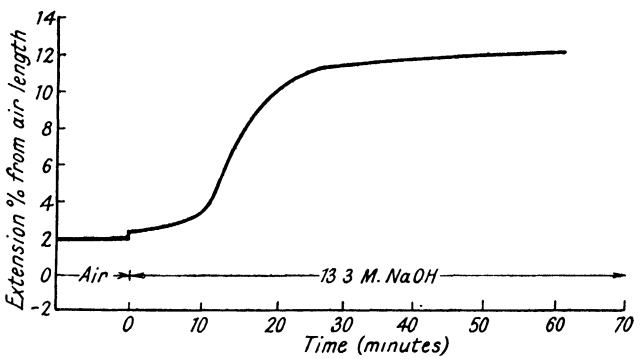


FIG. 81.—Transient swelling.
(Experiments with sheet viscose.)

strips of " cellophane " hung in tubes of the liquid which was rapidly changed and plotted against time, the complex phenomena was explained in terms of the osmotic theory of swelling on the grounds that the water diffuses through cellulose much more rapidly than does sodium hydroxide or its ions. If the external solution, i.e. sodium hydroxide, is suddenly replaced by water, the strong water attraction of the alkali cellulose phase is no longer partially balanced by the

opposing water attraction due to the alkali in the external solution. The osmotic pressure or swelling tendency is greatly increased momentarily, and this results in the temporary excessive swelling on account of the greater speed of the water molecules which enter the cellulose more rapidly than the alkali leaves it. After a short time, however, the alkali leaves the cellulose to such an extent that the osmotic pressure and hence the swelling become very small. These effects are shown by the following graphs. It will be noticed that in figure 80, which shows the change from 10·7 to 2·0 molar alkali, a similar transient swelling is observed to that which takes place with water (figure 79), but equilibrium is considerable and the contraction slight. Figure 81 shows the results of an experiment in which a strip was conditioned over 13·3 M alkali and then immersed. Since the cellulose was made isotonic with the alkali solution before immersion there was no rapid effect due to diffusion of water, and as the water and alkali diffused into the gel together the water following as required after the slowly moving alkali caused more gradual swelling. The initial lag period is probably due to the alkali swelling the outer layers chiefly in the direction of thickness.

The transient swelling effect was also observed by Willows, Barratt and Parker (loc. cit.) in experiments on the contraction in length of cotton hairs. Transient swelling is evidenced in the work of Birtwell, Clibbens and Geake on modified cellulose (see page 220), when a greater proportion of modified cellulose is dissolved by successive treatment with 10 N and 1·75 N sodium hydroxide than by a treatment with either single solution. (J.T.I., 1928, *19*, 349.)

The transient swelling effect is of considerable commercial importance, not only in the mercerisation of cotton, but chiefly in the mercerising of cotton-rayon mixtures which might result in such severe swelling of the rayon that it is completely destroyed from a textile standpoint. This is obviated by washing with hot water (B.P. 295,062) or by the substitution for water of a concentrated aqueous solution of common salt (B.P. 323,307), which has a high osmotic water attraction. This preliminary wash in brine removes the bulk of the absorbed alkali, without undue swelling.

Conclusions

Neale's explanation of the mercerising and swelling processes is based on the inference that the fibrillar micelles are roughly

parallel to the axis of the cotton hair or rayon filament. When the cellulose takes up water, the hydroxyl groups of the long chains attract water molecules, and the structure expands transversely as some of the mutual secondary valence linkages between the cellulose hydroxyl groups are broken and replaced by water-hydroxyl linkages. In alkali solution, the sodium ions replace some of the hydroxyl hydrogen atoms, setting up a system of high ionic concentrations. Water tends to enter such a system on account of the phenomenon of osmosis and in consequence more secondary linkages between the micelles are broken and replaced by linkages with alkali or water. When the alkali cellulose is washed, the sodium ions and hydroxyl ions diffuse away, and the cellulose gel contracts by virtue of its elasticity as the osmotic pressure falls. During this contraction the hydroxyl-hydroxyl linkages are reformed but not in such great numbers as before, and the orientation of the micelles in " mercerised " products is more random than in the original cotton cellulose. This accounts for the alteration in properties which will be described later (see page 187).

Orientation of the fibrillar micelles causes the swelling of cellulose to be directional; cotton hairs contract in length, whereas sheet or filament rayon swells transversely but shows comparatively little change longitudinally. The contraction of the cotton hairs has been ascribed to the spiral arrangements of the micelles, but it could also be explained by the transverse separation of the fibrillar micelles, between points of mutual attachment on lines roughly parallel to the axis, drawing the points nearer together, just as a trellis expands in one direction whilst contracting in another. The effect of tension in reducing the swelling of cotton hairs (Urquhart and Williams—J.T.I., 1925, *16*, 155), and the increased extensibility of mercerised cotton are corrollary to the fact that the hairs tend to shrink in length when swollen with alkali.

Neale's theory points to a maximum swelling pressure at moderate concentrations of alkali (about 15%), which is in agreement with the striking but previously unexplained phenomenon of maximum swelling concentration. It accounts in a quantitative manner for the observed alkali absorption, and for the observed heat of reaction/alkali concentration curve. The calculated curves of osmotic pressure as a function of alkali concentration show a temperature effect in agreement with observations. The theory also explains transient swelling and is supported by the satisfactory mercerisation of cotton

and viscose rayon mixtures with caustic soda followed by washing in brine.

Effect of Low Temperatures

Some interesting results of the effect of temperature on the shrinkage of yarn when placed in solutions of NaOH and KOH have been recorded by Birtwell, Clibbens, Geake and Ridge (J.T.I., 1930, *21*, 85). The results are shown in the following curves, and it is interesting to note that the great increase in shrinkage which takes place at very low temperatures is not reflected in the absorption ratio or reactivity ratio (see page 187).

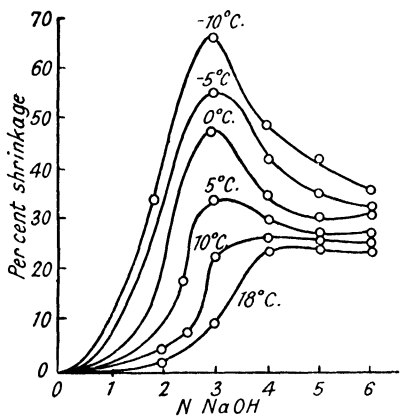


FIG. 82.—Effect of temperature on shrinkage.

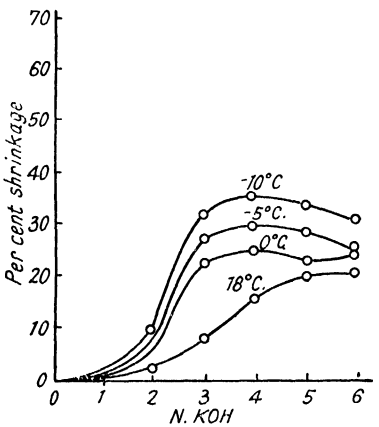


FIG. 83 —Effect of temperature on shrinkage.

Native Cellulose

The use of low temperatures to facilitate the preparation of solutions of cellulose in sodium hydroxide solution has been patented by Lilienfeld (B.P. 212,864). According to Foltzer ("Artificial Silk and its Manufacture"—Woodhouse's translation—London, 1921, page 103) Beltzer introduced wood pulp uniformly into caustic soda lye of 10° Bé. (sp. gr. 1·0744) at 0° to −5° C. Swelling took place and an almost complete solution is obtained when the temperature is lowered to −10° C.

The later B.P. 212,864 states that the cellulose should be mixed with alkali of less than 15% strength and the mixture cooled to below 0°—preferably to between −5° and −10° C., until solution is complete. The strength of caustic soda is

preferably 4% to 10%. Suitable coagulants for the cellulose solution are 10 to 20% H_2SO_4, salts, alcohol, etc. A solution prepared at −5° C. may give brittle films, whilst a solution of identical composition at −9° to −11° C. gives strong films. The cellulosic starting product may be in the form of bleached or unbleached cellulose, oxycellulose, mercerised cellulose, alkylated cellulose or regenerated cellulose. An example of the patent states that 10 parts of cotton wool or sulphite cellulose are mixed with 190 to 240 parts of 8 to 10% NaOH until homogeneous. The mixture is cooled with stirring to −9° to −10° C. when it is partially frozen. Cooling is then stopped and the temperature quickly raised with or without the application of gentle heat. At −5° to −3° C. the solution should be free from crystals and may be used at once, after filtering if necessary, or may be left to attain room temperature.

Hall (J.S.D.C., 1929, *45*, 98) states that attempts to dissolve cotton in 8% NaOH at 0° to −9° C. were unsuccessful, the resulting product always containing a large proportion of finely divided cotton. In contrast, viscose rayon easily dissolves under the same conditions.

It seems probable that some pre-treatment is necessary of the type now fairly general for most other preparations of solutions of cellulose either to damage the cuticle which normally restricts swelling, or slightly to degrade or modify the cotton cellulose and so facilitate solution.

Rayon

The affect of low temperatures in increasing the solubility of wood pulp and viscose rayon has been shown by D'Ans and Jager (Cellulosechem., 1925, *6*, 137).

Davidson (J.T.I., 1936, *27*, 112) examined the swelling of regenerated cellulose sheet in solutions of potassium hydrate adopting the technique of Neale as already described. The results are shown in figure 84. This investigation arose from the unusual nature of the solubility of oxycellulose in KOH (see fig. 134), when it became necessary to establish whether a similar feature existed in the swelling curves. Sheet viscose was utilised, on account of its low solubility in solutions of potassium hydroxide. The total swollen weight, the alkali absorbed and the water absorbed all pass through a maximum at an alkali concentration of between 4·5 and 6 N. When the temperature is reduced, the absorptions are increased and the maxima occur at lower concentrations. Comparison of the

total swollen weight curves with the solubility curves for oxycellulose showed that whereas the maxima correspond, the minimum in the solubility curves has no counterpart in the swelling curves. Solubility measurements were therefore made on regenerated cellulose under the same conditions—see Figure 85.

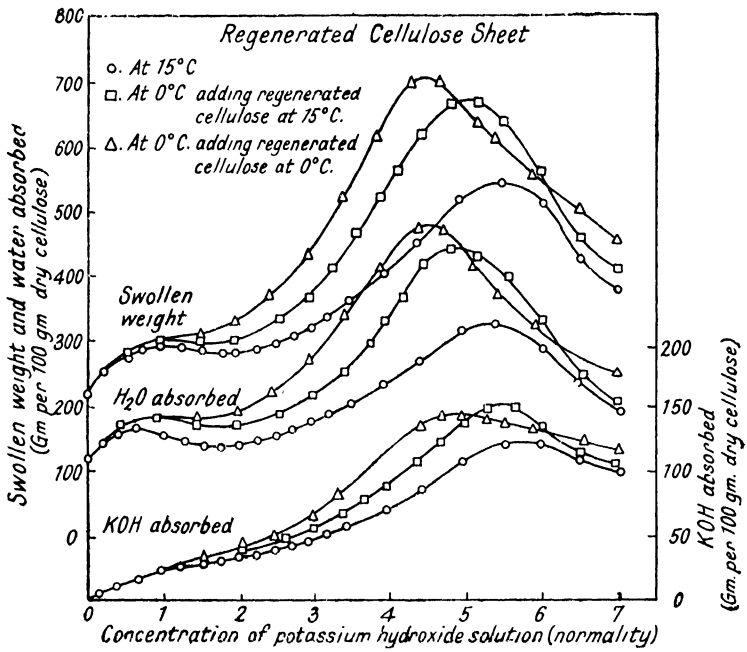


FIG. 84.—Swelling and absorption in KOH solutions (cf. Fig. 134).

The maximum fraction of the material dissolved was only 7% even at 0° C. With regenerated cellulose there is good correlation between swelling and solubility.

The solubility of regenerated cellulose in the form of " Cellophane " was also determined in solutions of sodium hydroxide at temperatures of 25, 20, 15, and 0° C. The results are shown in Figure 86, and indicate that at each temperature there is a certain maximum solubility at a certain alkali concentration, and that this maximum increases as the temperature is lowered. Neale (J.T.I., 1929, *20*, 373) found that at 25° C. the maximum swelling occurred at an alkali concentration of about 3·2 N,

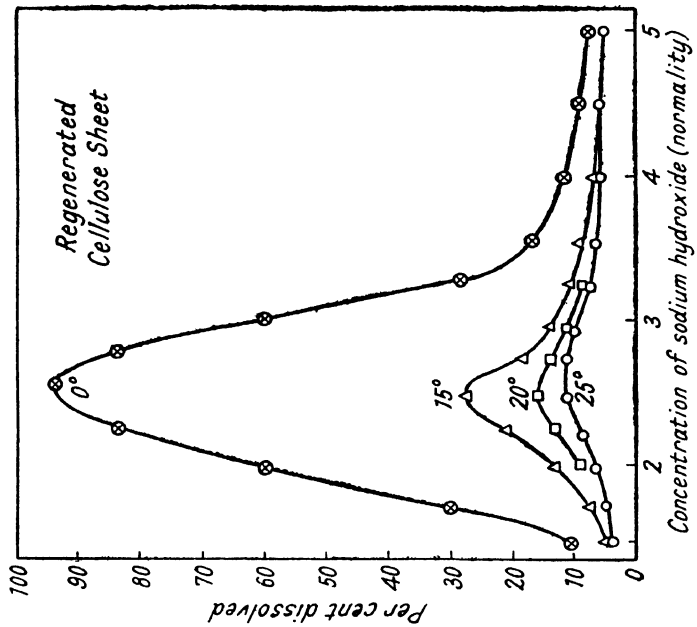


FIG. 86.—Solution of viscose in NaOH.

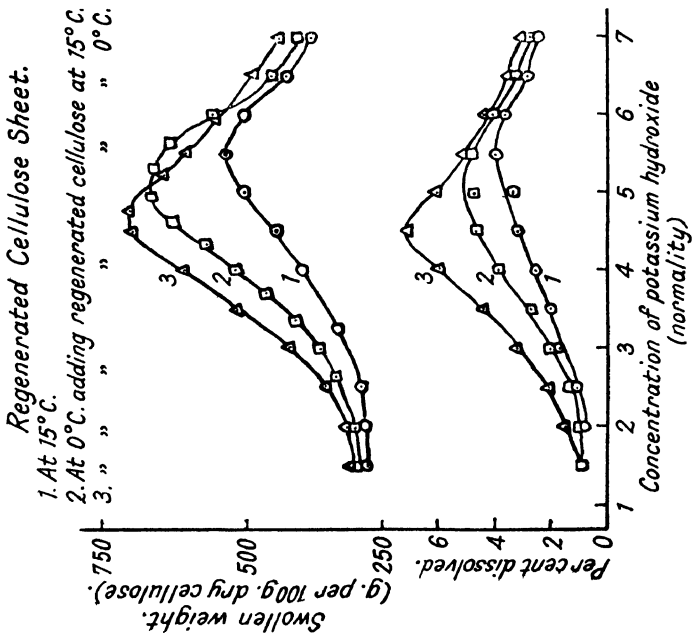


FIG. 85.—Swelling and solution of viscose in KOH.

but maximum solubility at the same temperature is shown with 2·75 N solution.

Hall (J.S.D.C., 1929, *45*, 171) had previously observed that viscose rayon swells and contracts to a much greater extent in solutions of NaOH than in KOH. It was not possible to dissolve viscose rayon in 10% KOH solution at 0° to -10° C., whereas under similar conditions the rayon readily dissolved in 8% NaOH. Hence by use of KOH solutions in place of those of NaOH it is possible to mercerise cotton and rayon mixtures without deleterious effect on the rayon—B.P. 295,488.

Strong Organic Bases

The swelling and solvent action of strong organic bases of the type of the quaternary ammonium compounds has received some little attention.

Quaternary Compounds

Knecht and Harrison (J.S.D.C., 1912, *28*, 224) and Dehnert and König (Cellulosechem., 1925, *6*, 1) have shown that tetramethylammonium hydroxide mercerises cotton, whilst the later work of Lieser and Leckzyck (Ann., 1936, *522*, 56) states that solutions of 2·3 N to 4·0 N tetræthyl ammonium hydroxide, 2·1 N to 3·6 N trimethyl-p-tolyl ammonium hydroxide and 1·7 N to 2·4 N tributylethylammonium hydroxide cause cotton cellulose to pass into solution. Above and below these concentrations strong swelling was observed.

Lilienfeld in B.P. 217,166 had already found the use of quaternary ammonium bases at low temperatures, and observed that 10 parts of cellulose when mixed with 190 parts of a 20 to 50% solution of tetræthylammonium hydroxide or phenyl trimethylammonium hydroxide at room temperatures and cooled to -11° C. readily passed into solution. Tetramethylammonium hydrate is also mentioned. The above example refers to undamaged cotton, but bleached or mercerised cotton is stated to dissolve at 0° C., whilst regenerated cellulose passes into solution at room temperatures.

According to Lieser (Ann., 1937, *528*, 276) the dissolution of cellulose in tetra-alkyl-ammonium, -phosphonium and -arsonium, and tri-alkyl-sulphonium and -selenonium bases increases with increase in the molecular volume of the solvent; thus, tetramethylammonium hydroxide does not dissolve cellulose but a 2·3 N solution of tetra-ethyl ammonium hydroxide gives a clear solution. The least concentration of the base

necessary for solvent action falls with increasing molecular volume, but solvent power is only exerted by solutions within a narrow range of concentration ; more concentrated solutions merely cause swelling. Lieser considers the solution is due to the formation of a molecular compound. If solutions in the bases under consideration are dialysed against sodium hydroxide, it is possible to obtain solutions of cellulose in sodium hydroxide as dilute as 0·7 N. From this observation it would appear that cellulose is fundamentally soluble in dilute sodium hydroxide solution, provided that the micellar structure has been disturbed by solvation of the main valencies of the micelles. Lieser points out that the solubility of cellulose in dilute alkali after regeneration from a solution in cold, super-concentrated hydrochloric acid may be explained on these lines.

B.P. 439,806 states that while the strong bases such as guanidine and dimethylguanidine appear to have less swelling action than solutions of the inorganic hydroxides, none of them give filterable solutions of cellulose suitable for spinning regenerated fibres. Quaternary ammonium bases containing a benzyl group, however, cause substantially complete and rapid dissolution of cellulosic materials. Aqueous solutions of benzyl substituted ammonium hydroxides possess this solvent property when the concentration is of the order 25 to 50 %, and when these solutions are diluted with water or alkali they become powerful swelling agents, depending on the degree of dilution. Solutions of trimethylbenzylammonium hydroxide with a concentration greater than twice normal, form clear solutions of cellulose, but when this hydroxide is diluted with water to give a normal solution it is no longer a solvent, but exerts powerful swelling action and may be used for gelatinising or mercerising. The normal solution when cooled to temperatures substantially below 0° C. exhibits an improved swelling action but does not become a true solvent for cellulose.

The temperature at which cellulose is dissolved has little effect on the rate of solution, but weak aqueous solutions of the bases are improved as swelling agents at temperatures below 0° C. Solvent action is usually found at concentrations of 25 % and over, but the minimum concentration depends on the chemical nature of the particular compound. For example, a 2·1 N solution of tri-methylbenzylammonium hydroxide, which is equivalent to a 35 % solution, is a very effective solvent for

cellulose, but on dilution to 1·9 N it loses its solvent action and becomes a swelling agent, whereas a 1·8 N solution of dimethylbenzylphenylammonium hydroxide, equivalent to a 42% solution, is a powerful solvent which also becomes a swelling agent on dilution. Other benzyl-substituted ammonium hydroxides mentioned in the patent specification are triethylbenzylammonium hydroxide, dimethylphenylbenzylammonium hydroxide, the corresponding diethyl com-

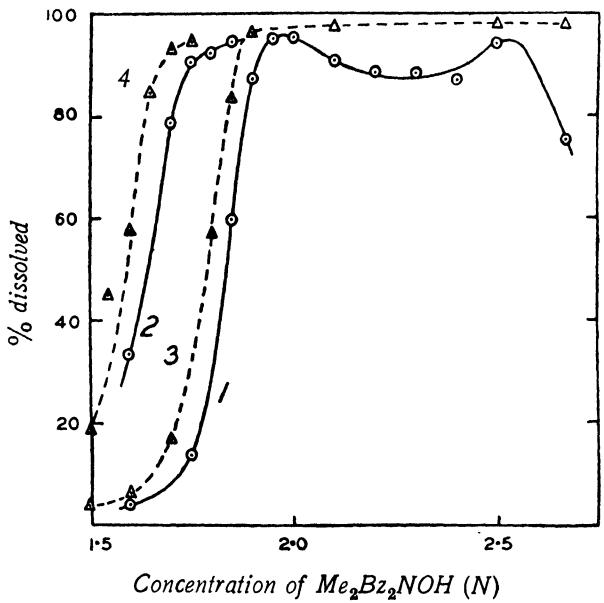


FIG. 87.—Fractional solubility of modified cottons in dimethyldibenzyl ammonium hydroxide. (1) Fluidity 5·6, temp. 20° C., (2) fluidity 5·6, temp. 0° C., (3) fluidity 17·2, temp. 20° C., (4) fluidity 17·2, temp. 0° C.

pound, dimethylamylbenzylammonium hydroxide, dimethyldibenzyl ammonium hydroxide and benzylpyridinium hydroxide.

Lieser (Ann. 1937, *528*, 276) has explained the swelling and dissolution of cellulose by the introduction of a large molecule between the cellulose chains so that solvent action increases with molecular volume of the solvated base; the molecular weight gives a measure of the molecular volume amongst the closely related substances forming the group of quaternary ammonium hydroxides. Sisson and Saner (J. Phys. Chem.,

1939, *43*, 687) by means of X-ray analysis, showed that the lattice of cellulose was extended during the formation of the "alkali cellulose," but there was no difference between trimethylbenzyl and dimethyldibenzyl ammonium hydroxides in spite of the large difference in molecular weight and solvent action.

Dimethyldibenzyl ammonium hydroxide is not only a powerful solvent for cotton but the resulting solution can be considerably diluted without precipitation of the cellulose. For

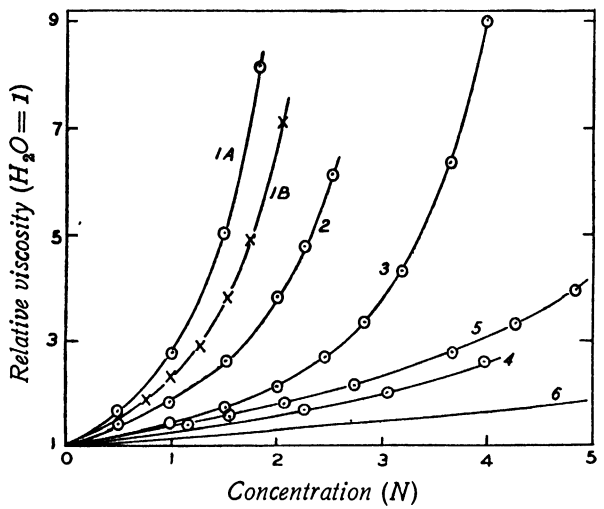


FIG. 88.—Relative viscosities of aqueous solutions of different bases at 20° C. (1) Dimethyldibenzylammonium hydroxide (deliveries *A* and *B*), (2) trimethylbenzylammonium hydroxide, (3) tetramethylammonium hydroxide, (4) sodium hydroxide, (5) lithium hydroxide, (6) potassium hydroxide.

instance, 1 % solution of cotton in the 2*N* base can be diluted to twice its volume or 0·75 % solution to four times its volume.

The solubility of cellulose in quaternary ammonium hydroxides has recently been examined by Brownsett and Clibbens (J.T.I. 1941, *32*, 32) when it was confirmed that the dimethyldibenzyl compound was the most powerful solvent. The solubility is shown in the following figure which refers to both unmodified cotton and modified cotton.

The percentage solubility of dissolved cotton or modified cotton is not calculated on the weight of solution but on the total weight of cotton originally treated with the base—the

curves, therefore, show the extent of complete dissolution under the particular conditions; this method of expressing the results is common for discussions on modified cellulose because the extent of dissolution indicates the chain length distribution, i.e., the results express the proportions of cellulose below a certain chain length.

Brownsett and Clibbens have compared the solvent action of various bases with their viscosity in equivalent aqueous solutions, in view of the suggested relation between solvent power and molecular volume. Except for sodium and lithium hydroxides there appears to be qualitative agreement between solvent power and viscosity, the more viscous bases being better solvents. This observation about viscosity is of particular interest for solutions of sodium and potassium hydroxides, whose solvent and swelling power increase with decrease of temperature; they also become more viscous. Sodium hydroxide is a better swelling agent than potassium hydroxide, and is more viscous in equivalent concentration.

An interesting point about the solutions of undegraded cellulose in quaternary benzyl ammonium hydroxides is that they may be diluted with NaOH solutions.

The American specification corresponding to B.P. 439,806 is U.S.P. 2,009,015, and in a later publication U.S.P. 2,040,065 the question of mercerising is discussed. Dimethylbenzylphenyl ammonium hydroxide in 42 % solution is a solvent for cellulose, but when diluted to 21 % concentration it loses its rapid solvent action and becomes a swelling or mercerising agent. In general, the quaternary benzyl ammonium hydroxides are good mercerising agents provided their concentration does not exceed 25 %. An example is given of 25 % trimethylbenzyl ammonium hydroxide producing 33 % increase in tensile strength of cotton after 5 minutes treatment at 0° C.; 20 % NaOH solution under similar conditions gave 16 % increase in strength.

Cellulose is likewise soluble in the oxides of tertiary amines according to B.P. 480,408, and may be regenerated by water, alcohol or dilute acid. Triethylamine oxide or dimethylcyclohexylamine oxide are exemplified as solvents for cellulose and seem to require temperatures of the order of 60 to 80° C.

Organic sulphonium hydroxides have also been protected as mercerising and swelling agents, e.g. B.P. 281,473 refers to the use of 4·8 N aqueous trimethylsulphonium hydroxide.

F.P. 723,600 discloses solvation effects by means of the salt

of a quaternary ammonium base dissolved in a nitrogen-containing solvent such as aniline or pyridine. Examples of suitable salts are benzylpyridinium chloride, allyl pyridinium chloride and ethyl pyridinium chloride. These cases, however, should really be considered in connection with the action of salt solutions on cellulose. All the examples require temperatures of the order of 100° C. in order to effect solution—a point of resemblance to the action of inorganic salts (see page 162) whereas the basic compounds previously considered require low temperatures and moderate concentrations.

Liquid Ammonia

Bernardy (Z. angew. Chem., 1925, *38*, 838) has recorded that when cellulose is treated with liquid ammonia at −33 to −35° C. swelling takes place. The use of liquid ammonia has been protected in B.P. 374,791 for the mercerising of rayon. The ammonia is removed by suction, and it is claimed that the viscose rayon is improved in respect of strength and elasticity. Barry, Peterson and King (J.A.C.S., 1936, *58*, 333) have examined the effect of liquid ammonia on ramie, and state that a very pronounced distention of the crystal lattice takes place as shown by the X-ray diagram. When the ammonia-cellulose was heated for several hours at 105° C., it lost its ammonia and gave a diffraction pattern which was very similar to that of mercerised cellulose. Hess and Trogus (Ber., 1935, *68*, 1986) have stated that when dry cellulose is treated with ammonia at −77 to −80° C., the latter condenses on the fibre, but after removal of the ammonia by distillation the fibre is unaltered. The X-ray diagram of the ammonia-cellulose indicated the formation of an addition compound, which was different from those previously obtained with hydrazine, ethylenediamine, etc. (Z. physik. Chem., 1931, *14*, 387), where the increase in the lattice was proportional to the length of the incorporated molecule. When the addition compound was decomposed by dilute acid or water, the pattern of the regenerated cellulose was found to be the same as that of the untreated material.

CHAPTER EIGHT

TREATMENT WITH HYGROSCOPIC SUBSTANCES

Solutions of Inorganic Salts

GENERAL.

The swelling of cellulose in salt solutions, discovered by Mercer, has been examined by von Weimarn (Kolloid Z., 1912, *11*, 41), who stated that any salt solution will disperse cellulose if applied under suitable conditions of temperature and pressure. Sodium chloride, for example, in concentrated solution at 170° C. requires eight atmospheres pressure and the sol is coagulated by cooling or dilution. The most efficient salts are those which become hydrated easily and are very soluble in water, e.g. the thiocyanates of barium, calcium, strontium and manganese and the iodides of sodium, calcium, strontium and lithium. The process follows the typically colloid course of passing through a gelatinous plastic state in which the cellulose is more or less transparent before reaching the sol condition. Schwalbe, however (Farber Zeit., 1913, page 434), denied that sodium chloride will dissolve cotton, whilst Herzog and Beck (Z. physiol. Chem., 1920, *111*, 287) stated that only certain salt solutions possess solvent properties and instanced negative results in a large number of cases. They put forward the theory that the solubility of cellulose in salt solutions is a function of the degree of hydration of the ions and increases with it, so that the solvent power of a salt follows from the series :

$NH_4 < K < Na < Li$; $Ba < Sr < Ca$; $\frac{1}{2}SO_4 < Cl < Br < I < CNS$.

As a working hypothesis it was suggested that complexes of cellulose, salt and water are first formed and then broken down by the carbohydrate adsorbing the water.

An interesting paper on the solubility of cellulose in solutions of inorganic salts has been published by Gerritsen (Chem. Weekblad, 1936, *33*, 405).

Deming (J.A.C.S., 1911, *33*, 1515) put forward the view that the solvent action of such solutions as zinc chloride is due to the acid formed by hydrolysis of the salt. Many solutions and mixtures were examined, mainly using filter paper, and were found to vary in efficiency but all the diluted sols coagulated on standing.

Williams (J.S.C.I., 1921, *40*, 221T) put forward a theory which bears certain resemblances to the hypothesis of Herzog and Beck, and which was based on his study of the action of the thiocyanates. Salt solutions which are solvents for cellulose must possess a positive heat of dilution, that is to say, the ions or molecules possess a power of combining with water. Cellulose is similarly capable of combination in view of its hydroxyl groups, so that when the temperature rises the water-salt complex tends to dissociate and the freed water molecules migrate to the cellulose, causing further swelling.

Thiocyanates

The solvent power of solutions of thiocyanates was discovered by Dubosc (Bull. Soc. Ind., Rouen, 1905, page 318), who worked mainly with the thiocyanates of ammonium, sodium, potassium, calcium and iron. The solvent power increases with the temperature of the solution, but some thiocyanates appear to be without action, according to Herzog and Beck (loc. cit.). A number of applications of thiocyanates to cellulose for technical purposes have been protected by patents. Calcium thiocyanate solutions are very efficient solvents and it is possible to obtain sols which set to solid gels. Their initial effect on cellulose is mainly one of swelling followed by the formation, on stirring, of a thick viscous system which slowly becomes thinner. The viscous stage may be eliminated by the previous addition of acetic acid. Williams also observed that the solvent action of thiocyanates is increased by the addition of acid and reduced by alkali. If no acid is added, then in order to effect direct solation, the salt solution must possess a certain minimum boiling point, minimum viscosity and positive heat of dilution.

A solution of $Ca(CNS)_2$ of such a concentration that it boils between 135 and 150° C., will dissolve cotton when heated to 80 to 100° C., but a solution boiling below 133 or above 150° C. has no solvent action, although the fibres parchmentised and swollen. Thiocyanate solutions must have a positive heat of dilution not greater than 3,500 calories, and the viscosity must be at least 3·3 times that of water at 20° C.

NaCNS is not a cellulose solvent at any concentration under atmospheric pressure, but as it has a positive heat of dilution when concentrated, additions may be made which increase its viscosity, but do not reduce the heat of dilution and so make the solution capable of dissolving cellulose. This result may be

accomplished by the addition of thiocyanates of Mn, Al, Zn, etc., the two latter not being themselves solvents for cellulose. The same result may be obtained by dissolving in the solution the sparingly soluble thiocyanates of Hg, Cu, Ag or Pb.

The fact that the high boiling solutions of $Ca(CNS)_2$ do not dissolve cellulose is not due to the increased viscosity of the solution according to Williams, but rather to the fact that as the concentration rises, the salt will tend to hold the water more firmly and thus retard the hydrating action, so that a point may be reached where the affinity of the water for the salt is so great as to transform any hydrating action into a dehydrating effect. The addition of a few drops of water to such a high boiling solution containing cellulose, sufficient to lower the boiling point to 148–149° C., causes solution of the cellulose in a few seconds.

In addition to the advantageous effect of acetic acid in facilitating solution (the presence of 2–4 % enabling solutions containing 10 to 12 % of cellulose to be obtained as easily as 4 % solutions in its absence), Williams found that part of the $Ca(CNS)_2$ may be replaced by certain salts which do not react chemically with it, but retain its boiling point and other necessary properties. Calcium chloride may be used in various proportions up to equal volumes of the two solutions, without interfering with the solvent properties of the $Ca(CNS)_2$ that is to say, the mixture will dissolve the same maximum amount of cellulose with the same ease as the $Ca(CNS)_2$ solution of the same boiling point. A solution of 7 % cellulose in the calcium chloride-calcium thiocyanate mixture and kept warm, may be used for the preparation of fine filaments by " spinning " through fine orifices into a precipitating mixture of water and alcohol (50-90 % C_2H_5OH).

Whereas cellulose only dissolves in the above solutions on warming, the interesting observation was made by C. F. Cross that solution may be effected in the cold by means of the intervention of formaldehyde. The actual technique is to soak cellulose for some hours in the cold in a mixture of four parts of $Ca(CNS)_2$ solution of sp. gr. 1·38 and one part by volume of 40 % formaldehyde. The fibres swell in the mixture but no other action takes place until the solution is diluted with an equal volume of cold water when the cellulose immediately passes into solution. Solutions containing up to 4 % of cellulose may be obtained in this manner. The reaction appears to be a general one as similar results are obtained by

using solutions of zinc chloride, strontium or lithium thiocyanate, etc., of appropriate strength mixed with 25% of 40% formaldehyde solution. The use of calcium chloride in the formaldehyde mixture has a retarding effect, probably on account of its dehydrating action. The addition of formaldehyde to the thiocyanate solution lowers the surface tension, but does not materially affect the viscosity or heat of dilution of the mixture; whilst the replacement of the formaldehyde solution by water lowers the viscosity and the heat of dilution, it does not alter the surface tension, but no solution of the cellulose takes place on dilution.

The use of strong solutions of $Ca(CNS)_2$ for parchmentising effects necessitates a mixture of calcium chloride-thiocyanate or calcium thiocyanate which boils at 155–157° C. and is used at 130° C. The material is in contact with the hot liquid for about 30 seconds and is well washed in running water afterwards.

A weaker thiocyanate bath cannot be used with success as it would partially dissolve the cellulose, but if the cellulose, when it leaves the parchmentising bath, is passed through a second bath at 40–60° C. of thiocyanate of slightly lower strength (b.p. 135–140° C.), squeezed, heated for 30 minutes at 120° C., cooled, washed and dried, a very fine vulcanised fibre is obtained resembling vegetable ivory. The dried mass contains no indication of the original paper.

Mercerising effects may be obtained on cotton cloths by treatment with 60% solutions of calcium thiocyanate; the fabric shrinks and the lustre and dyeing properties are enhanced. If, however, the material is immersed in hot solution of $Ca(CNS)_2$ then the fabric becomes stiff permanently whereas the cold solution leaves the material soft and pliable. Experiments on cotton yarn in cold solutions of 60% strength show that the cotton shrinks about 16% of its original length if added to the bath dry, and about 21% if a wetting treatment has previously been given.

It is interesting to note the calcium thiocyanate in concentrated solution will also dissolve cellulose acetate and natural silk but is without action on wool.

Iodides

Pope and Huebner (J.S.C.I., 1903, *22*, 70) found that when a cold, saturated solution of potassium iodide is applied to cotton, the material immediately wets and becomes glassy

and transparent. Shrinkage of the cotton hairs takes place and there is also slight swelling but without de-convolution, although there is an increased tensile strength. All the potassium iodide may be removed by washing with water, but the cotton retains some 15% of KI on being washed with absolute alcohol instead of water.

A hot saturated solution of KI at 120–140° C. produces definite swelling of cotton but the structure is still retained. Barium iodide exerts a similar effect, but a saturated solution of potassium mercuric iodide is a good solvent for cellulose, swelling and gelatinising the fibres immediately (*ibid.*, 1904, *23*, 404).

Sodium Sulphide

The use of 30% aqueous sodium sulphide solution for mercerising cotton was patented by Schneider in 1896 (B.P. 19,428), but when Huebner and Pope examined this reagent (loc. cit.) they found only slight swelling and de-convulution of the fibre. Lilienfeld, however, in B.P. 323,174 describes the mercerising of cotton in warm or hot solutions of alkali sulphide containing not less than 25% of sulphide calculated as Na_2S, $9H_2O$, whilst Franke (Zeit. Ges. Textil-Industrie, *13*, 1933) gives particulars of the treatment of cotton with a 100% solution of Na_2S, $9H_2O$ at 115° C. for five minutes, whereby the strength of the yarn is increased by 66% in the dry state and 59% when wet, compared with 16·5 and 17·3% respectively resulting from ordinary mercerising processes.

Zinc Chloride

Zinc chloride in 40% solution has been shown to gelatinise cotton at a gentle heat and produce a syrupy solution on further heating as described by Cross and Bevan (Cellulose, 1918).

Huebner and Pope (loc. cit.) found that at ordinary temperatures the effect of a 50% solution on single cotton hairs was one of slow swelling and slight untwisting. Puckered or crêpe effects combined with lustre were obtained by Grandmougin (Bull. Soc. Ind. Mulhouse, 1898, page 348) by printing with a 74% solution of zinc chloride and drying at 40–50° C., whilst Mercer himself in 1850 (B.P. 13296/1850) described the effect of a 59% solution at 65–70° C. Since then there has been quite a succession of patents dealing with various technical applications both for cotton and paper, and as would be expected from the results of swelling with other salt solutions

as already described, additions such as formaldehyde and also hydrochloric acid have proved of interest.

Other Salts

Calcium bisulphite solution has been shown by Councler (Chem. Zeit., 1900, *24*, 368) to modify and dissolve cellulose, but in the case of concentrated sodium bisulphite solution there appears to be no attack on cellulose even when heated in sealed tubes at 130–140° C. for 12 hours, according to Nastukoff (Bull. Soc. Ind. Mulhouse., 1892, *62*, 493), whereas oxycellulose is dissolved. Klason (Chem. Zeit., 1903, *27*, 585) records his opinion that cellulose proper is not dissolved by a solution of N/2 calcium or magnesium bisulphite but that hydrocellulose and oxycellulose are dissolved.

The action of perchlorates has been examined by Dobry (Bull. Soc. Chim., 1936, v. *3*, 312), and whilst some of these compounds dissolve cellulose acetate, cellulose itself is only soluble in the basic beryllium perchlorate.

Acids

The swelling action of acids on cellulose again requires the use of concentrated solutions as a general rule, although in the case of sulphuric acid swelling commences as the concentration rises above 50% and is followed later by solution. This, too, was discovered by Mercer.

Sulphuric Acid

The effect of 56% H_2SO_4 was examined by Girard (Ann. Chim. Phys., 1881, v. *24*, 337), and it was observed that the cotton hairs are swollen after a treatment of an hour. Huebner and Pope (loc. cit.) observed swelling, shrinkage and deconvolution of the cotton hairs when treated with 60% H_2SO_4 and that the cellulose slowly dissolved, but that the rate of solution was higher in more concentrated acid. When a solution of cellulose in sulphuric acid is diluted with a large volume of water amyloid is precipitated, but some of this is dissolved on further washing with water.

The products obtained from cellulose by the action of sulphuric acid for different periods of time have been classified by Bechamp (Ann. Chim. Phys., 1856, *48*, 458) as :

(1) the swollen or dissolved cellulose which is recovered as a gel and is insoluble in hot or cold water.
(2) a gel soluble in cold water ;
(3) cellulose dextrin ;
(4) sugars.

The action of sulphuric acid has been applied in industry for the treatment of paper and of cotton fabrics. The well-known parchmentised paper is obtained by passing the material through cooled acid at such a rate that the time of contact is very short—a matter of seconds and within the last 15 years a great deal of work has been done in applying similar processes to cotton goods. The momentary immersion is generally intended to increase the transparency and various strengths of acid have been suggested. For " mercerising " with sulphuric acid, however, the usual strength is 62% and the Heberlein Co., in particular, has taken out a large number of patents covering the treatment of cotton with sulphuric acid of various concentrations for certain definite times and temperatures, and sometimes in conjunction with mercerising by means of sodium hydroxide solutions before or after the acid treatment, in order to obtain a variety of effects ranging from linen-like, through transparent to wool-like. The addition of formaldehyde retards the action of sulphuric acid enabling the processes to be more easily controlled ; and Barrett and Foulds (B.P. 200,881) have described a process for the parchmentising of cotton fabrics at 10–15° C., with H_2SO_4 (sp. gr. 1·45–1·55), i.e. approx. 55–65%, containing 0·5 to 1% of 40% formaldehyde.

Cellulose is parchmentised by treatment with 78% sulphuric acid (sp. gr. 1·71), about 15 seconds at 10° C. being the usual conditions of treatment. The more concentrated acid, however, appears to act in a manner similar to that experienced with the 62% acid but more rapidly, and carbonisation is apt to take place unless the cellulose is pure. Parchmentising starts at 68 to 69% concentration.

Barrett and Foulds have also shown in B.P. 230,530 that cellulose which has been parchmentised by immersion for five seconds in sulphuric acid of 74% strength (sp. gr. 1·66) containing 0·5 of 40% formaldehyde may be softened by immersion in H_2SO_4 of 55% strength (sp. gr. 1·45).

Hydrochloric Acid

Concentrated hydrochloric acid causes slight swelling of cotton with a rapid untwisting of the hairs according to Huebner and Pope (loc. cit.). Cotton may be " mercerised " by the use of 36·3 to 37·2% hydrogen chloride ; at a slightly higher concentration (37·2 to 38·5%) it becomes transparent and highly swollen, whilst at concentrations of 38·9% and over the material is gelatinised and dissolves. The cellulose in

such a solution readily becomes degraded with time. Although hydrochloric acid is rarely used for dissolving cellulose, it has frequently been suggested in admixture with sulphuric or phosphoric acid or with inorganic salts.

Phosphoric Acid

Concentrated phosphoric acid causes a very slow untwisting and swelling of the cotton hairs followed by solution according to Huebner and Pope (loc. cit.). Here again the main suggestions as to its use are in admixture with sulphuric, acetic or formic acids.

Nitric Acid

Knecht (J.S.D.C., 1896, *12*, 89) observed that when cotton is steeped for a few moments in nitric acid of sp. gr. 1·415 it becomes gelatinous and on washing with water it shrinks, and gains both in lustre and tensile strength. According to patents specifications 67·5 to 74·4 % of nitric acid appears to be a suitable range of concentrations for mercerising. Huebner and Pope (loc. cit.) showed that 68·6 % HNO_3 causes the cotton hair to swell and untwist rapidly, but the swelling was not so severe as with caustic soda of mercerising strength. Haussermann (Z. angew. Chem., 1910, *23*, 1761) observed that 77·3 to 80·9 % nitric acid caused strong swelling, solution and nitration. The more concentrated acid showed a greater tendency to nitrate the cellulose although above 94 % a parchmentising or felting effect became apparent. Knecht, in a later paper (J.S.D.C., 1904, *20*, 68), stated that the nitric acid treatment increased the affinity of the cotton for direct dyestuffs and for moisture. A shrinkage of 24 % was reported, but with concentrations of acid lower than sp. gr. 1·415 there was less shrinkage and a diminution in tensile strength. The opinion was put forward that the treatment of bleached cotton with HNO_3 of density 1·415 leads to the formation of a nitrate $C_6H_{10}O_5.HNO_3$ which was hydrolysed by water to " hydrated " cellulose and nitric acid. This compound is sometimes referred to in the literature as Knecht's compound.

Budnikoff (Faser. u. Spinn., 1923, *5*, 64) confirmed many of Knecht's observations using HNO_3 of density 1·38 to 1·39 at 10–15° C., and recorded the increased lustre. Prolonged treatment of over 30 seconds, however, resulted in serious reduction of the tensile strength.

The chief technical application of nitric acid to cotton cloth, however, was that of the Philana A.G. of Basle, who worked

the " philanising " process of Schwartz (U.S.P. 1,384,677) for producing a wool-like texture. The unbleached unmercerised cloth is treated at room temperature with nitric acid of more than 65% strength, and then rapidly washed. The details of time and temperature varied according to the type of cloth, and examples range from 65 to 75% of acid for periods covering 1 to 5 minutes. It is also stated that the treatment may be prolonged up to even 30 minutes provided the temperature does not exceed 68° F., but even at 77° F. there is no material damage, but with acid concentrations over 75% the time of treatment must be very short indeed. The product is stated by Beil (Z. angew. Chem., 1924, *37*, 689) to have a harsh warm feel similar to that of wool. The tensile strength was increased by 50% and the wearing resistance by some 200-300%. The pale yellow colour, which resulted from the nitric acid treatment, was removed in the subsequent bleaching process.

Katz and Hess (Z. phys. Chem., 1927, *122*, 126) examined the X-ray spectra of philanised fibres of jute, ramie and flax which had been treated with 61% HNO_3, and found that the spectra did not resemble that of mercerised but of ordinary cotton, so that the process was physically distinct from mercerisation. Knecht's compound, however, had a distinctive X-ray spectrum.

Other Acids

Deming (J.A.C.S., 1911, *33*, 1515) observed that cotton is soluble in hot selenic acid, and also that arsenic acid will dissolve cellulose at ordinary temperatures and very readily on warming.

According to U.S.P. 763,473 of 1904, cotton is dissolved by treatment with sulphur dioxide gas in presence of water at 120 to 160° C.

Willstatter and Zechmeister (Ber., 1913, *46*, 2401) have stated that 48% hydrobromic acid gelatinises cotton and that partial solution takes place with 57% acid, whereas the use of 66% HBr causes complete solution at 6° C. The cellulose can be recovered quantitatively.

Concentrated solutions of hydriodic acid rapidly dissolve cellulose as observed by Deming (loc. cit.) whilst 70 to 75% HF rapidly swells and dissolves cotton according to the observations of Willstatter and Zechmeister (loc. cit.).

Methane sulphonic acid CH_3SO_3H is also stated to be a solvent for cellulose (F.P. 684,320).

CHAPTER NINE

TREATMENT WITH SPECIFIC REAGENTS

THE third type of substance which may be used consists of a group of particular reagents of a specific nature, which are generally supposed to act in virtue of purely chemical reaction.

Cuprammonium Hydrate

The effect of cuprammonium hydrate was discovered by Mercer and by Schweizer (J. pr. Chem., 1857, *22*, 109).

Cramer (J. pr. Chem., 1858, *73*, 1) investigated the action of cuprammonium-hydrate on cotton and observed that swelling generally preceded solution unless the reagent was very concentrated. Balls (Proc. Roy. Soc., 1918, *B90*, 542) was able to show the existence of daily growth rings in the cell walls by means of this reagent; unripe hairs do not swell appreciably or swell without dissolving. All the modified and regenerated celluloses swell and dissolve in concentrated cuprammonium and the solution of the cellulose is generally facilitated by previous treatments such as mercerising or bleaching. The existence of several cellulose copper complexes has been suggested, and Traube (Ber., 1921, *54*, 3220; 1922, *55*, 1899) formulated a theory of solvent action on chemical lines. Hess and Mesmer (Ber., 1922, *55*, 2432) concluded that when cellulose is dissolved in "cuprammonium," a complex copper-cellulose ion results, which forms with the cuprammonium cation the salt $[C_6H_7O_5Cu]_2Cu(NH_3)_4$. The hypothesis was based mainly on measurements of rotary power, but Neale (J.T.I., 1925, *16*, 363) pointed out that the solutions belong to the class of colloidal electrolytes, typified by soap solutions. According to this theory, the strong base cuprammonium hydroxide—$Cu(NH_3)_4(OH)_2$—which is only stable when the quantity of ammonia is greatly in excess of that demanded by this formula—forms with cellulose, which thus behaves as a weak acid, a soluble basic salt of which the cation is crystalloidal and the anion, colloidal. Cellulose neutralises the

cuprammonium to the extent of using completely the hydroxyl arising from the first dissociation of the substance; further action is presumably inhibited on account of the weaker dissociation of the base with respect to its second hydroxyl and by the impossibility of the existence of the soluble cellulose complex in any but a highly alkaline medium.

In addition to the regenerated celluloses, the modified celluloses (oxycellulose and hydrocellulose) are soluble in

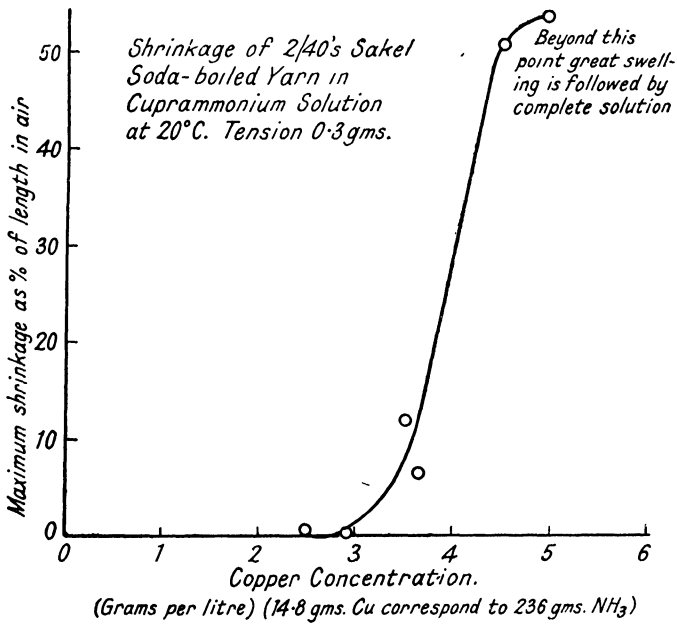


FIG. 89.—Swelling in cuprammonium hydrate.

cuprammonium hydrate. Solutions of other hydroxides in ammonia have been suggested, but they do not appear to be as efficient as copper hydroxide. Nickel ammonium hydroxide solutions dissolve cellulose, but according to Duyk (Chem. Zeit., 1901, *25*, 266) ammoniacal zinc hydroxide does not dissolve rayon although by the action of zinc on a cuprammonium solution of cellulose, Cross and Bevan (Cellulose, 1918) state that the corresponding zinc-ammonium solution could be obtained.

About thirty years ago, patents specifications disclosed the use of alkylamines and alkyleneamines as solvents for copper

hydroxide and hence for cellulose, but there have been no subsequent developments along these lines.

Traube (Ber., 1911, *44*, 3319) stated that primary aliphatic diamines saturated with cupric hydroxide have a greater solvent power for cellulose than cuprammonium solution with an equal ammonia concentration. Solutions containing as little as 2 to 8 % of ethylene diamine were effective solvents.

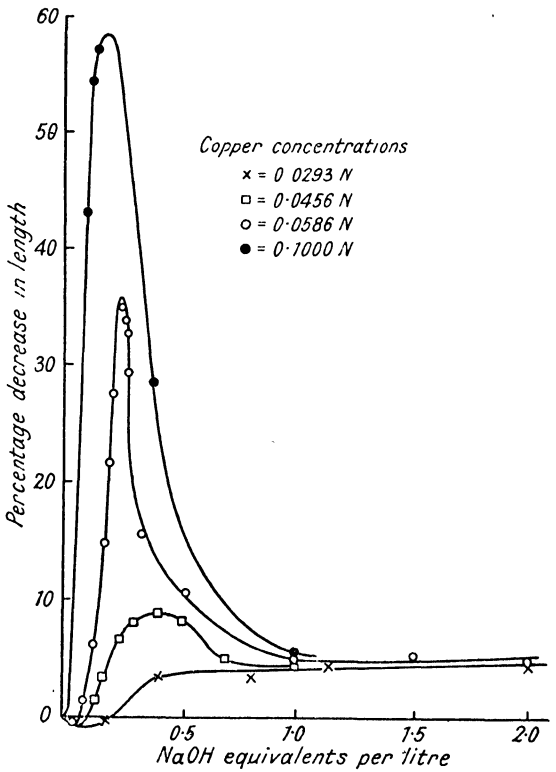


FIG. 90.—Addition of NaOH to cuprammonium hydrate as affecting shrinkage.

The relationship between the swelling of cotton and the concentration of this reagent as measured by its copper content has been demonstrated by Brownsett, Farrow and Neale (J.T.I., 1931, *22*, 357). [See Fig. 89.]

A solution containing less than 2·5 g. of copper per litre has no appreciable swelling effect.

It has been shown by Hess and Trogus (Z. physik. Chem.,

1929, *A145*, 401) that the addition of sodium hydroxide to the system cellulose-cuprammonium hydrate, causes an increase in the absorption of copper, whilst the amount of cellulose dissolved rises to a maximum and then falls. Neale and Stringfellow (J.T.I., 1932, *23*, 177) investigated the possibility of the addition of small amounts of alkali increasing the swelling effect and solvent power, it having previously been shown by Brownsett, Farrow and Neale (loc. cit.) that the alkali effects an increase in copper absorption even at concentrations so low that the cellulose is not swollen.

The linear contraction of cotton yarn was used as a measure of swelling. [See Fig. 90.]

Increasing the caustic soda concentration at a constant concentration of cuprammonium hydrate caused the shrinkage to increase to a maximum and then decrease. The maximum lies between 0·1 and 0·3 N. sodium hydrate according to the value of the copper concentration. The sharply defined maxima occur at values of NaOH concentration closely corresponding with those found by Hess and Trogus from measurements of the amount of cellulose dissolved. The effect of the added NaOH is considerable, as a solution of one tenth normal, both in copper and sodium hydrate, gives a shrinkage of approximately 50 % whilst a similar solution without caustic alkali is without appreciable effect. The yarn used showed a contraction of 18 % in the NaOH solution alone at a concentration of about 4 N. When the copper concentration was raised above 0·2 N the cellulose went into solution.

It was also found that the viscosity of the solution was unaffected by the presence of caustic soda up to the point where the solvent power of the solution was so reduced that the cellulose no longer dissolved completely.

Fluidity Measurements

The viscosity of a solution of cellulose in cuprammonium hydrate is extensively used as a routine test in textile laboratories for estimating the effect of technical processes on the strength of cotton goods. The work originated in connection with cellulose intended for the manufacture of explosives, and its historical development may be traced from the pioneer work of Ost (Z. angew. Chem., 1911, *24*, 1892), Gibson and his collaborators (J.C.S., 1920, *117*, 473 and 479) to that of Joyner (J.C.S., 1922, *121*, 1511 and 2395).

Farrow and Neale of the British Cotton Industry Research

Association, established a method (J.T.I., 1924, *15*, 157) of determining the extent of chemical attack on cotton during the processes of manufacture, which was based broadly on the technique developed by chemists in the explosives industry. The reagent recommended contains about 15 g. of copper and 240 g. of ammonia per litre, and sufficient cotton is dissolved to give a 2 % solution. An equation is given connecting viscosity and concentration over the range 0–3 % which may be applied to other solutions. The falling sphere method was used to measure the viscosity. It was found that the viscosity of a 2 % solution of a carefully bleached cotton cloth should lie between 300 and 10 c.g.s. units (log. η 2·5 to 1·0), and that the tensile strength of cotton hairs and yarn which had been chemically damaged by treatments such as oxidation or acid attack decreased with decreasing viscosity of the solution in cuprammonium hydrate.

Clibbens and Geake (J.T.I., 1928, *19*, 77) continued the work of their colleagues and reduced the technique to its simplest form, and embodied all the precautions found necessary as the result of considerable experimental work. The method is recommended by the Fabrics Research Committee of the Department of Scientific and Industrial Research. (The Viscosity of Cellulose Solutions, 1932.) See also J.T.I., 1936, *27*, 285.

As the most important feature of the measurements is the correlation with reduced tensile strength, it was found that neither the viscosity nor its logarithm was very suitable, but that the reciprocal of the viscosity or "fluidity" is more satisfactory, since when this is plotted against the extent of "tendering" the resultant curve approximates to a straight line. The increased extent of chemical attack is therefore accompanied by increased fluidity. The concentration of cellulose in the solution was lowered to 0·5 % in order to avoid a multiplication of apparatus. The absolute viscosity of a solution of cotton containing 0·5 g. per 100 cc. is generally about one poise, but more drastic conditions of preparation may reduce this to 0·2 without serious adverse effects on the quality of the material.

The cuprammonium solution contains 15 g. of copper, 240 g. of ammonia and less than 0·5 g. of nitrous acid per litre. It is prepared in a wide-mouthed earthenware bottle of about five litres capacity and closed by a cork carrying a centrifugal stirrer and air inlet tube, both of iron. The inlet tube ends in

an upturned jet which conducts the air into the trumpet shaped mouth of the stirrer. A mixture containing 2·6 litres of concentrated ammonia solution (sp. gr. 0·88), 0·4 litres of water and 3 g. of cane sugar is stirred at 400 r.p.m., with 180 g. of copper which has passed through a 60-mesh sieve, and air is blown in at the rate of 10 litres per hour through a wash bottle containing an ammonia solution of density 0·9. The approximate copper content of the solution can be followed by colorimetric comparison of a sample with a standard of the correct concentration, both diluted tenfold, and when it attains a value distinctly in excess of 15 g. per litre, the stirring and air supply are stopped. The preparation requires about five hours. If air is replaced by oxygen, the time may be reduced to one hour, but the solution generally contains more nitrous acid than is desirable. After standing for half an hour, the solution is syphoned off, and analysed for copper and ammonia, after the residual copper has been removed. The solution is adjusted to the desired concentration by dilution with the necessary amount of water and ammonia. The nitrous acid content is also checked by analysis and the preparation rejected if this proves to be above 0·5 g. per litre. The nitrometer method is used for the determination of nitrous acid, although this is apt to yield a maximum rather than an accurate value. For the analysis, 15 cc. of conc. H_2SO_4 are drawn into the nitrometer and carefully covered with water (1–2 cc.) before gradually admitting 5 cc. of the cuprammonium hydrate. If during the latter process, the mercury reservoir is held at its lowest position, and each small volume of cuprammonium solution is neutralised before the admission of succeeding portions, the reaction is not inconveniently vigorous. The cuprammonium hydrate solution is stored in a blackened bottle provided with a tubule and tap at the bottom, and connected at the top through a vessel containing alkaline pyrogallol with a gas holder (e.g. a Kipp's apparatus) filled with nitrogen.

The measurement of viscosity is based on the rate of flow and not on the " falling sphere " technique.

Preparation of the Cotton Solution and Determination of its Rate of Flow.

A viscometer of the form shown at *A* in Fig. 91 is used both for dissolving the cotton in cuprammonium and for determining

the fluidity of the solution. The wide body of the instrument has an internal diameter of 1 cm. and a length of approximately 26 cm., whilst the lower capillary *E* is 2·5 cm. long, 0·088 cm. in internal and 0·6 cm. in external diameter. The wide portion is etched with two rings, *D* and *B*, at heights of 6·2 and 24·2 cm. vertically above the flat end of the lower capillary, and the upper end of the instrument is closed with a rubber stopper carrying a second capillary *F*, the dimensions of which are unimportant. Each viscometer has an intermediate timing mark *C*. The measurement is made with a solution containing 0·5 g. of dry cotton in 100 cc. of solution, and for each instrument a record is kept of the weight of material required to yield a solution of this concentration when dissolved in the volume of cuprammonium necessary to fill the viscometer.

The cotton for measurement is preferably finely divided, and to secure this, yarn or loose cotton is cut across with scissors into lengths not greatly exceeding one-sixteenth of an inch, whilst cloth in narrow widths is similarly cut in a diagonal direction to break down both warp and weft threads. After the lower capillary has been closed with a short length of pressure tubing and clip, the viscometer with everything in position is filled three-quarters full with cuprammonium, a few drops are run out of the bottom, and the pre-determined weight of cotton added and mixed rapidly with the solvent by means of a thin glass rod. Mercury (0·7 cc.) is added, the viscometer is then completely filled with cuprammonium and the stopper inserted, so that excess of liquid, displacing all air, overflows through the top capillary and rubber tube. The latter is immediately closed with the clip, the stopper wired into position, and the viscometer, wrapped in black cloth, bound to the spokes of a bicycle wheel rotating at such a rate that during each half revolution the mercury falls from end to end of the liquid column. The agitation produced in this way by overnight running is sufficient to ensure complete and homogeneous solution of the cotton, a wheel rotating at the maximum rate of four revolutions per minute being suitable for the most viscous solutions encountered.

For the specification given above the volume is approximately 20 cc. so that roughly 0·1 g. of cotton is used in each determination. In view of this small weight care should be taken to ensure good sampling. Sufficient accuracy is attained for most purposes if unmercerised cotton, normal or modified,

is assumed to contain 6 % of moisture and allowance is made for this in calculating the weight of material to be used in each viscometer.

In order to measure the rate of flow of the cotton solution, the viscometer is removed from the wheel, the lower clip and rubber tube withdrawn, and the instrument hung in a wider tube in a thermostat at 20° C. After this temperature has

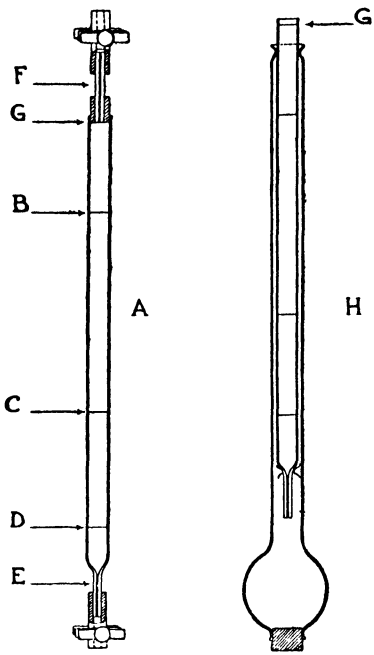


FIG. 91. FIG. 92.
Fluidity apparatus

been acquired the viscometer is placed in a glass jacket of the form shown at *H* in Fig. 92, which is supported vertically in the thermostat. The shape of the jacket is such that the viscometer rests on three glass points at the bottom, and is a sliding fit at the top in the constricted neck. The upper clip is then opened, the stopper removed, and the solution allowed to flow freely through the lower capillary. The time in seconds necessary for the liquid meniscus to fall from the upper to the lower ring is noted. The thermostat may be dispensed with in technical control work if the air temperature is not far from 20° C.

Standardisation of the Instrument and Expression of Result.

Owing to the fact that the rate of flow is dependent on the fourth power of the capillary diameter, it is not possible to make the viscometer so accurately to specification as to dispense with the necessity for separate standardisation. The instrument is calibrated by means of a mixture of pure glycerine and water, the specific gravity of which is 1·1681 in air at 20° C., compared with water at 20° C. (approximately 64·4% glycerine by weight). The viscometer is filled with this liquid, allowed to attain a temperature of 20° C., and measurement made of the time in seconds required for the meniscus to fall from the upper to the lower ring. For the purpose of routine works control, it is then sufficient to express the viscosity of any cotton solution as the ratio of the time taken by the cotton to that taken by the glycerine solution. The particular concentration of glycerine used for standardisation has, in fact, been chosen because its time of flow is equal to that of a 0·5% solution of cotton, which has suffered the maximum permissible chemical attack in bleaching and finishing. Thus the value one for the ratio referred to above represents a certain minimum standard which should be maintained in technical processes.

As will be explained later, it is more convenient for other purposes to express the results of rate of flow measurements in the form of absolute fluidities (reciprocals of the viscosities stated in poises). In order to do this it is only necessary to divide the "constant of the instrument," obtained as explained in the next paragraph, by the time of flow of the cotton solution.

At 20° C. the specific gravity (d) of the standard glycerine solution is 1·1681, and its fluidity (F) in absolute units is 6·83. If its time of flow in the standard viscometer is t seconds, the constant of the instrument,

$$C' = 1 \cdot 075 \ (dFt)$$

and can be readily calculated when F, d and t are known. A variation of 0·001 in the specific gravity corresponds with a change of fluidity of about 0·19 absolute units. The constant of instruments of the specified dimensions is approximately 2,000.

When the cotton is highly tendered, the solution consequently very fluid and hence rapidly flowing, it is necessary to apply a correction for the kinetic energy of the liquid. This

is conveniently done by subtracting from the time actually observed in the standard viscometer an amount which can be read from a table and which increases with decreasing time of flow. The calculations involved in compiling the table are explained (*ibid.*, *19*, 86). For technical routine purposes the correction can be neglected, as the following illustrations show. A fluidity of 10 corresponds with about 10 % loss of strength, and the time of flow in the standard viscometer is approximately 220 seconds ; the correction is 2 seconds. A fluidity of 20, corresponding with roughly 20 % tendering, gives a time of flow of about 110 seconds and a correction of 5 seconds. The correction evidently becomes rapidly more serious as the fluidity (tendering) increases, but when the tendering is as high as 30 or 40 %, an accurate measure is of minor importance in technical control.

The composition of the solvent as recommended by the Fabrics Co-ordinating Research Committee required less ammonia than required when following the method of Clibbens and Geake (200 g. compared with 240 g. per litre).

A further paper on the fluidity of cotton in cuprammonium solution was published by Clibbens and Little (J.T.I., 1936, *27*, 285), in which full details of the calibration and calculation of constants are given, together with an account of the applications of fluidity measurement as the result of accumulated experience. When requirements necessitate fluidity determinations on very small samples of material, a rolling sphere viscometer has been designed for use with 0·5 % solutions and requiring only 0·01 g. of cellulose. The instrument, calibration, use and limitations are fully described in the above paper.

The complete fluidity scale for cellulose solutions extends from about 2 down to 70, which is the fluidity of the pure solvent. When the fluidity of the material is 40, however, there is almost complete disintegration of the cotton hair, so that for practical purposes the useful range is from 2 to 40. In the case of regenerated cellulose, also measured in 0·5 % solution, the fluidity is about 40, and chemical damage may increase this to 60, at which point the filaments are too weak to handle. The fluidity of rayons is, therefore, usually measured in 2 % solution when the range of fluidities becomes about 7·5 to 35. These figures are approximately equal to those for cotton in 0·5 % solution, and the advantage is therefore gained of the practical measurements being confined to the same range. The fluidity figures for rayon may be recalculated to the basis

of 0·5 %. The equations of Farrow and Neale (J.T.I., *15*, 157) may be used, or, alternatively, the nomograms of Womersley (ibid., 1935, *26*, 165) are available.

Tankard and Graham (J.T.I., 1930, *21*, 260) point out that the early objections to the rate of flow method as opposed to the "falling sphere" were based on the point that the cellulose solution was prepared in a separate vessel from that in which the determination was made; elaborate precautions were therefore necessary. Clibbens and Geake overcame these objections by preparing the solution in the viscometer itself, but the method of closure does not ensure that the volume of cuprammonium is the same for any other tube, and further, it is only possible to make one determination on each solution. Tankard and Graham also point out that the rate of flow method has other objections such as clogging of the capillary, calibration of each tube being necessary, and the fact that corrections must be applied for surface tension effects and kinetic energy, the latter correction varying with the viscosity of the solution under examination. The rate of flow method was first employed by Ost and improved by Clibbens and Geake; the falling sphere method was utilised by Gibson and his collaborators, by Joyner and by Farrow and Neale.

Tankard and Graham's method is to determine the rate of fall of steel spheres, $\frac{1}{32}$ inch diameter, in the cuprammonium solution of cellulose prepared in the actual tube in which the measurement is to be made. The use of the $\frac{1}{32}$ in. diameter spheres instead of the $\frac{1}{16}$ in. previously used is stated to have definite advantages such as the accurate determination of viscosity over a range going as low as 1·4 log. viscosity with 2 % solutions; it is not necessary to calibrate each tube as Ladenburg's correction for wall effect is applicable, and as small variations in the diameter of the tube do not appreciably affect these calculations, it is possible to plot a graph of observed time of fall against log. viscosity of solution, which applies to all tubes having a diameter of approximately 1·0 cm.

This method requires only a small amount of cotton owing to the fact that the solution is prepared in the actual tube and duplicate readings can be made on each solution. A constant volume of cuprammonium solution for any one tube is assured by means of a new type of stopper.

Another method of studying the viscosity of cellulose has been suggested by Okada and Hayakawa (Cellulosechem., 1931, *12*, 153), involving the preparation of cellulose nitrate.

The cellulose is treated with a mixture of 63% H_2SO_4, 27·5% HNO_3 and 9·5% H_2O for two hours at 0° C. or less. The product is washed with water, dried over 40–50% H_2SO_4 and 0·5 g. dissolved in 50 cc. of acetone. The relative viscosity against acetone is determined with an Ostwald viscometer at 20° C. It is stated that this method does not involve such skilful manipulation as the cuprammonium method, whilst the degradation involved is of the same order as that produced by the dissolving of cellulose in the cuprammonium hydroxide solution. The cellulose nitrate fluidity has been utilised by Davidson (J.T.I., 1938, *29*, 195) as discussed on page 276. The newer quaternary benzyl ammonium hydroxides, described on page 157, have also been employed for viscosity determinations as mentioned on page 280.

Russell and Woodberry (Ind. Eng. Chem., Anal. Ed., 1940, *12*, 151) have compared fluidity measurements in Triton F (dimethyldibenzylammonium hydroxide) and cuprammonia. Measurements have also been made by Brownsett and Clibbens (J.T.I., 1941, *32*, 57) who found that the relation between the fluidities in the two solvents varies according to the method of modification of the cotton, but if the modified cellulose is first treated with dilute NaOH the relation is independent of the manner of modification.

For hydrocelluloses the relative or specific viscosity (0·5% solution) is lowest in cuprammonium solution and is followed in order by the values for solution in NaOH, Triton and cupriethylenediamine, the last giving the highest results.

The viscosity of cellulose in phosphoric acid solution has received attention by Ekenstam (Ber., 1936, *69*, 549), and by Stamm and Cohen (J. Phys. Chem., 1938, *42*, 921), but cuprammonia is still widely favoured for viscosity determinations, although the recent quaternary benzyl ammonium hydroxides appear to have definite advantages, as discussed on page 281, and may become the standard solvents for fluidity determinations with cellulose provided the bases can be obtained in commercial quantities and in a sufficiently pure state.

Comparatively little work has been done on the effect of mercerisation under different conditions, but it seems that the general tendency is slightly to lower the viscosity in cuprammonia, according to Farrow and Neale (loc. cit.) and also Clibbens and Little (loc. cit.).

As a broad generalisation it would appear that in terms of fluidities on the basis of 0·5% solution the most careful pre-

parations of cotton should lie between 1 and 5, whilst the normally bleached material may result in figures between 5 and 10. Fluidities of 20 to 30 indicate over-bleaching or other chemical attack which is dealt with in the section on modified cellulose. Most rayons give figures of 40 or more, but some may lie between 30 and 40. Ridge, Parsons and Corner (J.T.I., 1931, *22*, 117) give some interesting fluidity figures for rayons based on a 2% solution, and for wood pulp and cotton linters based on a 0·5% solution. The same authors show that the effect of mercerising on a few samples of cotton material is negligible in so far as fluidity is concerned.

Cuprammonium Rayon

The solubility of cellulose in cuprammonium hydrate was utilised by the Vereinigte Glanzstoff-Fabriken A. G. of Elberfeld, for the production of rayon. The raw material is usually bleached cotton linters, the preliminary treatment of which is carried out not only with a view to purification but also to increase its solubility. If the cotton is overbleached, then watery solutions will be produced which are unsuitable for "spinning" on account of the low viscosity. The cotton material is not dried but hydro-extracted, and stored in a damp condition when it is more readily soluble. The cuprammonium hydrate or Schweizer's reagent was originally prepared in the Glanzstoff process by the action of ammonia, water, and air on electrolytic copper. As the solubility of the cellulose is dependent on the copper content, it is necessary to cool the cuprammonium solution both during its preparation and storage, in order to obtain solutions as rich in copper content as possible. Temperatures of below 5° C. are employed, as otherwise decomposition occurs with precipitation of cupric hydroxide. The solvent and storage power of the cuprammonium hydrate may be increased by the addition of caustic soda solution or by additions of beet sugar, which has been denatured by treatment with copper sulphate.

The moist bleached linters are dissolved at a low temperature with powerful agitation, and a concentration of 6-8% of cellulose is obtained as the greater the concentration of cellulose, the stronger is the rayon produced from the solution.

The cotton dissolves in about six to eight hours, but an entirely homogeneous solution is not obtained so that it is necessary to filter the spinning solution through iron filter presses, the last being made of 200 mesh steel or nickel filter

gauze. Deæration next takes place to remove air bubbles from the solution by exposing it to reduced pressure in storage tanks. A certain amount of ammonia is also removed and the viscosity of the solution consequently is increased. The solution is then forced through spinnerets under 1·5 to 2 atmospheres pressure, into the coagulating bath.

The cuprammonium solution of cellulose may be caused to decompose by means of either sulphuric acid or alkali, with consequent regeneration of the cellulose. The original coagulating bath was composed of sulphuric acid containing about 500 g. per litre in order to produce a modified parchmentising action with beneficial effects on the tensile strength. In the Glanzstoff process, however, about 30% caustic soda solution was used as the coagulating bath with the addition of 6% of sugar or sodium lactate. The temperature was usually maintained at 50° C. The effect of the sugar in the bath was to produce filaments containing less precipitated copper, but in all cases it was necessary to remove the copper by rinsing in 2% H_2SO_4, either directly after the coagulating and washing or after the later twisting and reeling processes.

The Glanzstoff process yielded fairly coarse filaments and its manufacture was discontinued in 1914. The production of very fine filaments was made possible by Thiele and elaborated by the firm of J. P. Bemberg, A. G., of Barmen-Rittershausen, filaments finer than those of natural silk being made. In this modern method of manufacture the preparation of the spinning solution takes place in an entirely different manner. The beaten cellulose is intimately mixed with freshly precipitated cupric hydroxide to form cupric hydroxide cellulose which is soluble in concentrated ammonia. The cupric hydrate is prepared by running concentrated caustic soda solution at 0° C. into a concentrated copper sulphate solution at 15 ° C. with constant stirring until all the copper is precipitated as the hydroxide. The thick liquid is then mixed with the well-beaten cotton linters and mixing continued for 30 minutes. The mixture is then pressed and washed until the wash-water is free from sodium sulphate. The pressed mass or cakes containing about 40% of water are minced and squeezed through sieves to form fine threads, which are subjected to a vaccum in order to remove enclosed air. The necessary ammonia is added in a vertical dissolving vessel which is fitted with an agitator. After about 24 hours a concentrated solution of cellulose is obtained and this is diluted to 7–8%

by the addition of the necessary aqueous ammonia. The customary additions to the spinning solution, the deæration and filtering are carried out as in the older process.

The essential feature of the stretch spinning process is that the spinning solution emerges under slight pressure from the spinnerets into a feebly coagulating liquid such as water which moves with increasing speed in the direction of the forming filaments, which solidify incompletely at first and are stretched by means of the rapidly flowing coagulating bath and a mechanical device. Any air must be removed from the coagulating liquor in order to avoid the formation of bubbles which would cause the filaments to break. When the filaments have been drawn to the required fineness, they are coagulated completely by means of a second bath consisting either of dilute sulphuric acid or a solution of a metallic salt, such as 15% ferrous sulphate. The water used in the first coagulating bath should be as pure as possible as its slight coagulating action is due to the removal of some ammonia and copper from the spinning solution as it is forced through the fine orifices of the spinnerets.

Although cotton linters is the main starting material for the manufacture of cuprammonium rayon, wood pulp has been used with some success in England. It has been found, however, that the rayon produced, which nevertheless bleaches readily, is of a pale cream colour whereas that from cotton linters is almost completely white. It is also interesting to note that according to the data of Ridge, Parsons and Corner (loc. cit.) the fluidity range of cuprammonium rayons is considerably lower than those from viscose. There is also some evidence to show that the fluidity of cuprammonium rayon from cotton linters is slightly lower than that from wood pulp. This is in agreement with similar observations on the viscosity of cellulose acetates and nitrates, i.e. the viscosity is a measure of the quality of the starting material as distinct from indicating the effects of the chemical actions of solution and regeneration.

Other Reagents

NaOH and CS_2

The viscose reaction which is dealt with more fully on page 446, offers another example of the swelling of cellulose. Briefly, if cellulose is treated with caustic soda of mercerising strength and then with carbon bisulphide, without removal of the alkali and water, further swelling takes place above that due to the

alkali.. The mixture may be diluted with dilute alkali to form a solution of cellulose or more accurately, cellulose xanthate, from which cellulose may be regenerated.

A limited viscose reaction has been suggested and patented for mercerising and swelling effects in addition to other technical purposes (Lilienfeld B.P. 216,476 and 7), but is of comparatively little importance in the textile industry of to-day. The use of 9% sodium hydroxide and carbon bisulphide shows the existence of daily growth rings in the cotton hair, Balls (Proc. Roy. Soc., 1918, *B90*, 542) stating that ripe hairs show a forty-fold swelling whilst unripe hairs do not swell appreciably.

CHLORAL.

The solvent action of chloral on cellulose is described in D.R.P. 408,821. Four parts of chloral and eight of pyridine are mixed with one part of cellulose and the mass warmed to 90–95° C. when the cellulose swells and passes into solution in two hours. Ross and Payne, however, state that when 50 g. of cotton is condensed with 100 g. of chloral hydrate in presence of 100 cc. of conc. H_2SO_4 as condensing agent at 0° C. there is complete dissolution (J.A.C.S., 1923, *45*, 2363). The products of the reaction are dichloralglucoses and there is no trace of chloral-substituted cellulose or dextrins. According to D.R.P. 408,821, however, the chloral compound of cellulose is obtained as a clear transparent film by evaporation of the solvent or may be precipitated by water, acids, alkalies, hydrocarbons, alcohols, etc.

CHAPTER TEN

THE PROPERTIES OF DISPERSED CELLULOSE

SOME of the effects of swelling agents on cellulose have already been mentioned in connection with the actual action of the solvent or swelling agent, but there are certain properties of dispersed cellulose which have been examined in some detail more particularly in recent years.

Moisture Sorption

The original conception of rayons and mercerised cottons as cellulose hydrates or hydrated cellulose has now given way to the conception that they are merely cellulose in a more highly dispersed form. An examination of well dried samples of cotton, rayon and mercerised cotton by the classical methods of combustion reveals the common empirical formula $C_6H_{10}O_5$.

The idea of a cellulose hydrate was, no doubt, due to the fact that whilst cotton has a moisture regain of 6·2 %, mercerised cotton has a regain of 7·8 % and viscose rayon of 11·9 %. Higgins (J.S.C.I., 1909, *28*, 188) showed that this content of hygroscopic moisture depended on the conditions of mercerising. In the case of cotton mercerised without tension with various concentrations of caustic soda solution he observed the following increases in moisture content from a sample of cotton originally containing 6·2 %.

INCREASE IN MOISTURE CONTENT ON MERCERISING.

NaOH Concentration in degrees Twaddell	10	20	30	40	50	60	70
Moisture per cent.	6·37	6·68	8·40	9·41	9·43	9·57	9·69

Urquhart and Williams (J.T.I., 1925, *16*, 155) considered that most of the previous information was of doubtful value on account of the lack of controlled humidity, and examined the moisture regain of cotton mercerised without tension in order to obtain accurate knowledge of the regain at all humidities. They found that cotton has a maximum hygroscopicity when mercerised with solutions which are known to cause a maximum swelling, e.g. 15 % NaOH or 28 % KOH.

It was also established that the relation between the hygroscopicity of mercerised cotton and the concentration of the mercerising solution is very similar to that between the swelling and the concentration of the solution. The most striking feature, however, is that the ratio of the mercerised cotton to that of the original soda-boiled cotton at the same humidity is appreciably independent of the humidity. When

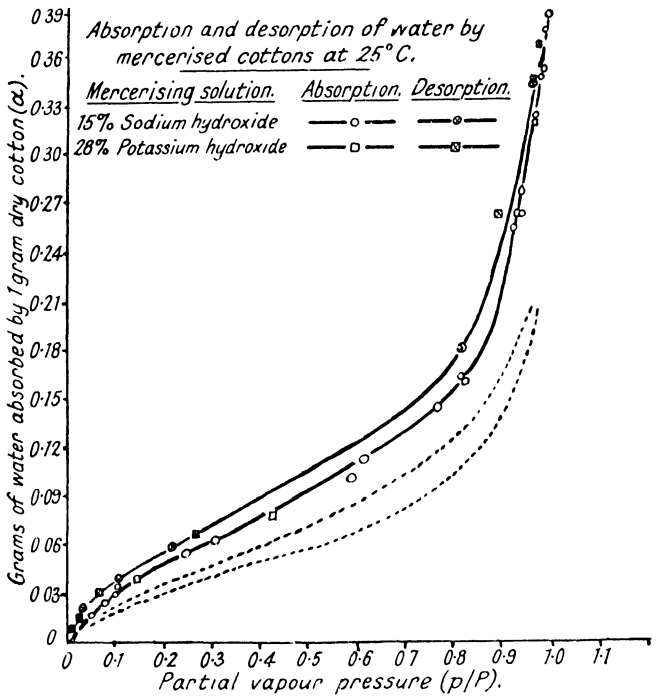


FIG. 93.—Moisture relations of mercerised cotton. (The dotted curve is for unmercerised cotton.)

mercerised with 15% NaOH solutions, for example, the regain is about 1·57 times as great when the material is absorbing moisture, and 1·46 times as great when losing moisture as the regains of unmercerised cotton, no matter what the prevailing humidity may be. This "absorption ratio" indicates quantitatively the effect of a given mercerisation process on the absorptive capacity of the material.

Urquhart (J.T.I., 1927, *18*, 55) in an examination of yarns mercerised with and without tension, broadly confirmed the

above results, any differences observed being explainable in terms of the effects of tension. As the applied tension acts in opposition to the swelling forces, the absorptive capacity of cotton mercerised with tension is less than that of the material mercerised loose. In the earlier paper it is pointed out that the absorptive capacity of a material depends on two factors, the absorptive power of the material which depends only on the substance of which it is composed, and the capacity factor which depends on the area available to an adsorbate, and hence on the state of aggregation of the substance. As mercerised cotton is chemically identical with cotton, it may be assumed that mercerisation produces an increase in the accessible surface of cotton so that the action of the mercerising solution is to increase the degree of dispersion of the material.

Urquhart and Eckersall (J.T.I., 1932, *23*, 163) examined the adsorption of water by rayon, and found that the highest hygroscopicity is exhibited by cellulose regenerated from cellulose nitrate. Regenerated celluloses gives curves for water absorption against vapour pressure similar to those given by cotton and mercerised cotton.

The main effects are illustrated by various typical examples taken from the data of Urquhart and his co-workers :

MOISTURE RELATIONS.

	Relative Humidity.					
Regains % of	10	20	40	60	80	90
Scoured cotton .	2·0	2·9	4·5	6·2	9·1	11·8
Mercerised cotton	2·4	3·6	5·6	7·8	11·1	14·3
Viscose rayon .	3·9	5·7	8·7	11·9	16·9	22·1

	Standard Sample as Unity.					
Absorption Ratio						
Scoured cotton .						
Mercerised cotton	1·2	1·23	1·24	1·26	1·22	1·21
Viscose rayon .	1·99	2·02	1·95	1·89	1·80	1·80

The increase of absorption is a roughly constant ratio at all humidities so that the effect of swelling is to increase the absorbing surface and not to confer increased powers of absorption but only the capacity.

It has already been stated that the swelling effect of alkali does not result in a permanent distension of the cellulose. This is supported by figures for the specific volume of cellulose according to Davidson (J.T.I., 1927, *18*, 175).

SPECIFIC VOLUME.
(ccs. per gram.)

	Helium.	Water.	Toluene.
Scoured cotton .	0·638	0·621	0·645
Mercerised cotton .	0·645	0·622	0·651
Viscose rayon . .	0·646	0·622	0·652
Cuprammonium rayon	0·653	0·625	0·657

It will be noticed, however, that the slight increase of about 1% in the case of dispersed celluloses is quite definite.

Affinity for Dyes

It will be remembered that Mercer not only recorded the shrinkage effects due to the use of sodium hydroxide solutions on cotton, but also the increased dyeing power. The earliest quantitative data, however, was obtained by Schaposchnikoff and Minajeff (Z. Farb. Text. Ind., 1903, *2*, 257; 1904, *3*, 163; 1905, *4*, 83), who stated that in the case of direct colours the unmercerised cloth contained 50% more dyestuff than the same fabric mercerised and dyed to the same shade. Similarly about 40% more indigo was required to give on unmercerised cotton, the same shade as on mercerised material.

With the development of accurate analytical methods for the determination of dyes, however, more reliable and quantitative data became available. Huebner and Pope (J.S.C.I., 1904, *23*, 404) made experiments of a partly quantitative nature in which they used Benzopurpurin 4B. They concluded that the adsorption of dye reaches a maximum for a concentration of alkali from 25% to 31·5% in the case of sodium hydroxide, and then diminished with increase of alkali concentration up to 36·5% NaOH.

Knecht (J.S.D.C., 1908, *24*, 67 and 197) showed that the dyeing capacity increases with increase in strength of the mercerising liquor, although the increase becomes less rapid as the concentration of the alkali rises above 13·5%. The different effects of mercerising with and without tension on the adsorption of benzopurpurin were also shown by Knecht using a mercerising solution containing 22·5% NaOH.

ABSORPTION OF DYE.

	% Adsorbed Benzopurpurin.	
Unmercerised cotton . . .	1·55	1·50
Mercerised with tension . .	2·90	2·86
Mercerised without tension . .	3·39	3·54

The first column represents unbleached and the second, bleached material.

Effect of Heating

Knecht (*ibid.*, page 197) also examined the effects produced by the drying of mercerised yarn on its capacity to absorb dyes, and found that the drying of yarn after mercerisation results in a greatly decreased adsorption of direct dye and that this decrease is greater the higher the temperature of drying.

EFFECT OF DRYING.

	% Adsorbed Benzopurpurin.	% Adsorbed Chrysophenin.
Mercerised and dyed without drying	3·24	0·96
Mercerised and air dried . .	3·03	0·92
Mercerised and dried at 110° C. .	2·51	0·84
Unmercerised yarn . . .	1·77	0·58

Coward and Spencer (J.T.I., 1923, *14*, 32) showed that the effect of drying the mercerised cotton was considerably to reduce its capacity for swelling in water. Mercerised samples, which had been well washed, centrifuged and weighed in order to determine the swelling capacity before drying, were heated for periods of two and eight hours in a steam oven, soaked in water, centrifuged and weighed. The results indicate that where the undried cotton gave a water absorption figure of some 120%, the dried material only showed a capacity for water of about 70% owing to the collapse of the swollen fibre. The eight hours' drying experiment gave a lower figure still.

The mercerised and washed cotton hair may also be caused to contract by boiling in water. For example, Coward and Spencer showed that a mercerised cotton, which after removal of alkali gave an absorption figure of 108 g. of water per 100 g. of cotton, retained only 88 g. of water after boiling for six hours. The contraction of the fibre in presence of water, but on application of heat, although slow, was quite definite; it is probably incomplete in comparison with the collapse on drying.

The amount of water held by 100 g. of acid or alkali treated fabric after washing and centrifuging in Coward and Spencer's centrifuge (2½ mins. at 7,000 r.p.m.) has been estimated by treating an open fabric (e.g. muslin) with the reagent and after the appointed lapse of time plunging into water and washing thoroughly in running water.

WEIGHT OF WATER HELD PER 100 G. OF DRY CELLULOSE

(*a*) Treatment followed by washing only.

(*b*) Fabric dried in air and re-immersed in water for 16 hours.

Time in secs	60° Tw. NaOH (27%)	100° Tw. H_2SO_4 (59·7%)	108° Tw. H_2SO_4 (63·4%)	110° Tw. H_2SO_4 (64·2%)	120° Tw H_2SO_4 (68·5%)	130° Tw. H_2SO_4 (72·7%)	140° Tw. H_2SO_4 (77·2%)
5 (*a*)	—	53	—	183	237	210	225
(*b*)	—	—	—	93	139	146	145
10 (*a*)	—	53	—	199	230	228	231
(*b*)	—	—	—	96	143	155	157
15 (*a*)	—	58	—	186	254	247	253
(*b*)	—	58	—	98	150	168	174
30 (*a*)	87	—	128	—	—	—	—
(*b*)	59	—	57	—	—	—	—

The water retention by the untreated fabric was 50.

The table shows the extremely rapid action of 110–140° Tw. H_2SO_4. Even after air drying, the imbibition of water still remains considerable in these cases.

Neale (J.T.I., 1931, *22*, 320) has also shown that the greater the amount of NaOH taken up from N/2 solutions by mercerised cotton, the greater is the corresponding decrease on heating at 110° C.

Bancroft and Calkin (Textile Res., 1934, *4*, 119) found that drying at 105° C. decreased the amount of NaOH taken up from dilute solutions by mercerised and air-dried cotton.

The partially irreversible contraction of the native fibre on drying after mercerising is less striking than the fact that boiling in water also causes contraction. This observation of Coward and Spencer has recently received support from the X-ray investigations of Sakurada and Hutino (Kolloid Z., 1936, *77*, 346). From the account of the molecular structure of cellulose on page 100, and anticipating the work on alkali-cellulose on page 430, it may be stated that the X-ray diagram of mercerised cellulose shows a more distended lattice than that of native cellulose. Sakurada and Hutino showed that the effect of washing the soda cellulose with water until free from alkali and then examining it in the wet state, was to give a new and fairly sharp X-ray diagram of a lattice

still more distended than that of the mercerised or " hydrate " lattice, indicating that water had penetrated into the crystal lattice. This super-swollen modification was termed " water-cellulose." If, however, the soda cellulose is washed at 100° C. then the usual mercerised lattice is obtained instead of the more extended form. Drying of the water-cellulose even at 25° C. caused a change to hydrate cellulose, but the change is slow at the lower temperatures. Water-cellulose was observed to swell more strongly in water than did mercerised cellulose. Similar extensive broadening of the lattice was observed in the case of cellulose from lithium cellulose, potassium cellulose and cellulose xanthate and the effect was also noted with other regenerated celluloses.

For purposes of comparison, the constants found were :

X-RAY DATA.

	Native Cellulose.	Mercerised Cellulose.	" Water " Cellulose.
a . .	8·35 Å	8·1 Å	10·03 Å
b . .	10·3 Å	10·3 Å	10·3 Å
c . .	7·9 Å	9·1 Å	9·98 Å
β . .	84°	62°	52°

Returning to the consideration of the affinity for dyes as a measure of the degree of dispersion of cellulose, it is well established that this increased affinity is higher again in the case of the more highly dispersed rayon than is the case with mercerised cotton. Here, however, is the added complication of the extent of degradation of the cellulose which again affects the dyeing properties. The combination of dispersion and degradation in the case of regenerated cellulose may account for the difficulties of producing a level-dyeing material.

Some interesting observations have been made on the recovery of the native modification of cellulose from the dispersed form and the first of these may be regarded as a somewhat indirect method of procedure.

Although cellulose does not appear to react with either ammonia gas or aqueous ammonia, yet some very interesting results have been obtained by Barry, Peterson and King (J.A.C.S., 1936, *58*, 333), also mentioned on page 161.

Ramie fibre was immersed in anhydrous liquid ammonia when a swelling took place which, according to X-ray examination, increased the *a* axis from 8·3 to 9·83 Å and the C axis

from 7·9 to 10·05 Å. The angle between *a* and *c* was found to have decreased from 84° to 53·5°. This pronounced distention of the lattice allows room for the introduction of ammonia molecules into the unit cell, and as might be expected this enlargement is not as great as that necessary to accommodate the diamines; Hess and Trogus (Z. physik. Chem., 1931, *14*, 387) found that the increase in the lattice was proportional to the length of the incorporated molecule.

When the ammonia cellulose was heated at 105° C. for several hours, it lost its ammonia and gave a diffraction pattern, which was very similar to that of hydrate cellulose, but a very interesting observation was made when the ammonia cellulose was decomposed by weak acetic acid, water or aqueous ammonia, then the pattern of the regenerated cellulose was found to be the same as that of the untreated ramie. This result is in conformity with the observation of Hess and Trogus (Z. physik. Chem., 1931, *14*, 387) in their examination of the effect of diamines on cellulose. This regeneration of native cellulose from a highly dispersed form had not previously been encountered

Hess and Gundermann (Ber., 1937, *70*, 525) have recorded results obtained from an examination of alkali-cellulose, which if washed with water at 100° C. gives the diagrams of both native and hydrate cellulose together.

Meyer and Bodenhuizen (Nature, 1937, *140*, 281) have shown that it is possible to convert hydrate cellulose to the native form directly. Lilienfeld rayon, i.e. highly stretched hydrate cellulose, when heated for 30 minutes in water at 200° C. gave an X-ray diagram which showed the interferences of native as well as hydrate cellulose. A period of eight days in water at 200° C. gave very little more native cellulose than the period of 30 minutes.

Viscose rayon, when immersed in glycerine for 30 minutes at 250° C., showed almost complete conversion to native cellulose. Immersion in boiling formamide (200° C.) for 30 minutes, also produced the picture of native cellulose, but the results when the temperature was only 130° C. showed a lower degree of transformation to native cellulose. Meyer obtained similar results to the above when using mercerised ramie in place of viscose, but less native cellulose was formed under the same conditions.

Dry viscose in a high vacuum for 20 minutes at 200° C. remained unchanged in so far as the X-ray picture is concerned,

but after 10 minutes at 300° C. a little native cellulose was formed. Water and other dipole containing liquids appear to increase the rate of transformation.

As native cellulose, in the form of ramie, was unchanged after five days in water at 150° C., Meyer concludes that native cellulose is the stable form and hydrate cellulose the unstable modification—the opposite state of affairs having previously been accepted by most investigators.

Hess and Gundermann (*supra*) obtained native cellulose interferences when alkali cellulose was washed at 100° C., but Meyer has detected native cellulose in preparations at 60° C. If, however, washing takes place with water at 20° C. and then the preparation is heated, no native cellulose appears even at 100° C. Fibres of alkali cellulose gave almost entirely native cellulose when dipped into formamide at 100° C. In all these cases it was observed that the temperature required for the formation of native cellulose from alkali cellulose was considerably lower than that necessary for the transformation of hydrate cellulose as such, into the native form.

The bearing of the above work on all processes involving mercerisation and hydration of cellulose is quite obvious, and it is interesting to note that the X-ray evidence now supports the early work of Knecht and of Coward and Spencer on the swollen or distended state of dispersed cellulose.

Activation

The effect of mercerising on the chemical properties of cotton was examined by Ridge, Parsons and Corner (J.T.I., 1931, *22*, 140) taking as criteria fluidity, copper number, methylene blue absorption and loss of weight in boiling alkali. Their results show that there is no significant increase in the respective values as a result of mercerisation. In the case of rayon, owing to degradation, there is an increase in fluidity and in copper number (see page 239).

Whilst the action of swelling agents on cellulose does not produce new properties, it results in an activation of the old. Modern terminology deals with this activation objectively, by reference to " absorption ratio " or " reactivity ratio " instead of the old " mercerisation ratio."

The increased chemical reactivity of swollen cotton is displayed by an increased rate of hydrolysis of the cellulose with acids. This was first shown by Schwalbe (Z. angew. Chem., 1908, *21*, 1321, and 1909, *22*, 197), who suggested the

term " hydrolysis number " defined as the increase in the copper number of cellulose materials which resulted from treatment with 5% H_2SO_4 for 15 minutes at the boil. This hydrolysis number is, therefore, a measure of the chemical reactivity of the cellulose. Birtwell, Clibbens, Geake and Ridge (J.T.I., 1930, *21*, 85) preferred the measurement of the copper number of cotton oxidised with hypobromite as a means of describing its reactivity, as the time and temperature of treatment with H_2SO_4 need most careful control, slight variations having a considerable effect on the copper number. The action of the hypobromite on the cellulose is to produce an oxidation product of aldehydic character, possessing reducing properties and, therefore, a high copper number. When cotton has been swollen the reactivity is increased, and the rate at which the reducing product is formed is also increased. The hypobromite solution is conveniently prepared from a stock standard solution of potassium bromate containing an excess of potassium bromide. By acidification of this solution, free bromine is liberated in quantity equivalent to the bromate, and the correct volume of standard caustic soda solution is then added to neutralise the excess acid, to react with the free bromine yielding an equivalent quantity of hypobromite, and to furnish the necessary concentration of excess alkali when the mixture is diluted to a convenient total bulk ; the concentration of the oxidising agent should lie between 0·95 N/10 and 1·05 N/10 and that of free alkali between 0·9 N/10 and 1·1 N/10.

100 cc. of the hypobromite solution are poured from a measuring cylinder into a 200 cc. stoppered bottle and 2·50 g. of the air dry cotton are introduced into the solution. The mixture is allowed to stand with occasional shaking for 1½ hours if the room temperature is between 20 and 25° C., or for 2 hours if it is between 15 and 20° C. At the end of this time, the cotton is filtered through a perforated plate and washed in the funnel with water, a dilute solution of H_2O_2, water, dilute (N/10) H_2SO_4, and finally with water to a neutral reaction. The cotton is pressed as dry as possible on the funnel, and transferred to a conical flask in which its copper number is determined as described on page 239. The copper number, referred as usual to 100 g. of oven-dry material is calculated on the basis of the 2·5 g. of air dry material orginally taken for oxidation, a correction being made for the moisture content. The next figure (94), shows the increased activity of mercerised cotton towards the sodium hypobromite treatment. It will

be noticed that although the oxidation is more rapid in the case of mercerised cotton yet it follows a course parallel to that of normal cotton. Normal unswollen cottons varying widely in origin and details of bleaching all yield values of copper number near to 1·5 *after* this standard treatment. The copper numbers resulting when mercerised or other swollen cottons are treated in the same way are, therefore, divided by 1·5 to obtain the reactivity ratio. The maximum reactivity ratio attained by normal cotton which has been swollen with caustic

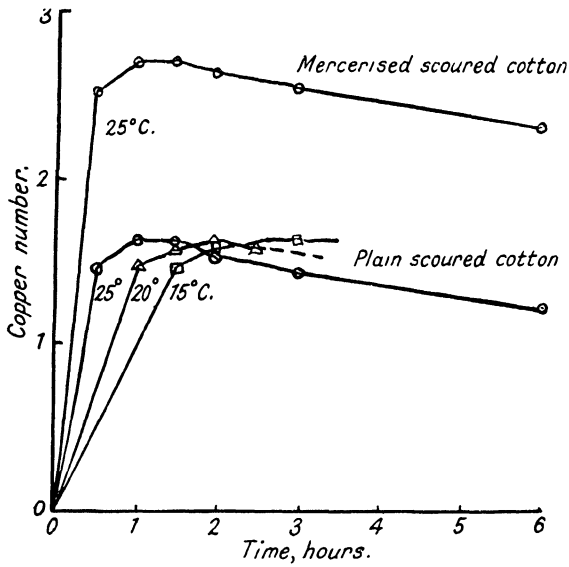


FIG. 94 —Reactivity ratio to hypobromite solution.

soda, i.e. mercerised, is about 1·8, unswollen material having a reactivity ratio of 1, whilst cotton materials parchmentised with strong sulphuric acid may possess reactivity ratios of 2 or even more. Reactivity and absorption ratios are always less for cotton mercerised under tension compared with mercerisation without tension; the effect of drying mercerised material at 100° C. is to reduce the absorption ratio but not the reactivity ratio.

The effects of swelling treatments with H_2SO_4 are striking; in the case of 62·5 % acid, both reactivity and absorption are increased by reduction in the temperature of the acid—as

with NaOH—but with 68·7% H_2SO_4 these ratios fall with falling temperature of the acid.

Quantitative Measures

The preferential absorption of sodium hydroxide from dilute solutions by cotton was noticed to increase with mercerisation. Vieweg (Ber., 1907, *40*, 3876) gave the following figures to show the relation between the weight of NaOH absorbed by 3 g. of mercerised cotton from a 2% solution of NaOH and the concentration of alkali used in mercerising the cotton:

ABSORPTION OF ALKALI.

% Concn. of alkali	0	4	8	12	16	20	24	28	32	50
% NaOH absorbed	1·0	1·0	1·4	1·8	2·8	2·8	2·8	2·9	2·9	2·9

and suggested that this might be a useful measure of the degree of mercerisation. Neale (J.T.I., 1931, *22*, 320) put forward the preferential absorption of alkali as a characteristic property, and in a later paper (*ibid.*, page 349) showed that as the absorption of barium hydroxide is greater in amount than that of sodium hydroxide it can be estimated relatively more exactly. Two grammes of the dried cotton are allowed to stand overnight with occasional shaking in 30 cc. of barium hydroxide solution, and 10 cc. are then withdrawn for titration with standard acid. The amount of alkali preferentially absorbed is calculated from the change in titre, with the appropriate corrections for dilution by moisture content and for differences in temperature between alkali and acid. The standard reagent is N/4 barium hydroxide and the standard temperature is 25° C.

Figure 95 shows the absorption ratios plotted against the concentration of the mercerising alkali.

The corrected absorption in millequivalents per 162 g. of cellulose divided by 71, gives the baryta absorption ratio relative to cotton.

The fact that the curves for cotton mercerised in the grey and scoured states cross at high alkali concentrations is no doubt due to local dilution of the concentrated alkali by the wetting liquor entrained in the grey cotton.

The work of Neale and his collaborators showed that where measurements of the absorption ratio to sodium hydrate or

baryta were made on cotton which had been treated in a loose state, the average result was about 2·6, compared with 1·7 for the moisture absorption ratio. The effect of tension confirms the previous and general observations that tension acts in opposition to the swelling forces of mercerising; maximum lustre is not compatible with maximum reactivity or sorption.

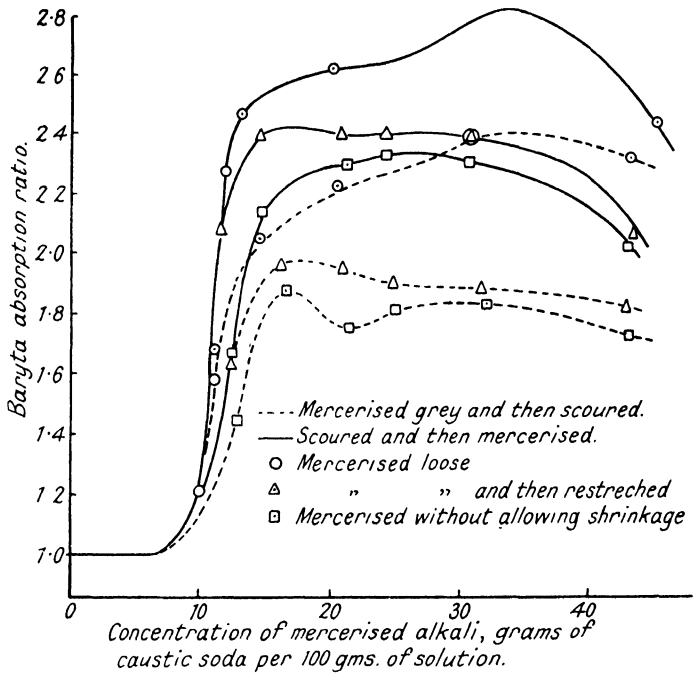


FIG. 95.—Baryta absorption.

By the use of cuprammonium hydrate too dilute to swell cellulose appreciably, Neale et al. (*ibid.*, page 357) were also able to show that the copper absorption is dependent on the pretreatment of the cellulose in much the same way as are the soda and baryta absorptions.

The various ratios of activation imparted by mercerisation have been collected by Neale (J.S.C.I., 1931, *50*, 177).

A more detailed account is given in "Mercerising," by Marsh (Chapman and Hall; London; 1941).

ACTIVATION RATIOS.

Concentration of NaOH in mercerising g/100g. of solution	Water Vapour.	Alkaline Hypobromite.	5% H_2SO_4.	Benzo-purpurin.	0·5 N NaOH.	0·2 N Ba $(OH)_2$.	Cuprammonium.
0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
10	1·1	1·0	1·1	—	1·2	1·2	—
12·5	1·4	1·3	—	—	1·9	1·9	—
15	1·6	1·6	1·7	—	2·3	2·4	—
20	1·5	1·6	—	2·2	2·4	2·6	—
25	1·6	—	2·2	—	2·5	2·6	2·6
32·5	1·6	—	2·2	—	2·6	2·8	—

The activation ratios of yarn treated loose with 25% NaOH solution washed and dried as under have also been recorded.

EFFECT OF DRYING.

	Water Vapour.	Alkaline Hypobromite.	0·5 N NaOH	0·2 N Ba $(OH)_2$.
Air dried	1·66	1·75	2·55	2·70
Dried at 110° C.	1·51	1·76	2·27	2·52

Rayon

In the case of regenerated cellulose, as already stated, there is degradation in addition to swelling. This is instanced by the low tensile strength of rayon compared with cotton, but also, there are the following properties to consider:

COMPARISON OF COTTON AND RAYON.

	Copper Number.	Fluidity (0·5%)	Mol. Wt. (Staudinger).
Scoured cotton	0·04	1·5	200,000
Viscose rayon	1·0	40	20,000

The measurable qualities of commercial rayons have been recorded by Ridge, Parsons and Corner (J.T.I., 1931, *22*, 117), from which it is shown that there is a greater loss in weight on boiling in 1% NaOH solution for one hour (amounting to

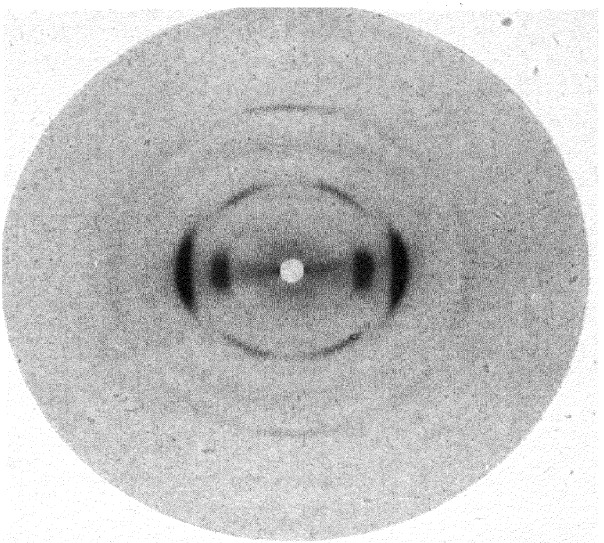


FIG. 96.—Ramie yarn.

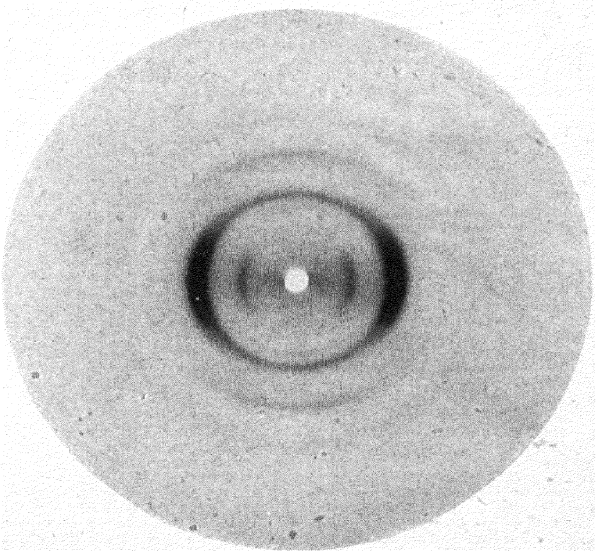


FIG. 97.—Ramie yarn mercerised without tension.

(*By courtesy of Dr. Astbury, F.R.S.*)

[*To face page* 200.

PLATE XXII.

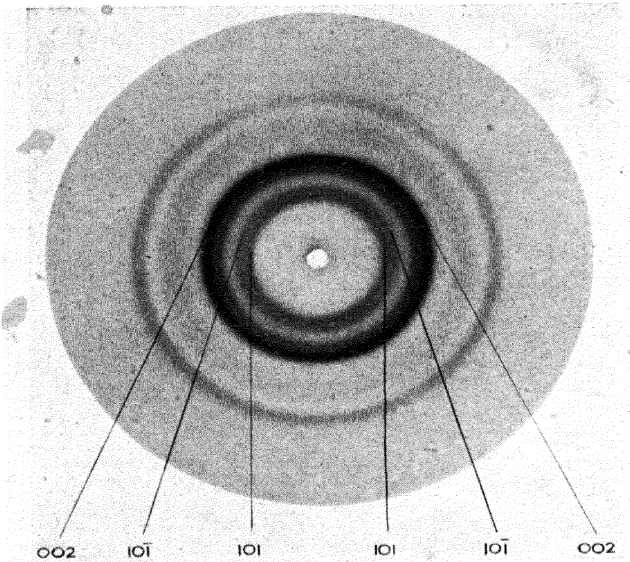


FIG. 98.—Photograph of disorientated native cellulose from an irregular arrangement of cotton hairs.

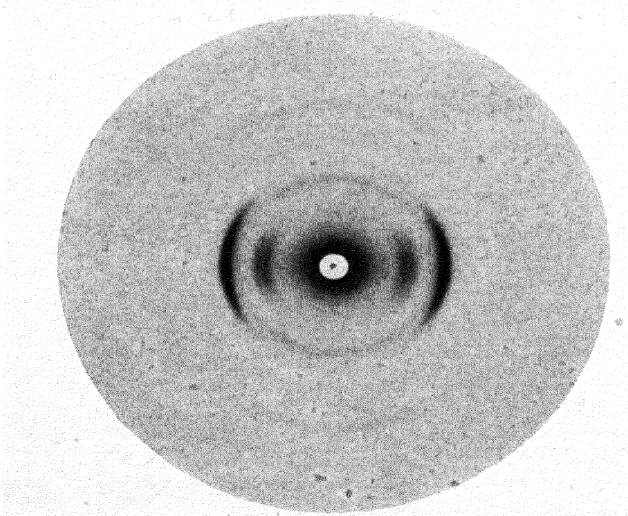


FIG. 99.—Cotton yarn.

(*By courtesy of Dr. Astbury, F.R.S.*)

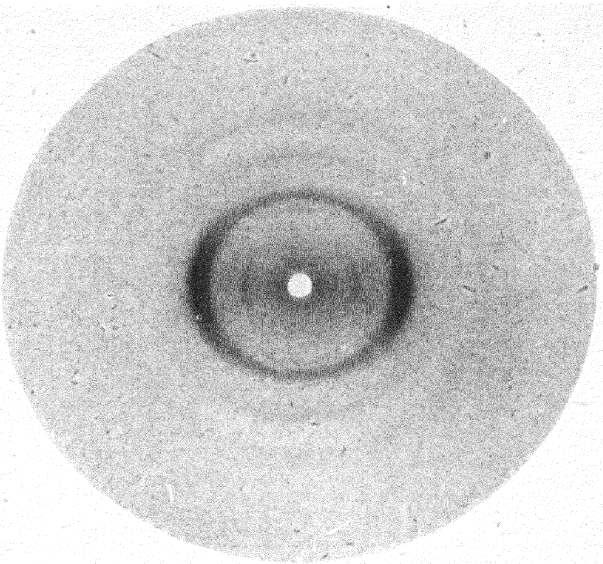


FIG. 100.—Cotton yarn mercerised without tension.

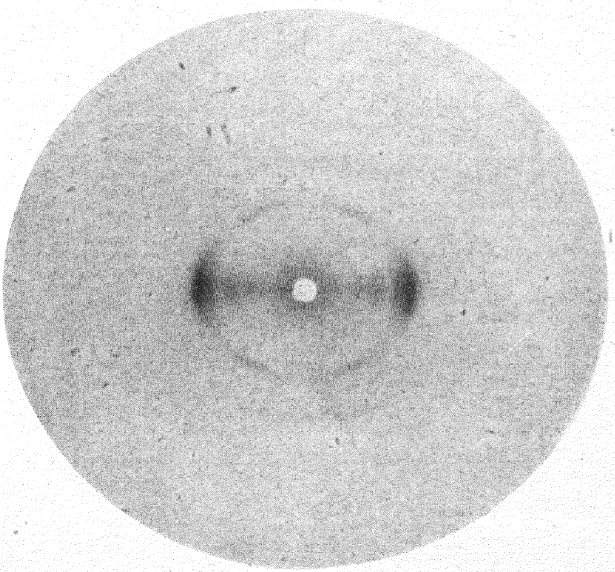


FIG. 101.—Cotton yarn mercerised with tension.

(*By courtesy of Dr. Astbury, F.R.S.*)

PLATE XXIV.

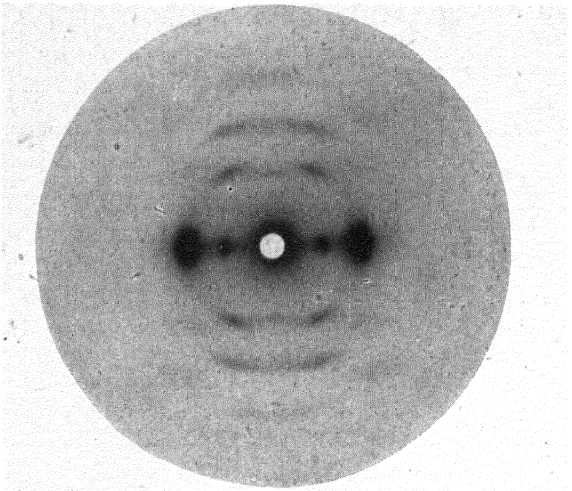


FIG. 102.—Highly orientated regenerated cellulose.

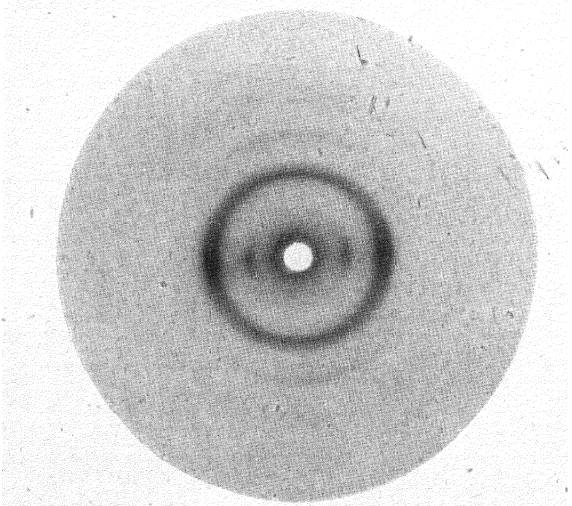


FIG. 103.—Poorly orientated regenerated cellulose.

(By courtesy of Dr. Astbury, F.R.S.)

[*To face page* 201.

approximately 7 % for regenerated celluloses) than with either mercerised or unmercerised cotton where the loss in each case is equivalent and of the order of 1·25 %. The methylene blue absorption value of approximately 1·15 is slightly reduced by mercerising, but in the case of regenerated celluloses values are given ranging from 1·3 to 4·5.

The general conclusion is that although the series cotton, mercerised cotton and rayon represent three stages of increasing dispersion of cellulose, yet in the preparation of the rayons some attack on the cellulose takes place with the result that the chemical properties of the rayon resemble those of the modified celluloses (page 207) rather than those of the unchanged material.

It will be remembered that tensile strength, fluidity and copper number are not adversely affected by the mercerising of cotton.

Typical activation ratios in the case of rayon are given below :

ACTIVATION RATIOS.

	Water Absorption.	Baryta Absorption.	Reactivity Ratio.
Scoured cotton .	1·0	1·0	1·0
Viscose rayon .	2·0	4·0	2·0

The *rate* of dyeing is known to be increased by swelling processes applied to native cellulose, and this aspect of activation has received attention by Boulton and Morton (J.S.D.C., 1940, *56*, 145) who found that mercerising cotton under tension produced a fourfold increase in the speed of dyeing.

Qualitative Tests

Some qualitative evidence for the activation of cotton by mercerisation is afforded by the work of Vieweg on benzoylation (Ber., 1907, *40*, 441, 3786), when it was shown that mercerised cotton gave a greater yield than the unmercerised material.

The nitration products of mercerised cotton are more soluble in the ether-alcohol mixture than the cellulose nitrates prepared from unmercerised cotton according to the same investigator and also Piest (Z. angew. Chem., 1909, *22*, 1215). It is also known that cotton when mercerised dissolves more easily both in zinc chloride solutions and in cuprammonium hydrate.

A number of tests for mercerising have been devised mainly

depending on the increased affinity for dyestuffs. The test originally due to Knecht (J.S.D.C., 1908, *24*, 67) and depending on the absorption of Benzopurpurin 4B, was later modified by Knaggs (J.S.D.C., 1908, *24*, 112). David (Z. angew. Chem., 1908, *21*, 1184) suggested spotting the material to be tested, with mercerising alkali, when on subsequent washing and dyeing the alkali-treated area would be distinguished if the material had not already been mercerised. Mennell (J.T.I., 1926, *17*, 247) suggests a test which makes use of the action of H_2SO_4 containing formaldehyde (B.P. 200,881—see page 168) on the suspected material, which after treatment is dyed with chlorazol sky blue GW. If unmercerised cotton is dyed to about 0·1% absorption then the mercerised material will show a colour equivalent to 0·8% dyeing. Ermen (J.S.D.C., 1931, *47*, 161) first steeps the material in iodine solution and then washes it until a similarly treated non-mercerised sample becomes colourless, and then places both in boiling dilute Indigosol Black IB solution when the mercerised sample turns blue or black whilst the unmercerised piece remains almost white.

According to Huebner (J.S.C.I., 1908, *27*, 105) the mercerisation of cotton causes an increase in its absorption of iodine from its solution in potassium iodide solution, and this was developed to form a test for mercerisation. The reagent is prepared by adding 20 drops of a solution containing 11 g. of iodine and 20 g. of potassium iodide in 100 cc. of water to 100 cc. of a solution containing 280 g. of zinc chloride in 300 cc. of water. The samples are immersed in water and pressed between filter papers and then laid in the reagent; the mercerised cotton becomes a deeper blue according to the concentration of the mercerising alkali, whilst unmercerised cotton remains practically colourless. Huebner describes many variations of this test. Similar tests are also described by Harrison (J.S.D.C., 1915, *31*, 198).

The change in double refraction (see page 45) may also be used as a test for mercerisation.

X-ray Diagrams

The change from native cellulose to hydrate cellulose has been followed by means of X-ray photographs which provide evidence of the internal change in structure. (It must be remembered, however, that only the crystalline cellulose is considered in the interpretation of the photograph and the

25 to 30% of non-crystalline cellulose does not figure; this, of course, does not affect the question of complete mercerisation as revealed in the photographs.)

Although the interpretation of an X-ray photograph is a matter for highly specialised knowledge, yet the main characteristic features of photographs of the various forms of cellulose are not difficult to appreciate.

Orientation

The result of orientation is seen most prominently in the diffraction effects due to the *002* planes where they are most intense. The lengthening of the arc is a measure of the disorientation of the cellulose and may be measured micrometrically. The same phenomenon occurs with other spots or arcs, but is not visible in such a striking manner. (This is not the whole story, for spirals also produce arcs.)

Another feature of a well-orientated fibre is seen by reference to the photograph of ramie where the clear presence of "outer spots" due to the more complex spectra is, among other factors, evidence of high orientation. The intensities of the higher orders are better defined, giving sharper spots, comparable with a good "crystal" photograph.

Comparison of an X-ray photograph of ramie and cotton shows this distinction in pronounced fashion, as in Figs. 96 and 99. Viscose rayon, highly oriented and poorly oriented, is shown in Figs. 102 and 103.

When well orientated native cellulose is mercerised without tension, the degree of orientation falls, as is seen by comparing Figs. 96 and 99 with Figs. 97 and 100. The effect of tension on orientation is also seen by comparing cotton mercerised with tension (Fig. 101) and cotton mercerised without tension (Fig. 100).

Mercerisation

Reference to good X-ray photographs of native cellulose fibres reveals the presence of two arcs close together and inside the prominent *002* arc. These reflections are from the $10\bar{1}$ plane and the *101* plane, the latter being nearer the centre of the photograph. They are not as intense as the *002* arcs.

In the case of completely mercerised or of regenerated cellulose, the X-ray photograph shows a change in position of these two shorter arcs. The $10\bar{1}$ arc is much nearer to the prominent *002* arc and the *101* arc is nearer the centre of the

photograph. This characteristic effect is a feature of dispersed cellulose and super-imposed upon it is the effect of orientation or disorientation, according to the tension.

During the change from native to mercerised cellulose the *10$\bar{1}$* and *101* arcs do not move apart but fade out in their old positions and reappear in their new positions. The extent of dispersion of the cellulose can be estimated quantitatively by the intensity of the arcs. Further, in the case of material which is not fully mercerised, then the *10$\bar{1}$* and *101* arcs each appear in two positions and even in regenerated cellulose the presence of native cellulose can sometimes be detected. The extent of mercerisation or dispersion may be estimated photometrically, as shown by Schramek (Monatschr. für Textil. Ind., 1934, *49*, 257) and for this purpose it is not necessary to have a complete X-ray photograph but only a section.

In this manner it is possible to produce a graded series passing from native cellulose to 100% mercerised cellulose where the comparative intensities have been measured and this series may be used as a standard for comparison with other photographs ; the degree of mercerisation may therefore be estimated.

It may be remarked, however, that the quantitative accuracy of this method is doubtful, for the regular X-ray diffraction pattern arises from the more organised or "crystalline" regions of the fibre structure and it can hardly be doubted that there are varying proportions of less organised material present.

On the basis of these estimations, however, Schramek concludes that in technical mercerising the efficiency seldom exceeds 60-70% for yarn and 35-40% for cloth. These figures show fair agreement with those obtained by the deconvolution count.

Fig. 100 refers to cotton yarn mercerised in the laboratory and shows complete conversion to hydrate cellulose ; the yarn was mercerised without tension. Fig. 101 relates to commercially mercerised cotton yarn, and although the effect of tension is seen in the better orientation, the presence of native cellulose is clear.

PART FOUR

MODIFIED CELLULOSE

CHAPTER ELEVEN

HYDROCELLULOSE

Introduction

THE term hydrocellulose has been employed since about 1880, to designate cellulose which has been weakened or tendered as the result of treatment with acids. As yet there is no proof of the chemical identity of such a substance, and it seems probable that what is known as hydrocellulose consists of a number of compounds less complex than cellulose itself and more or less related to it and to glucose.

Calvert (Pharm. J. Trans., 1855, *14*, 364) apparently was the first investigator to record the fact that cellulose suffers a pronounced change when heated with organic acids and Terreil (Bull. Soc. Chim., 1872, *17*, 3) showed that modification also occurs in the case of concentrated sulphuric acid.

The term hydrocellulose, however, will always be associated with the name of Girard who investigated the action of acids on cellulose in some detail (Comp. rend., 1875, *81*, 1105; 1879, *88*, 1322; Ann. Chim. Phys., 1881, *24*, 337). His main observations were that only the mineral acids have the property of forming hydrocellulose from cellulose by simple immersion. When H_2SO_4 (*d*.1·453) is used the fibre should be immersed for 12 hours at 15° C., but HCl (*d*.1·091) takes 24 hours. HNO_3 (*d*.1·424) produces a mixture of hydrocellulose and cellulose, whilst the more dilute acid fails to give any appreciable amount of hydrocellulose. Syrupy phosphoric acid has little effect. When dilute acids are used, however, Girard records the most generally utilised method for the preparation of hydrocellulose, namely the impregnation of cotton with a 1% solution of mineral acid followed by drying at 60–70° C.; where this method is used, hydrocellulose is formed in a few hours. If the immersion is followed by drying at room temperatures then the formation of hydrocellulose takes several months. Cold moist HCl or HBr gas transforms cellulose to hydrocellulose in about an hour, and if the gas is warm the reaction

is complete in a few minutes. The vapours from H_2SO_4 or HNO_3 react slowly while pure CO_2 and SO_2 are without effect.

HCl gas has no action on anhydrous cotton cellulose at room temperatures, according to Coward, Wood and Barrett (J.T.I., 1923, *14*, 520).

Girard also investigated the action of 5 % solutions of oxalic, tartaric and citric acids on cellulose by drying the impregnated material and then heating in closed vessels at 100° C. Oxalic acid effected a complete change, tartaric acid a partial change, but citric acid was less active. Acetic and formic acids exercised only a moderate action.

Some of this work was repeated by Stern (J.C.S., 1904, *85*, 336) who concluded from analytical data that there was no formation of hydrocellulose, but that the cellulose was partly hydrolysed with the production of soluble products. Cross and Bevan, however (J.C.S., 1904, *85*, 691), pointed out that Stern did not follow Girard's instructions, and that hydrocellulose differed from cellulose in its behaviour to alkali, Fehling's solution, and esterifying agents. Jentgen (Z. angew. Chem., 1910, *23*, 1541) found Girard's methods difficult to control, and therefore distributed the acid or a salt of the acid with a weak base, throughout the cellulose by means of a non-dissociating solvent such as glacial acetic acid, ether, amyl acetate, formic acid or glycerol.

Hauessermann (Z. angew. Chem., 1910, *23*, 1761) found that at ordinary temperatures, dilute HNO_3 exerts an action on cellulose similar to that of the other mineral acids.

Knoevenagel and Busch (Cellulosechemie, 1922, *3*, 42 and 58) prepared hydrocellulose from viscose containing its normal amount of moisture (11·5 %) by treating with hydrogen chloride until it contained 4–10 % of the acid which was then left in contact with the cellulose at ordinary temperature for 12 hours. This product (unlike Girard's hydrocellulose) is completely soluble in cold dilute 8 % sodium hydroxide.

Modern Developments

Birtwell, Clibbens and Geake (J.T.I., 1926, *17*, 145) pointed out the uncertainty of the exact experimental conditions employed by previous workers, and prepared a wide range of hydrocelluloses under reproducible conditions by treating cotton with a large excess of acid at temperatures between 20° and 100° C. as in the experiments of Coward, Wood and Barrett (loc. cit.). This is termed the acid steeping method.

In view of its technical significance the acid drying method was also studied by drying small quantities of acid into cotton fabrics. " Hydrocellulose " was defined as any preparation of cotton cellulose (other than esters) the properties of which have been altered to a greater or less extent by the action of acids; but the work described is limited to preparations which still retain the structure of the cotton hair.

In the acid steeping method, two temperatures were used, 20 and 40° C., and 40 g. of cotton were treated with one litre of the acid solution, the vessel being kept in a thermostat and every precaution being taken to ensure thorough wetting. The product was washed in distilled water and dried in the air. Where hair strength has to be determined, a more efficient wash is necessary in order to ensure the elimination of acid. The hydrocellulose is steeped in water for from one to three days and is centrifuged between the changes of water, until the steeping water shows an acid reaction of not more than 10^{-5} N in mineral acid.

Where the cellulose was boiled with acid, very weak solutions were employed, the boiling point of which scarcely differed from that of pure water. The cotton was boiled with 50 times its weight of the standard acid under a reflux condenser.

With the acid drying method it was found difficult to obtain even action but a moderately satisfactory technique is to wet the cotton cloth in a large volume of dilute acid with repeated mangling and impregnation until the weight has increased by 100%. In the case of phosphoric acid solutions the final weight was brought to two and a quarter times the air dry weight of the original cloth. The impregnated material was then allowed to " dry " overnight in the air and finally heated on a rotating glass frame in an electric oven maintained at the required temperature for the necessary time. With acid concentrations of not less than 0·025 N the results were uniform and reproducible, but with acid as dilute as 0·01 N no satisfactory method was found. Birtwell, Clibbens and Geake (J.T.I., 1926, *17*, 145) considered that it was possible to arrive at a more precise definition of hydrocellulose by means of a measure of the relation between any two quantitative properties. For instance, the fall in the tensile strength of cotton caused by the action of acids under any conditions of treatment is accompanied by a fall in the viscosity of the material in cuprammonium hydroxide solution, and by a rise in its reducing power or copper number. They have shown that for hydro-

celluloses formed under a wide range of different conditions there exists a definite relation between the loss of tensile strength and the viscosity; in other words, the same fall of viscosity corresponds to the same loss of strength irrespective of the mode of acid tendering. An acid attack which causes the log. viscosity (η) to fall to the value 1, produces a loss in strength of 10%, whilst a loss of 80% in strength corresponds to a log. viscosity (η) of -1. The following curves show the relationship between log. viscosity and breaking load for single hairs and single threads.

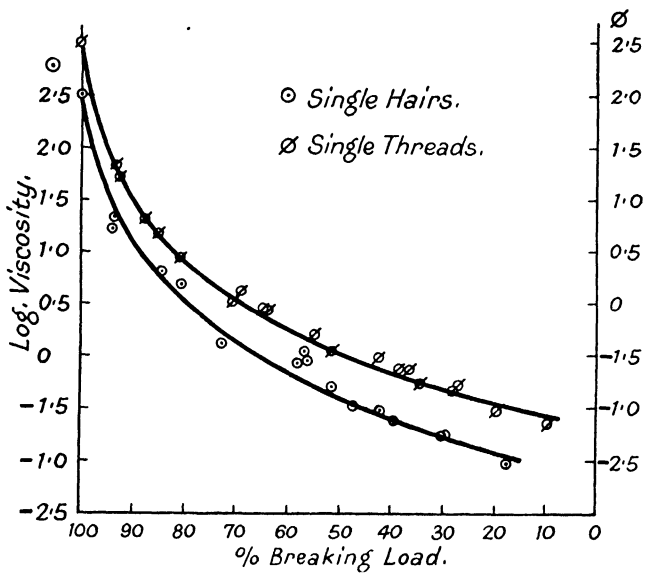


FIG. 104.—Relation between log. viscosity and breaking load.

A definite relation has also been shown to exist between the strength and the copper number of the hydrocelluloses examined, a diminution of 10% in breaking load, corresponding to a rise of 0·25 in copper number, and a decrease of 80% in breaking load to a rise of 3·5. As the copper number is greatly reduced by alkali boiling under conditions which have little effect on the viscosity, the latter measurement is more generally useful for the detection and estimation of acid tendering. The copper number—breaking load relationship is shown graphically on the next page.

From an examination of about seventy different hydro-

celluloses prepared by the widest range of acid action, Birtwell, Clibbens and Greake (loc. cit.) have shown that a given viscosity always corresponds to the same copper number irrespective of the conditions of acid treatment, and the relation between the two quantities can be expressed with reasonable accuracy over the most important range by a simple equation.

If η is the absolute viscosity of a 2% modified cellulose solution and η_0 is the absolute viscosity of the cuprammonium solvent (taken as 0·0152 poise), then η/η_0 is the relative viscosity

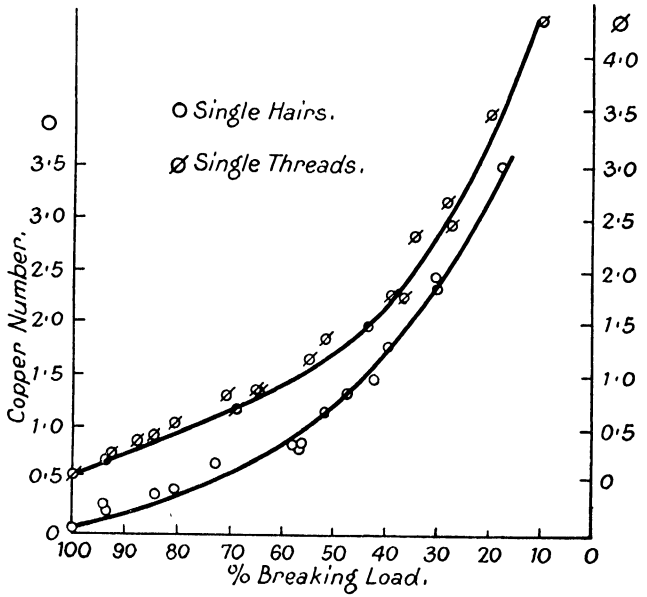


FIG. 105.—Relation between copper number and breaking load.

of the solution and the quantity log η, generally used in work on modified cellulose, will be replaced by log η/η_0, which will be designated by the symbol V, thus

$$V = \log \eta/\eta_0 = \log \eta - \log \eta_0 = \log \eta + 1{\cdot}82.$$

In order to obtain V, the logarithm of the relative viscosity, it is only necessary to add 1·82 to the recorded values of the logarithm of the absolute viscosity (log η). If the copper number is denoted by the symbol N_{Cu}, then the viscosity-copper number relationship is represented by the equation

$$N_{Cu}\ V^2 = 2{\cdot}6$$

These investigators have also demonstrated the relationship by the following curve:

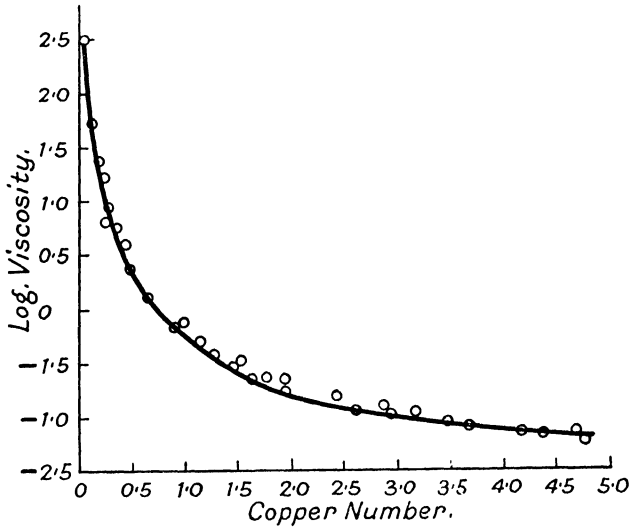


FIG. 106.—Relation between log. viscosity and copper number.

A specific test of hydrocellulose formation is to be found in this rise of copper number relative to the fall of viscosity, and by this means it is frequently possible to differentiate between hydrocellulose and those oxycelluloses which are otherwise indistinguishable from them.

Rate of Attack

Birtwell, Clibbens and Geake (loc. cit.) have also measured the rate of acid attack as affected by conditions of temperature and concentration. For normal hydrocellulose formation the copper number can be taken as a true measure of the extent of cellulose degradation, and it has been shown that under conditions of acid steeping the increase of copper number with increasing time of treatment is governed by the rule that the copper number is increased by 50 % when the time is doubled. This may be expressed by the equation

$$N_{Cu} = KT^{0.6}$$

where T is the time of treatment and K is a constant under defined conditions. If the time is measured in days, K is equal to the copper number which results from an acid treatment lasting one day.

Some typical results are shown below :

VELOCITY CONSTANT.

H_2SO_4 100 g./l at 20° C.	1	2	4	8	16	
Copper number .	0·17	0·23	0·36	0·52	0·77	Mean
Velocity constant K	0·17	0·15	0·16	0·15	0·15	0·15
HCl 100 g./l at 20° C.						
Copper number .	0·58	0·91	1·28	1·96	2·94	Mean
Velocity constant K	0·58	0·60	0·56	0·56	0·56	0·56

The mean value of K derived from a series of experiments covering a range of copper numbers is the best measure of the rate of attack of a given acid solution under definite conditions of concentration and temperature. This method has not been used in the case of hydrocellulose with a copper number greater than 4.

At any temperature the rate of hydrocellulose formation is approximately the same for solutions of two acids of equal molar concentration, HCl being, however, always slightly more active than H_2SO_4. Measurements at 20, 40, and 100° C. show that for the lower temperatures, the velocity constant is almost proportional to the acid concentration for values below 3 molar, but for increasingly rising concentrations the rate of attack increases much more rapidly than the acid concentration ; thus the activity of 8-molar HCl at 20° C. is nearly six times that of 4-molar acid. At 100° C. it is not possible to investigate such high acid concentrations as the rate of attack is too rapid for accurate measurement.

The mean temperature coefficient of hydrocellulose formation over the range 20 100° C. has been found to be 2·3, which means that the copper number resulting from a given acid treatment is increased 2·3 times for a 10° rise in temperature.

The addition of neutral salt to a dilute solution of hydrochloric acid has been shown to have a great effect in increasing the rate of acid attack when the salt concentration becomes high. For example, the rate of attack of the dilute acid (0·1 M HCl) is increased over threefold by making the solution 3·9 M in NaCl. Birtwell, Clibbens and Geake consider it probable that these observations have an important bearing on the action of concentrated solutions of zinc or magnesium chloride on cotton. The acidity of these solutions, which is a consequence of the hydrolysis of the salt, is not considerable, but the effect may be greatly enhanced by the high concentration of neutral salt.

General Properties

According to the somewhat ill-defined experiments of the earlier (i.e. prior to 1925) workers, where no attempt was made to preserve the fibrous structure of the material, hydrocellulose is a white friable powder, which if free from acid, remains unchanged when heated at 100° C., but in the presence of traces of acid it is converted into a dark coloured water soluble mass when heated at 80–100° C. for some hours. Ost (Annalen, 1913, *368*, 313) found that certain samples of hydrocellulose were decomposed by heat at 125–130° C. whilst Justin-Mueller (Bull. Soc. Chim., 1921, *29*, 937) suggested that the discoloration and caramelisation at 130–140° C. might form a test for hydrocellulose in the presence of cellulose and oxycellulose. Ost (loc. cit.) also found that hydrocellulose contains less absorbed moisture than cellulose.

Colour reactions for hydrocellulose have been observed by various workers; a blue-violet coloration is given by zinc chloride-iodine solution and by a solution of iodine in potassium iodide. The colour is transient and rapidly removed by water, whereas similar colorations in the case of hydrate cellulose, resist washing for some time. Hydrocellulose scarcely reacts with Schiff's reagent, but with phenylhydrazine it is coloured deep yellow or brown.

There are a number of contradictory statements in the literature regarding the affinity of hydrocellulose for dyestuffs, particularly methylene blue. This is probably due to the different methods of preparation employed by the various investigators, and perhaps in some cases to a failure completely to remove the acid from the material.

Harrison (J.S.D.C., 1912, *28*, 238) states that when dilute H_2SO_4 is dried into cotton the absorption of methylene blue is increased, and that of direct dyes is decreased. Briggs (J.S.C.I., 1916, *35*, 80) states that hydrocellulose does not show a greater affinity for methylene blue than ordinary cellulose does. Regarding the effect of acid on cotton, Birtwell, Clibbens and Geake (J.T.I., 1926, *17*, 145) have shown that its affinity for basic dyes varies with the concentration of the acid used; with the first increase in concentration, it suffers a loss of affinity for basic dyes, which is the normal effect of acid attack, but when acid of still higher concentration is used, the affinity increases. It differs from oxycellulose, however, in that it absorbs methylene blue from an acid solution quite as

well as from a neutral solution. The product contains sulphuric acid in a state of combination which is not destroyed by the most drastic alkali boil, and the increased affinity for methylene blue is due to this combination. The combined sulphuric acid exists as sulphate and may be removed by boiling alcohol (Wood—J.T.I., 1926, *17*, 101P).

In the case of cotton steeped in H_2SO_4 for 48 hours at 20° C. the following data have been obtained :

METHYLENE BLUE ABSORPTION.

H_2SO_4 in grams/litre	0	100	200	300	400	500	600	700
Methylene blue abs.								
pH 7 . .	0·89	0·82	0·83	0·82	0·79	0·79	0·94	1·30
pH 2·7 . .	0·31	0·28	0·26	0·25	0·27	0·36	0·72	1·76

With lower concentrations of H_2SO_4, at higher temperatures, there is no rise of methylene blue absorption, but a steady fall is also observed when cotton is steeped in HCl under any conditions. Hydrocellulose formed by impregnation with dilute H_2SO_4 followed by heating behaves in the manner described above, i.e. an initial fall in methylene blue absorption followed by a rapid rise as the acid concentration is increased. HCl when dried into cotton decreases the absorption except under drastic conditions, e.g. N-acid at 90° C. when an increase in absorption takes place. Phosphoric acid gives results similar to those from sulphuric acid. By using the method of Geake (J.T.I., 1924, *15*, 81) for estimating phosphoric acid, it is possible to show the relationship between the combined acid and the affinity for methylene blue. This has been done by Birtwell, Clibbens and Geake (J.T.I., 1926, *17*, 145).

Cotton impregnated with 0·1 M phosphoric acid and heated for two hours :

METHYLENE BLUE ABSORPTION.

Temp. of Heating.	Methylene Blue at pH 7.	Absorption. at pH 2·7.	H_3PO_4 content M. Moles/100g.
(untreated)	0·89	0·31	0·00
50	0·83	0·52	0·35
70	0·93	0·71	0·79
90	1·39	1·19	1·80
110	1·64	1·70	2·62
130	1·82	2·14	3·31

From the above table it will be seen that the methylene blue

absorption at pH 2·7 is proportional to the phosphoric acid content of the hydrocellulose except in the early stages.

Hydrocellulose is esterified much more easily than normal cellulose, and a great deal of work has been published in this connection, some of which is described in the section dealing with the esterfication of cellulose.

Berl and Klaye (Z. ges. Schiess und Sprengstoffwesen, 1907, *2*, 381) have prepared cellulose nitrates from cellulose and hydrocellulose under the same conditions, and found that the product from hydrocellulose showed a greater solubility in alcohol, a greater fixation of methylene blue and a lower viscosity than the nitrate from cellulose. This does not agree with the view of Girard (page 207), who considered the two products to be identical.

Hydrocellulose is acetylated much more rapidly then cellulose. Stein (Z. angew. Chem., 1913, *26*, 673) has prepared esters of propionic, butyric and valeric acid by the action of the anhydride on hydrocellulose in the presence of concentrated H_2SO_4. Esterification proceeds easily up to the tri-ester.

The dimethyl ether of hydrocellulose has been prepared by Heuser and von Neuenstein (Cellulosechemie, 1922, *3*, 89 and 101) in quantitative yield by the action of dimethyl sulphate on an alkaline solution of hydrocellulose prepared by the method of Knoevenagel and Busch. The product is soluble in cold water and on acetylation yields a monoacetyl dimethyl derivative of cellulose.

Beltzer, in an original communication at the 8th International Congress of Applied Chemistry in 1912, has stated that hydrocellulose is capable of absorbing large quantities of formaldehyde, thereby yielding a very tough product.

Solubility of Hydrocellulose

The effect of boiling water on hydrocellulose is to yield a considerable quantity of a soluble copper-reducing substance, and to produce a reduction in copper number from 5·4 to 0·8 after 70 hours extraction according to Heuser and Herzfeld (Chem. Zeit., 1915, *39*, 689). Treatment of the residue with 3% H_2SO_4 according to Girard's method formed hydrocellulose again, which had a copper number of 3·9 and behaved as before on extraction with boiling water.

Alkali Boil

The solubility of hydrocellulose in boiling solutions of sodium

and potassium hydroxide has been well established by many workers, including Girard, Cross and Bevan, Schwalbe, and Briggs. Schwalbe (Z. angew. Chem., 1909, *22*, 155) gives the following results obtained by boiling "Girard" hydrocellulose with sodium hydroxide solution:

EFFECT OF THE ALKALI BOIL.

Hydrocellulose.	15% NaOH.	Time of Boil.	Undissolved Residue.
10 g.	200 g.	10 mins.	48%
10 g.	200 g.	20 ,,	42%
10 g.	200 g.	30 ,,	40%
10 g.	200 g.	40 ,,	37%
10 g.	400 g.	60 ,,	33%

The hydrocellulose prepared from viscose cellulose by the method of Knoevenagel and Busch (loc. cit.) is completely soluble in cold 8% NaOH solution.

The action of boiling dilute alkali on hydrocellulose which has not lost its fibrous structure has been examined by Birtwell, Clibbens, and Geake (J.T.I., 1926, *17*, 145). The hydrocelluloses were prepared by steeping in H_2SO_4 of various concentrations for 48 hours at 20° C. For the determination of loss of weight the samples were boiled with 1% NaOH solution for four hours, but for examination of the other properties they were submitted to a technical kier boil of six hours duration with 1% NaOH at 20 lbs. excess pressure—a process which produced appreciably greater loss of weight than the analytical procedure.

EFFECT OF THE ALKALI BOIL.

% Loss in wt	Copper Number. Before	After	Log. Viscosity (2%). Before.	After.	Breaking Load (%) Before.	After.
1·40	0·04	0·03	2·5	2·03	100	105
1·69	0·205	0·01	1·33	1·20	93·3	97·8
3·06	0·425	0·06	0·69	0·40	84·7	84·2
5·14	0·80	0·08	0·02	$\bar{1}$·91	70·3	67·5
8·66	1·34	0·21	$\bar{1}$·53	$\bar{1}$·56	51·4	43·0
14·7	2·32	0·39	$\bar{1}$·23	$\bar{1}$·22	34·1	24·2
	3·48	0·56	$\bar{2}$·98	$\bar{1}$·00	19·5	12·1
	4·36	0·98	$\bar{2}$·85	$\bar{2}$·85	9·7	5·5

The copper number is, in all cases, greatly diminished by alkali boiling, and would evidently approximate to zero with prolonged treatment, but the viscosity is only slightly affected. The effect of alkali boiling on the single thread breaking load

of hydrocelluloses is not great until the loss of weight becomes considerable, and the less modified preparations suffer no change, or actually show an increase in strength after kier boiling, due no doubt to the swelling of the cellulose and the tighter binding of the component hairs in the yarn.

Clibbens, Geake, and Ridge (J.T.I., 1927, *18*, 277) have examined the effect of hot dilute NaOH solutions on modified cotton and found that as a result of a six hours' treatment with 1 % NaOH at the boil, oxycellulose suffers a fall in viscosity and differs in this respect from hydrocellulose and normal bleached cotton which are only slightly affected. An exactly similar behaviour occurs when the alkali boil is replaced by

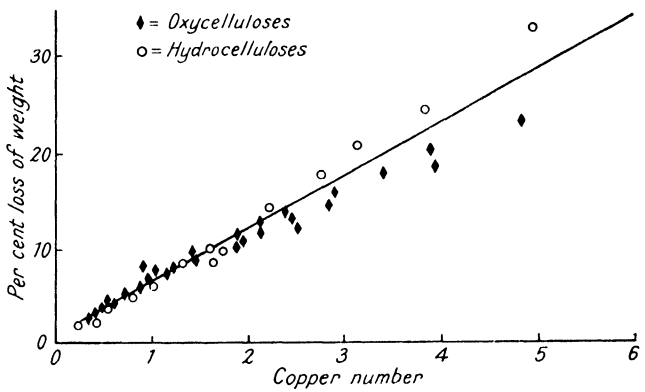


FIG. 107.—Relation between copper number and loss in weight.

the treatment used in the determination of copper number by Braidy's method. In this connection, it has already been shown by Birtwell, Clibbens, and Geake (loc. cit.) that with a given copper number, hydrocellulose has a lower viscosity than many oxycelluloses.

The enhanced copper number of modified cellulose is reduced on an average to one-fifth of the original value by a six hours' treatment with 1 % NaOH at the boil under atmospheric pressure and to one-tenth at 20 lbs. excess pressure.

The methylene blue absorbtion of hydrocellulose which is initially great owing to the presence of combined acid, rises still further on alkali boiling in spite of the partial removal of acid. As a general rule, the methylene blue absorption of all modified cellulose rises in consequence of alkali boiling.

The percentage loss in weight suffered by modified cottons

on boiling for four hours with a 1% solution of NaOH at ordinary pressure is about six times the copper number when the latter does not exceed 2·5, irrespective of the manner of modification of the cellulose. With copper numbers greater than 2·5, hydrocellulose experiences a greater, and oxycellulose a smaller loss, and this divergence increases with increasing cellulose modification.

The effect of hot dilute alkali on the strength of modified cotton had been observed by Witz (Bull. Soc. Ind., Rouen, 1883, *11*, 169), who found that oxycellulose suffered a further

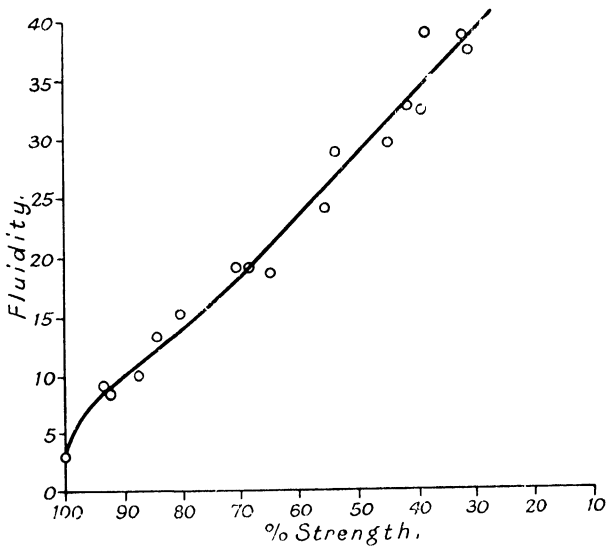


FIG 108.—Relation between tensile strength and fluidity.

loss of strength on treatment with hot dilute alkali but that hydrocellulose did not. Clibbens and Ridge (J.T.I., 1928, *19*, 390) examined the tensile strength and fluidity of chemically modified cotton, broadly confirming and extending the conclusions of Witz, but also showing that fluidity remains a valuable control of the extent of tendering, even when the chemical modification is followed by hot alkaline treatment. Chemical measurement of the extent of modification of cotton cellulose is, in most cases, of little value as a guide to the loss of strength. Cotton yarn was chemically modified between two kier boils, and it was found that yarn tendered by acid to an extent of 20% suffered very little extra loss of

strength as a result of the subsequent boil. Clibbens and Ridge give data for the action of acids on yarn, most of which were published in an earlier paper by Birtwell, Clibbens and Geake, but the measurements of rate of flow in cuprammonium were there recorded as logarithms of viscosities in 2 % solution, whereas Clibbens and Ridge express the results as fluidities in 0·5 % solution.

The relationship between tensile strength and fluidity is shown in the graph on the previous page.

Solubility at Room Temperature

The solubility of modified cellulose in sodium hydroxide solutions at ordinary temperatures has been investigated by Birtwell, Clibbens and Geake, and the results described in a later paper (J.T.I., 1928, *19*, 349). They found that the maximum solubility on treatment with any single solution at 15° C. occurs in 3 N sodium hydroxide and that the solubility falls rapidly with increase or decrease of alkali concentration.

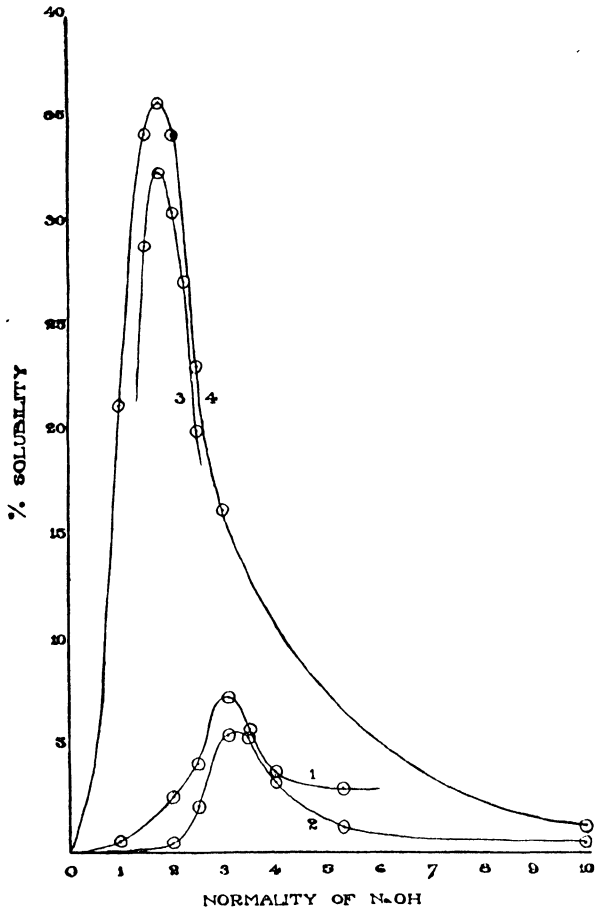
If, however, the modified cellulose is first treated with a more concentrated NaOH solution (6 to 10 N), and the alkali subsequently diluted by adding water to the mixture, then a much greater amount of modified cellulose may be dissolved than by the use of any single solution. The conditions under which maximum solubility is realised consist in first steeping the material in 10 N caustic soda solution and then diluting the alkali with water to 2 N while still in contact with the cotton. This process is described as treatment with 10 N—2 N caustic soda, and it is of importance to control the temperature to within one degree as the solubility is greatly affected by temperature changes.

The effect of treatment with such solutions of sodium hydroxide is illustrated by a hydrocellulose of copper number 3, which had a 6 % solubility in 3 N sodium hydroxide, but a 30 % solubility in 10 N—2 N, at 15° C. Other results are shown in the graph on the following page.

Since a washing treatment is equivalent to a series of rapid treatments with successively weaker alkaline solutions, it is obvious that the loss in weight by the 10 N–2 N sodium hydroxide treatment cannot be determined accurately by direct weighing, so that the solubility has to be measured by a volumetric analysis of the solution, dichromate being used for the complete oxidation of the dissolved cotton.

Solubility Number

Before determining the Solubility Number (which is the name for the result of the standard test), it is necessary thoroughly to disintegrate the material. This is effected,



Curves 1 & 2 ... 3 N. Curves 3 & 4 ... 10 N – 2 N.

FIG. 109.—Solubility in alkali.

in the case of cloth, by cutting narrow diagonal widths into shavings not more than one-sixteenth of an inch wide and rubbing these between the hands. 2·5 g. of the modified cotton are steeped in a stoppered bottle with 25 cc. of 10 N caustic soda for 15 minutes, 100 cc. of water are then added,

diluting the alkali to 2 N, and the mixture shaken occasionally during one hour. The temperature is maintained at 15° C. to within one degree throughout the process. The solution is separated from the residue by inverse filtration through a fritted glass filter, a preliminary separation being effected by centrifuging when filtration is difficult. The filter is of the " inversion " type, 4 cm. in diameter, and made of Jena glass with a glass filter disc of the coarsest grade (Schott. u. Gen., No. 11a, G3/2–3) ; it is dipped into the bottle containing the mixture, and the solution drawn off into a second vessel. To 10 cc. of the filtered solution, approximately neutralised with a small volume of sulphuric acid, 25 cc. of N potassium dichromate are added—or less if the solubility of the cotton is small—followed by 10 cc. of concentrated H_2SO_4, the total volume being adjusted to roughly 55 cc. with water. The mixture is boiled under reflux for one hour, cooled, made up to 100 cc. with water, and 20 cc. portions titrated with N/10 ferrous ammonium sulphate, potassium ferricyanide being used as external indicator. The ferrous ammonium sulphate is standardised immediately before use with N/10 potassium dichromate solution. From the volume of dichromate consumed, the weight of cellulosic material in the alkaline solution is calculated on the assumption that its composition is represented by the formula $C_6H_{10}O_5$ and that complete oxidation to water and carbon dioxide occurs. (1,000 cc. of N dichromate equivalent to 6·75 g. of cellulose.)

This method has been adapted by Nodder (J.T.I., 1931, *22*, 416) to form a *microchemical* test. The material to be examined is first boiled for six hours under reflux in a 2% solution of caustic soda. It is then washed free from alkali and carefully dried. The preliminary boil is an essential part of the method. Its object being to remove non-cellulosic impurities and cellulose degradation products soluble in boiling dilute caustic soda. The material is then cut into thin shreds. The air dry powder (exactly 0·1 g.) is weighed into a test tube provided with a ground glass stopper, a convenient size of tube being 5 ins. by $\frac{5}{8}$ in. The powder is tapped down into the bottom of the tube and caustic soda (10 N, 1 cc.) is added, the drops being distributed as evenly as possible. Uniform wetting may be promoted by tapping the tube smartly with the finger-tips.

If wetting is difficult, stirring with a thin glass rod is desirable. As soon as possible the tube is immersed in a water bath

maintained at 15° C. (Vacuum flasks have been found very satisfactory for water baths.) After 15 minutes distilled water (4 cc.) is added in order to dilute the caustic soda to 2 N strength. The tube is replaced in the water bath for a further period of one hour and shaken occasionally during that time. For filtering the solution from the undissolved residue, a small fritted glass filter (Schott u. Gen., 30a, G3) is used, this being cut down to within 2 mm. of the disc. The filter is attached to the lower end of a 2 cc. pipette by means of a suitable piece of thick-walled rubber tubing and immersed in the contents of the tube. The pipette is then filled by gentle suction from the water pump. The filtered solution (2 cc.) is run into a 100 cc. flask, and to it is added 10 cc. of a half normal solution of potassium dichromate containing 230 cc. of H_2SO_4 per litre. The flask is closed with a glass pear stopper and immersed for one hour in a vigorously boiling water-bath, being shaken occasionally. The evaporation from the flask is not so great under these conditions to necessitate the addition of water. After one hour, the contents of the flask are cooled and titrated with decinormal ferrous ammonium sulphate, using potassium ferricyanide as external indicator in the usual way. It is rather easy to overshoot the end-point, but if this occurs a back-titration with decinormal potassium bichromate may be made. The half-normal acid bichromate solution (10 cc.) is likewise titrated. If " a " is the number of cc. of decinormal ferrous ammonium sulphate required by 10 cc. of the half-normal acid dichromate and " b " is the number of cc. of decinormal ferrous ammonium sulphate required by the contents of the flask, then

$$\text{Solubility Number} = 1{\cdot}688\ (a-b).$$

This method is very useful for routine work. The solubility number as defined above is the percentage of cellulose (calculated, not on the original weight of the sample, but on the weight of the air-dry state after the preliminary boil in dilute caustic soda), which is dissolved by the caustic soda treatment at 15° C. under the conditions stated.

By means of the method of Birtwell, Clibbens and Geake (loc. cit.), a study has been made of the variation in the solubility of modified cotton, according to the manner of modification. In the case of hydrocellulose, the solubility is completely defined if the copper number is known, i.e. hydrocelluloses with the same copper number have the same solubility number. This is not the case with oxycellulose.

The relations between the properties of modified cottons described by Birtwell, Clibbens and Geake, do not apply to cotton which has been mercerised prior to modification. A hydrocellulose of given copper number, formed from unmercerised cotton, dissolves to a much greater extent than a hydrocellulose of the same copper number formed from mercerised cotton; the name is true for oxycelluloses.

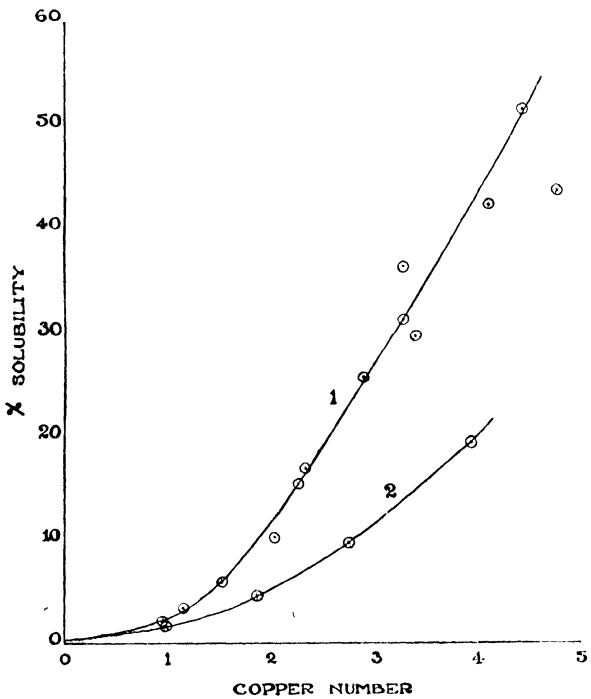


FIG. 110.—Relation between copper number and solubility.
(Curve 1 relates to bleached cotton attacked by acid; curve 2 to mercerised bleached cotton attacked by acid.)

Diminution in solubility, caused either by the mechanical form of the material or by mercerisation prior to chemical modification, is accompanied by an increase in the reducing value of the material dissolved.

Although the reducing substances in modified cotton (i.e. those substances which are responsible for the copper number) are dissolved in alkali, their presence does not account for the

loss of weight on extraction. This also has been shown by Birtwell, Clibbens and Geake (loc. cit.), by boiling a modified cotton with dilute alkali, e.g. N/4 NaOH under sufficiently vigorous conditions to reduce the copper number to zero, when

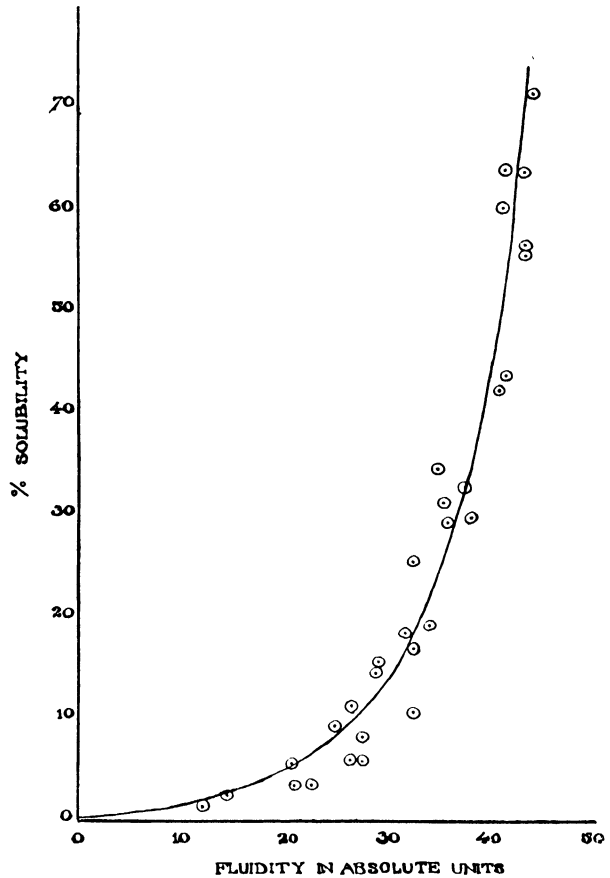


FIG. 111.—Relation between fluidity and solubility.

the solubility in 10 N—2 N NaOH at 15° C. was actually increased.

There is also a general correlation between the solubility number and fluidity which is independent of the manner of modification.

The *reducing properties* of the alkali-soluble fractions have

been measured according to the following method. From the 125 cc. of alkaline solution obtained by extracting 2·5 g. of modified cotton according to the standard method for solubility number, 75 cc. are measured into a conical flask of capacity slightly greater than 100 cc. and mixed with 11·3 cc. of 10 N NaOH. Carbon dioxide is passed into the mixture until the gain in weight of the flask and its contents is 6·9 g. The total volume is then brought up to 100 cc. by the addition of 5 cc. of the copper sulphate solution and 13·7 cc. of the carbonate—bicarbonate solution employed in the copper number method of Clibbens and Geake. The subsequent details follow the procedure for the determination of reduced copper except that a wad of well-scoured cotton fibre is placed above the filter paper to prevent choking. The weight of cotton in the 75 cc. of solution is known from the volumetric dichromate analysis, which can be carried out on another portion of the 125 cc. available. The reducing value is calculated from these analyses, as the weight of copper in grammes reduced by 100 g. of dissolved cotton, i.e. the reducing value is carried out on a constant volume of an alkaline solution varying in cotton content, whilst the copper number is determined on a constant weight of cotton.

When hydrocelluloses are extracted with 10 N—2 N NaOH, the reducing values of the extracts are roughly constant at the value 4, irrespective of the nature and extent of the acid attack within the limits examined. The constancy of the reducing values is not maintained in the earliest stages of cellulose modification.

Solubility at Low Temperatures

The solubility of modified cellulose in caustic soda at temperatures below the normal has been described by Davidson (J.T.I., 1934, *25*, 174). Here again the percentage of the material which dissolves is used as a measure of the solubility.

The results show that the solubility of hydro- and oxycelluloses at any temperature is at a maximum at a certain alkali concentration, and as the temperature is lowered from the normal, the maximum solubility is greatly increased and occurs a lower alkali concentration. Thus for a certain hydrocellulose, the maximum solubilities observed at 15°, 0° and — 5° C. were 8·2, 57·5 and 82·6%, and these maxima occurred at alkali concentrations of 3·0, 2·75 and 2·5 N. respectively. In the case of modified cellulose prepared from previously mercerised

cellulose, the maximum solubility at −5° C. occurred at a rather higher alkali concentration.

When modified cottons are boiled under pressure with dilute alkali, the residual material is more soluble in NaOH at −5° C. than the original modified cotton, in spite of the loss of weight that may occur during the boil. The increase in solubility is slight with hydrocelluloses prepared from unmercerised cotton, but is considerable with hydrocellulose from mercerised cotton and with oxycellulose of the hypochlorite series.

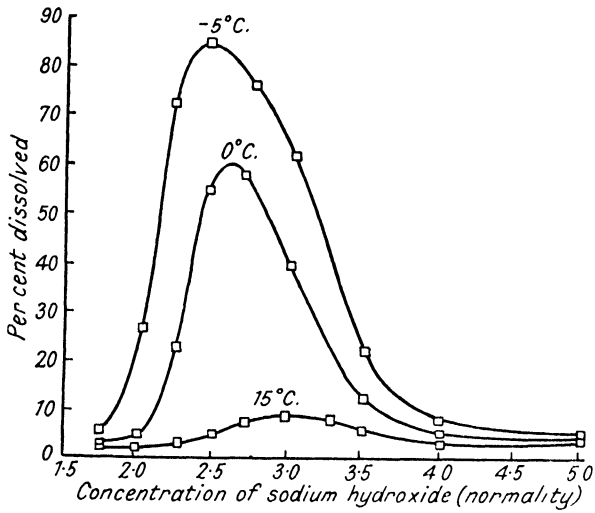


FIG. 112.—Effect of temperature.

When a modified cotton is treated with 5 N NaOH, and after dilution of the alkali to lower concentrations, the solubility at low temperatures is determined, it is found that the maximum solubility is lower and occurs at a higher alkali concentration than in the case of modified cotton not treated with the 5 N alkali solution. This is in contradistinction to the results of Birtwell, Clibbens and Geake using 6 to 10 N NaOH diluted to 2 N, but Davidson further examined the effect of the rate of dilution and found that slowing down the dilution results in a diminution of the solubility.

The solubility data for various concentrations of sodium hydroxide at 15°, 0° and −5° C. relating to hydrocellulose are shown in the graph (figure 112, above).

The solubility of any modified cotton, measured under the optimum conditions at $-5°$ C. increases with the fluidity, samples with very high fluidities being completely soluble. Hydrocelluloses made from unmercerised cotton, whether boiled after modification or not, have approximately the same fluidity-solubility relation, but the hydrocelluloses prepared from mercerised cotton are much less soluble than materials of equal fluidity similarly prepared from unmercerised cotton.

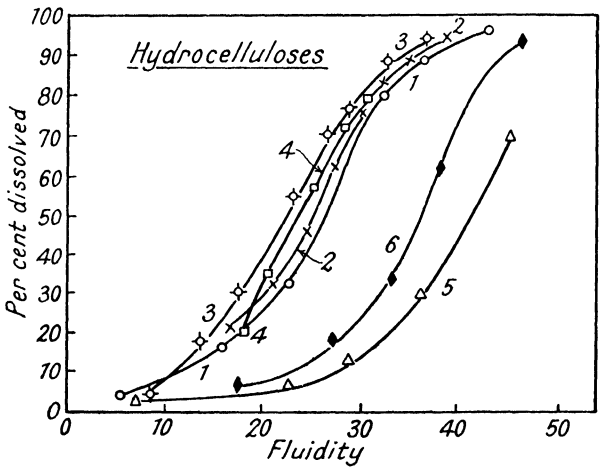


FIG. 113.—Effect of alkali-boil.

Curves 2 and 4 represent alkali-boiled cottons corresponding to those of curves 1 and 2; curve 5 represents mercerised cotton, and curve 6 the same material after an alkali-boil

Fractionation

Davidson has made use of successive extractions of a hydrocellulose with sodium hydroxide under suitably chosen conditions to effect separation into four fractions differing in fluidity. The fluidity of the original material (2% solution in cuprammonium) was 6·2, and fractions of fluidities 16·6, 10·8, 6·2 and 3·6 were obtained from it. These data, together with the observation that when progressively increasing amounts of a hydrocellulose are extracted with 100 cc. of 2·5 N NaOH solution at 0° C., the percentage of the available material dissolved is very nearly constant, are explained on the assumption that modified cottons consist of mixtures of chain mole-

cules of different lengths, the average length decreasing with increasing modification and that the tensile strength, fluidity and solubility are all functions of the chain length frequency distribution. This is in agreement with a similar assumption regarding the different viscosities, and other physical properties of cellulose esters separated into fractions all having approximately the same degree of esterification.

Solubility in various Bases

Davidson has recently shown (J.T.I., 1936, *27*, 112) that the solvent action of lithium and tetramethylammonium hydroxides is qualitatively similar to that of sodium hydroxide in the case of modified cellulose. In these solutions, the solubility of modified cotton, again defined as the percentage of the material dissolved, is at a maximum at certain alkali concentrations and as the temperature is lowered this maximum increases greatly and occurs at a lower alkali concentration. The maximum solubilities found with these three bases differ, the order of solvent action on modified cottons being LiOH < NaOH < $N(CH_3)_4OH$ at 15° C. and $N(CH_3)_4OH$ < LiOH < NaOH at 0° and −5° C. The concentrations of the alkalies that give maximum solubility also vary. The solvent action of $N(CH_3)_4OH$ at 15° C. has a minimum at 3·25 N. and increases again in a region where the solvent action of the other two bases falls continuously with increasing alkali concentration.

The solvent action of KOH on modified cottons is much less than that of the other three bases and is much less affected by temperature. In the case of unmercerised cotton the curves obtained with oxy- and hydrocelluloses have two maxima which become more pronounced at temperatures below the normal. Modified mercerised cotton gives a single maximum (*cf.* rayon). These effects are seen in figure 114.

In measurements of solubility with KOH at low temperatures, the temperature at which the modified cotton is added to the alkali solution is important, e.g. the solubility is greater when the modified cotton is added to the cooled solution than when the mixture is cooled. Partial precipitation of a modified cotton dissolved in NaOH solution may be produced by the addition of KOH of the same molar concentration, the concentration of modified cellulose in solution falling progressively as the KOH is increased.

The addition of alkali metal sulphates to 3 N. NaOH solution reduces the solvent action, the solubility decreasing with

increasing sulphate concentration. The effect of the sulphate increases in the order $Li_2SO_4 < Na_2SO_4, < K_2SO_4$.

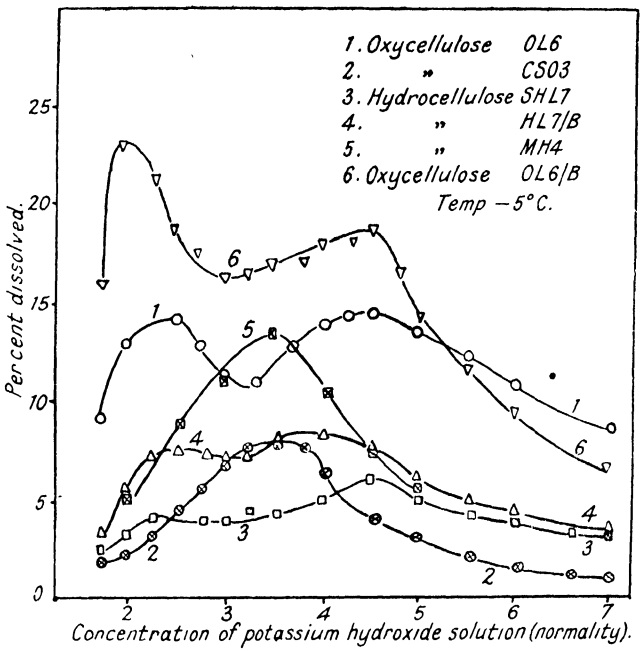
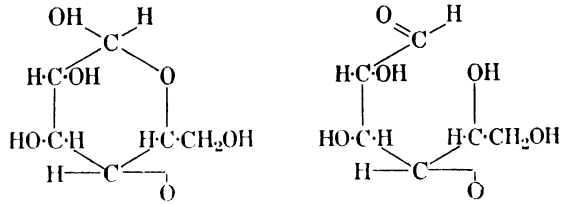


FIG. 114.—Solubility in KOH.
(Curves 2 and 5 relate to mercerised cotton.)

Hydrocellulose and the Chain Molecule

The properties of the hydrocelluloses are comparatively simple to explain in the light of the molecular chain theory.

The reducing power of cellulose is measured by means of a method depending on the determination of the amount of copper reduced from the cupric to the cuprous state; see "Copper Number," page 239. The reducing power of carefully purified cotton cellulose is never zero, but is only just significantly different (0·05 or less), which is accounted for by the fact that in the molecular chain of glucose residues the end residue is free to resume its tautomeric form and react as an aldehyde



The length of the chain accounts for the proximity of the reducing value to zero.

The copper number rises with increasing acid attack, resulting in the formation of a continuous series of hydrocelluloses characterised by progressively increasing reducing power. Whilst the hydrocelluloses are the insoluble products of acid attack, soluble products of high reducing power are also formed, and it seems likely that if the whole hydrolysis system of soluble and insoluble products were to be examined, then the copper number would increase in a continuous manner to about 300 for glucose.

The fall in tensile strength is the most striking physical feature of acid attack on the cotton fibre and this too increases continuously with a continuous variation in the conditions of acid treatment. The limit to progressive weakening is reached when the fibre falls to a powder with a copper number of about 5, thus illustrating the difference in importance between chemical modification from the textile and purely chemical standpoint.

Continuous variation is also seen in the fluidity, or reciprocal of viscosity, of cellulose subjected to continuous variation in the conditions of acid treatment.

It has been shown that in the case of a very large number of hydrocelluloses prepared under a variety of conditions, there is a definite relation between reducing power, tensile strength and fluidity, irrespective of the conditions of the acid treatment. In other words, when one of the above three properties is known for a particular hydrocellulose, then the other two are also defined. This interdependence is explained on the molecular chain theory. The action of acid consists in the hydrolysis of the glucosidic link between the glucose residues with the production of shorter chains, each possessing a terminal reducing group. The attack occurs at points distributed at random along the chains which are split into fragments of varying length, the average chain length and

distribution being measured by the fluidity. Hence the hydrolysis of a certain proportion of the glucosidic linkages defines the reducing power and also the average chain length.

As the tensile strength of the cotton hair is due to the strength of the primary valency chains together with the secondary valencies which tend to prevent the slipping of one chain on another when a longitudinal force is applied, it also follows that the rupture of the fibre will take place more easily with shorter chains.

Modified cotton cellulose also dissolves to a greater or less extent in *cold* concentrated solutions of sodium hydroxide and the dissolved fraction may be recovered by acidification without great change. The term " solubility " is not used in the orthodox sense but as defining the proportion of the material which dissolves. Under standard conditions (see page 221) the solubility also rises continuously with progressive attack and again irrespective of the conditions of acid treatment it is determined when copper number, tensile strength or fluidity is known.

Both modified and unmodified cotton celluloses swell considerably in cold concentrated solutions of sodium hydroxide and there is a direct connection between the swelling and solubility, as the greater the swelling the greater is the amount of the material which dissolves. For a certain degree of swelling, it is assumed that the chain molecules below a particular length are able to overcome the cohesive forces of the swollen material and escape into the solution. Solubility, therefore, becomes a fractionation into longer and shorter chains and measures the proportion of the material below a certain chain length. The relationship between the solubility of modified and dispersed or regenerated cellulose is thus explained. As the solubility is dependent on chain length distribution, it can be correlated with tensile strength, reducing power and fluidity as shown above. The fact that the reducing power of the soluble portion of a hydrocellulose is greater than that of the whole material confirms the idea that the shorter chain molecules are more easily dissolved.

The relationship between fluidity and solubility does not apply to the products obtained by the fractional dissolution of a hydrocellulose. If a fraction is derived from a certain hydrocellulose by separation from some of the longest and some of the shortest chain molecules, it is readily understandable that it may still have the same average chain length

and hence the same fluidity, as the original material, but the distribution of chain length will have been altered. The solubility of this fraction will, therefore, be less than that of the original hydrocellulose. The molecular chain hypothesis thus offers the explanation of the apparently peculiar observation that fluidity and solubility are no longer related to one another in the case of fractionated products.

General

Most of the preceding work on the effect of alkali on hydrocellulose refers to material which has not lost its fibrous structure; but the concluding remarks in this section do not refer to hydrocellulose prepared under conditions of careful control, but to the products of the earlier investigators.

Murumow, Sack and Tollens (Ber., 1901, *24*, 1427) and Schwalbe and Becker (J. prak. Chem., 1919, *100*, 19) have shown that when hydrocellulose is boiled with milk of lime for prolonged periods, it yields calcium iso-saccharinate and other calcium salts.

The action of acid on hydrocellulose is interesting for whilst cellulose dissolves completely to an almost colourless solution in 5 % H_2SO_4 when heated in a closed tube at 180° C., according to Girard, hydrocellulose leaves an abundant deposit of carbon, and on opening the tube there is a copious evolution of gaseous products. Ost (Annalen, 1913, *398*, 313) has shown that whilst hydrocellulose is very readily formed by the action of dilute H_2SO_4 on cellulose not more than one half of the cellulose can be hydrolysed to glucose by this method. Small amounts of glucose are formed by boiling hydrocellulose with dilute H_2SO_4 according to Stern and to Cross and Bevan (loc. cit.). Vignon (Compt. rend., 1900, *131*, 708) obtained 9·7 g. of glucose per 100 g. of hydrocellulose by heating with HCl (*d.* 1·125) on the water bath for six hours, whereas under the same conditions cellulose gave a yield of 3·29 g. of glucose. Heuser and Stockigt (Cellulosechemie, 1922, *3*, 61) state that hydrocellulose yields hydroxymethylfurfuraldehyde, but no furfuraldehyde when distilled with hydrochloric acid.

A very considerable amount of work has been done on the reducing properties of hydrocellulose. Kollman (Papierfabr., 1910, *8*, 863 and 890) has shown that hydrocellulose reduces solutions of potassium permanganate with the production of oxalic and saccharic acids. It does not react with Nessler's solution (Dietz, J. prak. Chem., 1908, *78*, 343), but it reduces

ammoniacal silver nitrate according to Buttner and Neuman (Z. angew. Chem., 1908, *21*, 2609). The reduction of Fehling's solution by hydrocellulose has been described by numerous workers, and is the basis of the " copper number " test devised by Schwalbe (loc. cit.) under carefully standardised conditions for determining the number of grammes of copper produced as a result of the action of 100 grammes of modified cellulose.

The copper numbers obtained by various investigators have been tabulated by Clifford in his exceedingly useful article " Hydrocellulose "—a summary of the literature. (J.T.I., 1923, *14*, 69) and the modern determination of " Copper Number " is described on page 239 .

CHAPTER TWELVE

OXYCELLULOSE

Introduction

THE term " oxycellulose " is generally recognised to include the intermediate products of the treatment of cellulose with oxidising agents, and must not be confused with the ultimate products of the oxidation of cellulose. As in the case of hydrocellulose, a differentiation may be drawn between the products obtained prior to about 1925 and the later products, and for the same reason, i.e. it is not at all clear from the description of the earlier work, whether it refers to material which has lost its fibrous character. The later work mainly refers to oxycellulose prepared under well defined conditions where the fibrous structure is retained. This is not due to any scientific reason, but to the fact that most research on cellulose has some technical significance and, therefore, applies to material with some textile value.

The discovery of " oxycellulose " is generally attributed to Witz, but there is evidence to show that in 1873, Jeanmaire observed that cotton goods which had been treated with dichromate solutions and were apparently quite strong, nevertheless became " tendered " when immersed in hot alkali. Even in 1868, Kolb had shown that ozone attacked linen. The discovery of Witz was in connection with the bleaching of cotton during an investigation of some fabrics which had been tendered. Cross and Bevan visited Witz about this time, and subsequently the term " oxycellulose " was coined to denote cellulose modified by oxidation.

An excellent summary of the early literature on the subject has been compiled by Clifford and Fargher (J.T.I., 1922, *13*, 189).

In the case of treatment with hypochlorites, the tendency to oxycellulose formation increases with the concentration of the solution, the presence of carbon dioxide or sunlight, and rise of temperature.

These factors were investigated by Witz (Bull. Soc. Ind.

Mulhouse, 1883, *43*, 334), and by Nastukoff (*ibid.*, 1892, *62*, 493).

Other earlier investigations include preparation by means of bromine in presence of calcium carbonate (Faber and Tollens: Ber., 1899, *32*, 2589); potassium permanganate (Nastukoff: Ber., 1900, *33*, 2237; Knecht and Thompson: J.S.D.C., 1920, *36*, 251, and 1922, *38*, 132; Cross and Bevan: Cellulose, page 62); persulphates (Dietz: Chem. Zeit., 1907, *31*, 833); hydrogen peroxide (Witz: loc. cit.; Bumcke and Wolffenstein: Ber., 1899, *32*, 2493, and 1901, *24*, 2415); ozone (Kolb: Bull. Soc. Ind. Mulhouse, 1868, *38*, 914; Witz: loc. cit.; Vignon: Compt. rend., 1897, *125*, 448; 1898, *126*, 1355; 1900, *131*, 558; 1903, *136*, 898, 969; Bull. Soc. Chim., 1898, *19*, 790; Cunningham and Dorée: J.C.S., 1912, *101*, 497) (a more recent paper has been published by Dorée and Healey (J.T.I., 1938, *29*, 27)); nitric acid (Cross and Bevan: J.C.S., 1883, *43*, 22; Tollens: Annalen, 1895, *286*, 296; Nastukoff: Ber., 1901, *34*, 3589; Vignon: Compt. rend., 1903, *136*, 818; Knecht: Ber., 1904, *37*, 549); electrolytic oxidation (Oertel: Z. angew. Chem., 1913, *26*, 246); ultra-violet light (Dorée and Dyer: J.S.D.C., 1917, *33*, 17); and heat (Knecht: J.S.D.C., 1920, *36*, 195).

Hess and Katona (Annalen, 1927, *455*, 221) repeated the experiments of some of these earlier workers and compared the results. The methods are interesting as representative examples of the preparation of oxycellulose. Bromine water oxycellulose (Faber and Tollens) was made by shaking 100 g. of cotton linters with 20 g. of bromine and 30 g. of $CaCO_3$ in 1·6 litres of water for 24 hours at ordinary temperatures. After two repetitions, the excess of bromine was removed on the water bath and the product well washed with 2% HCl in dilute acetic acid and dehydrated with methyl alcohol. The yield was 79 g. of oxycellulose slightly soluble in water. Nitric acid oxycellulose (Cross and Bevan) was made by heating 25 g. of cotton linters with 75 g. of HNO_3 (*d.*, 1·3) on the water bath for one hour. The fibres disintegrate owing to the vigorous reaction. The product was well washed with water and dehydrated with alcohol and ether yielding 19·2 g.

Permanganate oxycellulose (Nastukoff) was prepared by digesting 25 g. of linters with ten times the weight of a 10% solution of permanganate solution at ordinary temperatures for about 36 hours until the fibres disintegrated. The mixture was decolorised with sulphurous acid, filtered, washed with

2% H_2SO_4 followed by water, and dehydrated with methyl alcohol and ether. The yield was 19·6 g.

Chromic acid oxycellulose (Vignon) was made by heating 40 g. of linters on the water bath for three hours with a solution containing 60 g. of potassium dichromate and 80 g. of H_2SO_4 in 3 litres of water. The material was well washed with 2% H_2SO_4 and then with water, and finally dehydrated with alcohol. The yield was 33·7 g.

General Properties

Some of the properties are compared in the following table:

OXYCELLULOSE.

Method.	Yield.	COOH %	Solubility % in 2 N. NaOH	Loss % by extraction with $NaHCO_3$	Solubility % in 2 N. NaOH of residue from $NaHCO_3$ extraction.
Bromine .	79%	1·2	26·8	8·3	12·5
Permanganate	78%	0·9	33·8	5·1	21·9
Nitric acid .	77%	0·67	22·7	11·5	8·9
Chromic acid	84%	1·06	40·5	15·3	10·8
Original linters		0·43 0·22			

An important contribution was made by Knecht and Thompson (J.S.D.C., 1920, *36*, 251), who showed that much of the work previously done did not take into account the fact that caustic alkalis decompose oxycellulose into substances of small reducing value, and that a portion of the product also passes into solution. Some other oxidation processes, e.g. with the use of acids, are accompanied by hydrolysis and in general no attempt has been made to regulate and measure the mass ratio of oxidising agent consumed. Now Knecht and Thompson claimed that by the use of permanganate, these disadvantages could be avoided, and an oxycellulose obtained representing a higher degree of oxidation without degradation of the cellulose, but richer in aldehydic properties. Their method was to make a pulp of 30 g. of filter paper with 600–900 cc. of 15° Tw. NaOH and mix this with a slight excess of dilute H_2SO_4, filter, wash and whilst still moist, suspend the material in 600–900 cc. of 10° Tw. H_2SO_4 and stir rapidly. 12 g. of potassium permanganate (one atom of oxygen per $C_6H_{10}O_5$) was dissolved in the same H_2SO_4 and added gradually from a tap funnel over a period of one to two hours. The

solution became decolorised after four hours and the pulp disintegrated to a finely divided brown mass. This was removed by filtration, suspended in dilute H_2SO_4 and decolorised by the addition of hydrogen peroxide. The product was washed in distilled water to free it from acid and managanous sulphate, dried below 40° C. to avoid setting to a horny mass and to ensure subsequent pulping with water. The yield was 94·5%. Oxidation with two atoms of oxygen per $C_6H_{10}O_5$ unit gave a more gelatinous product which was difficult to free from acid.

This highly oxidised cellulose showed no acidic properties, but had strongly marked aldehydic reactions, dyeing a deep shade with Schiff's reagent and giving hydrazones containing considerable amounts of combined phenyl hydrazine. It also combined with ammonia and with hydrogen cyanide. The reaction with solutions of sodium bisulphite of 61° Tw. was accompanied by a marked increase in temperature. The oxycellulose was also very sensitive to alkali, giving an intense yellow colour on boiling with N/100 NaOH and with a 5 N solution in the cold, and differing in this respect from the oxycelluloses previously described. Strong reducing properties were demonstrated by a copper number of 14·2 (Schwalbe's method), the reduction of ammoniacal silver nitrate solution and also by the reduction of Cross and Bevan's ferric ferricyanide solution with the formation of Prussian blue. Methylene blue is reduced to the leuco compound in presence of alkali.

The preparation and properties of some other forms of oxycellulose are of interest. Bumcke and Wolffenstein (Ber., 1899, *32*, 2493 ; 1901, *34*, 2415) treated filter paper with solutions of hydrogen peroxide until completely disintegrated. The product was termed " hydralcellulose," but its properties are similar to those of oxycellulose. The solubility in boiling 10% NaOH solution was 33% and the residue resembled cellulose. The action of ozone was investigated by Cunningham and Dorée (J.C.S., 1912, *101*, 497), who found that the first stage of the reaction produced a cellulose peroxide. When ozone reacts with moist cellulose, acidity is immediately produced on the fibre and carbon dioxide is evolved continuously. Cotton and rayon threads, after a short exposure to ozone, are able to liberate iodine from potassium iodide solution. Dorée and Dyer (J.S.D.C., 1917, *33*, 17) examined the effect of exposure of cellulose to ultraviolet light, and found that the material was disintegrated and an oxycellulose

produced. The copper number (Schwalbe) was 4·0, the methylene blue absorption ·1·5 %, and the loss in weight in a boiling 1 % solution of NaOH was 13·6 % in 60 minutes after an exposure of several days.

Dorée, in his book, " The Methods of Cellulose Chemistry," page 120, has summarised some of the work on oxycellulose formation by means of nitric acid.

OXYCELLULOSE.

Investigator.	% HNO_3.	HNO_3/Cotton.	Time.	% Yield (insoluble product).
(*a*) Bull	60	6 : 1	24 hours	35
(*b*) Faber and Tollens	47·5	3·3 : 1	2½ ,,	70
(*c*) Nastukoff	47·5	1·2 : 1	—	90

In each case the temperature of reaction was 95–100° C.

The product from (*a*) did not reduce Fehling's solution, but was completely soluble in aqueous solutions of ammonia, pyridine, Na_2CO_3 and NaOH. The product from (*b*) strongly reduced Fehling's solution and dissolved in dilute alkali and in ammonia. Tartaric acid was observed as a by-product. Further oxidation produced a greater solubility in alkali. Product (*c*) was soluble in ammonia and gave a barium salt containing 5 % of barium. Vignon (Compt. rend., 1903, *136*, 818) has described the formation of oxycelluloses by reduction of the higher cellulose nitrates with ferric chloride.

Before consideration of the more recent work, a brief review of the typical reactions of oxycelluloses may now be given.

Reactions of Oxycellulose

Amongst the reactions characteristic of the presence of the carbonyl group, the compounds formed with oxycellulose and phenylhydrazine and its derivatives may be taken as typical. A number of observers have assumed that definite chemical combination takes place, but Knecht and Thompson (J.S.D.C., 1920, *36*, 251) showed that the amount of the hydrazine which enters into combination varies so considerably (2·7–8·5 %—according to various workers) with the experimental conditions that adsorption and not combination is the underlying cause.

Copper Number

The reduction of Fehling's solution has long been recognized

as a characteristic test for oxycellulose and C. G. Schwalbe (Ber., 1907, *40*, 1347) proposed the adoption of standard conditions in order to obtain comparable results. This led to the "Copper Number" test, which was later modified by Clibbens and Geake (J.T.I., 1924, *15*, 27) of the British Cotton Industry Research Association, who substituted for Fehling's solution the mixture of copper sulphate and sodium carbonate —bicarbonate as advocated by Braidy (Rev. Gen. Mat. Col., 1921, *15*, 35) and estimated the cuprous oxide by the volumetric method used by Knecht and Thompson (J.S.D.C., 1920, *36*, 255).

The following solutions are used in the determination :

(*a*) pure copper sulphate, $CuSO_4, 5H_2O$ . .	100 g.
water	to 1 litre
(*b*) sodium bicarbonate	50 g.
crystallised sodium carbonate . . .	350 g.
water	to 1 litre.

Immediately before use 5 cc. of solution (*a*) are run from a burette into 95 cc. of solution (*b*), the mixture is raised to the boil and poured over 2·5 g. of the material to be examined, contained in a conical flask of capacity only very slightly greater than 100 cc. By means of a glass rod the cotton is distributed through the liquid and any air bubbles are allowed to escape, after which the flask is closed with a pear-shaped glass bulb and immersed in a rapidly boiling constant-level water bath. The flask should be deeply immersed in the water, and care should be taken to cover the top of the bath sufficiently to prevent cooling of the reaction mixture by currents of cold air ; several determinations may, of course, be carried out simultaneously in a suitable bath. The flask is allowed to remain in the boiling bath for exactly three hours ; the contents are then filtered with suction, and the cotton, impregnated with cuprous oxide is washed first with dilute sodium carbonate and then with hot water. The cuprous oxide is dissolved by treating the cotton on the filter with the following solution :

Iron alum	100 g.
Concentrated sulphuric acid . . .	140 cc.
Water	to 1 litre.

Two portions of this solution, of volume 15 cc. and 10 cc., respectively, are usually sufficient for this purpose, though a

further treatment with 10 cc. may occasionally be necessary in the case of highly reducing products. The cotton is then washed with 2 N sulphuric acid, and the combined filtrates and washings are titrated with standard potassium permanganate solution of concentration approximately N/25, corresponding to about 2·5 mg. of reduced copper per cubic centimetre. The end-point of the titration is sharp and stable, which is not the case when Fehling's solution is used as the copper-containing reagent, owing probably to the fact that cotton absorbs tartrates from this solution, and that these, like the absorbed bivalent copper are only removed by acid washing. It is certainly the case that when Fehling's solution is used in this determination the pink colour produced by a slight excess of permanganate soon disappears when the titrated liquid is allowed to stand, and this may well be due to reduction of permanganate by the absorbed tartrates which have been extracted from the cotton by the acidic iron alum solution.

A micro-method of estimating copper numbers has been described by Heyes (J.S.C.I., 1928, *47*, 90).

Other Reducing Actions

The reduction of solutions of other metallic salts has also been described, e.g. Nessler's solution (Dietz—Chem. Zeit., 1907, *31*, 833); silver nitrate, in presence of sodium thiosulphate and sodium hydroxide (Harrison—J.S.D.C., 1912, *28*, 359) and ferric salts (Knecht—J.S.D.C., 1920, *36*, 251). Götze (Textilber, 1927, *8*, 624) has utilised the reduction of an ammoniacal solution of silver nitrate for the determination of the "*silver number.*" The colour of Schiff's reagent is restored by most forms of oxycellulose.

A rapid method of determining the reducing power of modified cellulose has been described by Foster, Kaji and Venkataraman (J.S.C.I., 1938, *57*, 310). The material is extracted with NaOH, acidified, treated with excess of ceric sulphate solution and the latter is then determined by titration with ferrous ammonium sulphate. The conditions of extraction and ceric sulphate oxidation are adjusted to give numbers for reducing power in accordance with the Braidy values. The new method gives lower values for copper numbers above 2 with oxycellulose but not with hydrocellulose.

Another type of reducing action was noted by Ermen (J.S.D.C., 1912, *28*, 132), who found that oxycellulose behaves in a similar manner to hydrosulphite in the reduction of

indanthrene yellow when it is dyed from a hot alkaline suspension. Scholl (Ber., 1907, *40*, 1692; 1911, *44*, 1312) had also remarked on the reduction of vat dyes by oxycellulose.

Presence of -COOH

A second set of typical reactions is regarded as characteristic of the presence of the carboxyl group. The solubility in alkaline solutions has already been mentioned, and is also seen in the case of hydrocellulose. Schwalbe and his co-workers (Zellstoff u. Papier, 1921, *1*, 100; 1922, *2*, 75), however, have suggested two methods for the measurement of the acidity of oxycellulose (*a*) estimation of the amount of barium absorbed from barium hydroxide solution and (*b*) estimation by titration with N/100 NaOH, the figures being corrected for ash alkalinity. The data, together with the other determinations are shown on page 245. [The resistance to baryta is the residue per cent. after boiling for one hour with a saturated solution of barium hydroxide.]

The evolution of carbon dioxide during acid hydrolysis is regarded as characteristic of oxycellulose, for Heuser and Stockigt (Cellulosechem., 1922, *3*, 61) have employed the reaction to measure the carboxyl content of oxycellulose.

Typical results are shown below.

ACIDITY OF OXYCELLULOSE.

Substance	%COOH
Oxycellulose (H_2O_2)	0·29
($KMnO_4$) . .	0·65 ; 1·04
(CrO_3) . .	1·32
($KClO_3$) . .	0·66
(HNO_3) . .	0·97 ; 0·83
Cotton cellulose . . .	0·03
Hydrocellulose (Girard) .	0·04

General Reactions

Amongst the more general reactions of oxycellulose, one of the more important characteristic features is that a larger proportion of furfuraldehyde is formed on distillation with HCl (*d.* 1·06) than is obtained from cellulose, the observed values usually being of the order of 1·5 to 3%, although variations of from 0·8 to 8·2% are recorded in the summary of the literature by Clifford and Fargher (J.T.I., 1922, *13*, 189). The furfuraldehyde is generally estimated as the phloroglucide.

Cross, Bevan and Beadle (Ber., 1893, *26*, 2527) appear to have been the first to study this reaction. Heuser and Stockigt (loc. cit.) have shown that the proportion of phloroglucide soluble in alcohol was large in the case of hydrocellulose, lower in the case of cellulose and much lower with oxycellulose.

The increased affinity of oxycellulose for basic dyes was first observed by Witz (loc. cit.), and the absorption of methylene blue in particular has been largely used as a test. Knecht (J.S.D.C., 1921, *37*, 76) found that oxycelluloses showing a high affinity for basic dyes resist dyeing with the direct azo colours.

A large number of colour reactions are also recorded in the literature. Whilst the production of a yellow colour on boiling with dilute sodium hydroxide indicates either oxy- or hydrocellulose, only the former gives the colour on steaming according to Freiberger (Farber Zeit., 1917, *28*, 221 ; 235 ; 249).

Jandrier (Compt. rend., 1899, *128*, 1407) has recorded a number of colour reactions characteristic of oxycellulose, prepared by the action of potassium chlorate. The material is tested, in presence of sulphuric acid, with various phenolic compounds. Berl and Klaye (Zeitschr. Schiess u. Sprengstoffe, 1907, *2*, 381) described a blue coloration with iodine and zinc chloride whilst the coloration with methyl orange was suggested as a test by Schwalbe and Becker (loc. cit.).

Witz (Bull. Soc. Chim., 1886, *45*, 309) observed that oxycellulose exerted an attraction for a number of inorganic salts, particularly those of vanadium, which were withdrawn from very dilute aqueous solutions. This was demonstrated by printing the material containing oxycellulose with an aniline black mixture.

Everest and Hall (J.S.D.C., 1921, *37*, 227) showed that whilst cotton cloths are normally unaffected by immersion in a solution of tetrazotised benzidine, which has been made alkaline by means of sodium carbonate, a yellowish brown colour, which is fast to washing, is developed if oxycellulose is present.

Nitric and acetic esters of oxycellulose have been prepared, and references are given in the summary by Clifford and Fargher (loc. cit.).

Acid hydrolysis has been examined by Vignon (Bull. Soc. Chim., 1901, iii, *25*, 130), who found that the relative copper-reduction of the soluble products was higher in the case of oxy- and hydrocellulose than with cellulose. Alkaline hydro-

lysis of oxycellulose was studied by Tollens and his collaborators (Ber., 1899, *32*, 2589; 1901, *34*, 1427), who treated the material obtained by the action of potassium chlorate and hydrochloric acid on cellulose with boiling milk of lime and isolated isosaccharic acid and dihydroxybutyric acid from the soluble products of the reaction.

Permetier (Bull. Soc. Ind. Rouen, 1883, *11*, 236) observed an interesting behaviour of oxycellulose towards cuprammonium hydrate; oxycellulose, when treated with this reagent does not exhibit the characteristic bead-like swellings of normal cellulose, but swells in a comparatively uniform manner.

COMPARISON OF THE PROPERTIES OF THE TWO EXTREME TYPES OF OXYCELLULOSE.

Tests.	"Methylene blue" type.	Reducing type.
Methylene blue absorption .	High	Low
Copper number . . .	Low	High
Loss in weight on alkali boil .	Low	High
Properties of residue . .	as original oxycellulose	as unmodified cotton (excepting viscosity)
Ash Alkalinity . . .	High	Low
Yellow colour with alkali .	Negative	Positive
Indanthrene yellow test .	,,	,,
Resistance to direct dyes .	,,	,,
Reduction of $AgNO_3$ . .	,,	,,

Modern Work on Oxycellulose

The descriptions of the methods of preparing oxycellulose are often vague concerning the physical state of the product (i.e. whether it is a powder or retained fibrous structure) and are frequently at variance as to its properties.

The work of Birtwell, Clibbens and Ridge (J.T.I., 1925, *16*, 13) is of the utmost importance in this respect for not only did they describe the properties of two different forms of oxycellulose (on a basis of differentiation essentially the same as that suggested by Witz in 1883 and again by Nastukoff in 1900), but they also found the experimental conditions for the

PROPERTIES OF MODIFIED CELLULOSES.

Material examined.	Copper No.	Furfuraldehyde. %	α-Cellulose %	Material resistant to Baryta. %	Barium taken up. %	Acidity in cc. N/100 NaOH per g.		Alkalinity of ash cc N/100 NaOH per g.	Total acidity.	Microscopic appearance with 20% I-KI.	Colour with methyl orange NaCl.
						litmus.	phenol phthalein				
Cellulose (cotton) . .	0·28	0·69	98·85	97·8	0·02	1·5	—	0·3	1·8	yellow	yellow
Oxycellulose from cotton (hypochlorite)	11·0	0·26	62·0	59·7	2·18	39·4	40·7	2·0	41·4	yellow	very bright red
Oxycellulose from wood . (hypochlorite)	33·2	3·32	58·6	61·5	—	12·7	13·8	20·7	33·4	violet	red
Oxycellulose from cotton ($KMnO_4$)	8·03	1·28	61·8	65·6	1·46	27·3	27·0	0·4	27·7	yellow	very bright red
Oxycellulose from cotton (H_2O_2)	5·8	0·94	78·3	77·2	0·34	10·1	11·6	0·3	10·4	yellow-brown	bright red
Hydrocellulose from cotton (Girard)	3·64	1·24	83·7	75·3	0·10	3·7	4·0	0·9	4·6	yellow-violet	yellow-brown
	6·22	—	—	62·0	—	—	—	—	—		
Hydrocellulose from cotton (Lederer)	5·67	0·76	88·45	76·3	0·17	—	—	—	—	pale violet	yellow

The results are calculated on water and ash free material.

preparation of these two extreme types. In the work about to follow "oxycellulose" is used to denote a cotton cellulose whose properties have been altered, however slightly, by the action of oxidising agents, but which still retains the outward form of the cotton hair.

Two Extreme Types

The two types of oxycellulose are characterised by a great affinity for methylene blue and an abnormal retentive power for alkali in one case, whilst the other possesses high reducing power (as expressed by copper number) and excessive loss of weight as the result of a boil with alkali.

The oxycelluloses were prepared by the action of chlorine water, acid permanganate and alkaline hypobromite, and the method consisted in shaking 25 g. of cotton with 1 litre of the solution of the oxidising agent until the whole of the latter was consumed. Five solutions of each oxidising agent were used, the concentrations being 0·01 N, 0·005 N, 0·003 N, 0·002 N, 0·001 N so that the experimental conditions corresponded to an oxygen consumption of 0·32, 0·16, 0·096, 0·064 and 0·032 % of the oxygen calculated on the weight of the air dry cotton and irrespective of the nature of the oxidising agent.

A normal bleaching process results in the consumption of 0·01 to 0·02 % of oxygen. Hypobromites differ in their action on cotton from hypochlorites, as they oxidise comparatively rapidly in strongly alkaline solutions in the dark and at ordinary temperatures.

The copper number, methylene blue absorption and percentage loss on alkali boiling were measured and are given in the following graphs:

Figure 115 shows that the rate of increase of copper number with progressive oxidation of the cotton varies widely with the nature of the oxidising agent, the chlorine series being characterised by high and rapidly increasing copper numbers, and the hyprobomite series by low copper numbers rising exceedingly slowly with progressive oxidation.

Figure 116 shows that exactly the opposite relations obtain with respect to methylene blue absorptions.

In Figure 117 copper numbers are plotted against loss of weight on alkali boiling irrespective of the oxidising agent used. The points lie on a smooth curve and over the range of oxidation examined, the loss of weight on alkali boiling may be determined by copper number alone. When the loss on boiling

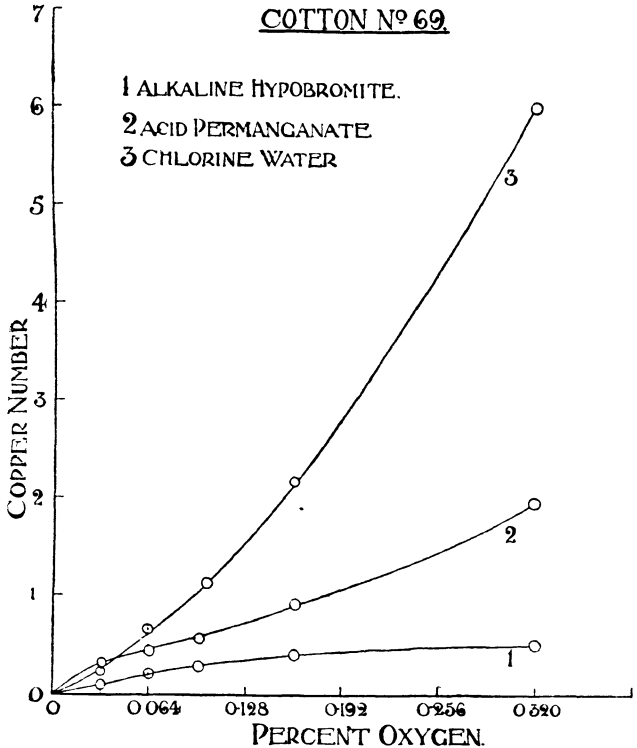


FIG. 115.—Rate of formation.

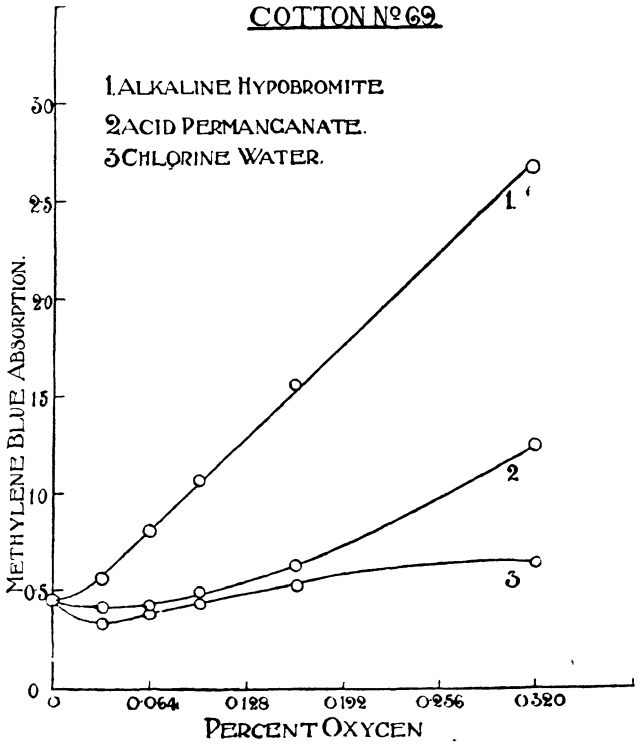


FIG. 116.—Rate of formation,

is low the results are not very accurate because the small loss is determined by difference, and the unoxidised material itself may suffer a loss of weight under the same conditions of alkali boiling.

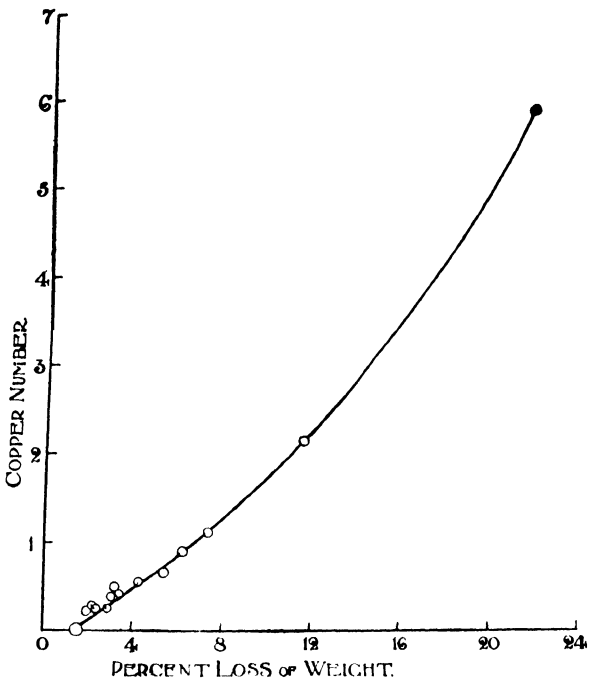


FIG. 117.—Relation between copper number and loss in weight after alkali-boil

Oxycelluloses with a high methylene blue absorption and a low copper number show only a slight loss of weight on boiling with dilute alkali. The following table shows that the absorption of methylene blue by oxycellulose is not greatly affected by alkali boiling. (The actual data refer to hypobromite oxycellulose.)

EFFECT OF ALKALI BOIL.

	Oxycellulose RB3.		Oxycellulose RB1.		Oxycellulose RB2.	
	Copper number.	Methylene blue.	Copper number.	Methylene blue.	Copper number.	Methylene blue.
Before alkali boil .	0·20	1·08	0·35	1·56	0·50	2·95
After 4 hours with 1% NaOH .	0·02	0·95	0·02	1·30	0·09	2·45
After 8 hours with 1% NaOH .	0·015	1·12	—	—	0·06	2·65
After 8 hours with 2% NaOH .	0·005	1·01	—	—	0·05	2·67

The copper number is so diminished by alkali boiling that the residue cannot be distinguished by means of this test from unmodified cellulose. The methylene blue absorption, however, diminishes slightly after the first alkali boil, but subsequent treatment fails to effect a further decrease.

Birtwell, Clibbens and Ridge had previously shown (J.T.I., 1923, *14*, 297) that the absorption of methylene blue depends on the ash alkalinity of the sample. The residual ash alkalinity was defined as the alkalinity possessed after the standard washing process of one hour with N/10 H_2SO_4. The later work now being described showed that those oxycelluloses which exhibit a high methylene blue absorption also possess a high residual ash alkalinity, a property not necessarily associated with high copper number, and further, that this is not reduced by further prolonged acid washing treatments.

A most important series of experiments revealed the properties of oxycelluloses prepared by hypochlorite solutions of equal oxidising value but of different hydrogen ion concentrations. In each case the amount of oxygen consumed was 0·32 %.

EFFECT OF HYDROGEN-ION CONCENTRATION.

pH	Copper number.	Methylene blue absorption.	Ash alkalinity.
14·6	0·42	1·30	1·28
13	0·54	1·91	1·82
12	1·31	2·28	2·57
11·2	0·65	3·26	2·78
9	1·37	3·20	3·18
7	3·64	2·23	2·24
4·6	5·5	1·04	1·23
2·7	6·0	0·90	1·06
1	3·79	0·81	0·98

The differences in properties as shown are due to variations of hydrogen-ion concentrations alone. The following curves are instructive.

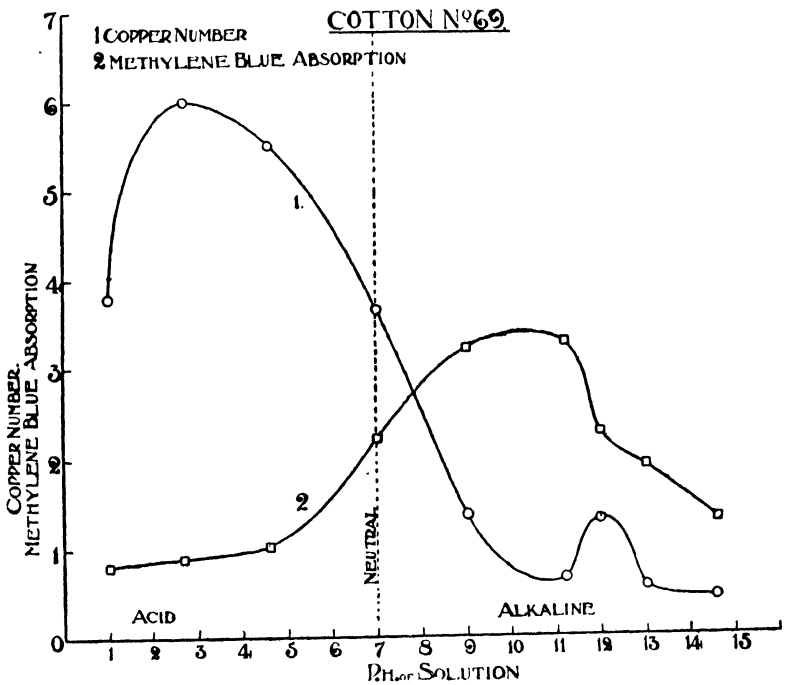


FIG. 118.—Effect of hydrogen-ion concentration.

Beginning from the extreme alkaline side, the methylene blue absorption rises with decreasing alkalinity and reaches a maximum on the alkaline side of the neutral point. It then falls continuously through the neutral point (pH 7) and continues to decrease on the acid side until it reaches a minimum. The behaviour of the copper number is the reverse of this. The peculiar " pincer " form of the curves shows very clearly that a maximum copper number is accompanied by a minimum absorption and vice versa, the two measurements being numerically equal for a preparation represented by the point of intersection of the curves, which lies close to the neutral point.

The very great changes from maximum to minimum copper numbers and methylene blue absorptions occur almost entirely within the range of hydrogen ion concentrations represented by pH 5 to 9. The small nature of this range and its proximity to the neutral point accounts for many of the apparent contradictions in the previous literature on oxycellulose. The range of properties previously obtained by the use of different oxidising agents can equally well be secured by employing one oxidising agent at various hydrogen ion concentrations.

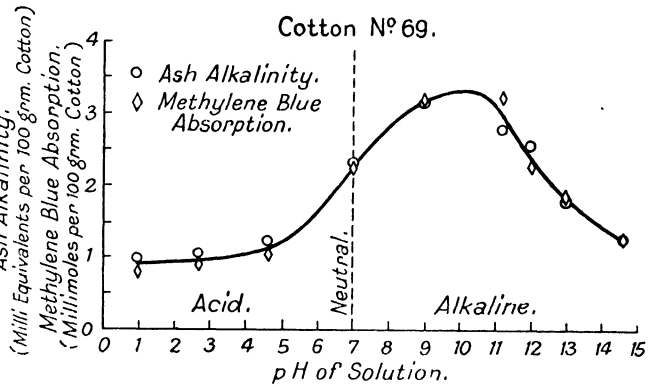


FIG. 119.—Effect of pH on ash alkalinity and methylene-blue absorption.

A very close correlation is again found to exist between methylene blue absorption and the residual ash alkalinity of oxycelluloses prepared is the above manner and when both values are plotted against hydrogen ion concentration, the two sets of values lie on the same curve. (Fig. 119.)

Fluidity of Oxycellulose

Birtwell, Clibbens and Ridge (loc cit.) examined the viscosity of the two types of oxycellulose in cuprammonium solution. It was found that the fall of viscosity caused by the consumption of a given percentage of oxygen was approximately the same, irrespective of the conditions of oxidation within certain limits. Differences were observed in the earlier stages of oxidation, where the action of alkaline hypochlorite (pH 12) producing a much greater fall in viscosity than that of acid

hypochlorite (pH 2·7) for the same oxygen consumption. The early stages of the reaction are complicated by the oxidation of the non-cellulose impurities in the scoured cotton, i.e. by the bleaching of the material—a process which, whilst consuming oxygen, is presumably without influence on the viscosity of the cellulose. (See Figure 120.)

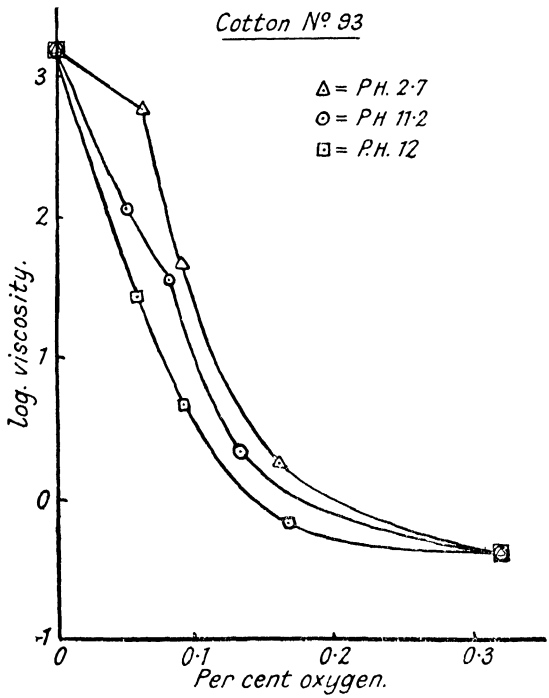


FIG. 120.—Rate of oxidation.

It has already been remarked that the copper number of an oxycellulose suffers diminution on alkali boiling in such a way as to approach the value of the unmodified cellulose (page 249). The viscosity, however, suffers a further reduction. Hence, an oxycellulose characterised by high copper number and low methylene blue absorption may, after alkali boiling, be indistinguishable from unmodified cellulose by either of these chemical tests, yet the evidence of oxidising attack and, therefore, a lowered tensile strength, is demonstrated by viscosity measurement. (J.T.I., 1925, *16*, 13.)

EFFECT OF ALKALI-BOIL.

Copper number.		Log. Viscosity in 2% solution.	
Before boiling.	After boiling.	Before boiling.	After boiling.
0·10	0·02	1·46	1·30
0·20	0·04	0·48	0·39
0·35	0·11	−0·25	−0·27
0·50	0·15	−0·63	−0·76
5·32	0·71	−0·65	−0·76
7·3	1·01	−0·86	−0·92

Rate of Formation

The rate of oxycellulose formation has been studied by Clibbens and Ridge (J.T.I., 1927, *18*, 135) by measuring the rate of consumption of oxygen and the rate of change in the properties of the material, when bleached cotton is treated with hypochlorite solutions of constant active chlorine content but of varying acidity or alkalinity. Within the range of hydrogen ion concentration pH 5 to 10, characteristic of technical bleach liquors, *the maximum rate of oxycellulose formation occurs at the neutral point.* Slightly acid hypochlorite solutions are less rapid in their action on cotton than neutral solutions.

This has been confirmed by the later work of Nabar, Scholefield and Turner (J.S.D.C., 1935, *51*, 5) as shown in Fig. 121.

Measurements of the rate of change of properties of the oxycellulose produced show that the rate of increase in copper number is extremely slow with alkaline liquors between pH 13 and 11·2. With less alkaline solutions (pH 9 and 8) the rate of increase rises rapidly and becomes very high at the neutral point. Broadly similar results were obtained by measuring the rate of change of methylene blue absorption and the viscosity. Figures 122, 123 and 124 show the rate of alteration in various properties, as a result of treatment with hypochlorite.

Comparisons made between the rate of oxycellulose formation with hypochlorite and hypobromite show the latter to be a much more rapid oxidising agent. The measurements were made in strongly alkaline solution.

The rate of oxycellulose formation with dichromate in aqueous solutions of varying acidity is much more rapid in the presence of dilute oxalic acid than in the presence of sulphuric acid of the same equivalent concentration.

It was also found that the presence of small quantities of chromium in cotton greatly increases the rate of cellulose

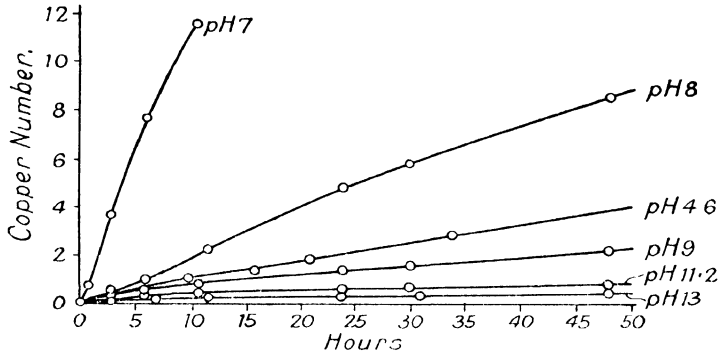


FIG. 122.—Rate of increase of copper number.

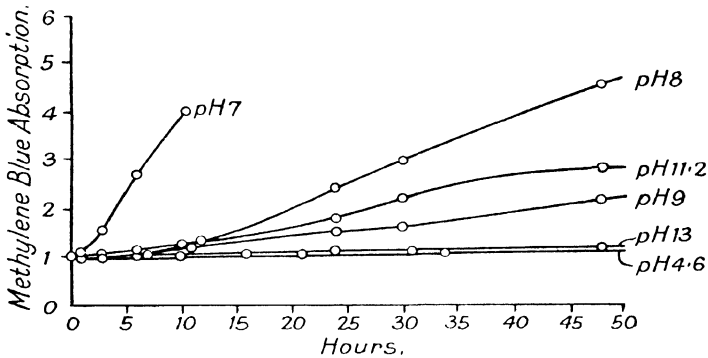


FIG. 123.—Rate of rise in methylene blue absorption.

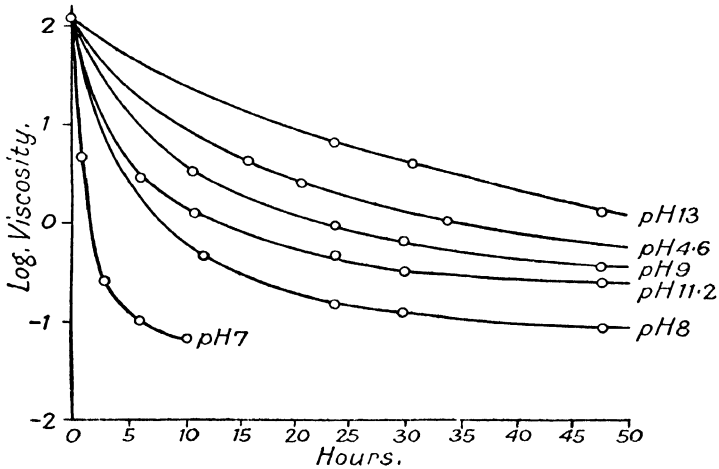


FIG. 124.—Rate of fall in viscosity.

oxidation by hypochlorite solutions. Oxycelluloses formed by the action of dichromate in sulphuric acid solutions contain traces of chromium which cannot be removed by washing; but this is not so with oxycellulose formed by the action of dichromate in oxalic acid solution.

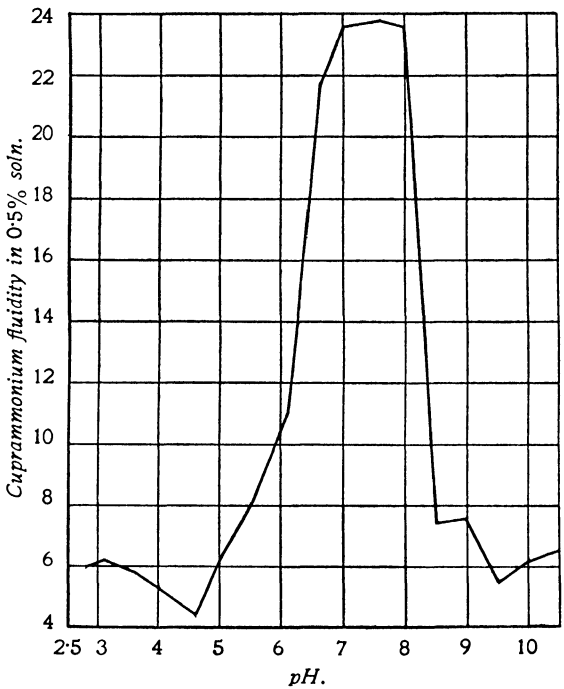
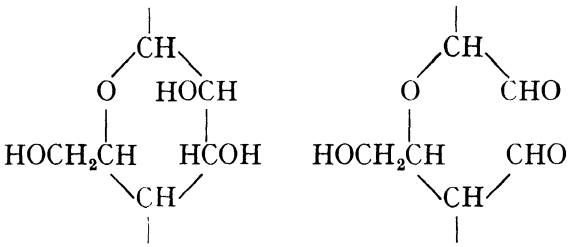


FIG. 121.—Degradation of cotton with self-buffered hypochlorite solutions (3 g. available chlorine per litre) after 5 hours' treatment.

Oxidation with Periodic Acid

For many years it was generally assumed that oxidative attack on cellulose occurred at the primary alcohol group, but the work of Jackson and Hudson (J.A.C.S., 1937, *59*, 2049; 1938, *60*, 989) showed that this was not the case for oxidation by periodic acid. The main reaction consisted in splitting the glucose ring structure between carbon atoms *2* and *3*, and converting the secondary alcohol groups to aldehyde groups.



Later work by Davidson (J.T.I., 1940, *31*, 81) showed that the oxycelluloses produced by periodic acid and by potassium metaperiodate belong to the extreme reducing type of oxycellulose and exhibit the property of alkali-sensitivity to a very high degree. When these oxycelluloses are treated with dilute alkali their tensile strength is very greatly diminished; for instance, a cotton yarn oxidised with periodic acid and still retaining 30% of its original tensile strength was completely disintegrated on contact with decinormal NaOH solution at 20° C.

Comparison of the periodic acid oxycelluloses with the dichromate oxycelluloses shows a resemblance in that they are both considerably stronger than hydrocellulose of equal cellulose fluidity, but after an alkali boil the relation between tensile strength and cellulose fluidity is much closer for all these types of modified cellulose.

The glucoside link between the *4* atom of the attacked unit and the *1* atom of the next unit, is similar to the linkage between glucose and erythrose in *2*-glucosidoerythrose, which is particularly susceptible to alkaline hydrolysis as shown by Evans and others (J.A.C.S., 1930, *52*, 294; 1931, *53*, 4384; 1936, *58*, 2388). This has an important bearing on the question of the alkali-sensitivity of certain oxycelluloses as discussed on page 275.

More detailed examination of the oxidation of cellulose by periodic acid over a wide range of oxygen consumption has given interesting results according to Davidson (J.T.I., 1941, *32*, 109). Apparently the crystalline portion of the cellulose becomes dispersed and accessible to the oxidising agent; this is shown by X-ray diagrams and supported by the changes in dimensions and the increased hygroscopicity. Chromic acid, however, only seems to attack the non-crystalline portions of the cellulose (*ibid.*, 132).

Oxidation with Permanganate

Potassium permanganate is well known to react differently with organic substances in acid and alkaline solution. Dorée and Healey (J.S.D.C., 1933, *49*, 290) carried out a series of experiments similar to those just described, but using potassium permanganate as the oxidising agent. The first set of experiments dealt with the time necessary to decompose a fixed amount of potassium permanganate, in solutions of

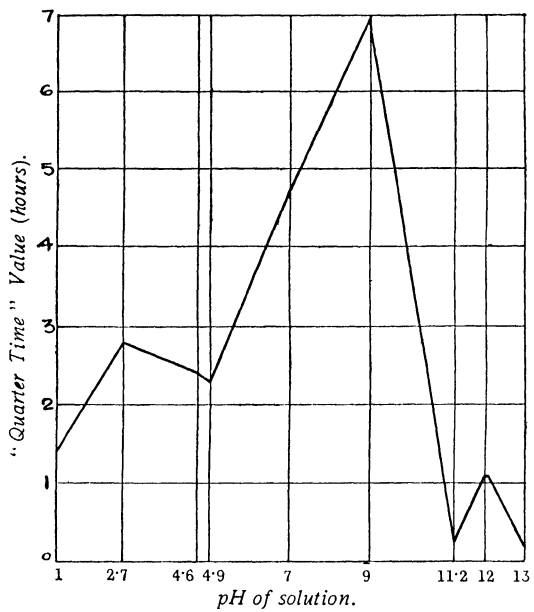


FIG. 125.—Variation of "Quarter Time" Value with pH of solution.

graded pH values, by a fixed weight of scoured calico. The unreduced reagent was titrated at intervals and "quarter time" values recorded as the measure of the rate of reduction. The "quarter time" value is the time taken for the available oxygen to fall from three-quarters to half of its original value. By taking this interval, uncertainties due to delay in the wetting of the material and to the oxidation of non-cellulosic impurities are avoided. The values are plotted for a range of pH from 1 to 13.

The minimum rate is at pH 9 (quarter-time 6·9 hours) and the maximum at pH 11·2 (0·2 hours). Subsidiary minima

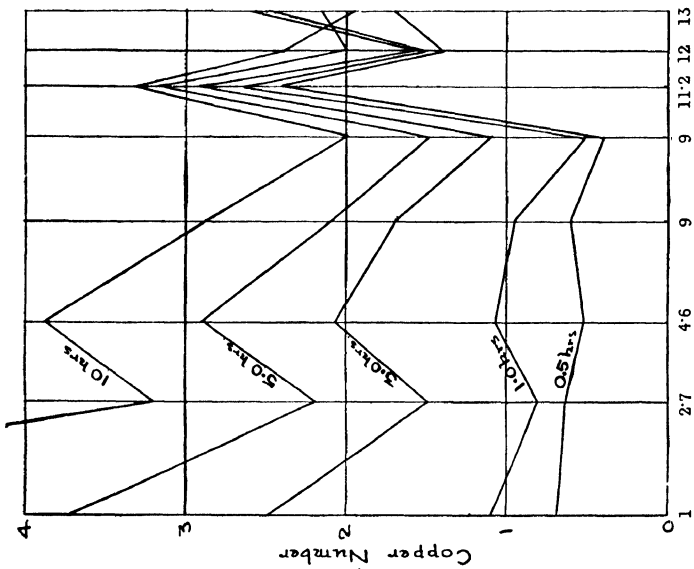


FIG. 127.—Effect of pH on copper number ($KMnO_4$).

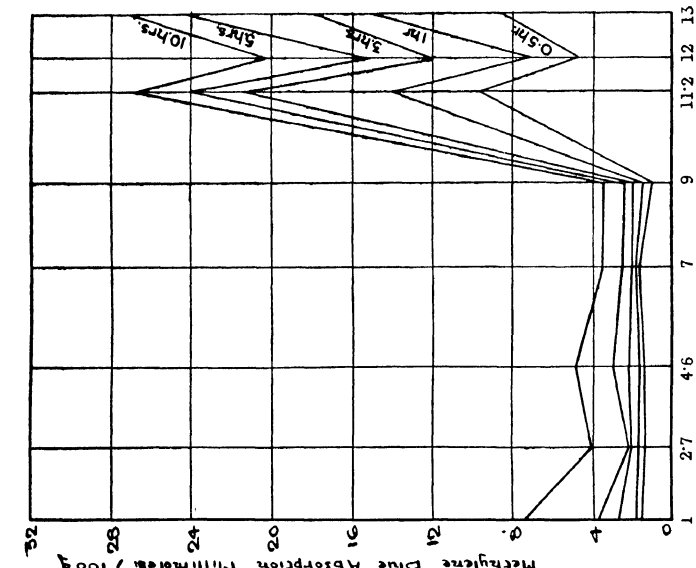


FIG. 126.—Effect of pH on methylene blue absorption ($KMnO_4$).

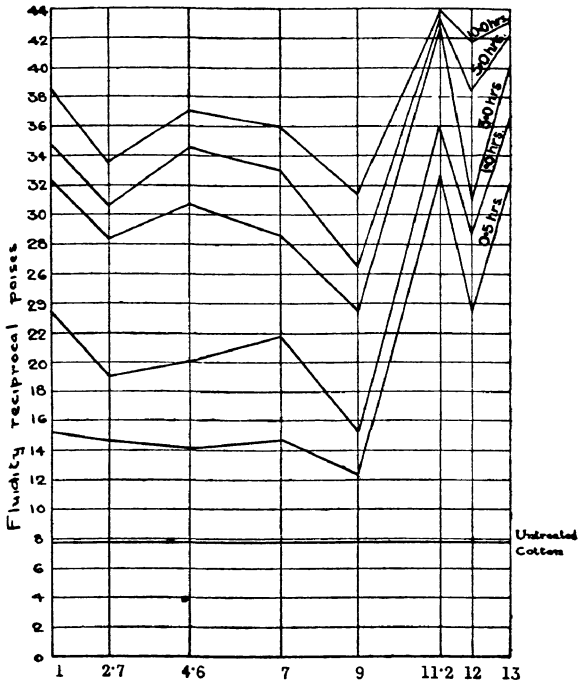


FIG. 128.—Effect of pH on fluidity ($KMnO_4$).

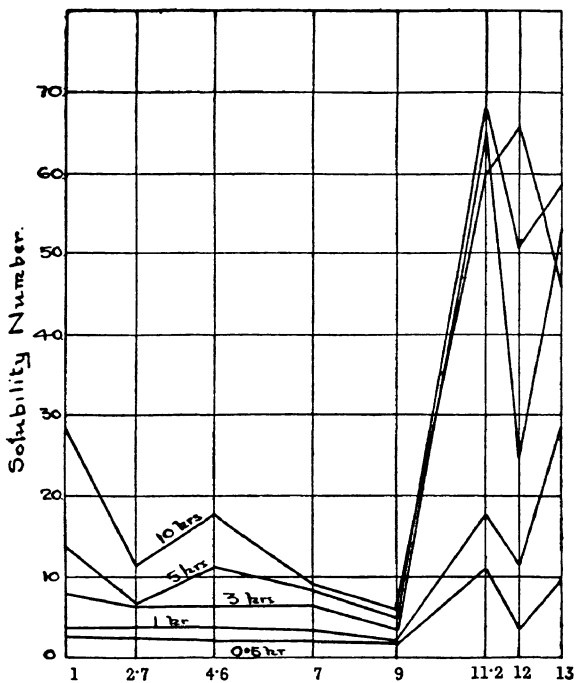


FIG. 129.—Effect of pH on solubility number ($KMnO_4$.)

occur at pH 2·7 and 12. Solutions of great alkalinity (pH 11·2 to 13) are decomposed with extreme rapidity whilst acid solutions pH 4·9 to 1) are rapidly decomposed.

The modifications produced in the properties of the cellulose by treatment with permanganate of graded pH in definite times was also examined. It was found that pH 9 marks a fundamental transition ; on the acid side, the products are of the reducing type whilst on the alkaline side the product is characterised by high methylene blue absorption. Little change occurs between pH 5 and 9. This distinguishes the results from those obtained with hypochlorite solutions where the changes are very marked over this range. Otherwise the main differentiation into two types according to the acid or alkaline nature of the oxidising agent is the same.

Various properties of the oxycelluloses produced at intervals were plotted against pH and some of these curves are shown on pages 258 and 259.

Although the initial increase in copper number is higher when cotton is treated with alkaline than with acid permanganate solutions, the rate of increase of copper number in alkaline solution is slow after a value of about 1·5 has been reached, so that eventually, higher copper numbers are obtained in acid than in alkaline solution.

The steady decrease in the activity of the permanganate as the pH rises from 1 to 9 is broken by a small maximum at pH 4·6, and the fuller exploration of the range 2·7 to 5·6 confirmed this point.

The properties of oxycelluloses prepared in solutions of extreme acidity and alkalinity were examined, using N-sulphuric, N-caustic soda and concentrated ammonia solutions. The quantity of permanganate used was calculated to provide 0·5 g. of oxygen for each $C_6H_{10}O_5$ unit. The product formed in ammonia resembled that formed in acid, having a high copper number which was reduced to a small value by boiling in alkali. The oxycellulose formed in caustic soda was of the other type with low copper number, not appreciably reduced by boiling with alkali.

Oxidation of Alkali-Cellulose

It is well known in the textile industry that the presence of air in the kier during the kier-boiling or scouring of cotton with dilute sodium hydroxide solutions leads to the formation of oxycellulose. Similarly during the " ageing " of alkali

cellulose in the first stages of viscose manufacture appreciable oxidation takes place even at room temperatures.

These points have been investigated by Davidson (J.T.I., 1932, *23*, 95), who pointed out that the conditions of the scouring of cotton made exact measurement of the rate of absorption rather difficult, but by approximating more to the ageing of alkali cellulose it was possible to examine the oxidation process. Concentrations of NaOH solution ranging from 2·5 N to 15·2 N were employed mainly at 40° C., as the oxidation of soda cellulose by oxygen is rather slow at room temperatures. The maximum absorption dealt with is about 3·5 cc. per gramme of cellulose, which represents the limit of the oxidation that is of interest in textile technology. The rate of absorption increases for some time and then becomes practically constant, showing that oxidation consists of several consecutive reactions. A similar hypothesis has been suggested by Birtwell, Clibbens, Geake and Ridge (J.T.I., 1930, *21*, 85). The comparison of rates of oxidation at different temperatures is complicated by the fact that the rate of absorption is not constant for any concentration of NaOH, but some idea of the relative rates of oxidation at 20, 40 and 60° C. is shown from the fact that when 10·3 N NaOH solution is used in the preparation of the soda cellulose, the volume of oxygen absorbed in 48 hours at 20° C. is absorbed in about six hours at 40° C. and in about 1·2 hours at 60° C.

The rate of oxidation of soda cellulose increases rapidly when the concentration of the alkali is increased from 2·5 N to 5 N. It then increases less rapidly as the concentration rises to about 10 N, where a well-defined maximum rate of oxidation is observed; as the concentration is further increased the rate of oxidation falls.

The presence of iron in the soda cellulose has a very important catalytic effect on the rate of oxidation, and whilst both nickel and copper also accelerate the reaction, their effects are less than that of iron.

The oxidation leads to an increase of fluidity and of copper number, the increase of both properties being rapid at first and then diminishing as the oxygen absorption increases. The copper number—oxygen absorption curve is thus of the same type as that obtained by oxidising cotton with alkaline hypobromite, according to Birtwell, Clibbens and Ridge (J.T.I., 1925, *16*, 13). The two types of oxycellulose also behave in the same way as regards methylene blue absorption.

Davidson is of the opinion that the rate of oxidation of soda cellulose is probably due to the combined effects of four separate factors, (*a*) the reactivity of the cellulose which is increased by swelling, (*b*) the concentration of NaOH in the cellulose phase, (*c*) the solubility of oxygen in soda cellulose, (*d*) the rate of diffusion of oxygen in soda cellulose.

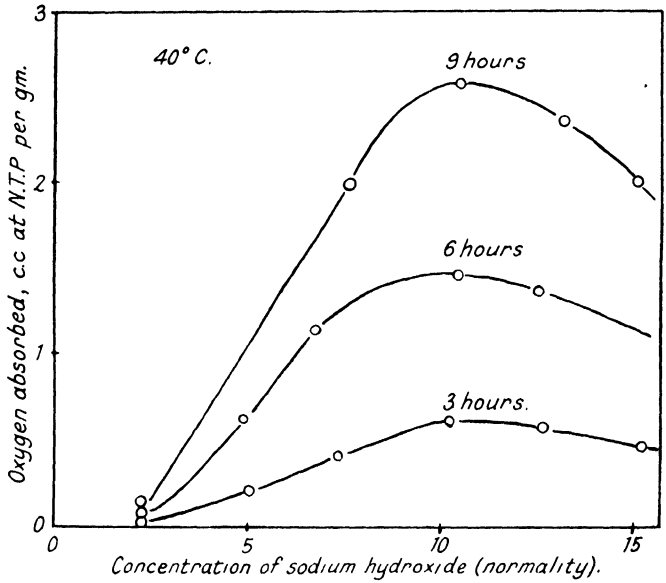


FIG. 130.—Rate of oxidation of alkali-cellulose.

These factors might be expected to lead to curves of the shape found when rate of oxidation is plotted against concentration of NaOH, the increase in rate of oxidation up to a concentration of 10 N being explained as increased reactivity due to swelling, and to the progressive increase in the concentration of NaOH in the soda cellulose. Meanwhile the solubility and the rate of diffusion of oxygen probably decrease gradually as the alkali concentration increases, and at concentrations above 10 N they become the predominant factors and so produce a diminution in the rate of oxidation.

Solubility of Oxycellulose

In considering the solubility of oxycellulose, mention is frequently made to the solubility of the hydrocelluloses also ;

indeed the latter are often utilised as reference substances in considering the solubility relations of modified cellulose as a class. The solubility of the hydrocelluloses is discussed on page 216.

Effect of Alkali-boil

Clibbens, Geake and Ridge (J.T.I., 1927, *18*, 277) have observed the action of hot dilute sodium hydroxide solutions on oxycellulose. All oxycelluloses suffer a fall of viscosity in cuprammonium solution as a result of six hours' treatment with a 1% solution of NaOH at the boil and differ in this respect from hydrocelluloses and normal bleached cotton, which are only slightly affected in viscosity by the same treatment. The magnitude of the viscosity change varies with the manner in which the oxycellulose has been formed, but is very great for neutral hypochlorite oxycelluloses. The following data illustrate the main variations in the properties of the oxycelluloses before and after an alkali boil.

EFFECT OF ALKALI-BOIL.

	Copper number		Methylene blue absorption.		Log. viscosity 2% solution.	
	Before.	After.	Before.	After.	Before.	After.
Hypochlorite	1·02	0·22	0·96	—	0·95	$\bar{1}$·96
at pH 7	1·41	0·34	1·01	1·18	0·46	$\bar{1}$·57
	2·02	0·47	1·08	—	$\bar{1}$·98	$\bar{1}$·39
	3·22	0·66	1·36	1·66	$\bar{1}$·56	$\bar{1}$·12
	4·58	0·79	1·51	1·89	$\bar{1}$·34	$\bar{1}$·09
Hypochlorite	0·65	0·09	1·02	0·90	0·81	0·38
at pH 4·6	1·07	0·17	1·04	1·02	0·24	0·02
	1·56	0·28	1·06	1·06	$\bar{1}$·98	$\bar{1}$·71
	2·46	0·39	1·10	1·21	$\bar{1}$·70	$\bar{1}$·53
	2·83	0·45	1·08	1·30	$\bar{1}$·62	$\bar{1}$·45
	3·78	0·51	1·18	1·48	$\bar{1}$·48	$\bar{1}$·35

The difference in copper number and methylene blue absorption offers no sharp distinction between the two extreme forms of oxycellulose nor between the oxycelluloses and the hydrocelluloses.

The effect of the alkali boil on the inter-relationship of the various properties has also been discussed in the section on hydrocellulose (see page 216).

In the same section, the work of Birtwell, Clibbens and Geake (J.T.I., 1928, *19*, 349) on the solubility in NaOH at ordinary temperatures and leading to the " solubility number " is described.

Solubility Number

Whilst the solubility of hydrocellulose is known if the copper number is available, very different relations obtain with the oxycelluloses. In any one series of oxidised cottons formed by the action of the same oxidising agent under the same conditions for varying times, the copper number of the material defines its solubility, but for different oxidising agents, or for

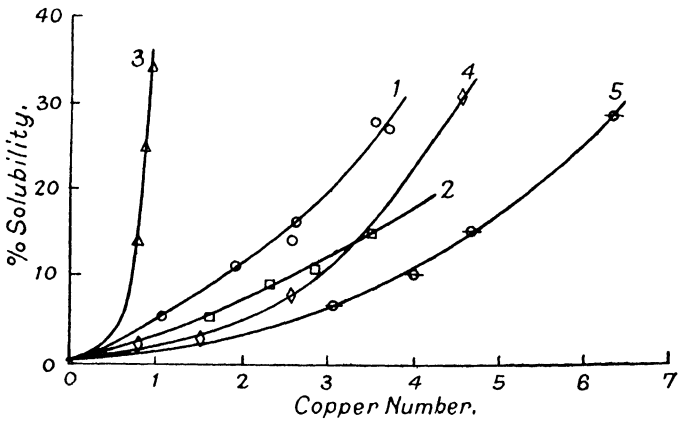


FIG. 131.—Solubility and copper number relationship for oxycelluloses.

the same oxidising agent acting under different conditions, there is no general relation between copper number and solubility number. This is shown from the above curves referring to neutral hypochlorite solution (1), hypochlorous acid (2), alkaline hypobromite (3), dichromate in presence of H_2SO_4 (4), and dichromate in presence of oxalic acid (5).

There is, however, a general correlation between fluidity and solubility number as in the case of hydrocellulose (see figure 111, page 225).

As with hydrocellulose, the effect of boiling an oxidised cotton with dilute alkali is slightly to increase its solubility number although the copper number is greatly reduced.

Reducing Value of Extract.

The reducing values (see page 226) of the extracts from oxycelluloses depend very largely on the nature of the oxidising attack. In the case of oxycellulose from neutral hypochlorite, the alkali extract has a reducing value of about 8, and the same is true for cotton oxidised with dichromate in the presence of H_2SO_4. Oxycelluloses formed by the action of hypochlorous acid on cotton, yield extracts with a reducing value near to 12, whilst those formed by the action of dichromate in presence of oxalic acid give extracts of reducing value from 16 to 20. Oxycelluloses, therefore, differ from hydrocelluloses in yielding extracts of a much higher reducing value, except in the case of oxycelluloses of the type formed by the action of alkaline hypobromite on cotton and all modified celluloses which have been boiled with alkalis. In other words, this reducing value of the extract may be used to distinguish between hydrocellulose and the reducing type of oxycellulose.

Mercerised Material.

It is necessary to point out that the relationships between, for example, copper number and solubility number do not apply to cotton which has been mercerised prior to modification. As with hydrocellulose, an oxycellulose of given copper number formed from unmercerised cotton, has a higher solubility number than an oxycellulose of the same copper number formed from mercerised cotton.

General Comparison.

Some data from the paper of Birtwell, Clibbens and Geake (loc. cit.) illustrating the properties of the oxycelluloses are shown in the following table.

Birtwell, Clibbens and Ridge (loc. cit.) have also shown that the properties of hypobromite oxycelluloses vary with hydrogen ion concentration in a manner similar to that for hypochlorite preparations.

PROPERTIES OF OXYCELLULOSES.

Method.	Copper number.	Fluidity.	Solubility number.	Reducing value.
N/25 NaClO pH 7	1·05		5·8	5·6
	1·92		11·6	6·5
	2·62		16·5	7·7
	3·73		27·5	8·0
	2·56		14·5	
	3·57		28·2	
N/25 HClO pH 4·6	1·61	20·5	5·6	12·1
	2·31	24·8	9·3	12·6
	2·83	26·3	11·1	13·1
	3·49	29·0	15·3	13·3
N/25 $K_2Cr_2O_7$	0·78	14·3	2·2	2·3
N/5 H_2SO_4	1·53	20·8	3·2	6·2
	2·54	27·5	8·1	8·3
	4·56	35·2	31·2	8·4
N/25 $K_2Cr_2O_7$	3·04		7·0	16·1
N/5 oxalic acid	3·98	32·3	10·5	
	4·65		15·4	
	6·33		29·1	17·9
N/100 NaOBr	0·35	12·0	1·2	2·5
N/10 NaOH	0·47		2·0	2·7
	0·57	27·5	5·9	2·6
	0·61		8·0	2·3
N/25 NaOBr	0·77	28·8	14·4	
N/10 NaOH	0·87	32·4	25·3	
	0·93	34·6	34·5	
N/10 NaOBr	1·50	41·1	60·2	
N/10 NaOH	1·48	44·1	71·2	

Solubility at Low Temperatures

The work of Davidson (J.T.I., 1934, *25*, 174) on the solubility of modified cellulose in caustic soda solutions at temperatures below the normal has already been mentioned in the section on hydrocellulose (see page 226). Much of this work refers to oxycellulose as well as hydrocellulose, the term " modified cellulose " covering both types.

However, when modified cottons are boiled under pressure with dilute alkali, the residual material is more soluble in NaOH solution at $-5°$ C. than the original modified cotton. The increase in solubility is slight with hydrocellulose from unmercerised cotton, but is considerable with hydrocellulose from mercerised cotton and with oxycellulose of the hypochlorite series examined.

The solubility of any modified cotton, measured under the optimum conditions at −5° C. was found to be greater the greater its fluidity. Oxycelluloses of the hypochlorite series were found to be more soluble than hydrocelluloses of the same fluidity, but after an alkali boil, these oxycelluloses showed a fluidity-solubility relation, which was nearly the same as that found for the hydrocelluloses prepared from unmercerised cotton (*q.v.*). The oxycelluloses made by the oxidation of

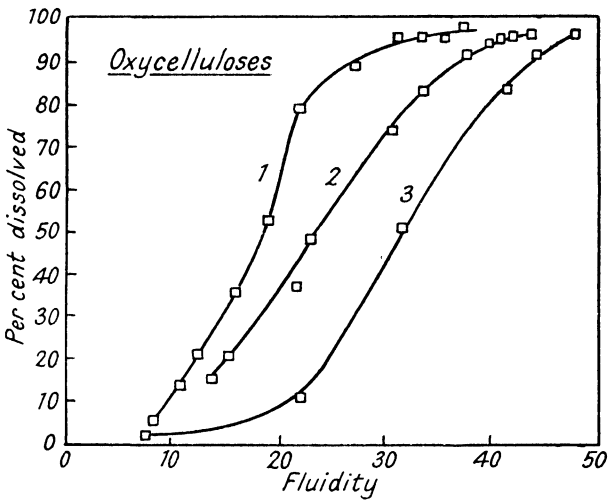


FIG. 132.—Relation between solubility and fluidity.

Curve 1 relates to the hypochlorite series; curve 2 to similar material after alkali-boil, and curve 3 to material from the oxidation of alkali cellulose.

soda cellulose, on the other hand, showed the effects of previous swelling in having relatively low solubility for a given fluidity. These results are shown in figure 132.

Further work by Brownsett and Davidson (J.T.I., 1941, *32*, 25) included a more comprehensive investigation of nine different modified cottons, prepared by the action of (1) alkaline hypobromite, (2) alkaline hypochlorite, (3) neutral hypochlorite, (4) acid hypochlorite, (5) dichromate-sulphuric, (6) dichromate-oxalic, (7) periodic acid, (8) metaperiodate and (9) hydrochloric acid to produce hydrocellulose. No two types gave exactly the same relation between fluidity and solubility in 2·5 N NaOH at −5° C., but the curves for alkaline hypochlorite, alkaline hypobromite, and the two dichromate series

were not very different from that for the hydrocelluloses. The neutral hypochlorite oxycelluloses, for a given fluidity, were more soluble than these five types and the acid hypochlorite oxycelluloses were still more soluble. Periodate oxycelluloses, on the other hand, are considerably less soluble than hydrocelluloses of equal fluidity.

Treatment of the modified cottons with cold or hot dilute NaOH solutions brings about certain changes which vary with

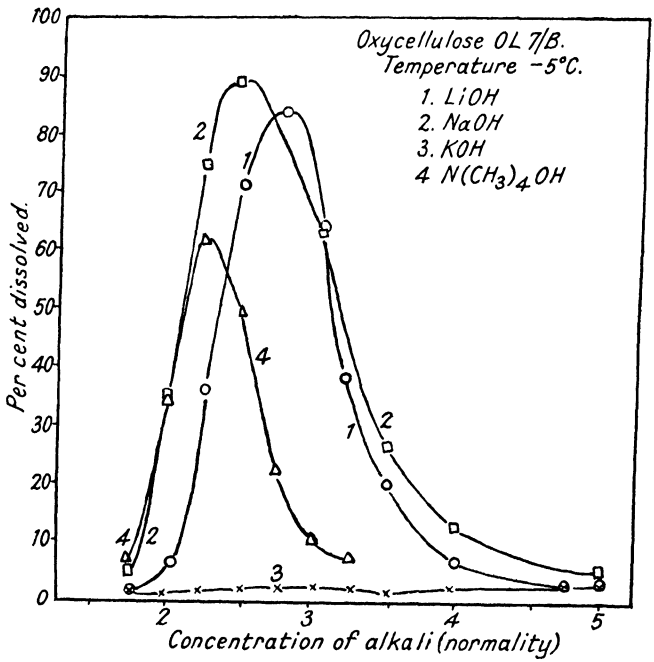


FIG. 133.—Solvent action of various hydroxides.

the type of modification, but after this treatment the relation between fluidity and solubility may be expressed by a single curve which is almost coincident with that for the hydrocelluloses before treatment with alkali.

The solvent action of solutions of lithium, sodium, potassium and tetramethylammonium hydroxides on modified cellulose, described by Davidson (J.T.I., 1936, *27*, 112) has also been referred to in the section on hydrocellulose. There are, however, certain data specifically concerning oxycellulose which are of interest. The graph, figure 133, represents the solubility

of oxycellulose prepared from scoured cotton linters by the action of sodium hypochlorite of pH 8·4 and subjected to an alkaline boil after modification. The outstanding feature is the relatively low solvent power of potassium hydroxide solution.

The solvent power of these hydroxides at 15° C. was also measured, and it was found that the order of solvent action varied with the temperature, i.e. at 15° C. the order of increasing solvent action is $LiOH < NaOH < N(CH_3)_4OH$ whilst at −5° C. it is $N(CH_3)_4OH < LiOH < NaOH$.

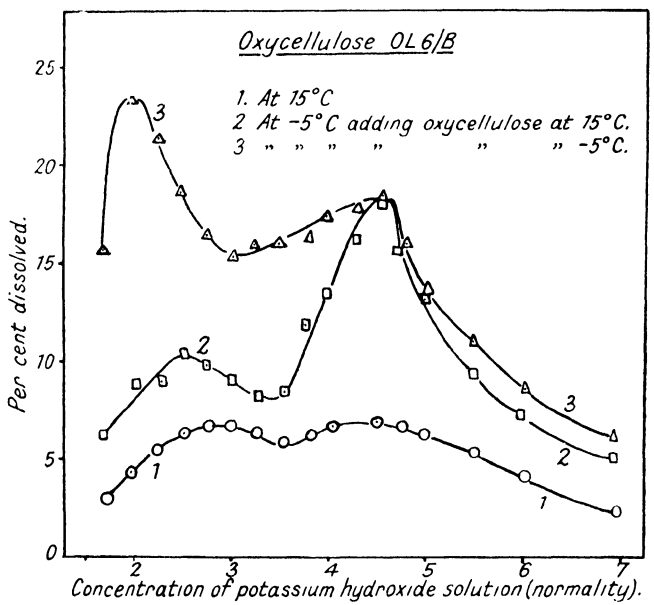


FIG. 134.—Effect of temperature on solubility in KOH.

The effect of the temperature on the solvent action of KOH was investigated, and it was found that if, instead of mixing the oxycellulose and the solution at 15° C., the solution is cooled to −5° C. before the addition of the oxycellulose, the effect on the solubility curve is striking. The maximum at an alkali concentration of 4·5 N is little affected, but at all lower concentrations the solubility is considerably increased, and a maximum, which is higher than at 4·5 N, occurs at a concentration of 2 N. (See Fig. 134.)

Reference has been made on page 157 to the new quaternary benzyl ammonium hydroxides and these have been included by Brownsett and Clibbens (J.T.I., 1941, *32*, 32) in a survey of the relation between the fluidity of modified cotton and the solubility in different bases at their optimum concentration. From the curves of Fig. 135 the six bases may be arranged in the following order of solvent power: dimethyldibenzylammonium, triethylbenzylammonium, tetramethylammonium, sodium, lithium and potassium hydroxides.

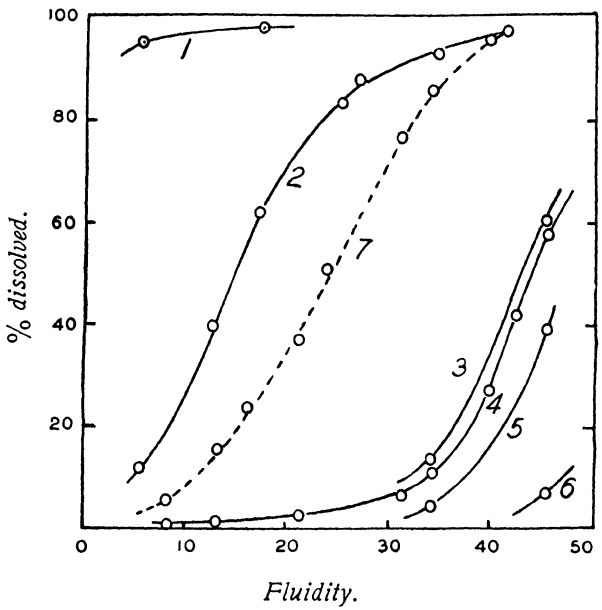


FIG. 135.—Relation between fluidity of modified cottons and their reactional solubility in different bases at their optimum concentrations. (1) Dimethyldibenzylammonium hydroxide at 20° C., (2) trimethylbenzylammonium hydroxide at 20° C., (3) tetramethylammonium hydroxide at 15° C., (4) NaOH at 15° C., (5) LiOH at 15° C., (6) KOH at 15° C., (7) NaOH at −5° C.

The above order refers to solvent power at the ordinary temperature, but it will be seen that the broken curve refers to NaOH at −5° C., when its solvent power is only slightly inferior to that of trimethylbenzylammonium hydroxide at 20° C.

Each curve in Fig. 135 refers to a different concentration of base, corresponding to the maximum in the solubility curve—

the first miaxmum where two exist. The modified celluloses were derived from native cotton cellulose and different quantitative results would be obtained for activated or hydrate cellulose. Subject to this condition, the solubility is not greatly affected by the method of modification provided that the material oxidised in neutral or acid solution receive a treatment with dilute alkali before examining the solubility.

Accelerated Oxidation

The oxidation of cellulose may be accelerated by the simultaneous oxidation of a compound additional to the oxidising agent and the cellulose itself. It is well known for example that when cellulose is treated with potassium dichromate and oxalic acid, both the oxalic acid and the cellulose are oxidised and the oxidation of the latter takes place much more rapidly than when cellulose is treated with potassium dichromate and sulphuric acid (Clibbens and Ridge, J.T.I., 1927, *18*, 135). Oxycelluloses of the extreme reducing type are conveniently prepared by treatment with potassium dichromate and oxalic acid.

More recently, however, the accelerated oxidation of cellulose has been studied by Turner, Nabar and Scholefield (J.S.D.C., 1935, *51*, 5; 1937, *53*, 5) who found that in the presence of certain reduced vat dyes, the cellulose was oxidised by hypochlorite to an extent which was only reached with undyed cotton and hypochlorite after several hours treatment. The most important feature of their work was the great acceleration of the oxidation of cellulose which occurs in the presence of reduced vat dyes, but it was also shown that there was close connection between the extent of the accelerated oxidation and the corresponding potential of the oxidising agent. For accelerated oxidation, the oxygen consumed is directly proportional to the increase in copper number and to the carboxyl content of the cellulose brought about by the hypochlorite treatment. The degree of modification of cellulose, dyed with a reduced vat dye, and treated with hypochlorite solution of pH 7·55, increases with increase in concentration of the accelerating dye. When the degree of chemical modification was varied by varying the concentration of the accelerating substance, the constant ratio between oxygen consumption and rise in copper number, and also between oxygen consumption and rise in carboxyl content was again established. It appears, therefore, that the ratio between the number of

reducing groups and the number of carboxyl groups produced during accelerated oxidation is a constant. The value of this ratio is approximately the same when the accelerator is constant and the pH of the hypochlorite varied, as when the pH of the hypochlorite is constant and the concentration of the accelerator varied. Hence, the ratio of reducing groups to carboxyl groups is not only constant but independent of the pH of the hypochlorite, the concentration of the accelerator and the composition of any buffers which may be present. The same conclusion may be applied to the ratio between the reducing groups formed and the oxygen consumed and also to the ratio between the oxygen consumed and the carboxyl groups formed. These simple relationships do not obtain in the case of prolonged unaccelerated oxidation.

Oxycellulose and the Chain Molecule

A progressive diminution in tensile strength and increase in fluidity is a feature of the progressive action of some oxidising agents on cellulose. Whereas the action of acids can hardly be interpreted in any manner other than that of hydrolysis of glucosidic linkages, oxidation might attack any of the hydroxyl groups in the molecular chain, nevertheless the strength and fluidity data point to progressive shortening of the chain-molecules.

The oxycelluloses also show increased reducing power, but this is probably due to oxidation of the primary or secondary alcohol groups to aldehyde or ketonic groups, and it was not clear why this should lead to reduction in chain length. It is possible that the oxidised chain is unstable and that a secondary reaction ensues. Instances are known of oxidation resulting in high copper number with relatively small loss of tensile strength. Whilst a copper number of 5 in the case of acid attack results in complete loss of strength, the same copper number produced by means of dichromate oxidation corresponded to a 20% decrease in strength. On the other hand, different methods of oxidation produced oxycelluloses characterised by much greater decreases in strength for the same copper number than is the case with hydrocelluloses.

In addition to the reducing power, the oxycelluloses also exhibit an enhanced affinity for methylene blue, which is not seen in the hydrocelluloses proper. The methylene blue absorption is regarded as a measure of the acidic character

of the oxycellulose and denotes that the oxidation process has produced carboxyl groups, most probably by oxidation of the aldehydic group derived from the primary alcohol groupings.

The action of different oxidising agents has resulted in the formation of two extreme types of oxycellulose, one characterised by high reducing power and low methylene blue absorption, whilst the other exhibits low reducing powers and high absorption of the basic dyestuff. In each series the progressive action of the oxidising agent results in the copper number of the methylene blue absorption increasing regularly, the changes being accompanied by continuous changes in fluidity, strength and solubility in cold solutions of sodium hydroxide. When the two series of oxycelluloses prepared under different conditions of oxidation are compared, then the relationship between reducing power or methylene blue absorption and tensile strength, solubility and fluidity is often quite different. It must, therefore, be assumed that the chemical mechanism of the oxidation processes is different in the two cases. The difference in relation between fluidity and tensile strength in the two series may be accounted for on the basis that for one method of oxidation the average chain length does not necessarily define the distribution of chain length in the other series, i.e. by a different method of oxidation.

The Chemical Action of Alkali

The action of cold aqueous solutions of sodium hydroxide on modified cellulose is regarded as a physical process of swelling followed by the dissolution of the shorter chain molecules, but Davidson (loc. cit.) also emphasised the fact that modified celluloses are chemically unstable to alkali, e.g. on boiling with 1% (0·25 N) NaOH solution the modified celluloses lose in weight and the dissolved portion is fundamentally changed, for it cannot be recovered by acidification as it is soluble in water. There is also a reduction in the copper number of the modified cellulose and a sufficiently long period of boiling will reduce it to that of the original cellulose. The loss in weight on boiling with alkali is correlated with the copper number, no matter whether the modification has been produced by acid attack or by means of oxidising agents, and is usually of the order of 6% for each unit of copper number. The methylene blue absorption also increases as the result of an alkali boil, no matter if the modification is hydro- or oxycellulose. The type of oxycellulose with a low copper number and high methy-

lene blue absorption does not undergo a further increase in methylene blue absorption nor does it suffer much loss in weight as the result of boiling in alkali.

Whilst the fluidity of the hydrocelluloses is not affected by an alkaline boil, yet with the oxycelluloses there is an increase which varies according to the manner of oxidation. The effect on the tensile strength is slight for hydrocellulose and the acidic type of oxycellulose, but more severe in the case of oxycellulose of high reducing power as produced by dichromate oxidation.

This behaviour is easier to explain in the case of hydrocellulose since the molecular structure is better understood. Whilst little is known of the chemical reactions which take place on boiling hydrocellulose with alkali, it is most probable that the chain is attacked at the terminal reducing group on account of the loss in reducing power and the correlation between loss in weight and initial copper number. The reducing group is most likely replaced by a carboxyl group on the evidence of the rise in methylene blue absorption, but the exact nature and mechanism is unknown. If the alkali attack on the reducing group results in the shortening of the chains and the decomposition of the shortest into soluble products, then the removal of the shortest chains and the shortening of the remainder would have opposite effects on the fluidity and even counterbalance each other leaving the fluidity unchanged. The shortening of the chains would also account for the increase in solubility in cold aqueous solutions of sodium hydroxide. The reduction in length of the longer chains by relatively small amounts need not seriously affect the tensile strength, whilst removal of the shortest chains should not produce any difference owing to their small contribution to the tensile strength even when present. The chief difficulty is to account for the large loss in weight without considerable shortening of the molecule chain which would produce a lower tensile strength.

The behaviour of the extreme acidic type of oxycellulose may also be explained on the above arguments ; the low copper number accounts for the small loss in weight and the slight change in fluidity and tensile strength as the result of an alkali boil.

The properties of the other type of oxycellulose, i.e. that produced by dichromate action and possessing high reducing power, cannot be explained by the same hypothesis.

The most pronounced effect of the alkali boil on oxycelluloses of high reducing power is the great loss in strength, which is not necessarily due to a loss in weight as this does not follow on boiling with soap solution or even water, which, nevertheless, cause considerable weakening.

It seems apparent that this loss in tensile strength must be due to actual rupture of the molecular chain and not to the usual progressive shortening which accompanies controlled oxidation. From this it follows that there must be an essential difference between the dichromate oxycelluloses on the one hand and the hydrocelluloses and oxycelluloses of the acidic type on the other, in that the former possess glucose residues and glucosidic residues in the chain molecule which, though physically intact, are yet so unstable as to be readily broken by boiling with water and very easily broken by boiling in dilute alkali. This assumption is confirmed by the observation that the fluidity of the dichromate oxycelluloses is abnormally high compared with the tensile strength ; in this case, however, the action of the boiling alkali is replaced by the strongly alkaline effect of the cuprammonium solution in which the fluidity is determined.

Alkali-Sensitivity

Although the properties of the various oxycelluloses vary according to the method of formation, there is always a fall in tensile strength and a rise in fluidity; the relation between these two properties has shown that the loss in strength for a given rise in fluidity is greatest for the hydrocelluloses and least for the oxycelluloses prepared by the action of dichromate in oxalic acid solution. If the modified celluloses are subjected to an alkali boil, the tensile strength is diminished and the fluidity increased to an extent which also depends on the manner of modification—the dichromate and periodate oxycelluloses suffering the greatest additional loss in strength. The changes of fluidity and strength produced by boiling are such that the fluidity-strength relation for the boiled material is approximately the same whatever the method of modification. The behaviour of the dichromate oxycelluloses and those prepared by oxidation in non-alkaline solutions is difficult to interpret on the theory of cellulose as a chain molecule, but Davidson (J.T.I., 1934, *25*, 174) suggested that oxidation does not necessarily result in the scission of the chain molecule but that the alcohol groups in the glucose residue are first oxidised

to an aldehyde or that the ring structure may be broken, causing a weakening of the glucosidic linkage.

On examination of the oxidation of the simple glycosides, such as the alkyl glycosides of glucose, mannose and galactose, Fleury and Lange (Compt. rend., 1932, *195*, 1395) and Fleury and Paris (*ibid.*, 1933, *196*, 1416) and Cherissey, Fleury and Joly (J. pharm. Chim., 1934, *20*, 149) concluded that in the case of periodic acid, the glycosides were oxidised to dialdehydes. The work of Jackson and Hudson (J.A.C.S., 1936, *58*, 378; 1937, *59*, 994; 2049) established the correctness of this view for they showed that the oxidation of methyl mannoside by alkaline hypobromite yielded the corresponding dibasic acid and in view of the similarity in structure between the methyl hexosides and cellulose, they suggested that oxidation by periodic acid should lead to a cleavage of the ring structure between carbon atoms *2* and *3*, whereby the secondary alcohol groups are oxidised to aldehyde groups. As previously stated the work of Davidson on the oxidation of cellulose with periodic acid, has shown that this oxycellulose is extremely alkali-sensitive and his work throws light on the whole question of the alkaline hydrolysis of the high reducing type of oxycellulose.

The earlier observations of Clibbens and Ridge (J.T.I., 1928, *19*, 389) on the fluidity of the dichromate oxycelluloses showed two important differences from the neutral-hypochlorite oxycelluloses—a definite rise in fluidity on modification corresponds with a smaller loss in strength, while alkali-boiling is accompanied by a large additional loss in strength with a comparatively small rise in fluidity. The general effect of the alkali-boil on some modified cottons is shown in Fig. 136; recent work has shown that the periodate oxycelluloses are even more sensitive than the dichromate oxycelluloses. The alkali-sensitive linkage may even be broken by boiling the oxycellulose with water and also by treatment with an alkaline solvent such as cuprammonium hydrate—processes which are without much action on hydrocellulose and have comparatively little effect on the oxycelluloses prepared in alkaline solutions.

The difficulties associated with the alkaline nature of cuprammonia may be avoided by observing the fluidity, in acetone solution, of the cellulose nitrates formed from the modified celluloses. Davidson (J.T.I., 1938, *29*, 195) showed that within each series of modified cottons there is a definite relation between cellulose fluidity and cellulose nitrate fluidity, and this relation differs widely for the various methods of

modification, but that boiling the modified celluloses with 1% NaOH solution under pressure brings about a change whereby the relation between cellulose fluidity and cellulose nitrate fluidity is expressed by a single curve, irrespective of the method of modification, and corresponding to that for hydrocelluloses before alkali-boiling.

The cellulose nitrate fluidity of the periodic acid oxycellulose is only slightly greater than that of the cotton from which it is produced, and is therefore much less than that of hydrocellulose of equal cellulose fluidity in cuprammonia; after

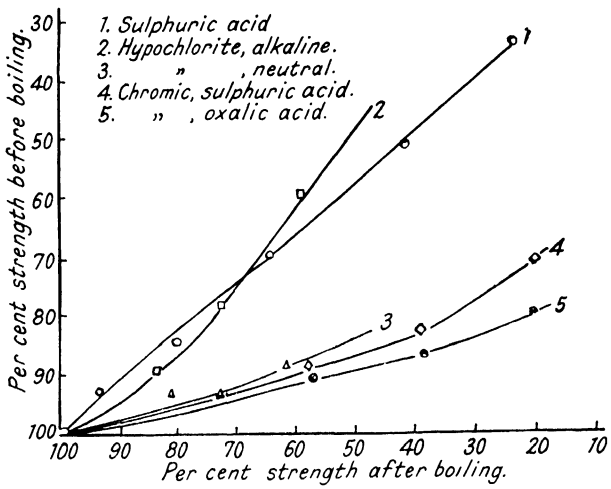


FIG. 136.—Effect of alkaline boil on the tensile strength of modified cellulose.

boiling with a dilute alkali, however, the periodic acid oxycellulose shows the same relation between cellulose fluidity and cellulose nitrate fluidity as do the hydrocelluloses and the other types of oxycellulose which have been subjected to an alkali boil. When the periodate oxycelluloses are treated with dilute alkali their cellulose nitrate fluidity may be greatly increased and their tensile strength seriously diminished. For the same cellulose nitrate fluidity the periodate oxycelluloses are considerably weaker than the dichromate oxycelluloses.

Boiling with alkali under pressure demonstrates the presence or absence of alkali-sensitive linkages in modified cellulose whose average chain length may be measured in the non-alkaline medium. The alkali-sensitive material shows an

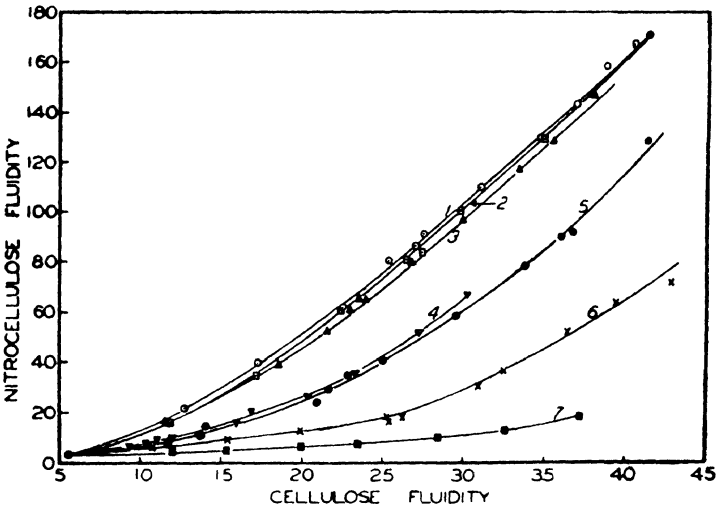


FIG. 137.—Relation between cellulose fluidity and nitrocellulose fluidity.
1-hydrochloric acid; 2-alkaline hypobromite; 3-alkaline hypochlorite; 4-acid hypochlorite; 5-neutral hypochlorite; 6-dichromate and sulphuric; 7-dichromate and oxalic.

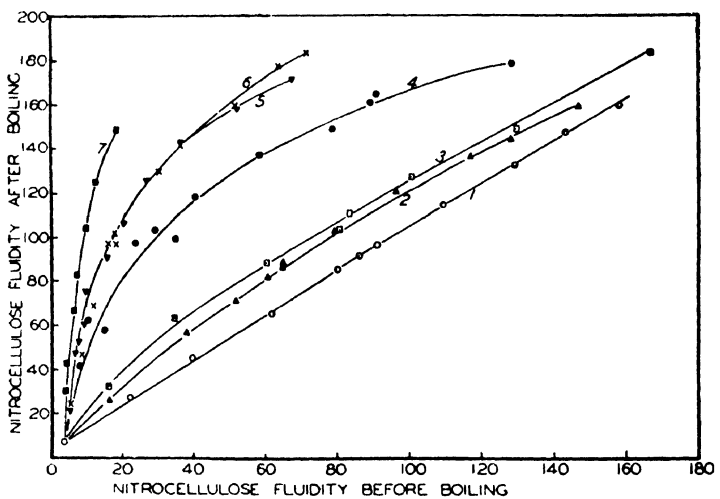


FIG. 138.—Cellulose nitrate fluidities of modified celluloses before and after an alkaline boil.
1-hydrochloric acid; 2-alkaline hypochlorite; 3-alkaline hypobromite; 4-neutral hypochlorite; 5-acid hypochlorite; 6-dichromate and sulphuric; 7-dichromate and oxalic.

increase in cellulose nitrate fluidity as the result of rupture of the chain. The results of Fig. 138 illustrate the point clearly. The hydrocelluloses are little affected, but the oxycelluloses from neutral or acid oxidising solutions show a great increase in cellulose nitrate fluidity as the result of the alkali-boil. Relatively small increases of cellulose nitrate fluidity are shown in the case of the oxycelluloses prepared by the action of alkaline oxidising agents.

Where milder conditions of boiling were employed, those oxycelluloses which show a large increase in cellulose nitrate fluidity when boiled under pressure with NaOH showed a smaller but nevertheless considerable increase when boiled with water. Intermediate increases were shown on boiling with soap or sodium carbonate solutions. The acid and neutral-hypochlorite oxycelluloses which show the greatest rise in cellulose fluidity on boiling with NaOH solution under pressure, show almost the same effect after boiling with soap or sodium carbonate solutions; hydrocelluloses and oxycelluloses of the alkaline hypobromite and alkaline hypochlorite types show small increases in fluidity, both for celluloses and nitrocellulose, when boiled in water, soap or sodium carbonate solution.

The effect of cold dilute solutions of alkali (NaOH or Na_2CO_3) is to increase both the cellulose fluidity and cellulose nitrate fludity of alkaline hypochlorite oxycelluloses, but there is little increase in the case of hydrocelluloses. The effect on neutral hypochlorite, acid hypochlorite and dichromate oxycelluloses is similar to that produced by the boiling alkali in that there is a great increase in cellulose nitrate fluidity, though somewhat less for the cold treatment.

Hydrocelluloses prepared from mercerised cotton show the same relation between cellulose fluidity and cellulose nitrate fluidity as hydrocelluloses from unmercerised cotton.

Consideration of the relationship between solubility and fluidity of modified cotton has given interesting results, as discussed on page 225; indeed as both the fluidity in cuprammonia and the solubility in alkali are functions of the frequency distribution of chain length, some functional relation should be expected. This relation should be the same for *different* methods of modification, provided two conditions are fulfilled, (*a*) the distribution of breaks (both actual and latent) in the chain molecules changes in the same way with progressive attack by various chemical reagents, and (*b*) if NaOH as used for solubility measurement and cuprammonia as used

for fluidity determination, are equally effective in breaking the alkali-sensitive linkage.

The first condition appears to be fulfilled by the types of modified cotton which do not contain alkali-sensitive linkages (hydrocellulose, alkaline hypobromite, and alkaline hypochlorite oxycellulose) and by all types after adequate prior treatment with NaOH. The abnormal fluidity-solubility relation shown by the periodate, neutral hypochlorite and acid hypochlorite oxycelluloses suggests that the second condition has not been met, i.e., NaOH and cuprammonia are not equivalent in their attack on the alkali sensitive linkage. From the work of Brownsett and Davidson (J.T.I., 1941, *32*, 25) it appears that all the weak linkages in the periodate oxycelluloses have not been broken by NaOH, under the conditions of the solubility determination, but may be broken by a more prolonged treatment with the same alkali; the abnormal low solubility of the periodate oxycelluloses as compared with hydrocellulose of equal fluidity is accounted for if the alkali-sensitive linkages which were not broken in the solubility measurement were affected in the fluidity determination.

The neutral and acid hypochlorite oxycelluloses showed an abnormal rise of fluidity when treated with dilute NaOH, so it appears that cuprammonia is not able to break all the linkages in these types of oxycellulose which are broken by NaOH.

The work of Brownsett and Clibbens (J.T.I., 1941, *32*, 57) on the quaternary benzyl ammonium hydroxides has contributed further information on the matter of alkali-sensitivity. One of the difficulties previously encountered was that the additional fragmentation of the oxycellulose chain molecules could be brought about by either the alkaline action of cold dilute sodium hydroxide, which is not a solvent for cellulose, or by the action of cuprammonia which is a solvent for cellulose; the extent of the fragmentation differs greatly with the two alkalies. The difference in their action is seen by considering the oxycelluloses from neutral or acid hypochlorite, where cold dilute NaOH produces greater additional degradation than cuprammonia. Comparison of the fluidities of modified cotton in cuprammonia and in Triton F varies according to the method of modification, but when considering the alkali-sensitive oxycelluloses, if these two alkaline solvents exert different fragmentation effects, then the fluidities will

relate to different chain length distributions. It was established that in the case of the dichromate-sulphuric oxycelluloses and also the neutral hypochlorite oxycelluloses, that NaOH produces a greater effect than cuprammonia but does not produce a greater effect than Triton F. Although these oxycelluloses suffer some reduction in chain length from both solvents they are less affected by cuprammonia than by Triton F. Hence the latter has a definite advantage when investigating the total modification (i.e., actual and latent), as otherwise it becomes necessary to treat the cotton material with NaOH before measurement of the fluidity in cuprammonia ; the degrading action of Triton F on the alkali sensitive modified cottons is similar to that of NaOH so that abnormalities connected with cuprammonia are avoided.

It is not yet clear if the Tritons (quaternary benzyl ammonium hydroxides) will be available in commercial quantities and of a sufficient degree of purity to replace cuprammonia for fluidity work as a standard solvent.

The rapid advances of recent years have clarified the question of oxycellulose formation and behaviour to a remarkable degree and it now appears that they may be divided into two classes.

1. Those prepared from alkaline oxidising solutions and giving almost the same relation between cellulose fluidity and cellulose nitrate fluidity as the hydrocelluloses ; these oxycelluloses are very slightly affected by alkaline treatment.

2. The oxycelluloses prepared with neutral or acid oxidising solutions and giving products which, although degraded to some extent, yet contain alkali-sensitive linkages which are responsible for further degradation when the original oxycellulose is treated with feebly alkaline solutions.

Modified Cellulose—Tests

The main differences between oxycellulose and hydrocellulose modifications, with certain reservations, may be shown by the following tests, which are taken from " The Methods of Cellulose Chemistry," by Dorée.

(i) The viscosity in cuprammonium hydroxide after boiling for six hours in a 1% solution of NaOH. Oxycellulose shows a marked fall in viscosity which is not the case with hydrocellulose or normal cotton.

(ii) The cellulose residue left after the determination of the copper number shows changes similar to those produced by the alkali boil.
(iii) Determination of the copper number (or better, the fluidity) of the residue from the solubility number determination.
(iv) Determination of the reducing value of the extract obtained during the determination of the solubility number. Hydrocelluloses have a value 4, and reducing oxycelluloses 8–20.
(v) The use of methylene blue absorption at pH 2·7 and pH 7·0 gives an approximate differentiation between damage caused by oxidation and that caused by acid attack.

The following points of difference have been recorded for the more highly modified products:

(*a*) evolution of carbon dioxide during hydrolysis with HCl is found with oxycellulose but not hydrocellulose.
(*b*) When methyl orange is added to a suspension of the material in water, an orange red colour is given by oxycellulose, changing to red on the addition of brine. Hydrocellulose does not give this test.

The "acidity" of one type of oxycellulose has been mentioned on page 242, and its quantitative estimation has recently received attention from Neale and Stringfellow (Trans. Farad. Soc., 1937, *33*, 881). The increased affinity for basic dyes varies so largely with the pH that it cannot be used as a measure of the carboxylic acid group to which it is presumably due. At the same time the affinity for direct dyes is decreased and in the case of the absorption of Sky Blue F.F. from solutions containing sodium chloride, it was shown by Hanson, Neale and Stringfellow (Trans. Farad. Soc., 1935, *31*, 1718) that this could be explained quantitatively according to the principle of the Donnan membrane equilibrium.

The decreased affinity for direct dye could therefore be attributed to the presence of carboxylic acid groups which entered into ionic equilibria with the solution.

If an oxycellulose of the acidic type is placed in sodium chloride solution, then the solution shows an acid reaction, since a certain proportion of the hydrogen ions arising from the carboxylic acid groups are replaced by sodium ions and are

thus able to escape from the cellulose phase, and to distribute themselves throughout the two phases in accordance with the principle of membrane equilibrium. On adding alkali to the system, the equilibrium is displaced until all the carboxylic acid groups have been neutralised.

The material must first be washed free from cations in order that the whole of the carboxylic acid may be originally present as such. This is done by leaving the oxycellulose in contact with cold 2 N. HCl for 30 mins., and then washing repeatedly with distilled water until the washings were neutral to brom-cresol-purple. The method of back-titration is the same as that adopted by Nabar, Scholefield and Turner (J.S.D.C., 1937, *53*, 5).

The method is stated to work quite satisfactorily and to be more reliable than the methods described by Lüdtke (Angew. Chem., 1935, *48*, 650) and by Schmidt and his co-workers (Ber., 1934, *67*, 2037). As oxycelluloses of the reducing type may partially dissolve on treatment with hot alkalis, it is desirable to avoid heating the solutions except for a brief period near the end of the titration, when it is necessary to boil in order to expel the carbon dioxide.

Qualitative Tests

The presence of oxy- or hydrocellulose may be recognised by the following qualitative tests:

(*a*) With iodine solution, cellulose gives a yellow colour changed to blue by H_2SO_4; oxycellulose gives an immediate blue destroyed by H_2SO_4.

(*b*) By dyeing in benzopurpurin 4 B, rinsing in H_2SO_4, and washing in water until the red colour reappears, any oxidised portions will be a blue-black colour.

(*c*) Indanthrene yellow is dissolved in concentrated H_2SO_4 and the solution poured into cold water and neutralised. A few drops of the suspension are added to 10% NaOH and the fabric is steeped, removed and squeezed. It is placed over a beaker of vigorously boiling water. In one minute oxy- and hydrocellulose give a deep blue stain, whereas, cellulose shows no change in five minutes. If the fabric is washed and scoured with acetic acid followed by scouring with soap, the unaffected parts wash light, and the changed parts remain coloured.

(*d*) Any modification of the cellulose is shown by the presence of red copper oxide after boiling with Fehling's solution.

Thomas (J.S.C.I., 1933, *52*, 79) has reviewed the main colorimetric tests for distinguishing between oxy- and hydrocellulose. In this case the oxycellulose was prepared by treatment with sodium hypochlorite solution containing 0·5% of sodium carbonate.

The stannous chloride-gold chloride test of Haller (Textilber., 1931, *12*, 257) was found to give inconsistent results on repetition. The test was also stated to be tedious and expensive for routine work, although the principle of absorbing metals from solutions of their salts is sound. The heat test described by Fort (J.S.D.C., 1932, *48*, 94) was found to be difficult to apply, and often oxycellulose and hydrocellulose discoloured to the same extent. The methylene blue test was stated to be fairly satisfactory but not specific, as both hydrocellulose and normal cotton become coloured though not to the same extent as oxycellulose. A negative test for oxycellulose with direct cotton dyestuffs was also found to be satisfactory but was not sufficiently selective.

New positive tests for oxycellulose were, therefore, devised by Thomas, based on the principle of the enhanced affinity of oxycellulose for metals from solutions of their salts. Solutions of iron salts gave very satisfactory results, lead salts were quite suitable, but copper salts did not give such discriminatory results.

Immersion of the oxycellulose-hydrocellulose material and white cotton in a solution of ferrous sulphate, followed by rinsing, and subsequent immersion in potassium ferricyanide solution resulted in the development of a deep blue coloration of the oxycellulose but only slight coloration of the cotton and hydrocellulose. Similar results were obtained by immersion in ferric chloride and potassium ferrocyanide.

Another selective test was evolved on the basis of the production of lead chromate by immersion in lead acetate solution and subsequent treatment in sodium chromate solution.

The reducing powers of oxycellulose, combined with its affinity for metals, furnishes a further selective test; thus on immersion in ferric chloride solution, a certain amount of reduction to the ferrous condition takes place on the oxycellulose material and probably on the hydrocellulose. On

rinsing, however, the iron salt is removed from the cotton and hydrocellulose but is fixed on the oxycellulose so that a deep blue coloration is obtained on immersion in a solution of potassium ferricyanide. In all these colorimetric tests developed by Thomas, it is essential to follow the experimental conditions rigorously.

PART FIVE

THE DERIVATIVES OF CELLULOSE

CHAPTER THIRTEEN

ESTERS OF INORGANIC ACIDS

Cellulose Nitrate

Introductory

The general method for the preparation of the nitrates of cellulose was indicated by Schönbein in 1845, the most suitable nitrating agent being a mixture of nitric and sulphuric acids. There is considerable doubt about the existence of a true mono- or di-ether or ester of cellulose, and in the case of the mono-nitrate of cellulose, X-ray analysis indicates that it is a mixture of unchanged cellulose with the higher esters. The nitrogen content of these esters may be varied continuously by suitable alteration of the conditions of nitration, and most cases of nitration produce a mixture of indefinite chemical compounds.

On the basis of a glucose residue $C_6H_{10}O_5$, the trinitrate should contain 14·2% of nitrogen and the di- and mono-nitrates 11·1% and 6·8% respectively.

It must be remarked, however, that many of these mixtures of nitric and sulphuric acids would not be employed for the preparation of cellulose nitrates of the corresponding nitrogen content. In each experiment, equal weights of nitric (*d.* 1·50) and sulphuric (*d.* 1·83) acids were taken, and the ratio of acid to cotton was constant. The cellulose was treated for 24 hours at 16–18° C., the acid pressed out, and the mixture treated with a large quantity of cold water, then filtered, and washed for two days with boiling water.

Concentrated nitric acid (*d.* 1·5) alone will nitrate cellulose, but in practice the mixture of nitric and sulphuric acids is invariably used. Lunge and Bebie (Z. angew. Chem., 1901, *14*, 486) have shown the influence of the water content of the nitrating mixture on the degree of esterification.

INFLUENCE OF WATER.

Nitration mixture.			$N_2O_5/C_6H_{10}O_5$.	Nitrogen %	Solubility in ether-alcohol.
H_2SO_4	HNO_3	H_2O			
45·31	49·07	5·62	2·8	13·65	1·50
42·61	46·01	11·38	2·7	13·21	5·40
41·03	44·45	14·52	2·5	12·76	22·00
40·66	43·85	15·49	2·4	12·58	60·00
40·14	43·25	16·61	2·4	12·31	99·14
39·45	42·73	17·82	2·3	12·05	99·84
38·95	42·15	18·90	2·2	11·59	100·00
38·43	41·31	20·26	2·0	10·93	99·82
37·20	40·30	22·50	1·7	9·76	74·22
36·72	39·78	23·50	1·5	9·31	1·15
35·87	38·83	25·50	1·3	8·40	0·61
34·41	37·17	28·42	1·0	6·50	1·73

The sulphuric acid appears to act as a dehydrating agent, for the highest degree of nitration is obtained from a system represented by $HNO_3+n(H_2SO_4.H_2O)$ and the lowest when the nitric acid is present as $HNO_3.H_2O$, according to Kullgren (Z. Schiess-u. Sprengstoffw., 1908, *3*, 146).

Cellulose nitrates containing more than 13·1% of nitrogen are very unstable and have no commercial value. All the nitrates of cellulose are readily inflammable.

The most highly nitrated cellulose is gun-cotton, which is prepared, according to Worden, by treating purified cotton waste with about 30 times its weight of a mixture of 75% of sulphuric acid, 15·75% of nitric acid, 1·30% of nitrous acid and 7·95% of water at 15° C. The temperature rises during the reaction to about 25° C., and finally falls to 20° C. Nitration takes from three to twelve hours, and the nitrated cotton is washed with cold water and finally with large amounts of boiling water. The crude nitrate is contaminated with some cellulose sulphate and certain nitro-compounds from impurities in the cotton itself. In this state the cellulose nitrate is subject to spontaneous decomposition and the careful removal of the impurities is essential. Purification must be carefully controlled as the conditions for decomposition of the sulphuric ester (loc. cit.) would affect the cellulose nitrate itself. Hence the usual procedure is to give a prolonged boil in weak acid solution followed by shorter treatments with boiling calcareous water. This is the so-called " stabilisation " process.

The fibrous form of gun-cotton burns quickly but quietly in the open, but when detonated in a confined space it explodes with great violence. The effect of gelatinisation by means of volatile or non-volatile solvents moderates the force and allows the nitrate to be used as a high explosive. When partially dissolved in nitro-glycerine and mixed with castor oil, or vaseline, it forms a gelatinous mass which is used as cordite and forms a smokeless powder (cf. gunpowder).

Gun-cotton is soluble in acetone, ethyl acetate, partly in amyl acetate but is insoluble in alcohol and ether-alcohol.

On the cellobiose residue system, gun-cotton is $C_{12}H_{14}O_4(NO_3)_6$, but by digesting cellulose at 45 to 55° C. with 55% sulphuric acid, 17% nitric acid and 28% of water for many hours, a soluble nitrate $C_{12}H_{15}O_5(NO_3)_5$ is formed. The solution of this is known as *collodion*, and is used in photography and surgery, as it leaves a thin waterproof film of the nitrate on any surface to which it is applied. It is also termed pyroxylin and is soluble in ethyl or amyl acetate, acetone, methyl alcohol and ether-alcohol. According to Worden, this name applies to all cellulose nitrates soluble in amyl acetate, and methyl alcohol. This nitrate of cellulose was first used by Chardonnet for the manufacture of artificial silk or rayon.

Cellulose nitrates containing 12·5 to 11·5% of nitrogen are used for the preparation of photographic films whilst compounds of 10·7% nitrogen content are mixed with camphor or camphor substitutes for the manufacture of celluloid.

Ullmann (Enzyklopädie der technische Chemie, 1917, *5*, 96) has shown that there is considerable variation in the solubility of the cellulose nitrates.

SOLUBILITY.

Nitrogen %	Percentage solubility. Acetone, ethyl acetate.	Ether-alcohol 2 : 1	Ethyl alcohol.
13·1–13·4	95–100	Insol	Insol
12·8–13·1	95–100	<30	Insol
12·5–12·8	95–100	50–100	<10
12·0–12·5	95–100	95–100	<50
11–12	95–100	90–100	50–100
10–11	95–100	80–100	<50
9–10	30–90	30–90	Insol
7–9	<30	<30	Insol
3–7	Insol	Insol	Insol

Preparation

The possibility of replacing sulphuric acid by phosphoric acid in the mixture for the nitration of cellulose has been examined by Krauz and Blechta (Chemicky Obzor., 1927, *2*, 1), who report that the nitration is slower and requires about four hours in absence of water. In the presence of even small quantities of water, nitration is very incomplete and the reaction products are largely soluble in the nitrating liquid. The chemical stability of the product, however, is good, and washing in pure water is sufficient to obtain a stable cellulose nitrate. Stability is the main advantage, but on the other hand the use of an anhydrous nitrating mixture is essential and the reaction is slower and more expensive.

Berl and Rueff (Ber., 1930, *63*, 3212) have shown that cellulose nitrate containing between 14·0 and 13·7 % of nitrogen can be obtained by the nitration of cellulose with mixtures of nitric and phosphoric acids of suitable composition. The nitration process is accompanied by a strong swelling of the fibre, which facilitates the entry of the nitric acid and results in regular nitration. The product again is stated to be stable, more stable than that containing less nitrogen but obtained by nitration with sulphuric and nitric acid mixtures. Nitrates with 11 to 11·5 % of nitrogen cannot be obtained in fibre form with phosphoric acid—nitric acid mixtures. Nitration proceeds slowly and appears to be preceded by a conversion of the cellulose into mercerised cellulose, as is shown by the change of the lattice from that of native cellulose to the lattice of hydrate cellulose. Sulphuric acid—nitric acid mixtures, however, do not change the native cellulose lattice provided the nitric acid proportion is not too high. The phosphoric acid method appears to give a higher degree of esterification with less degradation of the micelles.

Presumably the competition between HNO_3 and H_2SO_4 for the hydroxyl groups may be avoided by the use of H_3PO_4.

Berl and Rueff (Cellulosechem., 1933, *14*, 115) have shown that the use of anhydrous mixtures of HNO_3 and H_3PO_4 gives cellulose nitrates which produce acetone solutions of high viscosity. Apparently the high concentration during nitration may prevent dissociation of the acids and hence degradation of the cellulose (cf. Staudinger—Cellulosechem., 1934, *15*, 66). The fluidity of cellulose nitrate in acetone has been utilised for measuring the modification of cellulose as discussed on page 181.

In contrast to acetylation, the nitration of cellulose may be effected without degradation; tensile strength and extension at break are not affected in the case of viscose filaments, cotton or even ramie. Staudinger (Ber., 1937, *70*, 2296) suggests this may be due to the rapidity of the nitration which quickly changes cellulose into a derivative which is remarkably indifferent to acids. Unfortunately no method has been found of regenerating the cellulose from the nitrate without extensive degradation.

According to Trogus (Ber., 1931, *64*, 405) a cellulose nitrate of 7 to 13·9% nitrogen content may be prepared by the action of mixtures of concentrated nitric acid (*d.* 1·52) and acetic acid in the absence of water on fibrous cellulose material. The effect of the presence of water is to reduce the nitrogen content. Cellulose nitrates of higher nitrogen contents may be obtained by the addition of a little acetic anhydride or phosphorus pentoxide to the nitrating mixture. The fibres obtained in this manner resemble the original cellulose in feel and appearance, and are easily stabilised.

In order to develop a method of preparing cellulose nitrates of very high nitrogen contents, Lenze and Rubens (Chem. Zentr., 1931, *I*, 2993) treated bleached cotton linters with various nitrating mixtures: nitric and sulphuric acids; nitric acid and sulphur trioxide or sulphuric acid containing sulphur trioxide; nitric acid, acetic anhydride and glacial acetic acid; nitric acid and nitrogen pentoxide; also mixtures of nitric acid and phosphorus pentoxide in various proportions. The highest nitrogen content of the cellulose nitrate was obtained from the use of nitric acid and phosphorus pentoxide, i.e. 13·8–13·9%, but up to 14% could be obtained if the cellulose was given certain preliminary treatments. Almost the same nitrogen content is obtained by the nitration of gun-cotton and pyroxylin in solution in nitromethane, but the solubility of all these products in ether-alcohol is small.

Properties

The viscosity of the cellulose nitrates in solution is a matter of great technical importance and is, in general, decided by the viscosity of the original cellulose. Low viscosity cellulose nitrates, which may be required for the manufacture of lacquers for spraying and brushing, are obtained from a modified form of cellulose, which may range from mercerised cellulose to material which has been slightly degraded by acid action,

oxidation or heat. The higher viscosity nitrates are suitable for the manufacture of thin and pliable films, rayon or artificial silk, and are essential in the case of gelatinous explosives. Viscosity measurements are usually effected by means of the Ostwald viscometer and the falling sphere method.

By careful fractionation of commercial nitrates of cellulose, Spurlin (Ind. Eng. Chem., 1938, *30*, 538) has established a definite relation between viscosity and resistance to folding as measured on films by the Schopper fold-tester. The fractions gave higher values than the unfractionated material of the same viscosity, and this in turn was better than blends of high and low viscosity material. Plasticisation, however, tends to smooth out these distinctions and so obviates the need for uniformity of chain-length.

Cellulose nitrate is unchallenged in the field of organic material for protective coatings, and is frequently used for conferring waterproof properties on cellophane and similar material.

Tomonari, Trogus and Hess (Z. physikal. Chem., 1932, B*16*, 241, and 351) have shown that nitrocellulose forms addition compounds with certain ketones and give definite Röntgen diagrams. Acetone is stated to form two definite compounds, one of which is a derivative of cellulose and the other a derivative of cellulose hydrate. Cyclohexanone, p-methylcyclohexanone and fenchone also form similar addition compounds, which vary with the concentration and temperature. m-Xylene forms a compound with cellulose nitrate in the presence of acetone but not in its absence. These results appear to confirm the view that in the dissolution process the first action consists of the formation of a compound between the solvent and the ester. X-ray evidence also shows that camphor forms an addition compound with cellulose trinitrate, which in contrast to the mono-nitrate is soluble in many organic solvents.

The estimation of the nitrogen content of the cellulose nitrates may readily be done by means of the Schultz-Tiemann method (reduction with a saturated solution of ferrous chloride), which has the advantage that it may be applied in all instances, particularly those in which solution in sulphuric acid is slow and difficult. The nitrometer method is easily applicable where the cellulose nitrate can be obtained in a finely divided form. It is also possible to estimate the nitrogen by use of the Devarda alloy.

Details of these methods may be found in " The Methods of Cellulose Chemistry," by Dorée, p. 232.

In many of the technical and commercial applications of the cellulose nitrates, high inflammability is a great disadvantage, but it has been found that by treatment with reducing agents, such as ammonium sulphide, the nitrate groups may be removed leaving a regenerated cellulose which is not absolutely pure, but usually contains 1–2 % of nitrogen, sufficient to give the characteristic di-phenylamine test. This action of reducing agents is generally termed de-nitration. It may here be observed that the cellulose nitrates were originally and erroneously termed nitrocelluloses—a term which is still employed, to some extent, in spite of its inaccuracy. A true nitro-compound would be reduced to the amino-derivative on reduction, and would not be hydrolysed by treatment with acid or alkali into the original components, as occurs with the cellulose nitrates which are nitric acid esters of cellulose.

The de-nitrification process is, therefore, one of saponification or hydrolysis of an ester and not the reduction of a nitro-derivative.

The solubility of cellulose nitrate in *alkali* has been used by Heberlein (B.P. 262, 477) to produce ingenious pattern effects. Cloths are woven from ordinary cotton yarn and nitrated cotton yarn ; they are then printed with alkali in selected areas in order to remove the cellulose nitrate. When the embroidered effect has been produced the material is de-nitrated as usual.

Rayon

In view of the importance of cellulose nitrate in the manufacture of rayon or artificial silk, a brief description of the manufacture is, no doubt, of interest. The cellulose nitrate process for artificial silk is the oldest of such processes, and originated with Swan. The general scheme simply involves treating cellulose with nitric acid to form the nitrate which is soluble in a mixture of alcohol and ether. The viscous solution is then forced through fine orifices either into air (dry spinning) or into a liquid (wet spinning). In both cases solidification of the extruded filament takes place.

As the sulphite cellulose originally used by Chardonnet, one of the pioneers of the method, has proved unsatisfactory, cotton is the only suitable raw material for this particular process. The type of cotton used is in the form of linters,

which have been subjected to an alkaline boil in order to remove the cotton wax and other impurities, followed by a bleaching process which must be as mild as possible in order to avoid degradation of the cellulose. After careful washing, the purified cellulose is dried by means of hot air until the moisture content does not exceed 1%, when the dried linters must be cooled and nitrated immediately, before they can absorb moisture from the air.

A considerable amount of research, during 1914 18, was carried on in the Research Department of the Royal Arsenal, Woolwich, to correlate the preliminary treatment of cotton waste with the quality of the cellulose nitrate. Gibson and his collaborators showed that the viscosity of the cellulose in cuprammonia was correlated with the viscosity of the same cellulose, nitrated and dissolved in ether-alcohol (J.C.S., 1920, *117*, 473 ; 479).

The esterification with nitric acid proceeds according to the equation

$$C_6H_{10}O_5 + 2HNO_3 \longrightarrow C_6H_8O_3(NO_3)_2 + 2H_2O$$

from which it is seen that water is formed diluting the nitric acid, which only reacts properly when concentrated. The addition of sulphuric acid, however, absorbs the water formed and shortens the reaction period. The composition of the nitrating acid is usually adjusted to give a water content of 17–19%, and the amount of sulphuric acid should not be more than three times that of the nitric acid used. The temperature of nitration should not exceed 24° C. at the commencement of the reaction, and the amount of nitrating acid added should be such that the temperature does not rise above 40° C. Esterification usually proceeds for about two hours, after which the cellulose nitrate is removed from the nitrating mixture. It still contains some 30% of the acid mixture and must be brought quickly into admixture with a very large amount of water in order to avoid sudden decomposition. A very thorough washing process follows, during which the material is well beaten and thoroughly subdivided. Slight formation of cellulose sulphates has taken place owing to the action of the sulphuric acid, and the presence of these impurities is removed by boiling with water under pressure ; this is essential if the cellulose nitrate is to be dried and is termed *stabilisation*.

Solution of the cotton does not occur during the esterification process with nitric acid, indeed the fibre shows little physical

alteration, it feels harsher and has increased in specific gravity from 1·5 to 1·66. Occasionally the nitrate is coloured yellow by the presence of various metallic salts, but these impurities may be removed by treatment with dilute hydrochloric acid. About 150 lbs. of the cellulose nitrate are obtained from 100 lbs. of cotton.

The cellulose nitrate is usually hydro-extracted to contain 25–28% of water, as it has been found that the moist product is more easily soluble in the mixed solvent and is especially suitable for dry spinning. If, however, the cellulose nitrate solution is to be spun into water, then it must be dried or whitish filaments of low tensile strength will result.

Solution is effected in a mixture of ethyl alcohol-ether and although it proceeds rapidly at first, it is only complete in about 20 hours. The spinning solution must be viscous in order that the extruded filaments may be capable of extension; the viscosity increases with the concentration of the solution, but it is also dependent on the nature of the original cellulose, which if once degraded cannot be restored. The viscous solution of cellulose nitrate is well filtered through several presses in order to remove any traces of insoluble matter which would block the fine orifices of the spinnerets.

Wet spinning processes, now generally obsolete, required a 10 to 15% concentration, and were easier to filter than those for the dry process which requires 20 to 25% solutions. The filtered solution is allowed to stand for some time before spinning in order to allow the small air bubbles to pass away, as otherwise they would produce weak filaments. A type of ripening also takes place with the effect of imparting to the cellulose nitrate the property of rapid separation from the solvent during spinning—probably due to aggregation of the molecules, with a consequent reduction in solubility.

In the actual spinning process, which is the extrusion of the filaments through the fine orifices, the individual filaments are very weak, and it is usual to combine some 10 to 25 together to form a suitable thread, which hardens on account of the evaporation of the solvent, and is improved further by extension.

The threads are wound into hanks and "denitrated" by means of ammonium hydrosulphide or calcium hydrosulphide in 3% solution at 40° C. for about three hours, as a result of which the cellulose is regenerated and the nitrogen content falls from about 11% to a minimum of 0·05%. The loss in

weight is about 30 % and the tensile strength has fallen about 25 %, but the rayon is now as soft as natural silk and has lost its high inflammability. Owing, however, to the reduced tenacity in the wet state, the subsequent operations of washing and bleaching need great care.

The two main manufacturing advantages of nitrate rayon are the relative stability of the spinning solution, i.e. the cellulose nitrate solution, and the small amount of waste during manufacture.

Cellulose Sulphate

Braconnot (Ann. Chim. Phys., 1819, *12*, 185) observed that linen dissolved in cold concentrated sulphuric acid, and that if the solution was diluted with water, a clear solution resulted which contained H_2SO_4 and a product which he termed "acide végéto sulphurique." Blondeau de Carolles (Ann., 1844, *52*, 412) investigated this acid and found that its barium salt, which remained in solution, could be precipitated from the concentrated clear solution by means of alcohol. The composition of the salt varied with the time the sulphuric acid solution was allowed to stand before dilution, as is shown by the following cases :

$C_{18}H_{36}O_{18}(SO_3)_2BaO, 2H_2O$	after 30 minutes.
$C_{10}H_{20}O_{10}(SO_3)_2BaO, 2H_2O$	after 12 hours.
$C_4H_8O_4(SO_3)_2BaO, 2H_2O$	after 24 hours.

Fehling (Ann., 1845, *53*, 135) found a barium salt to correspond to $C_{90}H_{180}O_{90}BaO(SO_3)_2$ and Marchand (J. pr. Chem., 1845, *35*, 200) prepared a lime salt, $C_{33}H_{28}O_8(SO_3)_2CaO$. Honig and Schubert (Monat., 1885, *6*, 708) confirmed the observation of de Carolles in that the proportion of Ba to H_2SO_4 is invariably 1 : 2. The temperature at which the cellulose was dissolved (7–40° C.) had little effect on the composition of the compound, but had considerable effect on its optical activity. The proportion of acid to cellulose did not affect the composition or optical activity so long as it did not fall below two parts of acid to one of cellulose. With equal proportions, the resultant cellulose sulphate neutralised less base. The barium salts of these acids were white or yellow crystalline powders, soluble in water but insoluble in alcohol. They were decomposed in boiling aqueous solution.

Stern (J.C.S., 1895, *67*, 74) also found that the same substance is produced by dissolving cellulose in H_2SO_4 at different

temperatures (5-15° C.), but that the optical activity depends on the temperature of dissolution.

Stern prepared the barium salt of cellulose disulphuric acid $C_6H_8O_3(SO_4)_2Ba$, and used salts throughout this work as they are more convenient to manipulate than the free acid. The salts are not altered when heated to 100° C., but at a slightly higher temperature they are blackened, and, when strongly heated, decompose with almost explosive violence. The yield of the disulphate was 48% of the theoretical. The H_2SO_4 was estimated by boiling with HCl and a little $BaCl_2$ when the whole of the sulphate was precipitated.

The Ba salts containing a high percentage of H_2SO_4 start to decompose in presence of the slightest trace of acid. The disulphuric acid may be hydrolysed to the monosulphuric acid $C_6H_9O_4SO_4H$ by means of boiling with dilute H_2SO_4, but the resting point is not well marked, for if the digestion is continued for a few minutes too long or if the amount of hydrolysing acid is increased, then more H_2SO_4 is released and sugar is formed. Cellulose sulphuric acids containing less than the monoderivative are also formed, the barium salts of which reduce Fehling's solution whereas the barium salts of the mono- and disulphuric acids do not.

Caille (Chim et Ind., 1926, *15*, 189) showed that sulphuric esters of cellulose could be formed under conditions which precluded the formation of oxycellulose, and that these esters have an affinity for basic dyes, increasing with the SO_4 content, while the affinity for the acid and direct colouring matters diminishes. The esters were made (*ibid.*, 1925, *13*, 11) by treating cotton with 15 times its weight of a mixture of equal proportions of H_2SO_4 and glacial CH_3COOH at 45° C. for 30 minutes. The fibrous structure was unchanged. The product could be washed neutral with ethyl alcohol or with calcareous water, but not with ordinary water owing to continued hydrolysis. Stability tests by heating in the dry state indicate that stability increases as the acid function of the ester is neutralised by the mineral bases of the water.

Traube, Blaser and Grunert (Ber., 1928, *61*, B, 754) found that when cellulose in the form of filter paper is dried in a high vacuum at 100° C. it can absorb SO_3 with avidity, and when it has absorbed 50–75% of its own weight, the product may be converted to the potassium salt by cautious neutralisation with KOH. If a greater absorption has occurred then the product is treated with H_2O and $PbCO_3$, slightly in excess of

that required to neutralise the free SO_4. Potassium cellulose trisulphate A, may thus be prepared in about 65% yield. It is amorphous. The neutral aqueous solutions are stable when boiled, but the presence of HCl causes elimination of H_2SO_4 and the production of a substance with reducing powers (cf. the formation of dextrose). The salt is also stable to alkali. However, regeneration of the cellulose has not been accomplished.

Concentration of the mother liquor results in the isolation of a potassium cellulose trisulphate B, $C_6H_7O_5(SO_3K)_3$ of different optical activity and probably containing some of the "A" product. If preparations with more than three molecules of SO_3 are preserved, a brown viscous mass is obtained which dissolves in water and in ethyl alcohol without residue. Little or none of the "A" product is obtained on neutralisation, but a material of formula $C_6H_6O_5(SO_3K)_4$—potassium cellulose tetra-sulphate—is obtained. This is not a cellulose derivative as its formation involves rupture of the ring of anhydroglucose.

Gebauer-Fulnegg, Stevens and Dingler (Ber., 1928, *61*, B, 2000) found that cotton or filter paper may be converted by chlorsulphonic acid at 100° C. in excess pyridine to a clear gelatinous product which gives transparent colloidal solutions in water. The cellulose derivatives are precipitated by ethyl alcohol and also by NaCl, C_2H_5OH·NaCl, and C_2H_5OH·HCl. According to the nature of the precipitant, the product may be either a sodium or a pyridine salt.

When isolated, the barium salt is insoluble in water and other media, is little affected by boiling alkaline hydroxides and is only slowly decomposed by boiling HCl. A substance with the composition of the trisulphate may be obtained, but attempts to prove that it is actually a derivative of cellulose were hindered by the impossibility of removing the H_2SO_4 residues by means of acid or alkali without considerable decomposition of the cellulose component. This, however, can be done by treatment with a 5% solution of HCl in methyl alcohol (J.A.C.S., 1930, *52*, 2849) for six hours. The recovered cellulose shows a higher optical rotation in cuprammonium solution, but its triacetate and trimethyl derivative show properties identical with those of derivatives from pure cellulose; hence the cellulose units in the sulphate ester can only be slightly degraded at most. Direct conversion of the sulphate ester into other cellulose derivatives was not successful.

Traube, Blaser and Lindemann (Ber., 1932, *65*, 603) state that

prolonged action of chlorsulphonic acid on cellulose in presence of pyridine only leads to the introduction of 2·7 SO_4H groups per glucose unit, whereas the use of SO_3 always results in complete substitution. It is advantageous to replace the gaseous SO_3 by a solution of SO_3 in CS_2, and to use an excess of cellulose. The product is poured into excess of KOH, unattacked cellulose removed, and the product worked up for the K_3 salt (loc. cit.). The $(NH_4)_3$ salt has also been prepared. Addition of pyridine to a solution of SO_3 in CS_2, followed by evaporation of the latter and addition of cellulose gives an ester with 2·6 SO_4H groups.

The salts of the cellulose sulphates obtained by this method are more closely allied to cellulose than those obtained by the SO_3 process, for which the name " hydrocellulose sulphates " was suggested.

Examination of the products appears to indicate that the micellar structure of the cellulose is not destroyed unless all the OH groups are replaced by the SO_4H residue.

The behaviour of potassium hydrocellulose trisulphate as a protective colloid in inhibiting the precipitation of $BaSO_4$, $HgCrO_4$, and PbI_2 (shared by the pyridinium sulphate) indicates a high molecular weight, confirmed by non-elevation of the boiling point of water in which, however, it has marked electrical conductivity. Hydrocellulose trisulphuric acid is quantitatively hydrolysed by a solution of HCl in methyl alcohol which does not attack the potassium salt.

The viscosity of a 1% aqueous solution of the potassium salt of the trisulphate is practically the same as that of water, whereas the product with less than three sulphonic acid groups has a high viscosity.

Cellulose Phosphate

There appears to be but a small amount of information concerning the cellulose phosphates. Champetier (Compt. rend., 1933, *196*, 930) treated cotton linters with solutions of H_3PO_4, containing from 600 to 1300 grammes per litre, and found that the increase in the amount of acid taken up reached a maximum at 1050 g/l. Fixation appeared to be complete in 15 hours, with the formation of an addition compound containing no water of hydration and corresponding to $3C_6H_{10}O_5H_3PO_4$. This compound was completely destroyed on washing with water, and the cellulose regenerated without exhibiting any of the phenomena of mercerisation.

D.R.P. 547,812 states that cellulose in the form of paper may be treated with moderately concentrated phosphoric acid and phosphorus oxychloride with or without a diluent. After five days a product is obtained which contains 72% of H_3PO_4. A modification of this process is seen in D.R.P. 556,590 by omitting the $POCl_3$. Cellulose is treated with concentrated phosphoric acid containing a small amount of another inorganic acid, e.g. H_2SO_4, until it is completely esterified and the ester is precipitated with water. Examples contain from 50 to 65% of H_3PO_4.

Another patented method, B.P. 279,796, gives an instance of the treatment of alkali cellulose from cotton linters with an ice cold solution of phosphorus oxychloride in benzene, the heat of reaction raising the benzene to the boiling point. A tough magna settles to the bottom and this is washed with alcohol and ether, dried in a vacuum and dissolved in water. The solution is freed from electrolytes by dialysis and the cellulose phosphate precipitated by methyl alcohol.

Tanner, in U.S.P. 1,896,725, treats cellulose with a mixture comprising sulphuric acid, phosphoric acid and a small amount of a weak catalyst, such as acetic, boric or formic acid, to form cellulose phosphates which are stated to be suitable for lacquers, etc.

Cellulose phosphate may be formed by the methods of Plauson, described in B.P. 183,908, where cellulose is first dispersed by intensive mechanical disintegration at high speeds, e.g. in a colloid mill, until the particles are about 0·8μ in diameter. Four parts of cotton dispersed in water by these means are treated with two parts of orthophosphoric acid at gradually increasing temperatures, from 30 to 50° C., until esterification takes place, as is shown by the appearance of foam. The reaction is preferably effected in vacuo and in presence of 0·1 part of H_2SO_4, which acts as an accelerator. (Cellulose acetate may be prepared by similar methods.)

Esters of Other Acids

Plauson has also made cellulose sulphide by heating a gel of highly dispersed cellulose with an equal weight of sulphur, preferably with the addition of 1 to 5% of alkali or alkali carbonate, to a temperature of 150° C. until evolution of H_2S ceases and a homogeneous mass is obtained. Cellulose sulphide is a yellow-grey to brown-grey mass which evolves H_2S on treatment with water.

Cellulose derivatives containing inorganic acidic groups may be prepared according to B.P. 192,173, and are stated to resist decomposition by water or alkali. One hundred parts of cellulose are treated with caustic soda (preferably 12–20 %) squeezed until an equal weight of liquor remains, and then dried rapidly in air (or in vacuo) at a temperature not exceeding 40° C. The material is then treated with an inorganic acid chloride, e.g. thionyl chloride (9 to 35 parts), sulphuryl chloride (10 to 14 parts), phosphoryl chloride (15 to 20 parts) or chlorsulphonic acid, pyrosulphuryl chloride, etc., dissolved in 1500 to 2000 parts of an inert solvent. The temperature should not exceed 40° C., and the reaction is complete in 5 to 15 minutes.

Cellulose carbonates do not exist but some alkylated carbonic esters of cellulose have been prepared by Heuser and Schneider (Ber., 1924, *57*, B, 1389) by means of the action of an excess of methyl chloroformate on a solution of hydrocellulose in a cold aqueous 8 % solution of sodium hydroxide. The esters produced correspond approximately to the formula $C_6H_8O_3$ $(OCOOCH_3)_2$. The product is a white amorphous granular material, soluble in pyridine, chloroform, and acetic acid, but insoluble in ether, alcohol, acetone and benzene. The ester is readily hydrolysed, even in boiling water, when carbon dioxide is split off. The estimation of the CO_2 and a determination of the methoxyl content, provides the means of analysis.

CHAPTER FOURTEEN

ESTERS OF ORGANIC ACIDS

Cellulose Formate

THE formylation of cellulose does not need the theoretical counterpart of acetic anhydride, as formic acid itself, with the aid of a catalyst, is able to effect esterification. One function of the " catalyst " appears to be that of a " hydrating agent," and it must be chosen with some care in view of the fact that formic acid is easily decomposed. Suitable substances are gaseous hydrogen chloride, sulphuric acid in small amounts, zinc chloride, phosphorus pentachloride, chlorsulphonic acid, etc. Frey and Elöd (*Z. angew. Chem.*, 1930, *43*, 579) in an investigation of the action of formylating mixtures indicate the existence of complex acids, corresponding to $[ZnCl_3]$ H or $Zn\left[\begin{matrix}Cl_2\\HCOO\end{matrix}\right]$ H. There appears to be some connection between the acidity of these acids and their power of dissolving cellulose, and it is further suggested that cellulose is in a much more reactive state when it is beginning to dissolve. The action of the catalyst in esterification may also depend on its swelling power as is shown by the fact that regenerated cellulose may be esterified by formic acid alone. Vereinigte Glanzstoff Fabriken showed that regenerated cellulose would dissolve in 95 100% formic acid on warming, but that too high a temperature produced further hydration with impaired strength of the resulting formate.

When regenerated cellulose is not used then some dispersing process seems necessary either as a preliminary or coincident with esterification. Formylation is often incomplete, the triformate seldom being obtained. Clément and Rivière (La Cellulose, 1923, 53) state that the formate should contain 42·8% of formic acid, but only 38·4% can be incorporated without severe degradation of the cellulose. These formates slowly transform themselves into products containing only 10·8% of formic acid.

Uyeda and Hata (J. Cell. Inst., Tokyo, 1928, *4*, 1) state that

with anhydrous HCOOH and H_2SO_4, hydrocellulose yields a product containing 22·9 % HCOOH (cf. 24·2 % for monoformate) whilst that from regenerated cellulose yields a compound with 50·5 % (triformate requires 56·09 %). The degree of esterification is affected by the amount of H_2SO_4. Further work by Uyeda and Kato showed that the HCOOH content rises to a maximum, and subsequently decreases with the reaction period. Similar variations accompany increase in the amount of H_2SO_4, and in both cases the maximum formate content is slightly below the theoretical figure for the triformate.

Uyeda (*ibid.*, 1932, *8*, 33) treated cellulose regenerated from alkali cellulose with 100 % HCOOH and H_2SO_4 (*d.* 1·84) at 15–20° C. for periods varying from 20 to 120 hours, at the end of which time the product contains 24–25 % HCOOH. Investigation of the period from 20–55 hours at 20° C. shows that the HCOOH content reaches a maximum of 39·9 % at 40 hours. There is an increase in film strength from 20 to 40 hours, a decrease from 45 to 48 hours, and a sharp rise at 55 hours. Elongation and specific viscosity decrease with reaction time to minima at 48 hours and then increase.

Uyeda and Fujiwara (*ibid.*, 1933, *9*, 274) formylated 4 g. of regenerated cellulose with 40 g. of HCOOH and 3 g. of H_2SO_4 (*d.* 1·84) at 20° C.

The formates are soluble in pyridine and formic acid but are insoluble in most organic solvents. Aqueous solutions of many acids have a characteristic solvent action, as also have solutions of salts, particularly $ZnCl_2$ and the thiocyanates.

Tocco and Nyssens (Giorn. Chim. Ind. Appl., 1931, *13*, 325) state that a *cellulose diformate* of constant composition is produced by the action of formic acid on cellulose in presence of a dehydrating catalyst. This diformate is stable in dry air but slowly decomposes in the atmosphere. This effect is retarded by immersion in water or a neutral liquid.

The more important technical solutions of formates in thiocyanates and in pyridine follow a course of ripening similar to that of viscose, and the viscosity increases geometrically with the ester content. Pyridine solutions are more viscous than solutions of cellulose acetate in acetone and are affected by temperature changes to a greater degree than corresponding solutions in ammonium thiocyanate. The solution of the formate in formic acid yields films of pure cellulose on evaporation and this characteristic property serves as a useful method of preparing pure cellulose.

Tocco (*ibid.*, 414) states that the dry spinning of formic acid solutions of the diformate yields cellulose of good mechanical properties. Spinning is best effected in vacuo on account of the high boiling point of HCOOH. It is possible to incorporate protein substances in the solution, and casein, for example, has been found to confer plasticity. The manufacture is stated to be economical, the main difficulty being in corrosion of the plant. Films from the diformate are stated to be stronger than cellophane and less sensitive to water. It is also possible to produce films twice the thickness of cellophane produced by coagulation.

An *acetone-soluble cellulose formate* is produced according to U.S.P. 1,880,420 by prolonged digestion of undegraded cellulose at 35–40° C. in a mixture of 20 parts of 85% HCOOH and 40 parts of chloracetic anhydride. The ester is precipitated by water and contains 7 formyl groups per C_{24}. The formyl content may be increased by replenishing the reagents at intervals during the reaction.

Esterification at lower temperatures causes modifications in the product according to B.P. 260,650 and D.R.P. 498,157. The former method produces formates of high HCOOH content by treating cellulose with concentrated HCOOH at 0–5° C. in presence of a catalyst, e.g. PCl_3, H_2SO_4, $ZnCl_2$, SO_2Cl_2, etc. The dissolution requires 24–40 hours. The formate is stable at ordinary temperatures if the catalyst is rendered inactive by the addition of a salt of formic acid. Suitable coagulants are organic liquids or aqueous salt solutions, and it is stated that the filaments of the rayon produced have a high tensile strength even after saponification. The latter patent produces a triformate at 0° C., and it is claimed to be very stable to water and only slightly decomposed by boiling. The coagulated filaments are washed, bleached and dried in the stretched state and form a strong lustrous formate rayon.

Uyeda and his co-workers (J. Cell. Inst., Tokyo, 1939, *15*, 212) have investigated the methods of preparing cellulose formate. According to measurements of formyl content, viscosity and tensile strengths of films, the best mixture for the production of cellulose formate is cellulose 4 g., 98·5% HCOOH 40 g., and H_2SO_4 (*d* 1·84) 3 g.

Determination of the HCOOH content of cellulose formate is best done by the method of Tocco and Nyssens (loc. cit., 1930, *12*, 124) in which 1 g. of the well dried ester is treated with 135–150 cc. of N-potassium dichromate, and slowly and with

cooling, with 41 cc. of H_2SO_4. If necessary the evolution of CO_2 is restrained by further cooling. After a lapse of 30 minutes the beaker is left for eight hours on a boiling water bath, the excess of dichromate being determined by titration with ferrous sulphate or iodometrically. The number of c.c. of N- dichromate required for 1 g. is 148·14, 136·78, 128·43, and 121·95 for cellulose and the mono-, di-, and triformates respectively. This procedure has been used to control methods of hydrolysis by means of alkali, and is claimed to be very suitable for formic esters which are not readily attacked by normal sodium hydroxide or are only slightly soluble in thiocyanates.

Cellulose Acetate

Primary Acetate

Cellulose acetate was prepared by Schutzenberger in 1866 by heating cellulose with acetic anhydride under pressure. However, some difficulty was experienced in the early investigations on the esterification on account of the slowness of the reaction. It was not until catalysts were employed that cellulose acetate could easily be made.

The type of catalyst must be chosen with care as degradation of the ester occurs during formation, affecting the transparency and flexibility of the films and threads made from the resulting cellulose acetate.

The general scheme of reaction is to treat cellulose with a mixture of acetic anhydride, glacial acetic acid and a catalyst, such as zinc chloride, phosphoric acid, sulphuric acid, or chloracetic acid, etc.

Cellulose sulphoacetate $(C_6H_7O_4)_4SO_4(C_2H_3O_2)_{10}$ is stated to be formed when cotton is immersed in a mixture of 50 parts of acetic anhydride, 50 parts of glacial acetic acid and 4 to 6 parts of sulphuric acid. The cotton rapidly dissolves at 30 to 40° C.

According to Malm and Clarke (J.A.C.S., 1929, *51*, 274) the reaction between cellulose and acetic acid alone comes to equilibrium with the production of a compound containing 6 to 7% of acetyl, corresponding to $C_{24}H_{39}O_{20}(COCH_3)$. Hydrate cellulose, however, prepared from the regeneration of cellulose gives esters with a limiting composition expressed by the formula $C_6H_9O_5(COCH_3)$. Mercerised cellulose behaves in the same way as the regenerated cellulose. It is interesting to note that cellulose which has been regenerated from cellulose

acetate which has preserved its fibrous structure behaves more like native cellulose than hydrate cellulose.

Kreuger and Tschirch (Ber., 1931, *64*, 1874) have shown that perchloric acid has a greater catalytic effect than H_2SO_4. An addition of 15 mg. of perchloric acid to a mixture of 20 cc. of acetic anhydride and 20 cc. of acetic acid is sufficient to produce acetylation of 5 g. of cotton linters to the triacetate stage in 24 hours at 32° C. The acetylation may also be carried out at 0° C. with a mixture of acetic anhydride and benzene containing perchloric acid. Tests with methylene blue show that the primary acetate is free from combined perchloric acid.

According to Ost (Z. angew. Chem., 1919, *32*, 66) undue degradation of the cellulose may be avoided by the use of zinc chloride as a catalyst at low temperatures. 10 g. of cellulose are mixed gradually with a solution of 20 g. of zinc chloride in 40 cc. of glacial acetic acid. 40 cc. of acetic anhydride are added in portions with cooling and the temperature kept at 30° C. The duration of the reaction is dependent on the temperature, but usually within 36 hours the commencement of acetylation can be observed by the swelling of the fibres, whose structure will disappear in about two days and a stiff paste result. The reaction requires about two to three weeks at 10 to 20° C., and several days would be necessary at 40 to 70° C., but the higher the temperature, the more readily does degradation of the cellulose take place.

The syrupy solution of the triacetate is dissolved in about 200 cc. of glacial acetic acid, warmed to about 30° C. and well shaken. The acetate is precipitated by water and washed free from acid and zinc. The yield is stated to be about 16·8 g., and it contains about 62·5 % of acetic acid, corresponding to the triacetate.

There is considerable evidence from X-ray examination of cellulose acetate and nitrate for the belief that only the tri-acetate and trinitrate exist, and that the lower esters are merely mixtures of the triesters with unchanged cellulose.

Cellulose triacetate is insoluble in acetone but is soluble in chloroform, tetrachlorethane, formic acid, acetic acid, nitro-benzene, aniline and pyridine. It is resistant to boiling water but the threads and films from it are weak and brittle. These facts render it generally unsuitable for technical and commerical purposes. This chloroform-soluble acetate is referred to as the primary acetate and was prepared technically

in 1894 by Cross and Bevan, who considered it to be the tetra-acetate.

Secondary Acetate

Many other investigators were also concerned with the production of the triacetate, but a considerable technical advance was made by Miles in 1904 by the discovery that partial hydrolysis of the primary acetate resulted in the production of a secondary acetate soluble in acetone and other solvents and having a lower acetic acid content. This interesting point has a counterpart in the solubilities of the cellulose nitrates which vary according to the degree of esterification.

Cellulose triacetate contains 44·8 % acetyl, the diacetate 35 % and the monoacetate 21·1 % acetyl. Cellulose acetates which are soluble in acetone contain from 35·8 to 41·5 % acetyl, and the commercial acetates lie within this range. In general, the acetates for plastics contain 36·5 to 38 % acetyl, acetate rayons contain 38 to 39·4 % acetyl and the acetates for films contain 39·4 to 41·6 % acetyl; acetate rayon comprises 70 to 80 % of commercial cellulose acetate production.

The method adopted by Miles in B.P. 19330 of 1905 was to treat 100 g. of dry cellulose (5 % of H_2O) with a mixture of 270 to 310 g. of acetic anhydride, 390 to 410 g. of glacial acetic acid and 3 to 9 cc. of concentrated sulphuric acid at a temperature below 40° C.

The temperature is controlled by cooling and the cellulose is converted to a paste. At the end of the exothermic reaction the temperature begins to fall and the mass is then heated to 50–55° C., and maintained at that temperature for 36 to 40 hours, when the mass appears less viscous and more or less transparent. A test portion should be insoluble in acetone but soluble in chloroform. About 60 cc. of glacial acetic acid are diluted with an equal volume of water, and the mixture slowly added to the cellulose acetate solution with vigorous stirring in order to avoid precipitation. The reaction mass is maintained at a temperature of 40–50° C. for 12 to 16 hours until a test precipitate, on washing and drying, is completely soluble in acetone but only plastic in chloroform. The bulk is then precipitated by pouring into cold water, after which it is washed and dried, yielding about 130 to 145 g. of the secondary acetate. This product is insoluble in water, ethyl and amyl alcohol, amyl acetate, carbon tetrachloride, and benzene; it becomes plastic in hot chloroform and hot glycerol,

but dissolves readily in acetone, tetrachlorethane, and chloroform containing alcohols. It is less soluble in pyridine, ethyl acetate, and nitrobenzene, and only soluble with difficulty in acetic acid and formic acid. It dissolves in hot 70% aqueous ethyl alcohol but gelatinises on cooling. A warm mixture of ethyl alcohol and benzene also dissolves the secondary acetate which is deposited on cooling.

An important contribution to the solubility data for cellulose acetate (and also ethyl cellulose) has been made by Coltof (J.S.C.I., 1937, *56*, 363) and is discussed on page 479.

In connection with the solvents for cellulose acetate, a discovery of some technical importance was made by Eichengrun (D.R.P. 254,385 of 1909), who showed that certain mixtures of liquids, e.g. alcohol and benzene, although they have no solvent action will, nevertheless, when mixed with a good solvent such as acetone acquire considerable solvent properties for the secondary cellulose acetates.

General Preparations

It is important that the moisture content of the cellulose should be suitable for acetylation as completely dry cellulose reacts slowly and unevenly. Owing to the use of sulphuric acid, some cellulose sulphoacetates are first formed. These mixed esters, which are distinguished by their solubility in acetone and in 70% alcohol, are only intermediate products, and during prolonged stirring of the mixture are converted into the triacetate. The primary cellulose triacetate prepared in this manner should not contain more than 0·5 to 1% of combined sulphuric acid, for if it does the products prepared from it will later decompose with the liberation of sulphuric acid. Ost (loc. cit.) showed that the pure dry acetate may be heated to 125° C. or even higher without decomposition, but that the presence of more than 0·6% of combined sulphuric acid causes a brown discoloration at 100–120° C.

It must not be thought that the solution of the acetate is an essential part of the esterification process, for just as cellulose nitrate retains its fibrous form and does not pass into solution during the reaction, so cellulose acetate may be prepared with retention of the fibre structure by replacing the glacial acetic acid (which is a solvent for the acetate) by a liquid which is a non-solvent, but which is nevertheless miscible with acetic anhydride, e.g. benzene. This facilitates the recovery of the acetylation mixture. D.R.P. 184,201 gives an example where

10 g. of fibre are moistened with water until the moisture content is about 30% when the moist fibre is mixed with a solution of 60 g. of acetic anhydride in 180 g. of benzene to which 1·5 g. of H_2SO_4 has been added. When the whole is warmed to 70 to 75° C. for about eight hours, a chloroform-soluble product is obtained. The fibres are pressed, washed with benzene and later with alcohol and then dried. The yield is about 17·5 g. of pure white fibres containing 62·5% of acetic acid. (Hess—Die Zellulose, 1928.)

Fibrous esterification may also be effected by the addition of non-solvents or anti-solvents to the usual esterifying agents; these additions prevent dissolution of the ester. Ether, butyl-ether, benzene, toluene and so on may be used according to the methods of B.P. 464,843, U.S.P. 2,036,382, 2,066,571 amongst other specifications.

The Dreyfus process, described in F.P. 478,023 of 1914, concerns the treatment of air-dry cellulose with a mixture of glacial acetic acid, acetic anhydride and sulphuric acid at 0° C. The temperature rises to 5–15° C. and later falls to 5–10° C. The cooling is then stopped and the temperature allowed to rise to 15 to 20° C., after which the mass is stirred and cooled. When all the fibres have dissolved, water is added to promote hydrolysis of the primary acetate to the secondary which, according to this process, should have a high viscosity.

Hess and Ljubitsch (Ber., 1928, *61*, 1460) have developed a method for the preparation of cellulose triacetate which obviates the use of acidic catalysts and so reduces the possibility of degradation during the reaction. Cellulose is steeped in sodium hydroxide solution and then washed free from the alkali. The wet material is then steeped in pyridine which is changed from time to time so that the water is finally replaced by pyridine. The cellulose is then squeezed and treated with a mixture of 10 parts of acetic anhydride and 16 parts of pyridine for 24 hours with shaking. The mass is then heated for a number of days at 40-45° C., depending on the source of the original cellulose. The theoretical value of 62·5% acetic acid content for the triacetate was reached after 43 days in the case of cotton linters, and after 30 days in the case of viscose rayon. This triacetate resembles the original cellulose, but is chemically identical with the soluble acetate although it is insoluble in chloroform and pyridine.

On the other hand, Yarsley in his book "Uber die Herstellung und physikalishen Eigenschaften der Celluloseacetate"

describes the preparation of a primary acetate which is soluble in acetone.

This was done by cooling an acetylating mixture of five parts of acetic acid to three parts of acetic anhydride to below 5° C. and one part of cellulose in the form of cotton wool, was gradually added with constant shaking. The temperature was not allowed to rise above 20° C. and the mixture was stirred until the cotton was dissolved, after which it was allowed to stand for some time. Precipitation of the acetate takes place when it is poured into water, after which the product is washed and dried in air ; but if completely dried it is only soluble with difficulty in acetone. These acetates are more readily soluble in moist acetone than in the dry solvent ; they are also soluble in warm glacial acetic acid but insoluble in chloroform. The secondary acetates were obtained by saponification with equal parts of water and glacial acetic acid at 40 to 50° C. Complete acetone-solubility was obtained in 8 to 10 hours and the acetic acid content was constant at 53 % after 12 hours.

Further observations of Yarsley showed that it is necessary to use one part of cellulose to three parts of acetic anhydride and between 10 and 15 % of H_2SO_4 during the esterification. This does not cause degradation of the cellulose if the temperature of the reaction is not allowed to exceed 25° C. during the first hour, and 25–30° C. later. The content of combined H_2SO_4 (0·2–0·5 %) is lower according to the temperature at the commencement of the reaction (18–25° C.). Solutions of the primary acetates have a high viscosity, which is not uniform, whereas the secondary acetates give solutions of lower, but uniform viscosity in acetone. Although the primary acetates gave very tough and clear films yet they were useless for the preparation of filaments for artificial silk. Many of the acetone soluble primary acetates of Yarsley, when taken to dryness, give a residue which is no longer completely soluble in acetone.

Barnett (J.S.C.I., 1921, *40*, 8) has investigated the use of chlorine and sulphur dioxide as the catalytic agent for esterification, and found that if the ratio of Cl_2 to SO_2 is unity, a triacetate results, but if there is only a trace of SO_2, the composition of the product appears to be that of a di-acetate.

By this means, 5 g. of filter paper were treated in 20 cc. of glacial acetic acid and 20 cc. of acetic anhydride containing 0·32 g. of chlorine were added, followed by 2 cc. of acetic anhydride containing 0·26 g. of SO_2. Solution is rapid, being

complete in from 5 to 15 mins. When the mixture has been stirred for a few minutes about 20 cc. of chloroform is added, and the ester separated by the addition of excess of water, with stirring, a fine white powder is obtained, which is washed free from acid. The yield is quantitative and the acetic acid content is 62·4 %.

The diacetate may be prepared by adding 200 g. of acetic acid just coloured with chlorine gas, to about 50 g. of filter paper. After an interval for the initial reaction to occur, 250 g. of acetic anhydride are added and a few bubbles of SO_2 passed through the mixture. An exothermic reaction commences, but the temperature is not allowed to rise above 65° C. A clear solution is formed in about one hour ; this is allowed to stand overnight and the resulting jelly is diluted with acetic acid and chloroform or acetone. Excess of water is also added and the volatile solvent removed by distillation when the acetate is gradually precipitated. The diacetate is a fine white powder giving an acetic acid content of 48·8 %. It is soluble in acetone, chloroform, pyridine, and hot nitrobenzene, but is only slightly soluble in aniline and a benzene-alcohol mixture.

Liquid sulphur dioxide has been used in B.P. 301,036 and 306,531, as the medium in which cellulose may be acetylated. The temperature of the reaction is controlled by means of the pressure, and at the end of the reaction the SO_2 is allowed to boil away so that its recovery is easy.

Investigation of the reaction between acetic anhydride and soda-cellulose, according to Centola (Gazzetta, 1935, *65*, 1230), has shown that the proportion of combined acetyl groups depends on the amount of NaOH and H_2O in the soda-cellulose.

The acetylation of cellulose by means of acetylchloride, was examined by Hess, Weltzien and Messmer (Ann., 1923, *435*, 48 and 1924, *435*, 44) using about 12 parts of acetyl chloride to one part of cellulose. The mixture was well shaken at 15 20° C. and disintegration began after a few hours, and in four to seven days all the cotton had dissolved to form a solution of great viscosity. The flask was then cooled to 0° C. and opened when the gaseous products escaped. The HCl, however, is firmly retained and can only be removed by repeated treatments with chloroform followed by evaporation in vacuo. The residue forms a brittle mass which is powdered and freed from the last traces of acid by drying at 80° C. in vacuo over potassium hydroxide.

The yield is about 92 % of theory, but the product must be purified by means of solution in warm glacial acetic acid followed by filtering. The product is precipitated with ether and further purified by means of treatment with acetic acid and ether finally resulting in a 60 % yield of a fine white powder which melts at 270–275° C. with decomposition. It is soluble in chloroform and glacial acetic acid, partly soluble in acetone and in acetic ester, but insoluble in alcohol and in ether. This cellulose compound is termed " cellulose acetate A " because, on saponification, with normal methyl alcoholic sodium hydroxide solution, it yields " cellulose A," which is a white powder insoluble in organic solvents, but easily soluble in 2 N-sodium hydroxide solution and in concentrated acids. It has no definite melting point but gradually discolours above 120° C. The analysis agrees with $C_6H_{10}O_5$.

The preparation of cellulose acetate by the treatment of cellulose or hydrocellulose with ketene ($CH_2 : C : O$) is dealt with in B.P. 237,573 and 237,591. The cellulosic material may be treated with the ketene either alone or in the presence of an inert solvent such as benzene or toluene or in presence of acetic acid or acetic anhydride, which may be applied to the cellulose in order to moisten it before the addition of the ketene. A small proportion of a catalyst such as zinc chloride, chlorsulphonic acid or sulphuric acid may also be added to the moistening agent. The moistened material is placed in a closed chamber, which is exhausted to free the material from air and then the ketene gas is admitted. During the reaction, the mixture is stirred and the process may also be effected under pressure.

Substituted ketenes have been made by the methods of B.P. 522,033 involving the reaction between strong tertiary bases and the chlorides of aliphatic monobasic carboxylic acids of high molecular weight. These substituted ketenes may be condensed with cellulose to give waterproof finishes (B.P. 522,204). For instance, rayon material may be soaked in 20 % cetylketene solution in benzine for 20 to 30 minutes, pressed, dried and then heated to 110° C.

Many attempts have been made to prepare primary cellulose acetates (i.e. the triacetate), which could be used for purposes of artificial silk manufacture without having to be transformed into the secondary acetates (mixtures of di- and triacetate containing 2·5 acetyl groups per $C_6H_{10}O_5$ residue).

The Zdanowich processes utilise the smallest possible amount of the necessary catalysts for acetylation, and avoid, as far as

possible, those catalysts which tend to form unstable compounds. An aequous solution of formaldehyde is added in order to stabilise the solutions. The acetylation is carried out in two phases—first, a slow phase in which chlorine is used as a catalyst, whilst in the second phase very small quantities of sulphuric acid are employed, which, in conjunction with the HCl derived from the chlorine in the first phase, are sufficient to complete the acetylation in a short time. After acetylation, the excess of anhydride is saponified by means of formaldehyde solution. Corrosion of the apparatus is stated to be a serious drawback (B.P. 139,232; 190,732; 196,641; 200,186; 227,134; 244,148).

Recent movements in the manufacture of cellulose acetate are mainly concerned with some pre-treatment of the cellulose. Treatment with formic acid and acetic acid are mentioned in concentrated, dilute and gaseous form. Lactic acid has also been used and glacial acetic acid containing sulphuric acid. Reactivity may be increased by treatment with hydrohalide acids (B.P. 312,098), organic acids (B.P. 308,322), or with oxidising agents in presence of moderating agents (B.P. 305,096). Ferric chloride or bromide is used as catalyst in B.P. 312,095.

B.P. 240,624 states that acetone-soluble cellulose acetate is obtained directly from air-dried cellulose in about 18 hours when chromium sulphate is used as catalyst in addition to H_2SO_4, but that a chloroform-soluble acetate is obtained by the use of chromium sulphate as a catalyst for acetylation in absence of H_2SO_4 (B.P. 265,267).

Solubility in chloroform is almost entirely determined by the extent of acetylation and increases rapidly where more than two-thirds of the available hydroxyl groups are acetylated. The solubility of cellulose acetate in acetone depends on the type of cellulose as well as on the extent of esterification, but it is not possible to produce an acetate which is completely soluble in acetone merely by interrupting the esterification at any stage.

Pre-treatment with alkali has been examined by Scheidegger (Dissertation, Zurich, 1931), who finds a progressive retardation of acetylation with increase of alkali concentration in the pre-treatment. The passivity is most marked when alkali of mercerising strength is used, subsequent reaction being a matter of days instead of hours.

Deripasko (Cellulosechem., 1931, *12*, 254) has provided some

interesting data on the saponification and solubility of the cellulose acetates. Two cellulose acetate preparations were used for the tests. Acetate I was obtained by the acetylation of cotton paper for seven hours at 250° C. in the presence of 15 % H_2SO_4 as catalyst and contained 55 % acetic acid and 4 % H_2SO_4. Acetate II was prepared by acetylation for five hours at 30° C. with 7 % H_2SO_4 as catalyst and contained 61–61·5 % acetic acid and 1–1·2 % H_2SO_4. A mixture of water and acetic acid was used for forming the secondary acetates and during the saponification it was found that in the case of acetate I, the H_2SO_4 content decreased while the acetic acid content at first increased reaching a maximum after a few hours. The maximum appeared to be higher the greater the excess of acetic anhydride pressure in the reaction mixture, and at times it reached 60 % or over. The increase was not accounted for by the simple replacement of sulpho groups. The stability of the product was found to depend partially on the sulphuric acid content. With acetate II, the saponification process reduced the acetic acid content of the acetate to 57·6–56·4 %. Only acetates with acetic acid contents between 60 and 49 % were soluble in acetone.

A series of acetates with acetic acid contents varying from 60 % to 57·5 % and H_2SO_4 contents from 0·1 to 0·3 % was prepared, and only acetates containing 57·4 to 57·8 % were soluble in ethyl acetate. Acetates containing 57 % of acetic acid were often found to be soluble in both acetone and chloroform.

Acetone solutions were titrated with non-solvents and the amount for the production of turbidity was noted to decrease with decreasing acetic acid content of the cellulose acetate except, in the case of water, when an increase was observed. The differences between the solubilities of cellulose acetates of the same acetic acid content appeared to be due to differences in the H_2SO_4 contents.

The solubility of cellulose acetate has been modified by heating the triacetate with various alcohols; for instance, products may be obtained which are soluble in methylene chloride, or mixtures of methylene chloride and alcohol, but insoluble in acetone according to B.P. 443,564.

U.S.P. 1,998,267 reveals that the solubility of cellulose esters may also be modified by treatment with solutions of salts, e.g., $CaCl_2$, which swell but do not dissolve the acetate; a small amount of HNO_3 is advised.

Sakurada (J.S.C.I., Japan, 1938, *41*, 381) states that treatment of the triacetate with HNO_3 or perchloric acid at 30° C. gave products containing 58·5% acetyl, and which were entirely soluble in chloroform and almost completely soluble in acetone; with H_2SO_4 or HCl it was more difficult to obtain an acetone-soluble product.

Fractionation

Hess, Schultz and Messmer (Annalen, 1925, *444*, 266) have shown that cellulose triacetate soluble in chloroform can be prepared in crystal form and is the normal acetylation product of chemically unchanged cellulose. By treating an acetone-solution of the secondary acetate of the product with precipitants, the authors obtained a product in which the acetyl content was narrowed down to 51–53%, but not to 48·8%, which is required for the diacetate. Crystals of this product are only capable of existence when in contact with the solvent, and fall to an amorphous powder when the solvent evaporates. The ability to crystallise appears to be governed, not so much by symmetry in the position of the ester groupings, but by the greater solubility caused by the presence of bodies with a low degree of acetylation.

McNally and Godbout (J.A.C.S., 1929, *51*, 3095) have shown by fractionation of acetone-soluble cellulose acetate that the fractions have the same chemical composition but different physical properties; this is attributed to a difference in the state of aggregation of the chain molecules in the micellæ. The solubility of cellulose acetate in organic liquids is a function of the chain length as well as its acetyl content.

Ohl (Kunstseide, 1930, *12*, 468) has divided commercial cellulose acetate into three portions by fractional precipitation. The first fraction consisted of pure cellulose acetate but contained inorganic and organic impurities showing low degrees of acetylation. The second fraction consisted of almost pure cellulose acetate and gave solutions of the highest viscosity. The third fraction contained decomposition products and intermediate products and gave solutions of low viscosity. Filaments from the second fraction gave the highest tensile strength and those from the third fraction the lowest.

Somewhat similar work by Rocha (Kolloidchem. Beih., 1930, *30*, 230) confirms the point that separation due to fractional precipitation is not made according to acetyl content.

Iwasaki (J. Soc. Chem. Ind., Japan, 1931, *34*) has also studied fractional precipitation of the cellulose acetates, and finds that the physico-chemical properties such as viscosity, solubility, and melting point are different, but that the acid contents are about the same. Other papers on broadly similar lines have been published by Ohl (Kunstseide, 1932, *14*, 3) and Herzog and Deripasko (Cellulosechem., 1932, *13*, 25), the latter giving viscosity-concentration and osmotic pressure-concentration curves for the different fractions. Fractional precipitation as a means of obtaining more uniform products has been protected in B.P. 345,408 and in B.P. 357,781.

Sakurada and Taniguchi (J. Soc. Chem. Ind., Japan, 1932, *35*, 249B) have shown that similar separation to fractional precipitation may be made by means of mixtures of benzene and methyl acetate.

Viscosity

Mardles (J.C.S., 1923, *123*, 1951) investigated the viscosity of cellulose acetate solutions, and came to the conclusion that there was no simple relationship between viscosity and the concentration of solution used.

Werner (Z. angew. Chem., 1931, *44*, 489) describes some interesting data on the viscosity of cellulose acetates and the cellulose saponification products. Different qualities of commercial cellulose acetate were saponified by treatment with 2% methyl alcoholic potash for 16 to 18 hours, and ordinary linters and cellulose samples were treated in the same way. All the saponified commercial cellulose acetate samples had extraordinarily low viscosities in cuprammonium solution, the values being practically equal and independent of the different viscosities of the original cellulose acetate samples. Various samples of linters and wood cellulose were then acetylated and saponified in a similar way. These saponified products also gave low and almost identical values in cuprammonium solution, in spite of the fact that the acetates differed in viscosity. From these results it appears that the value of viscosity measurement for the size of the cellulose principal valency chains in cellulose derivatives is doubtful.

The viscosity of cellulose acetate in solution is therefore not directly related to film strength or filament strength, but there is evidence to show that the acetates which give high viscosity solutions, are, when tested as films, more resistant to weathering.

In connection with the observations of Werner (loc. cit.) it is interesting to note that according to Ost, technically useful cellulose acetate may be made from hydrocellulose. Films prepared from the resulting acetate were of the normal quality in spite of the lower viscosity of the hydrocellulose. (See Rowe's translation of "Artificial Silk," by Reinthaler, page 108.)

Sakurada and Hess (Ber., 1931, *64*, 1174) suggest that the viscosity data of cellulose acetate solutions should be regarded as an indication of the degree of purification and disorganisation of the fibre, which result in the removal of impurities affecting the viscosity, rather than as indications of the existence of molecules of different weights. Viscosity decreases with increasing purity of the fibre, and with increase in the sulphuric acid concentration in the acetylation process. The sulphuric acid phenomenon may be due to its action on the non-cellulosic substances which affect the viscosity of the solutions.

The influence of various inorganic and organic additions on the viscosity of solutions of cellulose acetate in acetone and benzyl alcohol was investigated at different concentrations by Nisizawa (Kolloid Z., 1931, *56*, 317). Water produces an increase in viscosity, and later, causes coagulation. The addition of benzine produces gelatinisation of the system, the jelly showing rapid syneresis. Glacial acetic acid and nitric acid lower the viscosity of cellulose acetate solutions, as also do softening agents, such as camphor and triphenyl phosphate.

Mono-acetate

There have been many attempts to produce a monoacetate of cellulose. Early in this century Cross and Bevan produced a low-acetylated cellulose fibre by treating bleached cotton with boiling acetic anhydride in presence of sodium acetate. The product was insoluble in organic solvents for cellulose acetates and also in the cellulose solvents. Severe reduction of tensile strength accompanied this esterification. Cross and Briggs, in B.P. 5016 of 1907, acetylated cotton at a lower temperature in a closed apparatus, but only obtained irregular and uneven results. The general line of attack for some years was to employ either no catalyst at all, or to use weak catalysts, avoiding those used for the preparation of the higher acetates. An insufficiency of acetic anhydride for the production of the higher acetates was also investigated. It was assumed at this time that the course of the acetylation process was an initial esterification product, consisting of a surface triacetate, which,

in presence of adequate reagents suffered swelling and solution, ultimately allowing the whole fibre to be esterified. A true monoacetate could not be produced on this hypothesis.

Rheiner, however, was able to transform cellulose into its mono- and diacetate by direct treatment with an acetylating mixture, as employed for the triacetate, but the composition of the mixture and the temperature must be chosen to moderate the reaction, so that acetylation even to the monoacetate takes 20 hours or even longer. Descriptions of the various processes are found in B.P. 280,493; 314,913; 323,500; 323,515; 323,548; and 324,780.

The material shows an increase in weight of some 20% and remains unaltered in structure. There is no loss of tensile strength. According to Chippindale (J.S.D.C., 1934, *50*, 142) the regularity of acetylation is shown by microscopical examination of the cross section of the fibre after dyeing with cellulose acetate dyestuffs, whereas many fibrous esters previously examined show the "ester layer" in a ring, round the unchanged cellulose. This low acetylated cotton is insoluble in the solvents for cotton and the solvents for primary and secondary acetates.

Acetate Rayon

The manufacturing process for cellulose acetate, which is intended for use as artificial silk, or perhaps better expressed, as acetate rayon, does not necessitate a full description, in view of what has gone before. The technical success of these processes for textile purposes is largely due to the work of the Dreyfus brothers.

Secondary cellulose acetate is the only cellulose derivative in the field of commercial rayon production.

Cellulose is acetylated, as already described, and then changed from the primary or tri-acetate to the secondary acetate by a process of hydrolysis, usually by means of water and acetic acid. The secondary acetate solution is then allowed to ripen at a fixed temperature—the ripening determining the physical properties, including solubility, of the final product. The acetone-soluble acetate is then precipitated by the addition of a large excess of cold water, as white flakes, which are washed, centrifuged and dried at a relatively low temperature, e.g. 20 to 30° C.

The purified secondary acetate is then dissolved in a suitable solvent for spinning, filtered and de-aerated. Where the wet

spinning method is employed, the solution of cellulose acetate in acetone can be spun, i.e. coagulated as a number of continuous filaments, into baths of hydrocarbons, oils or aqueous solutions of salts. It has also been possible to " spin " from the acetylating mixture containing the secondary acetate without going through the processes of isolation, purification and re-solution. In the wet spinning processes, the thread is collected on bobbins, washed, twisted and reeled, as in the case of the other methods of rayon manufacture.

Most cellulose acetate, however, is spun by the dry system, which consists in projecting the acetone or acetone-alcohol solution of the secondary acetate (5 to 20% concentration) into a closed compartment whereupon the solvent is evaporated by means of hot air. The uniformity of the filament is obtained by " spinning " vertically downwards, while a current of warm, dry air flows upwards. In these circumstanes the material is not coagulated too rapidly, but remains plastic, so that the filaments are improved by the drawing action of the spinning spool below the enclosed vessel into which the solution is projected through the spinnerets.

Regulation of the temperature is essential, and the speed of the current of air must be uniform.

It is possible to draw off and recover the greater part of the solvent vapours, some of which is mixed with warm air and returned to the enclosed vessel or cell, as this contributes to the formation of uniform filaments. It has been found that in order to obtain filaments with a round cross section, the spinning atmosphere must contain more solvent vapour than when filaments with a flatter cross section are required.

Recent work has been directed to the improved tensile strength of acetate rayon produced by stretching; this phenomenon is in accordance with similar observations on micellar orientation in regenerated cellulose production. The cellulose acetate filaments may be stretched in wet steam or water at 100 to 120° C. according to the methods of B.P. 438,588-91; 438,584-7; 438,656-6; 438,786; 443,707 and 443,773. Stretching acetate rayon filaments in a plastic state may also be accomplished by swelling agents which are organic liquids (or vapours with solvent properties) according to B.P. 454,580 or by balanced mixtures of solvents and non-solvents (B.P. 453,155).

Simultaneous hydrolysis and stretching of acetate rayon has been responsible for great advances in tensile strength of the

regenerated cellulose. The subject is covered in a large number of patent specifications from which it appears that the use of inorganic bases is accompanied by definite disadvantages such as the production of a core of unchanged ester surrounded by an outer layer of pure cellulose. Liquid organic bases, particularly aliphatic bases, give even results. For instance, according to B.P. 417,220, acetate rayon which has been softened and stretched, is passed through 20% methylamine solution at 60° C. for 3 minutes. A regenerated cellulose may be obtained which has been stretched 200% and possesses a tenacity of 2·5 to 3 g. per denier and an extension of 12%. B.P. 429,103 utilises ethylene diamine which is particularly valuable in this connection. The products contain less than 1% acetic acid after hydrolysis, and if necessary their affinity for colouring matters which dye cellulose, may be improved by treatment with NaOH or KOH (B.P. 501,768). These processes are believed to form the basis of "*Fortisan*." It may be that the advantages of these processes over stretch spinning viscose into strong H_2SO_4 lies in the comparative mildness of the processes, thus allowing more control and producing a uniform result.

Analysis

The methods of determination of acetyl groups have conveniently been summarised by Krueger (Farben Zeit., 1930, *35*, 2032).

Some additional references are also given :

ALKALINE HYDROLYSIS.

Cross and Bevan (sodium ethoxide). "Researches on Cellulose," 1895–1900, page 38.

Green and Perkin (methyl alcoholic ammonia). J.C.S., 1906, *89*, 811.

Schultze and Hess (methyl alcoholic ammonia). Annalen der Chem., 1926, *450*, 65.

Schwalbe (cold aqueous alkali). Z. angew. Chem., 1910, *23*, 433.

Irvine and Hirst (warm aqueous alkali). J.C.S., 1922, *121*, 1587.

Eberstadt (aqueous alcoholic alkali). Diss. Heidelberg, 1913.

Fermazin (aqueous alcoholic alkali). Chem. Zeit., 1930, *54*, 605.

Knœvenagel and Konig (aqueous alcoholic alkali). Cellulosechem., 1922, *3*, 113.

Ost and Katayama (aqueous alcoholic alkali). Z. angew. Chem., 1912, *25*, 1469.

Barnett (acetone-aqueous alkali). J.S.C.I., 1921, *40*, 9T.

Battegay and Penche (pyridine-aqueous alkali). Bull. Soc. Chim. de France, 1929, *45*, 132.

Murray, Staud and Gray (pyridine-aqueous alkali). Ind. Eng. Chem. (Anal. Ed.). 1931, *3*, 269.

Moehring (sulphydrates). Wissen u. Ind., 1922, *1*, 70.

ACID HYDROLYSIS.

Perkin (alcoholic H_2SO_4). J.C.S., 1905, *87*, 107.

Ost (50% aqueous H_2SO_4). Z. angew. Chem., 1906, *19*, 933; 1919, *32*, 66.

Ost and Katayama (50% aqueous H_2SO_4). Z. angew. Chem., 1912, *25*, 1469.

Fenton and Berry (phosphoric acid). Proc. Camb. Phil. Soc., 1920, *20*, 1, 16.

Berl, Rueff and Wahlig (phosphoric acid). Chem. Zeit., 1931, *55*, 861.

Sudborough and Thomas (aromatic sulphonic acids). Proc. Chem. Soc., 1905, *21*, 88.

Pregl and Soltys (Toluenesulphonic acid). Mikrochem., 1929, *7*, 1.

Freudenberg and Weber (Toluenesulphonic acid). Z. angew. Chem., 1925, *38*, 280.

Friedrich and Rapoport (Toluenesulphonic acid). Biochem. Zeit., 1932, *251*, 432.

Parsons (65% H_2SO_4). J.T.I., 1933, *24*, 167.

The estimation of combined sulphuric acid in cellulose acetate may be effected by fusion with alkaline oxidants with subsequent analysis of the sulphate, or by treating the material with nitric acid, or nitric acid-potassium chlorate mixture. These methods obviously involve destruction of the cellulose.

Cellulose Chlor-esters

The direct action of chloracetic acids on cellulose does not result in any appreciable degree of esterification. Barnett (J.S.C.I., 1921, *40*, T253) investigated the action of chloracetyl

chlorides, containing SO_2, in a pyridine-toluene mixture, on cellulose which had been moistened with CH_3COOH containing a trace of Cl_2. The reaction is difficult to control and charred products easily result. Barnett states that cellulose chloracetate is probably first formed, and then gives rise to cellulose glycollic ester

$$ClCH_2COOR \longrightarrow HOCH_2COOR.$$

The best method for smoothness of reaction is to use glacial acetic acid, containing traces of SO_2 and Cl_2 as the reaction medium, but even here there is a small yield of a powdery product owing to rapid degradation. The resulting substance has the general formula $(C_{14}H_{20}O_{10})ClH$, the chlorine content of 2·47% being easily removed by hydrolysis. Careful examination of the product shows the presence of esters of higher hydroxy acids than glycollic—probably mixed esters of acetic and hydracrylic.

Rudy (Cellulosechem., 1932, *13*, 49) states that the direct action of the chloracetic acids or their chlorides on cellulose does not esterify to any marked extent. In the case of hydrocellulose, the anhydride of monochloracetic acid, in the presence of a suitable catalyst, such as H_2SO_4 or $ZnCl_2$, yields a trichloracetate $C_6H_7O_5(COCH_2Cl)_3$, containing 26% of chlorine. This ester is soluble in HCOOH, $CHCl_3$, CH_3COCH_3, and C_6H_6. It is insoluble in alcohol. The di- and trichloracetic anhydrides under similar conditions give the di-dichloracetyl $C_6H_8O_5(COCHCl_2)_2$ and the di-trichloracetyl derivatives $C_6H_8O_5(COCCl_3)_2$, which contain 36·6% and 44% of chlorine respectively. These two esters are soluble in HCOOH, CH_3COCH_3, and pyridine, but only slightly soluble in $CHCl_3$ and benzol.

The effect of alcoholic ammonia on these three esters is to hydrolyse them to chloracetamides with the production of a reducing cellulose.

This method is not suitable for the production of the tri-derivatives of di- and trichloracetic acid. Cellulose tri-trichloracetate may be prepared by the action of PCl_5 on cellulose triacetate, but the tri-derivatives of mono- and dichloracetic acid cannot be made in a similar manner.

The tri-trichloracetate is made by digesting cellulose triacetate with PCl_5 in a mixture of $CHCl_3$ and $C_2H_2Cl_4$, at 120° C. The mixture of solvents is so chosen to allow of such a temperature. The reaction at 100° C. is very slow. Investigation of a reaction period of from 2 to 10 hours, shows that the tri-

trichloracetate, with a chlorine content of 53 %, may be formed in three hours, whereas only 10 % of chlorine appears to be fixed in two hours. Rudy has also found the isonitrile test to be of value in following the course of the reaction.

This ester is soluble in HCOOH and $CHCl_3$, a lower ester is soluble in CH_3COCH_3, but both are insoluble in alcohol.

The tri-trichloracetate of cellulose, $C_6H_7O_2(O.COCCl_3)_3$ has the very important property of resisting hydrolysis by both aqueous and alcoholic solutions of acids or alkalis (*cf.* ethers).

The action of monochloracetic acid on alkali cellulose is interesting. Sakurada (Bull. Inst. Phys. Chem. Res., Japan, 1929, *8*, 96) has found that in the cold the sodium salt of cellulose glycollic acid is produced. This is soluble in water but is precipitated by alcohol. The free acid may be precipitated on addition of mineral acid and is not hydrolysed by heating with acid or alkali. Only one molecule of $CH_2ClCOOH$ condenses with each $C_6H_{10}O_5$, and the product is, of course, an *ether* of cellulose :—R.O.CH_2.COOH.

In discussing the effect of the chloracetic acids on cellulose, it may be well to mention here the peculiar properties of chloracetic anhydride in the esterification process. In B.P. 313,408, may be found the announcement, that halogen substituted organic acid anhydrides act as "impellers" in the esterification process, but do not exert esterifying action themselves. Hence it is possible to prepare cellulose esters from acids which were previously believed to be unreactive, and necessitated the use of the acid chloride or anhydride. The temperature of the reaction varies from 50 to 80° C., and esterification takes place in the halo-acetic acid solution. Typical reaction conditions are shown below :

ESTERIFICATION OF CELLULOSE.

Acid	Parts of acid.	Parts of cellulose.	Chloracetic anhydride.	$Mg(ClO_4)_2$	Time. Hours.
Crotonic . .	15	5	30	0·05	5
Cyclohexanecarboxylic	10	2	15	0·02	3
Benzoic . .	15	3	20	0·05	8
o-methoxybenzoic .	10	2	15	0·02	4
o-chlorbenzoic .	10	2	15	0·02	5
Acetyl salicylic .	20	2	20	0·05	10
Phenylacetic . .	15	3	20	0·05	7
Hydrocinnamic .	15	3	30	0·05	3
Cinnamic . .	15	3	40	0·05	5

Completion of reaction is shown by disappearance of the fibres. This catalyst has been mentioned previously in connection with cellulose formates.

By the use of ethyl hydrogen phthalate as the esterifying agent, in 72 hours there may be obtained a phthalic ester, in which the phthalic group retains the alcohol residue. It is soluble in acetone, benzene and chloroform, but insoluble in ligroin, ether and carbon tetrachloride.

This " impeller " may also be used for mixed esters.

The use of a halogen-substituted organic anhydride as an impeller is not generally applicable to halogen-substituted fatty acids. B.P. 304,279 states that there is no esterification in the case of acids with five carbon atoms or less ; in the case of compounds containing more than five carbon atoms, the method is successful and cellulose esters have been made from α bromostearic acid, 9 : 10 dibromostearic acid (i.e. brominated oleic acid), dichlorostearic acid (i.e. chlorinated oleic acid), tetrachlorostearic acid (from chlorine on the acid from saponified linseed oil) and α bromocaproic acid. These cellulose esters all give films which are non-inflammable. Their mixed esters, with acetate, are soluble in acetone and chloroform.

Dreyfus, in B.P. 320,842, gives a description of the preparation of cellulose chloracetate by heating pretreated cotton with chloracetic anhydride in presence of chloroform and sulphuryl chloride until solution takes place. It may also be prepared by using chloracetic acid and chloracetic anhydride in presence of H_2SO_4, and the conditions controlled, to ensure retention of the fibrous structure, if desired—otherwise the mixture passes into solution and it is precipitated by the addition of water. The method of pretreatment of the cotton is with formic acid and is employed to increase reactivity. The cellulose chloracetate is stated to be soluble in acetic acid and in chloroform, but insoluble in petroleum ether and in benzene.

Cellulose Propionates

Many of the methods employed for the preparation of cellulose acetate are suitable for the propionate ; in general, propionic anhydride is used in presence of a fatty acid, such as acetic, and a catalyst. Clear viscous solutions are formed which can be precipitated by alkali or ammonia. Prehydration of the cellulose is often necessary, or alternatively, the use of hydrocellulose, in which case the tripropionate is

easily produced. Worden refers to a typical method of treating one part of cellulose with five parts of propionic anhydride, 4·5 parts of glacial acetic acid and 0·1 part of gaseous HCl. A solution of the propionate occurs after digesting for 12 to 24 hours at 70° C.

Dreyfus, in U.S.P. 1,824,877, recommends the pretreatment of cellulose with a lower fatty acid and propionic anhydride in the absence of a catalyst, after which H_2SO_4 is added as a catalyst to cause propionylation, and the product is partly hydrolysed.

Malm and Clarke (J.A.C.S., 1929, *551*, 274) find that by prolonged refluxing with propionic acid the limit of esterification is reached at 100 hours, after which there is severe degradation of the cellulose. The amount of combined propionic acid is 8·1%, corresponding to $C_{24}H_{39}O_{20}(COC_2H_5)$. In the case of hydrate cellulose and mercerised cellulose a higher degree of esterification is obtained, corresponding to $C_6H_9O_5(COC_2H_5)$. Cellulose regenerated from cellulose acetate behaves in this respect like native cellulose. The solubility of the lower esters is the same as that of cellulose itself, the main difference being that of dyeing affinity. These workers obtained similar results with butyric acid.

The higher cellulose propionates are soluble in acetone, alcohol, chloroform and ethyl acetate.

Propionates may also be made by heating cellulose with propionic anhydride in presence of a little H_2SO_4 as a catalyst; the primary product, which is soluble in acetone-benzene, is hydrolysed with aqueous propionic acid and H_2SO_4 until the acetone-soluble product is obtained (B.P. 449,183). Alternatively, the cellulose may be treated with propionic anhydride in presence of an " impeller " such as acetic anhydride together with a small amount of SO_2 and NO. For fibrous propionates, a non-solvent such as CCl_4 may be incorporated in the esterification mixture (U.S.P. 2,000,621).

Ohl (Kunstseide, 1938, *20*, 42) states that cellulose propionate is soluble in alkyl acetates, but only possesses limited solubility in acetone. It is capable of producing satisfactory filaments of lower strength but greater extensibility than the acetate. Because of its thermoplastic nature, the propionate may also be drawn into filaments.

Cellulose Butyrates

The general method of preparation is by the action of butyric acid, butyryl chloride and a condensing agent, such as $ZnCl_2$

or H_2SO_4, on cellulose. Malm and Clarke (J.A.C.S., 1929, *51*, 274) have obtained a butyric ester containing 9·9% of butyric acid by boiling cellulose with n-butyric acid for 100 hours. This figure may be increased to 10·9%, but with severe degradation of the cellulose.

Frank and Cohn (Cellulosechem, 1931, *12*, 68) prepared a cellulose butyrate containing 65 to 66% of butyric acid by steeping cellulose in 80 to 95% HCOOH, for 24 hours at room temperature, and then esterifying with a mixture of butyric acid, anhydride and $ZnCl_2$. The formyl groups were removed by hydrolysis with 93% butyric acid. This product is intermediate between the di- and tri-esters, and decomposes at 225° C. It is soluble in the usual cellulose ester solvents and gives viscous solutions. The filaments and films produced from this ester have a lower tensile strength and a higher degree of plasticity than those from cellulose acetate.

According to B.P. 323,869, cellulose, after pretreatment with butyric acid, is esterified in presence of the sulphonic acid of an aliphatic hydrocarbon and butyric anhydride and a suitable catalyst. The addition of benzene, which is a solvent for the ester, is preferred. The tributyrate may be dissolved in aqueous butyric or other aliphatic acid, and hydrolysed for 16 to 18 hours at 45 to 50° C. This process, B.P. 328,259, produces an ester, which, after precipitation by water is soluble in methyl alcohol.

Little's method, B.P. 167,143, is to soak 100 parts of cellulose in 1,500 to 1,600 parts of an acetic acid solution of H_2SO_4, comprising 1–5% of H_2SO_4 (*d.* 1·84), 5–8% of water and 94–97% of CH_3COOH. The mixture is pressed until it contains one and a half times its own weight of the solution, and then treated in a bath containing 400 parts of butyric acid, and 465 parts of butyric anhydride. There is a rise in temperature and the reaction is allowed to proceed until products of the desired solubility are obtained. When H_2SO_4 is used in small amounts it is advisable, on the product showing good solubility in $CHCl_3$, to accelerate the reaction by adding 5 parts of H_2SO_4 and 3–5 parts H_2O on the volume of the butyrating mixture. In a subsequent patent, B.P. 182,820, Little covers the addition of methyl, ethyl, or butyl alcohol, or acetone, to the mixture in order to prevent separation into two layers, which is likely to occur when butyric acid, containing small amounts of water, is used as a catalyst carrier.

The ester produced by these means is soluble at room tem-

perature, in a mixture of either methyl or ethyl alcohol, and 50–90% by volume of benzol. Cellulose butyrate is also soluble in many other solvents including acetone, chloroform, 90% phenol, etc.

More modern methods of preparation are shown by two French patents. F.P. 664,932, describes the use of butyryl chloride, which is allowed to act on cellulose in presence of a tertiary organic base, e.g. pyridine and a catalyst. The product is stated to be suitable for films, filaments and artificial leather. F.P. 286,906 states that tri-isobutyrates and tri-butyrates may be formed by first submitting cellulose to the regulated action of a chloro-derivative of acetic acid in presence of a suitable solvent, such as butyric acid or acetone, at a low temperature, and then esterifying at 15–25° C. in presence of a dehydrating agent, e.g. H_2SO_4, and an appropriate solvent.

Cellulose Undecylenate

Cellulose undecylenate has been prepared by Gault and Urban as a sequel to the study of the higher fatty acid esters of cellulose by Gault and Ehrmann. According to Compt. rend. (1924, *179*, 333) a 60% yield of cellulose undecylenate may be obtained by treating hydrocellulose, soaked in a mixture of toluene and excess pyridine, with undecylenyl chloride, by heating on an oil bath at 110–120° C., for one and a half to two hours. The ester is precipitated by alcohol, dissolved in benzene to remove the insoluble part of the ester by centrifuging, and reprecipitated by alcohol as short fibrous filaments. Cellulose undecylenate is soluble in aromatic hydrocarbons, chloroform, pyridine, etc., and is insoluble in water, alcohol, and acetone. The point of softening appears to be below 190° C. The hydrolysis of this ester appears to be difficult, according to these workers, for attempts at acid detection by saponification failed on account of its great stability, but the usual methods of combustion gave figures which are in agreement with the formation of a tri-ester.

The Higher Fatty Esters

Acid anhydrides of high molecular weight are not easy to prepare nor are they particularly reactive ; for these reasons the preparation of cellulose esters with the higher aliphatic, aromatic and heterocyclic acids utilises the Schotten-Baumann reaction, i.e. treatment with acid chlorides in presence of alkali, which is sometimes pyridine.

Only a slight degree of esterification is obtained by heating cellulose with palmitic anhydride in the presence of pyridine and chloroform, according to Kita and his co-workers (Cell. Ind., Tokyo, 1925, *1*, 227). On the other hand when cellulose is heated with palmityl chloride and pyridine, preferably diluted with benzene, progressive formation of esters takes place, with the ultimate production of the tri-palmitate soluble in benzene and ether. The esters are purified by washing the product with alcohol and extracting with ether or benzene. Grun and Wittka (Z. angew. Chem., 1921, *34*, 645) investigated the formation of the higher fatty esters of cellulose, particularly the laurate and stearate, finding that the mono-ester could be formed by four hours heating on the water bath, employing 20 g., of say, stearyl chloride, to 10 g. of pure dry cellulose in presence of pyridine. For the di-stearate a considerable excess of acid chloride is necessary, 60 c.c. of stearic acid chloride to 5 g. of cellulose. The reaction is carried out in benzene in presence of pyridine and takes longer than the mono-ester reaction. The laurates are similarly obtained. Tri-esters of stearic and palmitic acids may be obtained by heating paper with the acid chloride in presence of pyridine and benzene for 24 hours on the water bath. The product is washed with alcohol and extracted with benzene. In the case of the laurates only the di-ester is obtained, but further treatment gives a lauric ester, containing between two and three lauric acid residues.

Di- and tri-esters of the higher fatty acids have been prepared from hydrocellulose and regenerated cellulose by Gault and Ehrmann (Bull. Soc. Chim., 1926, *39*, 873) by similar methods. Di-esters may be made by reacting one part of hydrocellulose with five parts of the acid chloride in presence of three parts of pyridine and five parts of toluene at 110° C., with constant stirring.

Every 15 minutes samples are removed and examined for solubility in benzene, and when completely soluble the mixture of esters is precipitated by alcohol, dried and treated with benzene. On centrifuging the benzene solution the insoluble mono-ester (10–20%) separates, and the clear solution is treated with alcohol to throw down a 60–80% yield of the di-ester, from which the tri-esters are best prepared by dissolving in a mixture of four parts of pyridine, one part of toluene and five parts of the acid chloride, and the whole heated to 100° C. for two hours. It is also possible to obtain

the tri-esters directly by using twice as much acid chloride as prescribed above.

The properties of these esters varies according to the degree of esterification and also according to the starting material. In the case of the palmitates, for example, the melting points, ranging from 180° to 220° C., are lower in the esters from hydrocellulose than in those from normal cellulose. The monopalmitate is still fibrous and only slightly swollen, whilst the higher palmitates are highly swollen and completely deformed. The tripalmitate from hydrocellulose is completely soluble in ether and the dipalmitate in benzene, but the esters from normal cellulose are only partly soluble. The mono-esters of the higher fatty acids are insoluble in the ordinary solvents, but the di- and tri-esters are soluble in many organic liquids, especially benzene, chlorinated hydrocarbons, fatty acids and oils.

Some interesting observations on the solubility of the higher fatty acid esters of cellulose have been made by Kita and his co-workers (Sci. Pap. Inst. Phys. Chem. Res., Tokyo, 1927, *7*, 153). Di- and tri-esters of the higher fatty acids are prepared by the action of the acid chloride on cotton cellulose in presence of pyridine and benzene. They are partly soluble in organic liquids, but are rendered soluble by heating for several hours in naphthalene at 200° C., or for two hours in the corresponding fatty acid. The presence of benzene sulphonic acid is advantageous. The esters may also be heated in benzene containing H_2SO_4, rich in benzene sulphonic acid. There is no hydrolysis, so that the change in solubility is due to physical changes, probably in the nature of molecular arrangement. Heating near the boiling point or at a lower temperature with a catalyst, e.g. benzene sulphonic acid, are conditions where molecular rearrangement might be expected. The cellulose produced from the soluble ester is soluble in NaOH, whilst that from the insoluble ester is only partly soluble. Pringsheim and Ward (Cellulosechem., 1932, *13*, 119) in an informative paper on the fatty acid esters of cellulose have compared the methods of converting the insoluble primary ester into a soluble form by means of heat treatment in presence of benzenesulphonic acid, tetralin, acetic acid, benzyl acetate and camphor. The type of ester so produced is slightly coloured and films from it are weak. Esterification at high temperatures produces the soluble form of ester directly, but with inferior properties.

The work of Nowakowski (Compt. rend., 1930, *191*, 411)

and Trillat (*ibid.*, 1933, *197*, 1616) has shown that the ester chains are perpendicular to the axis of the cellulose fibre. The esters up to the butyrate have a crystalline structure and the higher esters are mesomorphic, and increasingly plastic. The fatty acid character predominates increasingly with chain length tending to mask the cellulosic character (Trillat, J. Phys. Radium, 1934, *5*, 207).

As the solvents for the higher fatty esters are common, and the nature of the esters renders them suitable for flexible films, and for lacquers there is, naturally, a number of patents covering various methods of manufacture, but a novel aspect of the patent literature on this subject is the modern development of a surface esterification of the cellulose in the form of cloth, insufficient to destroy the character of the structure. A textile fabric so treated is resistant to the action of water, and, if the weave is correctly designed, may become completely waterproof, e.g. B.P. 343,104.

The analysis of the esters is effected by saponification with alcoholic potassium hydroxide to which benzene should be added, to cause swelling and promote the reaction.

Properties of the Fatty Esters

An interesting review of the properties of the cellulose esters of the aliphatic acids is given by Hagedorn and Möller (Cellulosechem., 1931, *12*, 29). They point out that no accurate comparisons can be drawn between compounds from differently degraded celluloses; they have, therefore, made use of preparations which give homogeneous products, and attack the cellulose micelle as little as possible, in order to retain the original structure. The general method adopted, with the exception of the formate, was to treat cellulose with the necessary acid chloride in presence of pyridine in an indifferent solvent. In all cases the highest degree of esterification was aimed at, i.e. the tri-ester, so that the basis of comparison is the primary ester, and not the secondary ester obtained by subsequent hydrolysis. The reaction was conducted, in each case, under optimum conditions of time, temperature, and proportion of reagents. In some cases the ester first comes out of solution in an insoluble form, but it is possible to produce such esters in soluble form by means of organic solvents peculiar to the compound. It was found that the viscosity of the cellulose derivatives varied within wide limits, but in general, it may be said that it falls with the diminution in the

size of the particles. Since this diminution in particle size is bound up with careful treatment of the ester during and after its preparation, a deterioration of the product occurs in most cases, and the esters lose the characteristic properties of cellulose and become brittle. This happens with the esters of the lower fatty acids, but with increasing length of the carbon chain in the acid residue, this influence becomes less defined, and it is possible to prepare a cellulose laurate solution of low viscosity, but with retention of its elastic properties, so that it resembles rubber in this respect.

Hagedorn and Möller state that none of the esters is soluble in water; nevertheless the individual esters differ in their sensitivity to water. This is shown by the deformation of their films on wetting and may be attributed to the degree of swelling. This property is of some technical importance. The sensitivity to water decreases with the number of carbon atoms in the acid radicle, so that from the laurate, onwards, the esters are unaffected by water. Apart from the formate all the esters are soluble in chlorinated hydrocarbons. In the acetate and propionate, the influence of the cellulose itself is still predominant, so that solubility is limited to a small number of solvents, but with the higher fatty esters (i.e. lower weight of cellulose), the solubility of the ester begins to be determined by the acid residue. Hence the number of solvents for the esters increases up to the valerate, and reaches a maximum with the caproate. The highest member is influenced by the acid residue. In the case of the hydrocarbon solvents, those of the aromatic class commence to be effective for the butyrate, whilst the aliphatic hydrocarbons dissolve only those cellulose esters from the laurate, onwards. Acetone is mentioned as occupying a peculiar position, for it dissolves the esters from the propionate to the caproate easily, the pelargoate on warming, but has no solvent action on the higher esters.

From the tables showing tearing strength and extension of films from the cellulose esters, it will be seen that the strength falls with increasing length of the acid chain, whilst extension increases, the product of strength and extension being approximately constant. In the higher esters the increasing extension is remarkable, for in the case of the stearate it exceeds the elastic limit, on account of plastic deformation. Total extension comprises elasticity (reversible) and plasticity (irreversible), both of which occur together in the cellulose esters of the higher fatty acids.

Solubility of Esters.

	Water.	Alcohol.	Ether.	Acetone.	Acetic Acid.	Benzine.	Benzol and homologues.	Chlorinated Hydro-carbon.
Formate .	v. slight swelling.	insol.	insol.	insol.	insol.	insol.	insol.	insol.
Acetate .	insol.	,,	,,	strong swelling.	,,	,,	,,	sol.
Propionate .	,,	,,	,,	sol. hot.	sol. hot.	,,	,,	,,
Butyrate .	,,	slight swelling.	strong swelling.	sol.	sol.	,,	sol.	,,
Valerate .	,,	,,	sol. hot.	,,	,,	,,	,,	,,
Caproate .	,,	insol.	sol.	,,	,,	slight swelling.	,,	,,
Pelargoate .	,,	,,	str. swell. hot.	sol. hot.	,,	insol.	,,	,,
Laurate .	,,	,,	sol.	strong swelling.	,,	sol. hot.	,,	,,
Stearate .	,,	,,	slight swelling.	slight swelling.	strong swelling.	swelling.	,,	,,
Naphthenate	,,	slight swelling.	sol.	swelling.	sol.	sol.	sol.	sol.

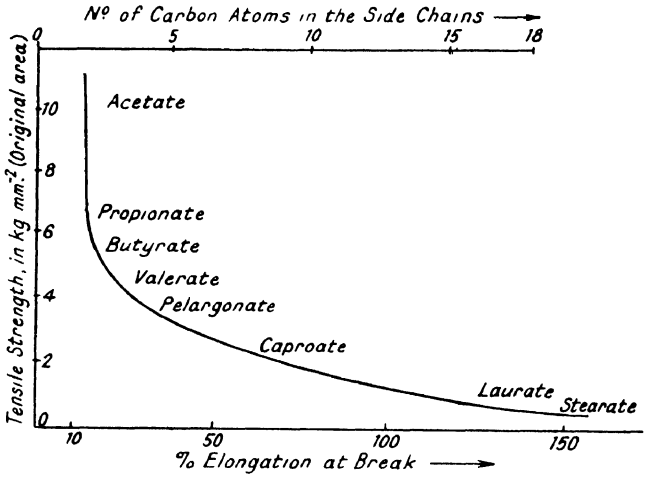


FIG. 139.—Variation in physical properties of cellulose esters with increasing length of the substituted side-chain.

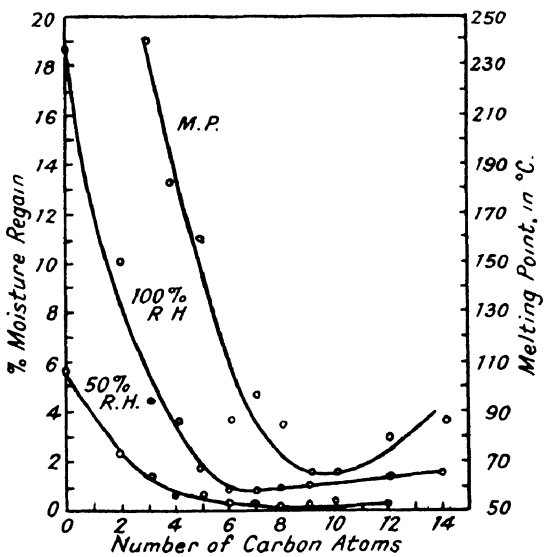


FIG. 140.—Progressive changes in the tri-esters of cellulose, with increase in molecular weight of the fatty acid.

STRENGTH AND EXTENSION DATA.

	Strength Kg/sq. mm.	Extension %
Acetate	9–12	15–25
Propionate	6–7	10–15
Butyrate	5–6	8–10 (?)
Valerate	4–5	18–25
Caproate	2·5	60
Pelargoate	3·5–4·0	20–30
Laurate	0·8–1·0	100–130
Stearate	0·5	> 140
Naphthenate	0·3	110

The alteration in strength and extension according to the acid grouping is shown in Fig. 139.

Sheppard and Newsome (J. Phys. Chem., 1935, *39*, 143) have studied the progressive changes in cellulose tri-esters as the molecular weight of the fatty acid is increased. Some of these effects are shown in Fig. 140. The moisture regain passes through a minimum near cellulose heptoate for no apparent reason, as it might be expected to decrease with the increase of carbon atoms in the side chain.

The effect of the degree of substitution has not been examined to such a great extent in the case of the higher fatty esters of cellulose as with cellulose acetate or, indeed, the cellulose ethers. It appears, however, that products soluble in organic solvents may be obtained with a lower degree of substitution as the molecular weight of the acid group is increased.

Esters of Hydroxy Acids

Cellulose esters of the hydroxy aliphatic acids may be prepared by the methods of B.P. 316,160, which employ the corresponding anhydride. The cellulose is pretreated by any of the usual means already indicated in the general technique of cellulose ester formation. The reaction is carried out in acetic acid at a temperature not exceeding 50° C., but 20–30° C. is preferred, or the cellulose may be treated in suspension in a non-solvent diluent in presence of a catalyst. If the preparation is effected in acetic acid then the reaction is continued until solution is complete and the ester is precipitated by the addition of water. Mono- di- and tri-esters may be prepared, and in the case of the tri-ester, the solubility may be altered by hydrolysis to the secondary ester in the usual manner.

The cellulose esters of glycollic, lactic, hydracrylic and other acids may be prepared by these means ; cellulose glycollate is soluble in acetone and in chloroform diluted with ethyl alcohol, and on hydrolysis to the secondary ester it becomes progressively soluble in acetone containing more and more water. As these esters contain free hydroxyl groups, they may be esterified, e.g. from cellulose glycollate, the cellulose derivative of acetylglycollic acid may be made.

Cellulose esters of hydroxy acids may also be made by the hydrolysis of the esters of the halogen substituted fatty acids, as described in B.P. 320,842. For example, cellulose chloracetate is treated with alcoholic sodium hydroxide at room temperature. The alkali is added at intervals, with stirring, until 32 parts of NaOH has been added to 100 parts of the chloracetate. The cellulose glycollate is separate and washed. The product is stated to contain no chlorine, and to possess properties similar to those of the glycollate prepared according to B.P. 316,160, except for solubility in solvents containing more water.

Substitution products of cellulose acetate, and its homologues, may be formed by treating cellulose with the anhydrides of the ethers of the hydroxy fatty acids (see B.P. 314,918). For instance, cellulose methoxyacetate may be prepared by treating cellulose with methoxyacetic acid and its anhydride until the cellulose passes into solution. The product may be precipitated and purified in the usual manner, and is soluble in methoxyacetic acid, acetic acid, and in chloroform-alcohol. Cellulose ethoxyacetate may be made by similar means.

All the alkyl ethers of the fatty acids, e.g. glycollic, lactic, hydracrylic, etc., may be reacted with cellulose according to the above fashion, and in general, the secondary esters obtained are found to be soluble in alcohol-benzene, acetone and in acetone-water.

Dicarboxylates

The early attempts of Knecht to obtain an oxalic ester of cellulose were not successful, and his experimental evidence led to the opinion that as cellulose formate was produced, the oxalic acid decomposed, to form formic acid on the cloth. There was no degradation. Briggs (J.S.C.I., 1912, *31*, 521) conducted experiments which showed that when oxalic acid is heated in the dry state with cellulose, even at moderate temperatures, there is some combination, but at the same

time the cellulose is converted to hydrocellulose. The cellulose-oxalic-ester formed showed a tendency to hydrolyse during washing. The fact that it is impossible to prepare the ester without a proportional conversion to hydrocellulose, coupled with the small amount of oxalic acid which entered into combination, even under extreme conditions, led to the conclusion that the reaction is with the hydroxyl groups of hydrocellulose rather than with those of the undegraded material.

Frank and Caro (Ber., 1930, *63*, 1532) state that oxalic acid esters of cellulose are not produced by the action of the acid, or its acid chloride, on cellulose. Insoluble, infusible derivatives are obtained probably due to cross-linking of the type usually produced with polyhydroxy compounds and polybasic acids. There appears to be no technical application for these derivatives, which are of limited interest. If, however, one of the chlorine atoms in the acid chloride is replaced by an alcohol radicle and the cellulose treated with this ester-half-chloride, then a product is obtained corresponding, approximately, to $C_6H_7O_5$ $(COCOOR)_3$. One carboxyl of the dibasic acid has reacted with the cellulose, and the other has been esterified with an alkyl group.

The properties vary according to the nature of the hydrocarbon residue. With increasing size of the residue, the density and softening point decrease, the solubility in non-polar solvents increases whilst that in polar solvents decreases, the plasticity of the film increases and the tensile strength falls.

The preparation is readily accomplished in presence of pyridine and nitrobenzene, and in some cases, proceeds at ordinary temperatures. The degree of esterification appears to lie between the di- and tri-ester.

Attempts to saponify the alkyl group, without splitting the cellulose oxalic acid linkage, were not successful. On hydrolysis of the ester, the product was found to consist of hydrocellulose. Further work by Caro (Bied. Zentr., 1934, A, *4*, 442) shows that mixed cellulose oxalates are formed by the action of the ester chlorides of oxalic acid and pyridine on cellulose. Cellulose ethyl oxalate may be formed under mild conditions of reaction. It was also shown that the activity of the ester chloride diminishes as the alkyl group becomes more complex. The ester chlorides of succinic and adipic acids do not react with cellulose under these conditions.

It is possible to produce cellulose esters of dibasic acids in which one carboxyl group remains unesterified, by making

use of the reaction with the acid anyhdride in presence of pyridine, according to B.P. 410,118.

Cellulose esters of the dicarboxylic acids may be prepared by the methods of B.P. 410,125, which make use of the anhydride. In this manner esters of succinic, glutaric, diglycollic, dilactic, and thiodiglycollic acids may be formed, characterised by superior adhesive properties. The combination is believed to take place between the cellulose and only one of the two carboxyl groups, the other combining with the base used in the preparation, and freed from it by addition of acid in the usual manner $C_6H_7O_2$ $(O.CO.R.COOH)_3$.

Five g. of cellulose may be treated with 25 g. of succinic anhydride in 75 cc. of pyridine, at 60-65° C., for a week, until a "dope" is formed. This is poured into methyl alcohol and the precipitate dried to form the pyridine salt of the acid ester. The pyridine may be removed in the usual manner, giving a compound containing 62% of succinic acid (tri-succinate requires 65%).

Where regenerated cellulose is used as the starting material, 10 g. is treated with 50 g. of diglycollic anhydride in 100 g. of pyridine, at 85–100° C. for three days. The reaction product is diluted with methyl alcohol-acetone and precipitated with 10% HCl.

Salts of these acid esters are covered by B.P. 410,126; the alkali salts are soluble in water and in methyl alcohol. Copper, cobalt, zinc and iron salts have also been formed, which may be slightly soluble in water, according to the metal, but are all soluble in water to which a weak base has been added.

Malm and Fordyce (Ind. Eng. Chem., 1940, *32*, 405) have made use of chloracetic anhydride as an "impeller" to bring about esterification with the half-esters of dicarboxylic acids.

$$C_6H_7O_2(OH)_3 + R\begin{matrix}\diagup COOR' \\ \diagdown COOH\end{matrix} \longrightarrow C_6H_7O_2(OCORCOOR')_3$$

Numerous cellulose alkyl esters have been made in this way, and those given below are completely soluble in acetone, ethyl acetate and ethylene dichloride. The higher alkyl esters (propyl and butyl) are also soluble in benzene and toluene.

CELLULOSE ALKYL ESTERS OF DIBASIC ACIDS.

Cellulose Ester.	M.P.
Methyl succinate . . .	195° C.
Ethyl succinate . . .	128° C.
Propyl succinate . . .	108° C.
Butyl succinate . . .	106° C.
Methyl phthalate . . .	180° C.
Ethyl phthalate . . .	178° C.
Propyl phthalate . . .	175° C.
Butyl phthalate . . .	155° C.

The cellulose acid dicarboxylates themselves, $C_6H_7O_2(OCORCOOH)_3$, possess limited solubility in organic solvents, and this makes the mixed esters, containing both acetyl and dicarboxylic acid groupings, of greater technical interest.

Carbamates

Carbamic esters of cellulose may be prepared, according to the methods of B.P. 130,277, of 1919, where cellulose is caused to react with aliphatic or aromatic isocyanic esters, with or without the addition of a base.

Thus, dried cellulose may be heated with about three times its weight of phenyl isocyanate or other isocyanic ester in presence of anhydrous pyridine, which promotes the reaction and also acts as a diluent. The resulting phenyl carbamic ester is isolated by pouring the mass into a large volume of water.

$$\text{Cell. OH} + C_6H_5N : C : O \longrightarrow \text{Cell. O}-\overset{\overset{C_6H_5NH}{\diagdown}}{\underset{\underset{O}{\diagup}}{C}}:O$$

The carbamic esters from stearyl iso-cyanate are described on page 426.

Esters of Unsaturated Fatty Acids

There appears to be little information concerning the preparation and properties of these esters. The crotonic esters of cellulose are prepared (B.P. 328,492) by treating cellulosic material with crotonic anhydride in the presence of the usual

esterification catalysts and a diluent. In a subsequent specification (B.P. 329,704) these crotonates may be partially saponified to yield lower crotonates of different solubilities. The tricrotonate is insoluble in water, ether, ligroin and CCl_4; but soluble in acetic acid, acetone, chloroform, benzene and benzene-alcohol. The dicrotonate is insoluble in benzene, but soluble in acetone, chloroform, and benzene-alcohol. The mono-crotonate of cellulose is soluble in acetone-water.

The esters of the higher unsaturated aliphatic acids are prepared by heating the cellulosic material with the acid chloride in presence of pyridine or dimethylaniline (B.P. 239,726). The linolenic acid ester of cellulose is an oil which is soluble in hydrocarbons, oils, turpentine, etc. Esters of oleic acid, linoleic acid and the unsaturated acids of train oils have also been prepared. Unlike the saturated acid esters, the unsaturated esters are made insoluble by heating. They also oxidise in the air to insoluble products.

According to D.R.P. 478,127, however, the esters of oleic, linoleic, ricinoleic and other acids, are insoluble in all solvents and the external appearance of the cotton fibre is preserved. They can only be brought into solution by treatment in a colloid mill. It is also stated that the strongly unsaturated esters, as for example, cellulose linoleate, tend towards spontaneous inflammability and, therefore, can only be stored in a moist condition. Hagedorn and Möller (Cellulosechem., 1931, *12*, 29) state that the unsaturated esters with a short carbon chain give brittle masses with little strength or elasticity. They point out that in the cellulose esters of the oleic acid series, the difference between the cis and trans isomers is clearly shown. Cellulose oleate is insoluble in all solvents, but the elaidate is soluble in organic solvents, and films formed from such solutions resemble those from the fatty acid esters of cellulose.

Esterification of cellulose, by means of maleic anhydride, is protected in B.P. 315,434. This is of particular interest as reaction is rapid and no catalyst is necessary. Two methods are given. One Kg. of cotton yarn is treated with 10 Kg. of fused maleic anhydride for 30 minutes at 50–95° C., and then washed. Another treatment gives the proportions of 1 Kg. of cotton, 1·2–1·5 Kg. of maleic anhydride and 9 Kg. of acetic acid, and the reaction is stated to require four hours. The use of copper sulphate as a catalyst shortens the time of reaction.

Aromatic Esters

Cellulose Benzoate

Cellulose esters of benzoic acid may readily be obtained by the action of benzoyl chloride on cotton or hydrocellulose, but the general method is to follow the Schotten-Baumann reaction, in which the material is treated with benzoyl chloride in presence of caustic soda solution. The degree of esterification depends on the alkali concentration. This interesting and important fact was first observed by Cross and Bevan ("Researches on Cellulose," 1895–1900, p. 34), and confirmed by Ost and Klein (Zeit. angew. Chem., 1913, *26*, 437), who showed graphically the relationship between benzoyl content and alkali concentration. This reaction may also be regarded as one of the general esterification methods for cellulose by treating soda cellulose with an acid chloride.

$$C_6H_{10}O_5NaOH + C_6H_5COCl \longrightarrow C_6H_9O_4\,(O.CO.C_6H_5)$$

Repeated applications of this process appear to produce a limit of esterification corresponding to between two and two and a half benzoyl groups for every $C_6H_{10}O_5$ residue. Lower proportions of benzoic acid, combined with cellulose, have been assumed to be mixtures of cellulose with the higher ester, but Herzog and Londberg (Ber., 1924, *57*, 329) have obtained a residue of cellulose from the lower esters. Cross and Bevan obtained a fibrous mono-benzoate by careful adjustment of the alkali concentration and removal of cellulose and the higher benzoates by means of suitable solvents. A structureless dibenzoate resulted from an increase in the amount of alkali and benzoyl chloride. Kita and his colleagues (J. Cell. Inst., Tokyo, 1926, *2*, 30) obtained products, which, after extraction with cuprammonium hydrate solution, appear to be mono-esters. In this case the reaction was effected with various concentrations of alkali. The acid content of the ester increased rapidly with alkali concentration up to 15% (by vol.) and then slowly up to 35%.

Mono-substituted esters also result from the use of halogen substituted benzoyl chlorides.

Wohl (Zeit. angew. Chem., 1903, *16*, 285) has obtained a cellulose tribenzoate by treating cellulose with an excess of benzoyl chloride in presence of pyridine and employing nitrobenzene as a solvent for the ester produced. The reaction was effected at 110 to 130° C.

Atsuki and Shimoyama (Cell. Ind., Tokyo, 1926, *2*, 336) report that cellulose di-benzoate is prepared by treating regenerated cellulose with 35 % sodium hydroxide solution, ageing for 24 hours and then shaking with benzoyl chloride dissolved in benzene. The proportions of the reagents were $C_6H_{10}O_5$: 4 NaOH : 10 C_6H_5COCl. The reaction was completed by heating at 50-60° C., for one to two hours. The dibenzoate from regenerated cellulose gives clear solutions in chloroform, but that from normal cellulose is not completely soluble, and the viscosity is very high. The higher benzoates appear to be soluble in chloroform, and in some cases, nitrobenzene. Dibenzoates are also soluble in acetone, acetic acid, pyridine and phenol. They are insoluble in ether and alcohol.

According to Cross and Bevan, the saponification of cellulose benzoates with alcoholic sodium hydroxide is unsatisfactory, and for purposes of analysis, it is preferable to digest the ester with alcoholic sodium ethylate solution in the cold for 12 hours.

Cellulose Furoate

It seems probable that pyromucic acid is the compound referred to, as furoic acid, by Kobe and Montanna (J.A.C.S., 1931, *53*, 1889). Cellulose furoate was prepared on account of its suggested similarity to cellulose benzoate and also because of the novelty of making an "all cellulose ester," as furoic acid may be prepared from furfuraldehyde—a decomposition product of cellulose.

Cellulose di- and trifuroates were prepared by treating standard cellulose with furoyl chloride in presence of pyridine. The esters were dark-coloured fibrous products, insoluble in the usual solvents for cellulose esters. A considerable degradation of the cellulose takes place during the reaction.

Cellulose O-Chlorbenzoate

Cellulose o-chlor-benzoate has been prepared by Clarke and Malm (U.S.P. 1,704,283). The previous attempts to prepare hydro-cellulose esters of monochlorbenzoic acids (Zeit. angew. Chem., 1913, *26*, 137) had resulted in the formation of mono-esters, i.e. one atom of halogen for each $C_6H_{10}O_5$ residue, and these esters were not soluble. However, by the use of chlor-acetic anhydride and magnesium perchlorate the esterification was carried above the mono-ester state sufficiently to impart solubility in chloroform. The amount of combined halogen

was found to be 14 to 18% of the weight of the ester. The halogen is stated to be so firmly combined that it does not injure photographic light-sensitive emulsions when the latter are placed in contact with the purified ester.

The ester is stated to be formed in about five hours at 60 to 65° C., and is isolated by precipitation into methyl alcohol.

Cellulose Naphthenate

The naphthenic acid esters of cellulose have been prepared by Kita, Mazume, Nakashina and Sakurada (Cellulose Ind., Tokyo, 1926, *2*, 31). Naphthenic acid fractions, having acid values from 199 to 250, and freed from hydrocarbons, were used in the form of the anhydride and acid chloride. With the former, the degree of esterification is low, but with the latter, in presence of pyridine, compounds were obtained containing 2·5 molecules of naphthenic acid to one molecule of cellulose. Hydrocellulose reacts more readily than normal cellulose. Alkali cellulose and the acid chloride produce a compound containing up to one molecule of naphthenic acid to four molecules of cellulose.

These esters resemble those of the higher fatty acids and those with high naphthenic acid contents show definite melting points. Esters from normal cellulose are substantially insoluble, being only partly soluble in benzene. Solubility depends on the state of the original cellulose as well as the naphthenic acid content. The diester from hydrocellulose is completely soluble in benzene, chloroform, carbon tetrachloride and ether. The originally insoluble esters become soluble in these media after fusion.

B.P. 305,947, describes the production of cellulose naphthenate by heating 100 g. of cellulose on the steam bath with 700 cc. of chlorbenzene, 400 cc. of naphthenic acid chloride (b.p. 95–120° C. at 12 mm.) and 200 cc. of α picoline for about three hours. This forms the insoluble cellulose naphthenate, which is made soluble by heating for 20 minutes at 135° C. The ester is precipitated into acetone and is soluble in benzene, dichlormethane, chloroform, ether, and in ethyl acetate. It swells strongly in benzine.

Cellulose Phthalate

The possibility of the use of cellulose phthalate as a " dope " to replace cellulose acetate, was investigated by Levey

(Ind. Eng. Chem., 1920, *12*, 743). A compound of formula $C_8H_4O_3 8C_6H_{10}O_5\ 4H_2O$, was prepared by heating hydrocellulose for 24 hours at 70° C. with phthalic anhydride in presence of a condensing agent. The use of $ZnCl_2$, or other catalyst, appears to be essential. Ethyl phthalate or acetic acid is used as the medium in which the reaction takes place. The resulting ester is well washed and dried in vacuo, at a temperature not exceeding 70° C. The cellulose phthalate thus prepared is insoluble in ether, alcohol, acetic acid, ethyl phthalate and other ordinary solvents.

Further work on the phthalic ester is described in U.S.P. 1,704,305—B.P. 410,118, where the triester is obtained by treating cellulose with phthalic anhydride in presence of an organic base until a dope is obtained. One of the carboxyl groups reacts with the cellulose, and the other with the organic base and the free acid ester is liberated by treatment with acid.

Natural cellulose requires a week at 60–65° C., but the reaction is quicker at a higher temperature or when pre-treated cellulose, particularly regenerated cellulose, is used. In all cases the temperature must not exceed 95° C. The ester is precipitated into a non-solvent, e.g. the compound containing 74 % combined phthalic acid is precipitated into methyl alcohol. The use of phthalic anhydride, in varying proportions, enables esters containing 72, 54, and 21 % phthalyl to be made. These are soluble in water containing a base, and in mixtures of pyridine and benzene, pyridine and tetrachlorethane, etc.

Cellulose Cinnamate

Frank and Mendrzyk (Ber., 1930, *63*, 875) have prepared cellulose tricinnamate by the action of the acid chloride and pyridine on cellulose. If the product is heated with trichloracetic acid, then a secondary cinnamate is obtained, which is soluble in hot acetone, and in cold benzene. When the solution in hot acetone is cooled, then a crystalline constituent may be separated and also an amorphous fraction precipitated with methyl alcohol. Both the fractions have the same specific rotation and appear to lie between the di- and tri-esters in composition. Saponification of the crystalline fraction yields a product which is soluble in dilute sodium hydroxide solution, and gives an X-ray diagram corresponding to cellulose hydrate.

Cellulose Phenylacetate

Cellulose phenyl acetate may be prepared according to the methods of B.P. 313,408, by the use of the acid in presence of chloracetic anhydride and magnesium perchlorate. It has also been prepared from phenylacetic acid chloride (B.P. 305,947). The example refers to the preparation of a mixture of 480 cc. of commercial pyridine bases, 1500 cc. of chlorbenzene, 700 cc. of phenyl-acetylchloride and 200 cc. of chlorbenzene. This was heated to 80° C. and 100 g. of cotton linters introduced. The mixture was heated with stirring for one hour at 115–120° C., when the cotton dissolved. The solution was then precipitated into alcohol and the crude ester extracted four times with boiling alcohol. Cellulose phenyl-acetate prepared in this manner contains 77% of combined phenyl-acetic acid. It is hard and brittle when cold, but softens at 80° C. and melts at 140° C. Suitable solvents are the benzene hydrocarbons and the halogenated aliphatic hydrocarbons.

Other Esters

The halides of cyclic substituted fatty acids, or of alicyclic carboxylic acids, may be caused to react with cellulose in a suitable diluent in presence of pyridine at a temperature of above 100° C., according to B.P. 305,947, to form cellulose esters which are soluble in the usual solvents, but if the cellulose is esterified below 100° C. then it is necessary to heat the primary ester to above 100° C. in order to obtain the desired solubility.

B.P. 347,451 describes the esterification of cellulose by halides of saturated, or unsaturated, heterocyclic carboxylic acids, or of heterocyclic substituted fatty acids, e.g. the carboxylic acids of furane, coumarone, thiophene, pyrrole, indole, piperidine, pyridine, quinoline, pyrazine, etc. The resulting cellulose esters possess the properties peculiar to their class and also to the acid radical introduced. Hence the esters with nitrogen in the ring form salts with acids, and also addition compounds, many of which are soluble in water.

Cellulose Esters of Sulphonic Acids

Comparatively little work has been done on the cellulose esters of the sulphonic acids, presumably, on account of the high cost, but p-toluenesulphochloride has been used, as it is

readily obtainable as a by-product in saccharin manufacture. Benzene sulphochloride has also been used.

B.P. 195,619 discloses the treatment whereby bleached cotton, yarn or cloth is allowed to stand for some time in an alcoholic solution of sodium hydroxide. It is then rinsed, dried and immersed at 15–20° C. in carbon tetrachloride containing the sulphochloride. The temperature rises with the course of the reaction and is then allowed to fall, and is finally raised nearly to the boiling point. The material is subsequently passed through a soap bath at 60° C. and is later washed and dried. The final product is yellowish-white, and may have had its weight increased by as much as 20%.

Cotton material treated in this manner is immune to the usual cellulose dyestuffs, as are all cellulose esters. The amount of esterification is small, and the view was expressed by Tagliani that the surface layer of ester prevented deeper action. Sakurada and Nakashima (Sci. Papers Inst. Phys. Chem. Res., 1927, *6*, 214) investigated the influence of temperature, time, concentration and mass of reagents in the esterification of cellulose by aromatic sulphonyl chlorides. They obtained compounds containing one molecule of acid to one or two $C_6H_{10}O_5$ groups. Further work (Cellulose Ind., Tokyo, 1926, *2*, 405) shows that the acid content of the ester is not influenced by the temperature of the reaction between 8 and 30° C., but at 30–80° C. the product contains a lower proportion of acid. Excess of acid chloride merely reduces the time of reaction. The reaction proceeds further with excess of alkali, but a definite maximum esterification is reached. In this behaviour and also in the fact that there is no sudden liberation of heat, the reaction differs from those between alkali cellulose and the carboxylic acid chlorides. Alkali cellulose prepared by the action of a 15 to 35% by volume alkali solution yields, with p-toluene sulphonylchloride, an ester containing one molecule of acid to two molecules of $C_6H_{10}O_5$. If an excess of alkali is added before esterification, the product consists mainly of the monoester, but if the esterification is repeated five times, the acid content of the product corresponds with that of a mixture of the mono- and diesters. An ester with a higher acid content is difficult to obtain even by esterification in presence of pyridine under conditions, which in the case of the carboxylic acid chlorides, give di- and triesters. The ester with an acid content above that required for the monoester is more stable to heat than esters of lower acid content.

Chippindale (J.S.D.C. 1934, *50*, 144) states that microscopic investigation shows that only the outer layers have been transformed to the ester, as cross sections of yarn dyed with acetate dyes show a dyed ring surrounding non-esterified fibre. The thickness of the ring is stated to depend on the alkaline pretreatment, but in all cases, the esterified portion is only a small proportion of the whole. Cuprammonium solution attacks the fibre only in those parts where it has been cut, the cellulose swells under the esterified coat, bursts the ester layer and disconnects itself. The cellulose finally dissolves, leaving the ester layer as a spiral tape. Alternatively, the outer esterified layer of these fibres can be dissolved with pyridine, leaving the unesterified centre as a somewhat thinner fibre.

Riesz (Bull. Soc. Ind., Mulhouse, 1933, *99*, 349) has examined the reaction between alkali cotton cellulose and aromatic sulphochlorides, whereas the work of Kita and his colleagues refers to regenerated cellulose.

The determinations of Riesz are analagous to those of Karrer (Helv. Chim. Act., 1926, *9*, 597) and of Wolf (Text. Col., *53*, page 171), who found one toluene sulphonic acid group to 9 or 10 $C_6H_{10}O_5$ groups. Riesz found that in the case of aminobenzene trisulphonic acid chloride one equivalent of the acid chloride can esterify three times as many $C_6H_{10}O_5$ residues.

Other reactions with aminosulphonic acid chlorides are described in B.P. 322,556.

CHAPTER FIFTEEN

MIXED ESTERS

THE greater part of the information on the preparation and properties of the mixed esters of cellulose comes from patent specifications. This is probably due to the fact that research along these lines has been developed from purely technical motives, i.e. to produce esters which have certain novel properties which may lead to commercial exploitation, or to obviate known defects in the existing simple esters and so improve their properties, thus rendering them more valuable.

A survey of this work would amount to an annotated catalogue of patents, many of which are without scientific value: it is, therefore, proposed to give a brief survey of the main types of mixed ester, and readers who require more information are referred to the first volume of the comprehensive "Celluloseverbindungen und ihre besonders wichtigen Verwendungsgebiete," by O. Faust (1935).

Nitrate-acetate

A typical example of a mixed ester is cellulose nitroacetate, which seems to have received more attention than any other mixed ester, probably on account of the possibility of improving the technical properties of cellulose nitrate and the fact that a great deal of information is available concerning both cellulose acetate and nitrate. Kruger (Cellulosechemie, 1930, *11*, 220) has given an interesting account of his investigations of the action of mixtures of nitric acid, sulphuric acid, acetic anhydride and glacial acetic acid on cellulose. For a considerable concentration region, the product obtained was pure cellulose nitrate, which showed a variation in solubility in ether-alcohol, with variation in nitrogen content similar to cellulose nitrate prepared in the usual manner. With a decrease in the proportion of nitrating acid there followed a region in which nitro-acetates were produced. These, at first, showed the same solubilities as the pure nitrates, but the resemblance decreased with a decrease in the nitrogen content.

It was not found possible to produce a nitroacetate, combining reduced inflammability with satisfactory solubility, for practical application. Owing to the unstable nature of acid mixtures of certain composition it was not possible to pass continuously from nitroacetates to pure acetates by changing the composition of the acid mixture. The same author has reviewed the literature relating to the acetylation of cellulose nitrate and the nitration of cellulose acetate (Kunststoffe, 1930, *20*, 73). Fibrous cellulose triacetate, treated for a short time at 0° or 30° C., with nitrating acid containing 15% of water, is not nitrated, but saponified. If the acid only contains 9·1% of water, a nitrated product gradually separates from the solution. Highly nitrated cellulose is only slowly attacked by the usual acetylating agents. A typical example shows that if 2·4 g. of dry cellulose nitrate (12·5% N) are treated with 9·5 cc. acetic acid, 9·5 cc. acetic anhydride and 0·29 g. H_2SO_4 for one hour at 30° C., and slowly cooled to room temperature over a period of about 20 hours, and the gelatinous mass precipitated with water, the product contains 8·32% of nitrogen. The analysis of the nitroacetate is also dealt with by Kruger (*ibid*, page 193). The sulphuric acid saponification mixture is diluted with water and distilled directly, or steam distilled. The residue is evaporated and extracted with absolute alcohol. The acetic acid in the dry residue of the alcohol extract may be determined microchemically, as sodium uranyl-acetate, in the presence of a large excess of nitric acid. The same process may be applied to the analysis of other mixed esters; with mixed organic esters an alkaline saponification without distillation may also be used. The uranyl reagent consists of one g. uranyl formate, one g. sodium formate, one g. of 50% formic acid, 3·5 g. of 96% alcohol and 3·5 g. of water.

According to B.P. 341,147, cellulose nitroacetate may be prepared by simultaneous application of the organic esterifying agent (i.e. the acetylating agent), and the nitrating agent. Catalysts are stated to be unnecessary, for the HNO_3 acts as a catalyst for the introduction of the acetyl group whilst the acetic anhydride acts catalytically towards the nitration of the cellulose. Mixed nitroacetates of very high nitrogen content may be obtained, and these may even be stable. An actual example refers to the mixing of 1,100 parts of acetic anhydride with 400 parts of fuming nitric acid, both liquids being cooled before mixing. The mixture is further cooled in

ice-water and 100 parts of cotton linters added. The mass is well stirred and allowed to stand for 24 hours. Any free anhydride is then hydrolysed by the addition of the requisite amount of water. An excess of water is added and the mass allowed to ripen for 24 hours at a temperature of 20–30° C., or until a sample precipitated in water shows the desired solubility, e.g. in acetone. The whole of the ripened ester may then be precipitated. The product was found to have a nitrogen content of 13·79%, and an acetic acid content of 32·34%.

Phosphate-acetate

The manufacture of cellulose phosphoacetate is described in B.P. 8647 of 1910, where one kg. of cellulose is mixed with two litres of acetic acid to which 50 cc. of sulphuric acid and the same amount of phosphorus oxychloride are added. As soon as a thin paste is produced, about three kg. of acetic anhydride are slowly added with cooling. As soon as all the cellulose has dissolved, 200 cc. of 10% phosphoric acid are added. This is allowed to stand for 10–12 hours, and is then precipitated with water. The solubility of the ester is stated to be high, e.g. 50–75% in acetone.

The method of B.P. 300,942 is illustrated by the following example, which deals with the esterification of an ester of cellulose containing free hydroxyl groups, i.e. incompletely esterified.

Five hundred g. of cellulose acetate, containing 54% combined acetic acid, is swollen in 2,000 cc. of heated pyridine and 1,000 g. of monophenyl phosphate added. The mixture is boiled for two hours and the product then precipitated by alcohol. This process yields a cellulose-acetate-phosphate, containing from 10·8 to 11% of PO_4, and soluble in ethyl alcohol, butyl alcohol, and acetone.

Other Inorganic-organic Esters

The same specification mentions the preparation of cellulose laurate phosphate by the partial esterification of cellulose with lauric chloride; the product is not separated but treated with phosphorus oxychloride in presence of pyridine. The mixed ester resulting, contains 65·5% of lauric acid and 4·2% of phosphoric acid, and is soluble in chloroform, methylene chloride, xylene and benzene.

Mixed esters may be obtained from cellulose nitrate by the methods of B.P. 219,926, where the nitrate is treated with chlorides of the higher fatty acids in presence of pyridine. Cellulose - nitrate - laurate and cellulose - nitrate - oleate are mentioned.

A somewhat large range of mixed esters of indefinite composition may be made by D.R.P. 556,951, where the cellulose ester of a fatty acid is treated with such inorganic acid chlorides as phosgene, thionyl chloride, sulphuryl chloride, silicon tetrachloride, etc., to form mixed organic-inorganic esters of cellulose.

F.P. 717,623 describes the preparation of cellulose acetochromate and cellulose acetosilicate. The former is prepared by the treatment of cellulose acetate, containing 56% acetic acid, with chromium oxychloride at room temperature under reduced pressure. The product is soluble in acetone. The acetosilicate is also prepared from a cellulose acetate of similar composition by treatment with silicon tetrachloride. The mixed ester is insoluble in acetone and contains 6·4% silicon dioxide. The sulphate-acetate has been mentioned on pages 307 and 310.

Mixed Organic Esters

Cellulose acetate-formate has received only slight attention compared with other mixed acetates—a typical method of preparation is given in B.P. 266,300, where cellulose is first treated with formic acid, containing a small amount of H_2SO_4, and the product then treated with acetic acid, containing a larger amount of the catalyst. The mixed ester is stated to be soluble in formic acid, formaldehyde, pyridine, and solutions of urea, cyanates, sulphocyanides, alkali nitrates and calcium chloride.

The manufacture of cellulose acetate-butyrate and cellulose acetate-propionate is covered by a large number of patents. The main methods, however, have already been described in the section dealing with esterification, and for the production of the mixed ester the same methods apply. It is possible to begin with cellulose and esterify with a mixture of the esterifying agents, or partially to esterify with one agent and complete esterification with another, often without isolating the first product.

Hence we may have an esterification mixture made of :

(i) acetic anhydride or acetyl chloride, and the chloride, or anhydride, of a higher fatty acid.

(ii) acetic anhydride or acetyl chloride, and a higher fatty acid.
(iii) acetic acid and the chloride or anhydride of the higher fatty acid.
(iv) acetic acid and a higher fatty acid.

The last instance may appear remarkable, in view of the more active nature of the previous mixtures, but the methods developed by the chemists of Kodak Ltd., employing an " impeller," such as a halogen-substituted fatty acid anhydride, and mentioned in the section on the simple esters, allow of this method of preparation.

Mixed esters of higher fatty acids have been made, e.g. cellulose propionate-butyrate is prepared by an esterification mixture of propionic anhydride and butyric acid (B.P. 356,665); and cellulose stearate-crotonate is made by treating cellulose with a mixture of stearic and crotonic acids in presence of chloroacetic anhydride and magnesium perchlorate (B.P. 289,582).

Fibrous mixed esters may be made from a reaction mixture containing an acyl halide, the sodium salt of a different fatty acid, a catalyst and an anti-solvent as described in U.S.P. 2,051,217.

Mixed esters may be made by treating cellulose with keten, and an organic acid other than acetic, as disclosed in U.S.P. 1,990,483. Keten has also been used in reaction with a cellulose ester containing 0·25 to 1·5 acyl groups per glucose residue; U.S.P. 2,053,280 refers to the catalyst perchloric acid in presence of a halogenated hydrocarbon as solvent for the end-product.

Cellulose acetate-carbamate has been prepared by treating cellulose acetate with phenyl carbimide in pyridine or cyclohexanone as mentioned in U.S.P. 1,991,107; the product is stated to be resistant to heat and to alkali.

Mixed esters from dibasic organic acids have been discussed by Malm and Fordyce (Ind. Eng. Chem., 1940, *32*, 405). Cellulose acetate phthalate is readily accessible on account of the availability of phthalic anhydride. The physical properties of the mixed ester vary with the amount of combined phthalyl, the melting point falling with increase in phthalyl content. Only minor changes in solubility are seen up to some 15% phthalyl, when the product becomes soluble in dilute NaOH and in organic solvents such as mixtures of benzene and alcohol.

Solubility of Mixed Esters

	Water.	Alcohol.	Ether.	Acetone.	Acetic Acid.	Benzine.	Benzol & homologues.	Chlorinated Hydro-carbons.
Acetate propionate	insol.	insol.	insol.	sol.	sol.	insol.	insol.	sol.
Acetate butyrate .	,,	,,	,,	,,	,,	,,	slight swell.	,,
Acetate laurate .	,,	,,	swell.	sol. hot.	,,	slight swell.	sol. hot.	,,
Acetate butyrate laurate	,,	,,	strong swell.	sol.	,,	insol.	sol.	,,
Butyrate laurate .	,,	,,	swells.	,,	,,	,,	,,	,,
Napthenate laurate .	,,	swells.	sol.	swells.	sol. hot.	sol.	,,	,,
Napthenate oleate laurate .	,,	,,	,,	,,	,,	,,	,,	,,

With higher phthalyl contents, the ammonium salt of the mixed ester is soluble in water and the ester itself is soluble in a wider range of organic solvents. Insoluble metal salts may be made from these derivatives by utilising heavy metals. (These mixed esters are described in U.S.P. 1,969,741; 2,040,093; 2,082,804 and 2,108,455.)

The use of mixed acid chlorides is shown in B.P. 300,207, which refers to the esters of estolidic acid—the inner condensation products of the higher hydroxylated fatty acids. In some of these mixed esters with the higher fatty acids, the amount of cellulose residue may be a very small proportion of the ester, 1·5 to 6%, being mentioned. A method of preparation is to heat 10 parts of cotton linters with 35 parts of lauryl chloride and 10 parts of triricinoleyl chloride in chlorbenzene and pyridine, for 90 minutes, at 125 to 135° C. The mixed ester may be used as a substitute for cork.

The use of mixed chlorides is also seen in B.P. 305,947. Here the product is sometimes heated for a longer period than that necessary to produce the ester, for the purpose of improving its solubility. Cellulose butyrate-ricinoleate is prepared by treating 100 g. of cellulose with 200 g. of butyric acid chloride, 350 g. of ricinoleic acid chloride and 500 g. of pyridine in 700 g. of chlorbenzene, for 12 hours at 85 to 90° C. A further 10 g. of butyryl chloride is then added, and heating at 135° C. maintained for one hour. The mixed ester is precipitated by ethanol and purified by extractions with warm methyl alcohol. It is soluble in the benzene hydrocarbons and in aliphatic halogenated hydrocarbons.

Cellulose acetate-palmitate may be prepared by similar means, 100 g. of cotton linters is added to a mixture of 1,180 cc. of chlorbenzene and 235 g. of pyridine, which is warmed to 50° C. About 47 cc. of acetyl chloride is added and the mixture heated for several hours on the steam bath, when 70 g. of pyridine bases and 424 g. of palmityl chloride are added and heating continued for 20 hours. The mixed ester, which has been made in two stages, is converted to the soluble ester by heating at 120° C. It is soluble in aromatic hydrocarbons and halogenated aliphatic hydrocarbons.

General Properties

The properties of some of the mixed esters have been described, and compared, by Hagedorn and Möller (Cellulosechemie, 1931, *12*, 29), and are shown in the following table:

STRENGTH AND EXTENSION DATA.

	Strength kg./sq. mm.	Extension %
Acetate-propionate	9·7	12
Acetate-butyrate	7·3–8·5	20–25
Acetate-laurate	2·0–3·0	60–85
Butyrate-laurate	3·5–5·0	60–70
Acetate-butyrate-laurate	3·5	85
Acetate-benzoate	8·3	12
Butyrate-benzoate	7·0	35
Naphthenate-laurate	1·2	200

Cellulose acetobutyrate and acetopropionate are in full commercial production in America and offer considerable promise. They are soluble in a wider range of solvents than the acetate, they are more easily plasticised and are more resistant to water and weather.

Fordyce and Meyer (Ind. Eng. Chem., 1940, *32*, 1059) have made a comparison of cellulose acetate (38·5% acetyl) and cellulose acetobutyrate (37% butyryl and 13% acetyl) in respect of plasticising with methyl, ethyl and methoxyethyl phthalates; the mixed ester always possesses superior properties.

Unsaturated Esters

Mixed esters, from unsaturated fatty acids, may be prepared by the methods disclosed in the Kodak patents. Cellulose nitrocrotonate is soluble in acetone and acetic acid, but insoluble in chloroform and in ether. It is prepared by treating nitrocellulose with crotonic acid in presence of chloracetic anhydride and magnesium perchlorate (B.P. 290,570). Cellulose acetate-crotonate is prepared by treating cellulose with a mixture of crotonic acid, acetic anhydride and chloracetic acid in presence of magnesium perchlorate. It is soluble in chloroform and in acetone. The cellulose may first be partially converted to the crotonate and the mixed ester prepared by acetylation. Cellulose aceto-undecylenate may similarly be prepared in the manner involving one esterification only. This, too, is soluble in either chloroform or acetone. Saturated groups from the higher fatty acids may similarly be introduced along with unsaturated groups, e.g. cellulose crotono-stearate may be formed and is soluble in chloroform, acetone and benzol. These instances of mixed

esters, containing unsaturated groups, are taken from B.P. 289,582. Another method (D.R.P. 550,260) is to use acetyl chloride and crotonic acid chloride.

Metathesis

A somewhat unusual method of making mixed esters is shown in F.P. 702,116, where cellulose acetate or some other organic ester of cellulose is heated with an organic acid of higher ionisation constant. The acid should, preferably, be one which is a solvent for the initial ester, and in some cases, the presence of water is desirable. Amongst the interesting compounds obtained in this manner are cellulose acetate-oxalate, which is soluble in water and in alcohol; cellulose acetate-tartrate, which is soluble in acetone-water, cellulose acetate-lactate (from acetone soluble acetate) which is soluble in acetone-water, whereas the acetate-lactate from acetone-insoluble cellulose acetate is soluble in alcohol-water. Cellulose acetate-maleate has thus been prepared for the first time, and contains 16·7% of maleic acid and 7 to 7·5% of acetic acid. A water soluble cellulose acetate-glycerate has also been made. Cellulose acetate-pyruvate is soluble in acetone, but gelatinises in water and in ethyl alcohol. A cellulose pyruvate-benzoate has been made by this method from cellulose tribenzoate and found to be soluble in chloroform, ethylene chloride and chloroform-alcohol, but insoluble in acetone and benzol. Cellulose acetate-phenylglycollate is soluble in chloroform and in acetone. Cellulose acetate-salicylate melts at 248–271° C., and is soluble in alcohol-water, acetone-water and alcohol-chloroform, but insoluble in acetone, water and benzol-alcohol.

Halogenated Esters

Mixed esters containing halogen-substituted fatty acid groups have received comparatively little attention. Cellulose nitrocrotonate (see B.P. 290,570) may be brominated in acetic acid solution in about two hours. Cellulose dibromobutyrate-nitrate is soluble in acetone, acetic acid and ether, but insoluble in chloroform and in alcohol. The product contains 17·8% of bromine and 6·8% of nitrogen.

U.S.P. 1,698,049 reveals that in the case of halogen-substituted fatty acids containing more than 5 carbon atoms, the inhibiting effect of the halogen on esterification does not apply as in the case of the lower fatty acids. The reaction is carried out in the presence of monochloracetic anhydride and a catalyst.

Hence, by the use of say, α-bromostearic acid and acetic acid, the mixed ester cellulose aceto-α-bromostearate may be obtained. This is soluble in acetone, chloroform and benzene. It is stated to contain 11·3% of bromine. Other mixed esters prepared in this manner are cellulose acetate-9:10 dibromstearate (containing 23% Br.), the corresponding dichlorstearate, cellulose acetate-tetrachlorstearate, and cellulose aceto-α-bromocaproate.

Cellulose acetate dibromostearate may also be made from cellulose acetate by the treatment of the latter with an unsaturated acid (oleic acid). The acetate-oleate is prepared in presence of chloracetic acid, chloracetic anhydride and magnesium perchlorate and then brominated in chloroform solution. The product is stated to contain 34·5% of acetic acid and 19% of bromine (U.S.P. 1,698,048).

Hydroxy-esters

Certain patent specifications contain examples of mixed esters containing hydroxyaliphatic acid groups. Cellulose lactate-formate may be prepared, according to D.R.P. 239,701, by dissolving cellulose formate in lactic acid. The anhydrides of hydroxy fatty acids are employed in conjunction with other acid anhydrides to produce mixed esters of cellulose in B.P. 316,160. Examples mentioned are those containing glycollic, lactic, hydracrylic acid, etc., in conjunction with, say, acetate. Corresponding esters are referred to in B.P. 314,919, where the alkyl ether of the hydroxy fatty acid forms part of the mixed ester and which is prepared in a similar manner, e.g. cellulose acetate-methoxyacetate.

The process of digesting cellulose acetate solution with a hydroxy acid is covered by B.P. 338,210. The reaction is effected at about 100° C., and it is essential that the initial ester be soluble in the acid employed. For example, an aqueous solution of 65–85% of lactic acid will dissolve cellulose acetate as will a 77% solution of tartaric acid; but if glycollic acid is used, the addition of water is unnecessary. Water soluble mixed esters thus produced are cellulose acetate-lactate; acetate-glycollate; acetate-tartrate; acetate-glycerate; acetate-malate. Mixed esters may be prepared containing varying proportions of the substituent acid radical, and these differ somewhat in their properties, e.g. the progressive solubility of cellulose acetate-malate has been observed from solubility in acetone, in a mixture of 75% alcohol, 25%

water, in a mixture of 50% alcohol-water to final solubility in water alone, as the proportion of malate increases in the mixed ester.

The method of heating a cellulose ester with an acid of higher ionisation constant already referred to, may also be employed to produce mixed esters containing hydroxy aliphatic acid radicals.

Ketonic-esters

The method of digesting a simple ester with another acid has also been used to produce mixed esters from a carboxylic acid containing a ketonic group in the α or γ position, e.g. pyruvic, levulinic, etc., and the examples mentioned (B.P. 338,202) generally employ cellulose acetate as the basis of the mixed ester.

Treatment of the cellulose ester with an acid of higher ionisation constant than that of the acid incorporated in the ester may also be used for mixed esters containing a radical from a carboxylic acid with a ketonic group (U.S.P. 1,861,200), and also for the production of mixed esters containing esters of dicarboxylic acids.

Aromatic Esters

Mixed cellulose esters containing residual groups of aromatic carboxylic acids are also dealt with in various patent specifications. Cellulose nitrate-benzoate may be made by the methods of D.R.P. 411,208, where cellulose nitrate is treated with the aromatic acid chloride in the presence of an acid binding compound, e.g. pyridine. The product contains 4·5% combined benzoic acid.

Cellulose acetate-benzoate may be made by the method of F.P. 435,507, which utilises a mixture of the anhydrides of acetic and benzoic acids in presence of a halogen catalyst.

The previously described methods involving the use of chloracetic acid or the anhydride may also be used for this class of mixed ester. U.S.P. 1,704,306 refers to the fact that in the case of the reaction between cellulose and phthalic acid, it has been found advisable to esterify one carboxyl group of the acid with an alcohol before reacting with cellulose. If ethyl hydrogen phthalate is allowed to react with cellulose in presence of acetic acid, using the chloracetic acid, chloracetic anhydride, magnesium perchlorate method, then the mixed

ester, cellulose acetate-phthalate, may be isolated. It is soluble in acetone, chloroform and benzol.

The method of " impelling " by chloracetic anhydride has been employed to make cellulose acetate-orthochlorbenzoate utilising o-chlorbenzoic acid. According to the proportions of the reactants the mixed ester is soluble in either acetone or chloroform. It is important to note that according to U.S.P. 1,704,283, all the halogen substitutes esters of cellulose produced in this manner have the halogen so strongly held to a carbon atom in the ring that it does not tend to split off and attack other substances with which the ester may be mixed in technical application.

Some interesting mixed esters containing aromatic acid groups have been prepared by the " higher ionisation constant " method. For example, in U.S.P. 1,785,466, there is mention of cellulose acetate-salicylate m.p. 248–271° C., soluble in 75% solutions of alcohol-water, acetone-water, alcohol-chloroform; cellulose acetate-mandelate soluble in chloroform and acetone; cellulose acetate-metatoluate m.p. 215–232° C. and soluble in 75% aqueous 1 : 4 dioxan.

Cellulose acetate-phenyglycollate has similarly been prepared. It is soluble chloroform and in acetone (U.S.P. 1,861,200).

Cellulose phenylacetate-laurate has been made by the method of B.P. 305,947, where the chloride of a fatty aromatic acid and a higher fatty acid are brought into reaction with cellulose in presence of a tertiary organic base at a temperature of 80° C. The mixture is then heated for two hours at 130° C. and then poured into methyl alcohol. It is purified by repeated extraction with this reagent and is soluble in the benzene hydrocarbons and in the halogenated aliphatic hydrocarbons.

The same specification mentions the preparation of cellulose laurate-naphthenate by reacting cellulose with lauryl chloride for 12 to 20 hours on the steam bath, followed by the addition of the naphthenic acid chloride and pyridine. A further period of heating for 1 to 3 hours at 110 to 120° C. results in the formation of the mixed ester which is separated by precipitation and extraction with ethyl alcohol. Owing to the presence of the naphthenic acid group, this ester softens at a temperature of over 50° C. It is soluble in the benzene and halogenated aliphatic hydrocarbons.

Another example from the same patent is the formation of cellulose acetate-naphthenate from cellulose acetate by treat-

ment with naphthenic acid chloride at 110-120° C. until the desired solubility in chloroform and in benzene is obtained. The mixed ester is separated and purified by means of alcohol, as in the previous examples.

According to B.P. 355,172, mixed esters may be prepared by the treatment of a cellulose ester containing free hydroxyl groups, with the chloride of a polybasic acid ester. For example, when cellulose dinitrate, monobutylphthalate, ethyl acetate and sulphuryl chloride react, the chloride of the acid ester is formed and this reacts with the free hydroxyl group of the cellulose dinitrate to form cellulose dinitrate-butyrophthalate. The mixed ester is stated to dissolve in acetone, methyl acetate, etc., and to be insoluble in benzene, ether and alcohol.

Methylcyclohexyladipic acid ester may also be utilised in the same manner.

Multiple Esters

Frequent references have been made to the method of preparing mixed esters of cellulose by treating a simple ester with an acid of higher ionisation constant than that of the acid in the simple ester. This method has been further developed in B.P. 300,058 for the production of multiple esters of cellulose. The selection of the " parent ester " is governed by the desired nature of the final product and the solvent to be used. One method of manufacture consists in dissolving a simple cellulose ester in a bath containing two or more organic acids, each of which must have an ionisation constant greater than that of the acid combined with the cellulose. For example, where the starting material is cellulose acetate, then the acids which are to be used to displace in part, the acetic acid in the ester, must have an ionisation constant greater than $1{\cdot}82 \times 10^{-5}$, which is the ionisation constant for acetic acid. When a mixed ester is under treatment it is necessary that the organic acid which is to introduce the further acyl group should have an ionisation constant greater than that of one of the acids combined with the cellulose.

In some cases, e.g. where the reacting acid is solid at the temperature of the reaction, it is necessary to dissolve it in a suitable solvent before the introduction of the cellulose ester. This solution may be made in any solvent which acts as a medium for bringing the ester into intimate contact with the displacing acid, and is not affected by the esterifying reaction.

In many cases 1 : 4 dioxan, ethylene dichloride or propionic acid have been found suitable. Water is also advantageous, as it has a tendency to accelerate the reaction. At the same time, it must be borne in mind that too great a concentration of the solvent has a tendency to decrease the rate of reaction. A suitable temperature of reaction is 100° C., and this must be kept well under 150° C. or degradation of the cellulose may result.

It is stated that the multiple esters have solubilities surprisingly different from those which would be expected from a knowledge of the mixed esters of cellulose. This is especially so with the multiple esters containing both an acetyl and two or more acyl radicals of the α-hydroxy acids or the α- or γ-ketonic mono- or dibasic acids. In the manufacture of the dual esters of cellulose containing an acetyl group and one of the above acyl groups, a product has never been obtained which is soluble both in acetone and in water. However, multiple esters which contain lactyl, acetyl and pyruvyl are soluble in acetone, 50 % ethyl alcohol, methyl alcohol and also in water. The properties will also naturally vary according to the amounts of the different combined acids.

In one example, 20 g. of cellulose acetolactate soluble in 75 % ethyl alcohol and containing 5–8 % of acetyl and 8 % of lactyl was dissolved in 50 cc. of chemically pure pyruvic acid. The mixture was heated on a steam bath for 5½ hours and then precipitated in a mixture of ether and methanol. After washing to neutrality with this precipitant, a whitish powder was obtained which contained all three acyl radicals and melted at 215–241° C. It was soluble in acetone, 50 % alcohol and in water.

Another example, commences with 20 g. of acetone-soluble cellulose acetate containing 39·8 % of acetyl. This was dissolved in a mixture of 25 cc. pure pyruvic acid and 25 cc. of lactic acid of 85 % strength. The mixture was heated to 100° C. for 17½ hours, yielding a water soluble product which was precipitated from solution and washed in a mixture of ether and acetone. This product also contained acetyl, lactyl and pyruvyl groups, but had a m.p. of 232–250° C.

The general methods of treatment with an acid of higher ionisation constant may be seen in B.P. 338,201 ; 338,202 and 360,417.

A triple ester of cellulose is also mentioned in B.P. 287,880, where chloracetic acid is used. The example refers to the

treatment of 5 parts cellulose with a mixture of 25 parts of commercial stearic acid (consisting of equal quantities of stearic and palmitic acids), 15 parts of acetic anhydride, 40 parts of chloracetic acid, and 0·05 parts of magnesium perchlorate. The reaction was carried out at 60 to 65° C. for about five hours, and a clear mixture was obtained. The ester was isolated by pouring the whole into methyl alcohol and washing the precipitate with warm methyl alcohol. The product was cellulose acetopalmito-stearate, and about 7% of its weight is due to the presence of the higher acyl groups. It is acetone-soluble.

Triple esters are also described in U.S.P. 1,984,094, which mentions cellulose acetate-phthalate-benzoate in particular; U.S.P. 2,000,596 describes cellulose acetate-lactate-phthalate.

It is obvious that a large number of mixed esters may be prepared and it is only considered necessary to outline a representative range rather than a comprehensive list.

The analysis of mixed esters of cellulose is described in U.S.P. 2,069,892. The general method is to treat the mixed ester with a hydrolysing base such as aqueous alkali, and then treat the solution of the alkali metal salts with dilute phosphoric acid to combine with the alkali metal content of the solution. The organic acids are separated by distillation so that the normality is 0·1 and a determination is made of the amount of standard alkali necessary to neutralise a given amount of the distillate. The percentage partition between the water and the extractant is determined and hence the percentages of the acyl groups may be calculated as described in the specific examples of the patent specification.

CHAPTER SIXTEEN

CELLULOSE ETHERS

CELLULOSE esters have been known for 100 years but no work on the ethers of cellulose appears to have been done before 1905, when Suida (Monat., 1905, *26*, 413) studied the behaviour of cotton wool after alkylation, towards dyestuffs, such as pararosaniline. His work was mainly of an academic nature and concerned with the dyeing properties of various colouring matters in relation to carbohydrate structure. Patented processes for the preparation of cellulose ethers were first published in 1912, by Leuchs, Lilienfeld and Dreyfus, as the result of independent work.

Etherification of other carbohydrates had attracted attention many years previous to work on cellulose, for Berthelot (Ann. Chim. Phys., 1860, *60*, 103) had treated sucrose with ethyl bromide and potassium hydroxide, Fischer (Ber., 1893, *26*, 2400) had prepared the alkylglucosides of carbohydrates, Tollens (Ber., 1899, *32*, 2585) had reacted glucose with formaldehyde containing hydrochloric acid, and Purdie and Irvine (J.C.S., 1903, *83*, 1021) worked out a method for the alkylation of glucosides by treatment with silver oxide and alkyl iodides. One of the chief technical defects of the cellulose esters is the lack of resistance to hydrolysis, but the ethers of cellulose show very attractive properties in this respect, their stability to acids, as well as alkalies, being of great importance. The methylene ethers of cellulose are an exception to this general statement, inasmuch as they are decomposed by acid but show complete resistance to alkali.

Some of the ethers of cellulose are discussed in the chapter on Aminocellulose.

Methylene Ethers

The first methylene ether of cellulose was prepared by Eschalier, who published a series of patents on processes for improving the strength of regenerated cellulose, particularly in the wet state, by means of treatment with formaldehyde in

presence of an acid. Eschalier did not recognise his products as methylene ethers.

His work was published in F.P. 347,724, of 1906, and followed by the patents of addition 8122, of 1908, 9904, 9905 and 10760, of 1909. The essence of Eschalier's process consists in the impregnation of cellulose with a mixture, such as 15 parts of 40% aqueous formaldehyde solution, five parts of 80% lactic acid and 75 parts of water. The excess of the acid formaldehyde liquor was removed by means of the centrifuge, and the impregnated material was then desiccated in a closed vessel and the reaction assisted by raising the temperature to some 40 to 50° C., for a period of from four to five hours. It was found that some difficulty was experienced in obtaining uniform results, even if the material was revolved during the desiccation. Eschalier's process caused the combination of about 0·35 to 0·8% of formaldehyde as cellulose methylene ether. This reaction has also been examined by Beltzer (Les Matières Cellulosiques, Paris, 1911, page 193) ; Bruckhaus (Oesterr. Chem. Z., 1926, *29*, 156 ; Kunstseide, 1926, *8*, 115) and Meunier and Guyot (Compt. rend., 1929, *188*, 506). Some of the differences observed by these investigators have been explained by Wood (J.S.C.I., 1931, *50*, 411 ; 1933, *52*, 33).

The Eschalier process was never a commercial success and its objects have since been achieved together with crease resistance, by means of the well-known anti-crease processes of Foulds, Marsh and Wood, of the Tootal Broadhurst Lee Co. (B.P. 291,473 and 4 ; U.S.P. 1,734,516, etc.). Anti-crease and other effects produced by means of a modification of the Eschalier processes have recently been described in B.P. 445,243, 447,651, 450,620, 452,150, 455,472, and U.S.P. 2,080,043. Still more recent processes have been protected in B.P. 460,201 ; 462,005 and 477,084. The experimental conditions vary in the different treatments, but as a wide generalisation the method is to impregnate the textile material with formaldehyde solution (the concentration varies in different treatments) containing an acid or acid forming catalyst. The material is then dried and heated and a temperature, which may vary from 90 to 150° C. for various times, according to the desired effect, the concentration of reagents and the temperature.

The type of ether produced by the general reaction, described above, is non-swelling, but high swelling cellulose methylene ethers are obtained by immersing cellulose in mixtures of

sulphuric or hydrochloric acid and formaldehyde. The main facts relating to this protective action of formaldehyde in parchmentising, as described by Foulds and Barrett (B.P. 200,881) have also been discussed by Wood (loc. cit.) and by Spietel and Schenk (Bull. Soc. Ind., Mulhouse, 1934, *50*, 109). This type of reaction is exemplified by immersing an open weave cotton fabric in a mixture of 73% H_2SO_4, containing 4 to 5% of para-formaldehyde for five minutes and then washing well with cold water. It is then refluxed with 20% ammonia to remove free formaldehyde, washed and dried. The product contained 7·3% of combined formaldehyde; it was capable of swelling with water and had an enhanced affinity for direct dyestuffs. Processes which employ acid catalysts or solutions which liberate acid during the reaction, do not give complete conversion of the cellulose to its methylene ether. This may be effected by condensing soda-cellulose with the methylene esters of inorganic acids, e.g. methylene sulphate, dichlordimethyl sulphate or chlormethoxysulphonic chloride. The last two are the most effective, according to Wood, and may be prepared by the methods of Fuchs and Katscher (Ber., 1927, *60*, 2288). The temperature of the reaction system is maintained at 60° C., as in the case of methylation, and the mixture is well stirred.

Cellulose methylene ether obtained in this manner had the formula $C_6H_7O_2(OH)(O_2CH_2)$, and on hydrolysis with mineral acid it gave 17·2% of combined formaldehyde. The ether was stable to alkali and insoluble in cuprammonium hydrate solution: it can be methylated, but complete methylation is difficult, for although there is still one free hydroxyl group per glucose residue, the product does not swell in alkali.

Most of the processes suggested in patent specifications involve a heating treatment with formaldehyde in presence of acid. This type of reaction has been examined by Saegusa (J. Cell. Inst., Tokyo, 1941, *17*, 17) who found that the product became more brittle with increasing methylenation; only products with less than 1% CH_2O could be stretched more than 10% without breaking in the case of rayon. For resistance to creasing it appears necessary to have at least 2% combined CH_2O, but for the maximum increase in wet strength (1·5 times the original) from 3 to 9% combined CH_2O is required. It does not seem possible to obtain a product containing more than 17·2% CH_2O even by repeated treatments.

Schenk (Helv. Chim. Acta., 1932, *15*, 1088) obtained a partially methylenated cellulose from a methylene cellulose acetate prepared by heating 3 g. of regenerated cellulose at 100° C. for 220 hours with 30 cc. of acetic anhydride and 25 cc. of di-isopropyl formal. The material was then washed in water and dried at 100° C. The acetic acid content was found to be 5·7% and the formaldehyde content 7·52%. The acetic acid, in combination, may be split off by hydrolysis to leave the partially methylenated cellulose.

Water-repellent textiles have been described in B.P. 477,029 by surface etherification of the material with aldehydes containing an alkyl or naphthene residue $> C_{10}$. For example, viscose rayon is treated with a 0·5% solution of stearyl aldehyde ($C_{17}H_{35}$.CHO) in light benzine, dried and heated five minutes at 150°. This reaction is not confined to the simple aldehydes nor to cellulose.

Methyl Cellulose

The original work of Suida (loc. cit.) involved the use of methyl sulphate and caustic soda; the same method was utilised by Denham and Woodhouse in a series of researches into the constitution of cellulose, which involve the hydrolysis of methylated cellulose, and which are described on page 52, where the nature of cellulose is considered.

Methyl cellulose was first described in 1912, in B.P. 12,854—the original master patent of Lilienfeld—according to which cellulose was treated with esters of inorganic acids, such as alkyl halides or sulphuric esters, in presence of basic substances. In the same year, Dreyfus published F.P. 462,274, but in January of 1912, Leuchs had filed a German application for a process involving the action of alkyl halides of cellulose derivatives, and this appears to have been allowed to remain unrecognised until it appeared as D.R.P. 322,586, in 1920.

Methyl cellulose is generally prepared by the action of methyl sulphate or chloride on soda cellulose. If methyl chloride is used then the reaction is carried out in an autoclave, on account of the low boiling point ($-24°$ C.). The methyl ether of cellulose is now an industrial product and is usually supplied in the form of its water-soluble variety. It may be prepared in two types—soluble in water, and insoluble in water but soluble in alkali, the difference in solubility depending on the degree of substitution. In the original Lilienfeld patent (q.v.) the ether passes through a water soluble stage, but

according to B.P. 164,374, the ether is not soluble in water at any stage of treatment.

Most of the patents specifications describe processes for the ethylation of cellulose as well as the methylation. The main publications of Lilienfeld may be seen in B.P. 12,854 (1912); 6036 (1913); 149,320; 156,735; 163,016-8; 181,391-5; 203,346-7; 177,809-10; 200,815-6; 200,827 and 200,834, whilst the Dreyfus patents include B.P. 176,420; 187,639; 269,531; 164,377; 164,379 and F.P. 530,891.

The classification according to solubility, involved three types (*a*) soluble in organic solvents (*b*) soluble in water and (*c*) soluble in aqueous alkaline solutions. The first type represents the highest degree of substitution, and many examples are plastic or thermoplastic. They are also extremely resistant to water and good films may be made from their solutions, but they have found little application in the textile finishing industry. The water-soluble cellulose-ethers have a lower degree of substitution and have found application in printing pastes as they are precipitated from solution on warming. The alkali-soluble ethers possess the lowest degree of alkylation, and are generally soluble in solutions of NaOH of between 5 and 12%, outside this range precipitation takes place. In some cases it is necessary to cool the alkali in order to bring about solution, which, when once effected, is stable at ordinary temperatures. The general strength of solution for practical use is up to 8 or 9% of cellulose ether.

An interesting property of the ethers which are soluble in organic solvents lies in their behaviour towards mixed solvents. For instance, the ethyl celluloses of ethoxy content between 42 and 45%, are insoluble in benzene and in alcohol, but if a 10% suspension in benzene is added to a 10% suspension in ethyl alcohol, solution occurs. Some other ethyl celluloses are not soluble in a 50 : 50 benzene-alcohol mixture, but readily dissolve in a 9 : 1 benzene-alcohol mixture.

COMPOSITION OF ETHERS.

Cellulose ether.	Methoxyl.	Ethoxyl.	Propoxyl.
Mono- .	17·61%	23·68%	28·93%
Di- . .	32·61%	41·28%	47·97%
Tri- . .	45·58%	54·87%	61·46%

The water-soluble type is probably the best known of the methyl celluloses and may be obtained under the trade marks,

Colloresin, Tylose or Glutoline. The methoxyl content varies from 22 to 26%, corresponding to the substitution of 1·5 hydroxylhydrogens per glucose residue. The type of methylcellulose which is only soluble in dilute alkali, shows a lower degree of etherification, amounting to an approximate methoxyl content of 5%.

With regard to the soluble ethers of cellulose it is stated in B.P. 469,391, that the alternate application of alkyl sulphate and alkyl chloride during the preparation of the ether gives a product of better water solubility than that obtained by the use of the alkyl sulphate only.

In B.P. 452,506 the use of the complex Na-Cu-cellulose is described. Apparently the copper protects one hydroxyl group per glucose residue. The properties of the ethers made in this way differ from the standard product. For instance, methyl cellulose as ordinarily prepared is only soluble in water when 1·2 hydroxyls have been etherified per glucose unit, but when the aqueous solution is warmed the methyl cellulose separates. On the other hand, the use of the Na-Cu-cellulose complex provides a methyl cellulose which is completely soluble in water (and not precipitated on warming) over a range of 0·72 to 1·1 methoxyl groups per glucose residue.

The preparation of *trimethyl cellulose* from cellulose is a long and tedious task, for complete methylation is difficult. The easiest method is that described by Haworth, Hirst and Thomas (J.C.S., 1931, page 821), which involves the simultaneous deacetylation and methylation of cellulose acetate. This involves one operation, whereas even finely divided cellulose requires at least three treatments. Ten g. of acetone-soluble cellulose acetate (40% acetic acid content) was dissolved in 200 cc. of acetone in a flask fitted with a stirrer and maintained at 55° C., during the gradual addition of 120 cc. of dimethyl sulphate and 320 cc. of a 30% aqueous solution of sodium hydroxide. The acetone was removed by distillation and the hot mixture filtered. The solid was then triturated with one litre of boiling water until the soluble impurities were removed, and the trimethyl cellulose separated by filtration. The product may be rendered free from ash by trituration with acetone and ether. Trimethyl cellulose obtained in the above manner is a fine white powder of m.p. 215 to 216° C.; it is insoluble in boiling water, acetone, ethyl and methyl alcohol, ether and light petroleum, but is soluble in benzene, toluene, acetic acid, ethyl acetate, pyridine, chloro-

form, tetrachlorethane, carbon tetrachloride and hot isoamyl alcohol. Solutions in the three last mentioned solvents deposited amorphous trimethyl cellulose on cooling, but slow evaporation of a 10% solution in chloroform gave microcrystalline aggregates. Trimethyl cellulose dissolves very slowly in ice-cold water.

The methylation of various modified celluloses was fully investigated by Heuser and Hiemer (Cellulosechem., 1925, *6*, 101; 125; 153), who used ten different products, ranging from cotton linters, through regenerated celluloses to cellulose dextrin, obtained by treating cotton with 72 to 74% H_2SO_4, for 10 hours. The degree of methylation, in all cases, was carried to the stage where 2 to 2·5 methoxy groups were introduced per glucose residue in order that molecular weight determinations could be made on the water-soluble product. The main general conclusion reached was that the milder forms of pre-treatment of the original cellulose correspond to lower solubility in cold water, higher molecular weight, higher softening point and a greater number of operations to produce a required degree of methylation. The methylated products, which were soluble in cold water, may be precipitated on boiling, and this represents a method of purification. An increased degree of depolymerisation of the original cellulose resulted in increased solubility in warm water. Heuser and Hiemer also established the fact that the methylation process may be considerably shortened by acetylation of the dimethyl derivative of viscose, e.g. monoacetyl dimethylcellulose in one operation gave 44·3% OCH_3, and by a further methylation, 45·4% OCH_3, compared with the theoretical 45·6% for trimethyl cellulose.

Two methylations of cellulose triacetate gave a product containing 38·3% OCH_3, which by a further methylation was increased to 45%. The product melted at 220–5° C., and was fairly soluble in cold water but completely soluble in acetic acid and in chloroform. The molecular weights of the products, containing 32 to 39% OCH_3, prepared from various cellulose modifications, ranged from 900 in the case of cellulose dextrin, through 3,280 for cuprammonium staple fibre, to 6,000–8,000 for pure cotton; the last values were obtained by extrapolation.

The original work of Denham and Woodhouse (J.C.S., 1913, *103*, 1735; 1914, *105*, 2367) on the methylation of cellulose showed that repeated treatment of the cellulose was

necessary to obtain even a fairly high degree of etherification. The cellulose was treated with three to four times its weight of sodium hydroxide solution of mercerising strength, and then with the necessary amount of dimethyl sulphate, when it was shown that there was a gradual increase in methoxyl content. These methods were later re-investigated by Berl and Schupp (Cellulosechem., 1929, *10*, 41), who subjected unmodified cellulose to the methylation process 28 times. With the increase in the number of operations, the portion soluble in water gradually diminished as did the solubility in cuprammonium hydroxide solution. One methylation process produced about 17·5 % OCH_3, corresponding to the monomethyl stage, six methylations gave a product with a methoxyl content of about 31·6 %, whilst 15 were necessary for 38 % OCH_3; 28 operations gave the trimethyl stage with 43·8 % OCH_3. Apparently two free hydroxyl groups per glucose residue are necessary for the product of methylation to be soluble in cuprammonium hydroxide solution. The water soluble methyl cellulose was easily and completely soluble in glacial acetic acid, pyridine and formic acid; it exhibited swelling in alcohol.

The methyl celluloses have no reducing properties and this fact has been offered as evidence that in the methylation process there is no cleavage of the chain of glucose residues, of which cellulose is now generally assumed to consist.

One of the most interesting features of the lower methylated celluloses, from the technical standpoint, is that they are soluble in cold water but insoluble in hot water.

The introduction of the methyl group into cellulose by means of diazomethane or substances producing it, has been used to a small extent. According to Nierenstein (Ber., 1925, *58*, 2615) Geake and Nierenstein utilised this means to make a product containing 1·5 to 4·2 % OCH_3. More recently, Lieser (Cellulosechem., 1929, *10*, 156) adopted similar methods in his examination of the viscose reaction; he described a monomethyl dicellulose. Reeves and Thompson (Contrib. Boyce Thompson Inst., 1940, *11*, 55) made a fibrous methylated cellulose, containing 4·6 to 7·0 % methoxyl, by treating raw cotton, linen or wood pulp, with 0·5 to 0·9 *M* CH_2N_2 in ether or methyl alcohol for one week at 0 to 5° C. After seven treatments the methoxyl content of the cotton rose to 9·8 % but mercerised fibres methylated more readily and after nine treatments were found to contain 17·7 % methoxyl.

Complete methylation of cellulose to the theoretical value OMe has recently been secured by Freudenberg and Boppel (Ber., 1937, *70* (B), 1542), who take the product showing 43·44% OMe and suspend it in liquid ammonia, treat with metallic sodium and after 1½ hours add methyl iodide. The ammonia is removed in vacuo at 100° C. when a pure white fibrous material is obtained insoluble in water (in absence of NaI). The loss of viscosity in $CHCl_3$ is remarkable.

Triphenyl-methyl Ether

The triphenyl-methyl ether of cellulose has been prepared by Helferich and Koster (Ber., 1924, *57*, 587) by treating one part of regenerated cellulose with six parts of triphenylmethyl chloride in presence of four parts of pyridine at 100° C. for 14 to 32 hours. The compound formed melted with decomposition at 250° C. and analysis showed that it was the monoether. The product gave colloidal solutions in pyridine and in chloroform, but was swollen by many organic solvents. More prolonged reaction or the use of a greater excess of reagents did not lead to a higher degree of etherification, but a further hydroxyl group was acetylated by treatment with acetic anhydride on the water bath. A still further degree of esterification was obtained by the use of chloracetyl chloride and pyridine.

Triphenylmethyl cellulose easily hydrolyses when treated with hydrogen chloride in chloroform. Apparently an accumulation of electro-negative groups in the methyl radical renders the ether sensitive to acid.

According to B.P. 359,249 the triphenymethyl ether has also been prepared by first stirring regenerated cellulose with benzyl pyridinium chloride and pyridine at a temperature not exceeding 110° C. until solution is obtained. A solution of 8 parts of cellulose in 160 parts of the pyridine and benzyl-pyridinium chloride mixture was then stirred at 90 to 100° C. with 20 parts of triphenylchloromethane for 90 minutes. The product was then poured into methyl alcohol when the ether separated as a soft fibrous mass, which soon became hard and brittle. It was pulverised and extracted with methyl alcohol. The triphenylmethyl-cellulose was obtained as a pure white brittle mass, soluble in pyridine and slightly soluble in chloroform.

Ethyl Cellulose

Reference to patents specifications shows that many of them cover the preparation of ethyl as well as methyl cellulose,

and in some cases, aralkyl ethers are also described. The relative amounts of cellulose, water and alkali are of great importance, and it appears that high proportions of etherifying agents and still higher proportions of alkali are commonly used. Nitikin and Orlova (J. App. Chem. Russ., 1933, *6*, 1093), in a general study of alkylation, found that the reactivity increased in the order Cl<I<Br and isoamyl<n-amyl<sec. butyl< n-butyl <sec. propyl<n-propyl<ethyl; increase in temperature resulted in an increase in the degree of alkylation.

Triethyl cellulose has been prepared by Hess and Muller (Ann., 1927, *455*, 209) by the slow addition of ethyl sulphate to alkali cellulose at a temperature of 50 to 55° C. Seven treatments were required to produce an OC_2H_5 content of 55·2%, compared with the theoretical 54·8%. The starting product for triethyl cellulose is preferably regenerated cellulose. The triether was filtered on a hot jacketed funnel and well washed with hot water; yields of 65 to 85% were reported. The dry ether was purified by solution in glacial acetic acid, filtering, and pouring into cold water after mixing with methyl alcohol. A crystalline product may be obtained by slow evaporation from a solution in benzene. One of the characteristic properties of triethyl cellulose is its comparatively high positive optical rotation compared with the negative rotation of trimethyl cellulose.

Berl and Schupp (loc. cit.) have also studied the ethylation process and established that, whereas methylation may be effected at room temperatures or even 0° C., ethylation with diethyl sulphate only begins at 70 to 80° C. Slow addition of the reagents gave a higher ethoxy content than if they were added at one time.

The solubility of the ethyl celluloses varies with the degree of ethylation. The lower ethers containing about 5% OC_2H_5 are soluble in sodium hydroxide solutions on freezing in a similar manner to the methyl celluloses. Where the ethoxy content reaches some 27%, the product is soluble in water, ethyl alcohol and acetic acid and it corresponds to the mono-stage. The usual commercial product is the di-ethyl cellulose containing 40 to 48% OC_2H_5 and this is soluble in a wide range of solvents including drying oils. The solutions obtained in organic solvents are typically colloidal and show a feeble opalescence. Berl and Schupp (supra) showed that when cellulose was ethylated to the stage of about 34% OC_2H_5, an alcohol soluble part and an alcohol-insoluble part were obtained

—both with the same ethoxyl content. They assumed that this indicated some depolymerisation of the cellulose during ethylation. The same authors obtained a methyl-ethyl cellulose by the ethylation of Denham and Woodhouse's dimethyl cellulose. The product was insoluble in water.

The use of the Na-Cu-cellulose complex (B.P. 452,506) as discussed on page 369, gives an ethyl cellulose which readily dissolves in water and only separates on warming to 70° C.; the degree of etherification was 1·0 to 1·2 hydroxyl groups per glucose residue.

Nitikin and Rudneva (J. App. Chem. Russ., 1933, *6*, 45) found that the maximum degree of ethylation was obtained when excess of ethyl chloride was added to cellulose suspended in 44% NaOH at 100° C., and when excess of common salt was added it was possible to obviate the side reaction of hydrolysis to some extent. They demonstrated that fibrous products were obtained where the degree of etherification did not exceed 1·5 OC_2H_5 groups per glucose residue but that the fibrous character was lacking where the proportion exceeded 2·5 OC_2H_5 groups. The use of ethyl iodide (*ibid.*, 716) by heating at 120° C. in presence of 40% NaOH for eight hours produced a maximum of 2·75 OC_2H_5 groups per glucose residue.

The best results in ethylation, according to Uschakov and Schneer (Plast. Massi, 1931, *1*, 17), were obtained by the use of 20 molecular proportions of NaOH for 48 hours to soak the cellulose, after which, the excess of alkali was removed until the product contained 110 to 125% of liquid. The alkali cellulose was then treated with 4 to 35 molecular proportions of ethyl chloride—six molecular proportions were found to be sufficient. It was found that an increase in the time of heating from 8 to 18 hours increased the yield and also the ethoxy content up to 99% yield of a product containing 39% OC_2H_5. The optimum temperature of reaction was stated to be 129 to 130° C. When the residual water in the alkali cellulose was removed by benzene or toluene, the ethoxy content could be increased at the expense of viscosity and tensile strength.

B.P. 470,994 describes the introduction of *one* alkyl group per $C_6H_{10}O_5$ by treatment of disintegrated cellulose pulp with strong aqueous ($>$50%) NaOH and aqueous sodium ethyl sulphate.

Okamura (Cellulosechem., 1933, *14*, 135) has shown that the fractionation of ethyl cellulose dissolved in glacial acetic acid by means of precipitation with water, gave products which

demonstrated that the iodine number and osmotic pressure increased from the higher to the lower fractions; specific viscosity and molecular weight decreased. Good agreement was found for the molecular weight estimations by means of osmotic pressure, specific viscosity and iodine number.

The stability of the ethyl ethers of cellulose to acid is shown by the observation of Uschakov and Schneer (supra) that where the ethoxy content is 45% and over the loss in weight was only 0·3% when left in accumulator acid at 48° C. for six days, but if the ethoxy content is below 42% then the ether was rapidly decomposed by H_2SO_4 and even 6% loss in weight took place in water after six days.

The ethylation of the alkali soluble and degraded form of cellulose precipitated from solution in H_2SO_4, has been carried out by the Baeyer method (ethyl chloride and NaOH).

A product was obtained containing 46·8% of OC_2H_5 (approximating to the di-ether) and this was soluble in alcohol, pyridine, chloroform and acetylene dichloride.

The manufacture of phenylethylcellulose and similar compounds has been protected by Dreyfus in B.P. 164,375 and 7. The reaction takes place at 50 to 100° C., and six to seven molecular proportions of the alkylating agent are necessary. The cellulose was first converted into soda cellulose by treatment with 0·5 to 1·5 times its weight of water and 12 to 16 molecular proportions of NaOH. The alkylation, which takes some seven hours, is preferably effected by means of the chloride.

Alkyl Ethers

Other alkyl ethers have been prepared by the general method already described. Propyl cellulose was first suggested as a varnish by Leuchs in 1917, on account of its solubility in benzene. The method employed was to heat one part of alkali cellulose with nine parts of benzene and eleven parts of propyl bromide in a closed vessel at 100° C. with stirring for 60 to 80 hours. The ether was precipitated from solution by water.

The preparation of the propyl, butyl, and amyl ethers of cellulose has been described by Young in B.P. 184,825, and U.S.P. 1,504,178. Propyl cellulose was made by first forming soda cellulose through the reaction between two parts of cellulose, two to three parts of NaOH and one and a half parts of water (i.e. 40% solution of NaOH); the product was then treated with 20 molecular proportions of propyl chloride, the

excess of which was later recovered by distillation. Etherification was effected in a one stage process by means of a revolving autoclave at a temperature not exceeding 130° C. The cellulose ether was washed with water and purified by solution in acetic acid. The product was also soluble in methyl and ethyl alcohols.

The butyl and amyl ethers of cellulose differ little from propyl cellulose, except for decreased solubility and increasing difficulty of formation with increasing magnitude of the alkyl group.

If a mixture of the isomeric propyl chlorides was used in stoichiometric ratio, then the n-propyl isopropyl cellulose resulted; other mixed ethers are also possible.

F.P. 664,932, described the preparation of butyl cellulose by treating cellulose with butyl chloride in presence of a base such as pyridine, dimethylaniline, etc.

Butyl cellulose has been prepared by Nowakowski (Cellulosechem., 1932, *13*, 105), who found that butyl chloride did not react with soda cellulose, but that the bromide gave a 6 to 18% OC_4H_9 content in one operation. A more complete treatment gave a product which appeared to lie between the di- and tri-ether; it was soluble in benzene, toluene, chloroform and acetylene dichloride. High plasticity and strong hydrophobic properties were also observed. The reported non-reactivity of butyl chloride is interesting in view of B.P. 326,865, which states that butyl chloride (or propyl chloride) in admixture with methyl or ethyl chloride reacted with soda cellulose at 120° C. to give a product, the films from which were little affected by water.

Benzyl Cellulose

The action of benzyl chloride on soda cellulose results in the formation of a fibrous product which is insoluble in the usual organic and inorganic solvents. The composition is close to that of the benzyl dicellulose—a product which is not of great technical interest on account, not only of its insolubility, but also owing to the fact that unlike the dibenzyl cellulose, it is not truly thermoplastic. Repetition of the treatment with alkali and aralkyl chloride leads to the di-ether which is soluble in a wide range of solvents and has a definite melting point.

According to Gomberg and Buchler (J.A.C.S., 1921, *43*, 1904), the benzyl dicellulose may be prepared by soaking cotton for three days in a 15% aqueous solution of NaOH,

followed by squeezing until the material holds three times its own weight of solution. Excess of benzyl chloride was then added and the mixture allowed to react for five hours at 100° C. after the excess of benzyl chloride was removed by steam distillation. The product was then digested for two days in cuprammonium hydroxide in order to remove unchanged cellulose, and finally washed with water, dilute HCl, and alcohol and ether.

The dibenzyl cellulose was prepared by treating 5 g. of filter paper for two days with a solution of 10 g. of NaOH in 30 cc. of water. The mass was squeezed and heated with 30 g. of benzyl chloride for seven hours at 100° C., after which the product was treated as described above. The benzylation was then repeated to give a product which was soluble in ethyl acetate and precipitated by alcohol. It softened at 165° and melted at 175 to 177° C. This dibenzyl ether was soluble in chloroform, chlorhydrin, and nitrobenzene; it was gelatinised by acetone.

If the filter paper is steeped in 40 to 50 % solution of NaOH and then caused to react with benzyl chloride in benzene or toluene, the dibenzyl cellulose is obtained in quantitative yield in one operation according to Nakashima (J.S.C.I., Japan, Suppl., 1929, *32*, 8B), but when only 10 to 20 % NaOH solution is employed a monobenzyl ether is produced from which the unchanged cellulose may be removed by means of cuprammonium hydroxide solution.

Atsuki and Kagawa (J.S.C.I., Japan, 1934, *37*, 128) found that the extent of aralkylation increased with increasing amounts of NaOH, measuring the etherification by means of the proportion of the product soluble in a mixture of 10 parts of alcohol and 90 parts of benzene. The optimum concentration of NaOH was found to be 40 to 50 %. Increasing amounts of benzyl chloride from 170 to 280% were investigated. Benzylation appeared to proceed from the outside to the inside of the fibre and was controlled by the dispersion of the benzyl cellulose and the diffusion of the aralkylating agent into the fibres.

A technical method of manufacture is described in B.P. 360,409, when 1·4 to 3 times the theoretical amount of benzyl chloride was added to well-pressed soda cellulose at a low temperature. Solid NaOH was then added at intervals and the mass slowly heated to 80–100° C. and maintained at that temperature for 24 hours. The product was then treated with alcohol, filtered, sodium chloride removed and the residue washed with alcohol and dried. The reaction mass sets to a

stiff gelatinous mass when cold, and isolation of the benzyl cellulose is not easy. The dilute alkali and sodium chloride are readily removed by water, but the other by-products benzyl alcohol and benzyl ether soften the benzyl cellulose and volatilise slowly. The benzyl chloride itself is lachrymatory and yields HCl on hydrolysis so that its removal is essential.

In one method of purification (B.P. 265,491) the reaction mass is ground with a water-soluble salt such as sodium chloride, and the mixture extracted with alcohol or a similar solvent. The salt is later removed from the extracted mass by washing with water. Another process (F.P. 615,349) employs castor oil in place of the salt. The function of both of these products is to enable the subsequent solvent to reach the by-products more easily. The mass is then lixiviated with alcohol which removes both the castor oil and the by-products. A later method of purification has been described by Traill in his review of the cellulose ethers (J.S.C.I., 1934, *53*, 337). The benzyl cellulose may be extracted with a solvent consisting of approximately equal parts of aliphatic and aromatic hydrocarbons. The aromatic hydrocarbons with the aid of the by-products swell the benzyl cellulose so that the reaction mass becomes a viscous solution whilst the aliphatic hydrocarbons have a moderating effect and allow the by-products to be extracted.

A higher degree of aralkylation than that corresponding to dibenzyl cellulose is difficult to obtain and necessitates the use of large excess of benzyl chloride. When 2·5 benzyl groups have been introduced per glucose residue, the resulting ether is only soluble in toluene.

The technical benzyl cellulose resists alkali attack up to 20 % NaOH, is unattacked by accumulator acid and is not affected by water. The viscosity of the solution is usually high, and where it is intended to use the ether as a lacquer it may be advisable to have a product of lower viscosity. Treatments which are applied after purification of the benzyl cellulose are usually of an acid character at high temperatures and sometimes under increased pressure. B.P. 342,391 states that the viscosity may be reduced without change in solubility, but according to Traill (loc. cit.) acid treatments of the type under consideration generally do affect the solubility. Various acids and some salts have been employed (B.P. 277,111) and the treatments are those which are generally regarded as causing some degradation of the cellulose structure. When the viscosity

is reduced too far, the effect is seen in the film strength of the product and the result is similar to that obtained when degraded cellulose is used as the starting product for the preparation of the cellulose ether. An interesting process for reducing the viscosity is described in B.P. 333,902, when the unpurified mass is treated with superheated steam which destroys the excess benzyl chloride and produces HCl which effects the necessary reduction in viscosity. The usual solvent mixture for the preparation of lacquers is an aromatic hydrocarbon to which 10 to 20% of alcohol has been added. Whilst both benzyl alcohol and phenol are solvents, the necessary benzene ring and hydroxyl group appear to best advantage in a mixed rather than a single solvent. The uses of technical benzyl cellulose include the formation of plastic masses in the same manner as cellulose acetate or nitrate. The moulded products may be plasticised by the incorporation of products such as triphenyl phosphate, ditolyl ether of glycerol and polychloronaphthalenes.

The refractive index is 1·57 and the hygroscopicity is very low—1% at 72% R.H.

Xylylcellulose has been described in D.R.P. 384,007 as being useful for the production of varnishes and plastics of the celluloid type.

Where ortho or para sulphonated benzyl chloride replaced the benzyl chloride in the reaction with soda cellulose, there resulted sulphobenzyl cellulose ethers which are soluble in water (B.P. 277,317), and as the corresponding calcium or barium salts are only sparingly soluble in water, they have been suggested as a means of fire-proofing textiles.

Properties

The general properties of the better known ethers of cellulose have been compared by Hagedorn and Möller (Cellulosechem., 1931, *12*, 29), whose tables are reproduced in the following pages. The degree of etherification is not stated, but apparently the di-ethers are considered.

STRENGTH AND EXTENSION DATA.

Cellulose ether.	Strength Kg./sq. mm.	Extension %
Ethyl . . .	5·5–6·5	25–30
Propyl. . .	5·5–6·0	25–30
Butyl . . .	3·0	27
Benzyl . .	5·0–6·0	25–30

Solubility of Ethers.

	Water.	Alcohol.	Ether.	Acetone.	Ethyl acetate.	Benzine.	Benzene	Chlorinated hydro-carbons.
Methyl .	sol. in cold only.	insol	insol.	insol.	insol.	insol	insol.	insol.
Ethyl. .	slight swelling.	sol.	sol.	sol.	sol.	slight swelling.	sol.	sol.
Propyl .	slight swelling.	sol.	strong swelling	swells	sol.	swells on warming.	sol. hot	sol.
Butyl. .	very slight swelling.	sol.	strong swelling	swells	sol.	swells on warming.	sol. hot.	sol.
Benzyl. .	insol.	slight swelling.	slight swelling.	sol.	sol.	swells on warming.	sol.	sol.

The physical reaction of the cellulose ethers to water is not only of great technical importance but shows many points of scientific interest. The researches of Dorr (Cellulosechem., 1932, *13*, 85) have shown that the resistance to water depends on two factors—first the degree of etherification and secondly, the nature and length of the radicle which is introduced. In general the whole sensitiveness to water decreases with higher degrees of etherification and also with increasing length or complexity of the alkyl or aryl substituent. These observations only apply to the ethers of cellulose in which there is no further active or polar group and do not hold in the case of, say, hydroxyethyl cellulose, which, as will be seen later, is soluble in water under certain conditions. With the exception of methyl cellulose, the ethers of cellulose which have found technical application, show a small sensitivity to water. The method adopted by Dorr was to measure the change in length of a strip of film after immersion in water at 20° C. for several hours. AT cellulose BS (a di-ethyl cellulose) showed an elongation of 2% whilst AT cellulose B (approximating to the triethyl stage) gave an elongation of less than 1%. BZ cellulose (di-benzyl) showed only 0·1 to 0·2% elongation.

The different behaviour of the cellulose esters in comparison with the ethers may appear somewhat paradoxical, but Adam (Trans. Farad. Soc., 1933, *29*, 90) has shown that the esters of cellulose do not spread completely on water, whereas the ethers do spread. There is a much greater lateral cohesion between the cellulose ester chains than between those of the cellulose ethers. Measurements were made of the surface pressures and areas of extremely thin films of cellulose ethers. The benzyl ethers spread completely on water from a benzene-alcohol solution and the pressure-area curves obtained were completely reversible. Methyl and ethyl cellulose also spread completely on water from a chloroform solution. It was concluded that the cellulose chains lie flat in the water with every hexose group in contact with the water.

A mixed diacetyl-monomethyl cellulose showed incomplete spreading. It is also interesting to note that whilst trimethyl cellulose showed complete spreading on water, trimethyl starch did not exhibit this property. This is comprehensible on reference to the accepted atomic models for cellulose and starch.

Lorand (Ind. Eng. Chem., 1938, *30*, 527) has given an important review of cellulose ethers. Their physical properties

are determined by (*a*) the substituent group, (*b*) the degree of substitution, (*c*) the chain length of the product, and (*d*) the uniformity of the product. In the main reaction of their preparation, the important features appear to be the ratio of alkali to cellulose, the ratio of alkali to water, and the ratio of cellulose to the etherifying agent.

PROPERTIES OF CELLULOSE ETHERS.

Ether.	Substitution.	M.P.	Moisture Sorption.	Benzene.
Ethyl .	2·15	158° C.	3·001 %	Insol.
Butyl .	2·28	65	1·673	Sol.
Amyl .	1·91	45	0·975	Sol.

The presence of non-polar groups, such as benzyl and even butyl, prevents solubility in water and in alkali even at low temperatures. For alkali-solubility, ethyl cellulose must contain 0·5 ethoxyl groups per glucose residue, and 0·8 to 1·3 for water-solubility. The property of water-solubility for low degrees of substitution may be due to the moving apart of the cellulose chains which are held apart by the slight amount of etherification and thus provide many accessible hydroxyl groups.

SUBSTITUTION AND SOLUBILITY.

(Ethyl cellulose.)

0·5 . .	Alkali (4·8 % NaOH).
1·0 — .	Water.
1·4 to 1·8 .	Swelling in organic polar/non-polar mixtures.
1·8 to 2·2 .	Soluble in organic polar/non-polar mixtures.
2·2 to 2·4 .	Increased solubility in alcohol.
2·2 to 2·5 .	Maximum solubility.
2·5 to 3·0 .	Rapid drop in alcohol-solubility, dissolve in non-polar solvents only.

The solubility in water is interesting in the homologous series.

SOLUBILITY IN WATER.

Methyl cellulose .	Soluble up to a substitution of 1·8.
Ethyl cellulose .	Soluble up to a substitution of 1·2 to 1·4.
Butyl cellulose .	Insoluble.

The sorption of moisture is also linked with the number of free hydroxyl groups.

The maximum solubility in organic solvents and the lowest softening temperature go together and are similarly affected by the extent of substitution; the solubility is not a function of degree of substitution as there is a maximum and minimum. For benzyl cellulose, this is 2·0, but for ethyl cellulose the degree of substitution is 2·4 to 2·5.

Slight differences in the degree of substitution make their effect on the solubility as may be seen for organic solvents applied to benzyl cellulose.

SOLUBILITY OF BENZYL CELLULOSE.

Substitution.	Benzene/ Alcohol.	Benzene.	Toluene.	Xylene.
2·0	S	PS	Sw	Sw
2·1	S	S	PS	Sw
2·2	S	S	S	PS
2·3	S	S	S	S

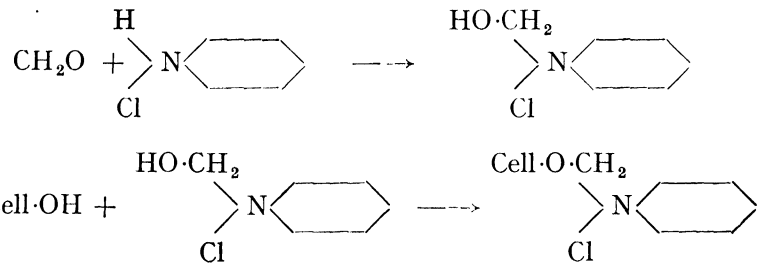
where S denotes soluble, PS partially soluble and Sw swelling. The influence of the polar group on the softening temperature of the lower ethers is interesting; ethyl cellulose softens at 142° C., ethylhydroxyethyl cellulose at 152 and cellulose glycollic acid at 170° C.

The uniformity of substitution also exerts a considerable influence on the solubility of the cellulose ethers. Bock (Ind. Eng. Chem., 1937, *29*, 985) prepared ethyl cellulose under homogeneous conditions (ethylating in a solution of trimethylbenzyl ammonium hydrate) and obtained a product whose degree of substitution was 0·6 to 0·7 and which was completely soluble in water. Substitution of 1·0 or more hydroxyl groups per glucose residue is necessary for water-solubility if the heterogeneous vapour phase ethylation is utilised. Traube (Ber., 1936, *693*, 1483) methylated the NaOH-copper hydroxide cellulose complex and obtained a water-soluble methyl cellulose whose degree of substitution was only 0·8 to 0·9, whereas commercial methyl cellulose requires 1·3 to 1·7.

The solubility in alcohol is also affected by the uniformity of the product. A uniform product is soluble over a wider range (2·2 to 2·5) than the non-uniform product (2·4 to 2·5).

Hydroxy-and Alkoxyalkyl Ethers

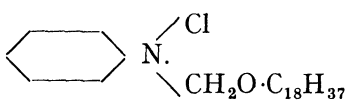
The hydroxymethylether of cellulose has not been obtained but may exist temporarily in solutions of cellulose in sulphuric acid containing formaldehyde (*vide* Samec and Ferjancec, Kolloid. Beiheft, 1921, *14*, 209). A product which may be considered its nitrogenous derivative is probably formed according to the reaction described in B.P. 426,482 (see also page 365) where formaldehyde was mixed with pyridine and pyridine hydrochloride and allowed to react with cellulose for three to four hours at 90 to 100° C. The course of the reaction appears to be



In another example of the same specification, one part of butyl chlormethyl ether is stirred into 10 parts of pyridine and after the evolution of heat is completed, one part of cotton is introduced and left for four hours at 100° C.

The product, after washing, is stated to be water repellant, and also to dye with direct colours which then show excellent fastness to washing. In the example under consideration, a butyl cellulose methylene ether is formed—$(Cellulose)_n \cdot O \cdot CH_2 \cdot O \cdot C_4H_9$—a mixed formal.

The *water-repellency* has been improved by the use of octadecyl chlormethyl ether, which may be dissolved in toluene with a little pyridine as an acid absorbing substance in the reaction with cellulose, which takes place at 90° C. for three hours (B.P. 469,476). Alternatively, a quaternary ammonium salt may be made with pyridine and the resulting compound octadecyloxymethylpyridinium chloride



dissolved and dispersed in water (B.P. 466,817). The fabric is passed through the solution, dried quickly, and then heated

at say, 130° C., for five minutes, when presumably a compound of the type $C_{18}H_{37}\cdot O\cdot CH_2O$ (Cellulose)$_n$ is formed. Excellent results are obtained with only 1 to 3 % of octa-decyl oxymethyl pyridinium chloride. Sodium acetate is added to the solution in order to prevent tendering of the cellulose when heated.

The waterproofing effect is fast to washing as the ether linkage (R.O.CH_2O.Cell.) is stable to alkali.

There appears to be little doubt that a cellulose ether is formed, for U.S.P. 2,083,554 and 2,084,125 describe the preparation of cetyloxymethyl ethers of cellulose (see page 389).

The chlormethyl ethers are made in the usual manner from paraformaldehyde, HCl gas, and the fatty alcohol; they are described in B.P. 394,196. The cetyl ether of oxymethyl-pyridinium chloride and the stearic ester of oxyethylpyridinium chloride are also discussed in B.P. 390,553.

Other fatty compounds of similar composition to those described in B.P. 466,817 and giving similar alkali-fast linkages in cellulose are described in B.P. 475,119, where the sulphite $C_{12}H_{25}.O.CH_2.NC_5H_5$ | $SO_3.NC_5H_5$ and the pyrosulphite

$C_{12}H_{25}.O.CH_2.N.C_5H_5$ | $S_2O_5.NC_5H_5$ are described.

Essentially similar results are obtained by the use of bodies containing nitrogen in addition to pyridine-nitrogen, obtained from paraform, hydrogen chloride and amides or urethanes followed by quaternary salt formation such as $C_{17}H_{35}.CO.NH.CH_2N(Cl)C_5H_5$ (B.P. 475,170) and $CH_3.O.CO.N(C_{17}H_{35}).CH_2.N(Cl)C_5H_5$ (B.P. 471,130).

These nitrogenous derivatives of cellulose are discussed in Chapter XIX, where the modern production of hydrophobic fibres is again considered.

The first reference to hydroxy ethers utilising *ethylene oxide* was by Humbert (D.R.P. 363,192), who treated modified cellulose at a fairly high temperature in presence of a catalyst, such as dimethylaniline. At about the same time, Dreyfus (B.P. 166,767) disclosed the method of preparing glycol cellulose (Cell.O.CH_2.CH_2.OH) by means of the halogen derivatives of polyhydric alcohols; soda cellulose was treated in the cold with ethylene chlorhydrin. A process of Lilienfeld (B.P. 231,807) describes a method in which the reaction mixture

is heated. The reaction of cellulose with ethylene oxide is almost unique, its only counterpart being in the esterification of cellulose by means of ketenes (see page 314).

The theory of the reaction is illustrated in the following manner.

$$\text{Cell.OH} + \underset{\diagdown\,\diagup}{\overset{\text{CH}_2\text{—CH}_2}{\text{O}}} \longrightarrow \text{Cell.O.CH}_2\text{.CH}_2\text{.OH}$$

The etherification may be carried to any desired extent by controlling the proportions of the etherifying agent and the cellulose. The three hydroxyl groups of the glucose residue can react with the alkylene oxide or chlorhydrin and in addition the terminal primary hydroxyl group of the attached alkoxy groups may also react.

Experimental details of a later process (B.P. 359,618) deal with the action of ethylene oxide on semi-moist soda cellulose, the mixture being stirred in an autoclave for 16 hours at a temperature not exceeding 30° C. The product is similar in appearance to the original soda cellulose, but its solubility varies according to the degree of substitution of the hydroxyl groups. In the case of three or more molecules of ethylene oxide per glucose residue, the product is soluble in water; with 1·5 to 2·5 molecules the ether is incompletely soluble in water, but soluble in dilute alkali, whereas, with 0·5 to 1 molecule it is only soluble in 5 to 10% alkali. The method of purification varies according to the solubility, the lower ethers being precipitated from alkaline solution by means of acid, whilst extraction with alcohol may be employed in the case of the water soluble varieties.

Permanent finishes and pattern effects have also been produced by ethylene oxide under such conditions that the fibrous character of the cloth is not affected. The range of finishes includes organdie effects, linenised effects, parchmentising and damask effects as described in B.P. 439,880; 475,906; 481,191 and 482,942. The general method is to impregnate the cloth with NaOH solution (usually of mercerising strength) and then subject it to the action of ethylene oxide which is preferably applied from solution in carbon tetrachloride. It is possible to apply the ethylene oxide in a solution of brine or even in the caustic soda solution usually employed in the preliminary impregnation.

Propylene oxide and glycide are capable of producing similar

effects ; a full account of this work has been given by Lawrie, Reynolds and Ward (J.S.D.C., 1940, *56*, 6).

Some work of Schorger (U.S.P. 1,941,276 to 8) has been applied to the still lower ethers in which less than one hydroxyl group per glucose residue reacts with the ethylene oxide. The reaction between alkali cellulose and ethylene oxide took place at room temperature to give products almost completely soluble in dilute alkali. Freezing the reaction product with dilute sodium hydroxide solutions gave complete solubility.

The reaction is said to be quantitative and no excess of ethylene oxide is required. The method may also be employed in the case of chlorhydrins. Ethylene oxide was introduced at a rate somewhat in excess of the absorption until a sufficient quantity was present in the reaction mixture which was then agitated and the temperature kept below 45° C. as the reaction is vigorous and exothermic. Excellent solubility resulted when 13 % or more of ethylene oxide was used estimated on the basis of the dry cellulose ; water-solubility started at about 75 to 85 % ethylene oxide. Where 14 to 15 % of the oxide is absorbed, probably two units of glucose react with one of ethylene oxide and on this account Schorger termed the product ethylene glycol dicellulose or dicellulose hydroxyethylether. With refrigeration it is possible to produce a degree of etherification corresponding to one ethylene oxide molecule to four glucose residues. A good account of this work has been published by Schorger and Shoemaker (Ind. Eng. Chem., 1937, *29*, 114). In the case of ethylene chlorhydrin the minimum amount used consistent with good solubility was 24·8 % estimated on the dry cellulose ; this corresponds to 13·5 % of ethylene oxide or one glycol group to two $C_6H_{10}O_5$ units.

The ethyleneglycol dicellulose retains the physical form of the material from which it was derived and is light and fluffy in appearance. It is less soluble in potassium hydroxide solutions than in those of sodium hydroxide. The greatest solubility appears to be in 10 % solution of sodium hydroxide, a marked diminution taking place at 20 % and over. Where the concentration of ether in the alkali solution exceeds 8 %, the solutions are too viscous to be of technical interest. The following table from Schorger and Shoemaker (supra) shows how the amount of ethylene oxide as a percentage of the dry cellulose affects the solubility of the resulting cellulose ether in various concentrations of sodium hydroxide.

PERCENTAGE SOLUBILITY OF HYDROXYETHYL CELLULOSE.

Ethylene oxide.	NaOH (per cent.). Not frozen.			
	2·05	5·0	15·0	19·8
4	7·0	16·5	27·6	14·7
6	6·8	14·3	—	10·7
8	3·5	33·0	—	7·0
10	6·5	58·3	—	19·0
14	4·5	68·6	—	—
18	15·0	85·1	54·2	—
24	25·7	—	—	—
30	43·3	—	81·7	2·9
	Frozen.			
4	50·5	64·2	39·2	30·4
6	36·8	69·6	—	17·5
8	82·1	80·0	—	22·4
10	78·3	92·0	—	33·3
14	95·3	97·1	—	—
18	95·7	99·2	—	—
24	97·6	99·7	—	—
30	95·1	100·0	98·2	34·3

Glycol cellulose may be obtained under the trade name Cellofas—there is a range of products which differ in the degree of alkylation so that their properties pass from solubility in cold alkali, solubility in alkali and in cold water, solubility in water to solubility in various organic solvents. The lowest degree of alkylation of the technical product corresponds to less than one-quarter of a molecular proportion of glycol per glucose residue. The chief use of these products appears to be as permanent finishes and adhesives for textile materials.

According to Traill (J.S.C.I., 1934, *53*, 340) these glycol celluloses have certain advantages over viscose in the matter of the production of artificial silk. The solutions are more stable than viscose, there is no desulphurisation process, nor bleaching, no careful control is required and the solutions may be stored for an indefinite time. Schorger and Shoemaker (loc. cit.) have also stated that when filaments were spun from the cellulose ether solution, the rayon resembled viscose rayon. The dry strength was excellent but the wet strength was low. The product is also capable of forming some interesting derivatives. It can be nitrated readily to yield an excellent lacquer base

with low viscosity and good clarity and stability. The hydroxyethyl dicellulose on acetylation yields a product soluble in acetone in one step and as the degree of alkylation increases, the ether may be acetylated more readily. The stearate, xanthate and benzoate were made, and these together with the methylated ether were similar to the corresponding cellulose derivative. The hydroxyl group of the hydroxyalkyl ether may also be ethylated and an example of the ethylation of trihydroxyethyl-cellulose is given in F.P. 629,099.

Hydroxyethyl cellulose has been used to some extent for finishing textiles on a large scale in the U.S.A.; the trade product was termed Ceglin and an account of its application has been given in Textile World (1940, *90*, 55).

B.P. 343,873 by Schorger refers to the higher hydroxy alkyl ethers of cellulose. They were prepared by means of propylene oxide, butylene oxide, amylene oxide, etc., or the corresponding chlorhydrins. The higher homologues were found to be more difficult to make.

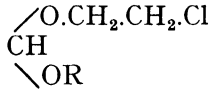
According to Traill (loc. cit.) dihydroxypropyl cellulose was prepared by the treatment of alkali cellulose with glycerol-monochlorhydrin. In this case the optimum concentration of the NaOH for making the soda cellulose was found to be 25%, compared with 43% in the case of ethylene chlorhydrin.

The reaction between ethylene oxide and alkali-cellulose appears to have been indicated in B.P. 277,721, in which the alternative use of ethylene chlorhydrin was also mentioned. Examples of other etherifying agents such as $C_2H_5O.CH(CH_3)Cl$ were also given, and in all cases the reaction was carried out with alkali-cellulose, that is, with the cellulose as a solid phase.

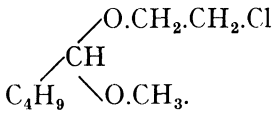
These fibrous reactions are not easy to perform satisfactorily and there is always some difficulty in characterising the product. In view of the large amount of work on the production of hydrophobic fibres, it is interesting to note that similar reactions have in fact been utilised to prepare definite cellulose ethers, as mentioned on page 385. Use is made of the new quaternary benzyl ammonium hydroxides which are sufficiently basic to take part in this type of reaction and also to dissolve the cellulose.

U.S.P. 2,083,554 discloses the preparation of new cellulose ethers by reacting halogen derivatives of acetals with cellulose dissolved in the new solvents above mentioned. The reacting halogen compound is made by bringing together an aldehyde,

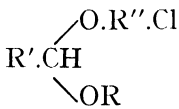
an alcohol and a chlorhydrin of an olefine, HO.R.X, where R is alkylene and X is a halogen atom. In this manner, it is possible to produce reagents such as β-chlorethyl alkyl formals



where R may be methyl, ethyl, butyl, capryl, etc. It is also possible to prepare β-chlorethylmethyl butanal



The general formula for the etherifying agent is therefore



where R is an alkyl radicle, R' is a hydrogen atom or alkyl radicle, and R'' is a hydrocarbon group carrying at least two carbon atoms.

The general method may be illustrated by an example. A mixture of 165 g. of bleached sulphite pulp and one litre of trimethylbenzyl ammonium hydroxide (39% solution) was prepared in a mixer fitted with a steam-jacket. The mixture was stirred at 75 to 100° C. for 1·5 hours and then cooled to 60° C., when 186 g. of chlorethylmethyl formal was added over a period of two hours with continuous stirring. The mass was heated at 80° C. for 3 hours, at the end of which period it appeared as a smooth viscous syrup with a little unreacted formal floating on top. It was then cooled, and the excess of base neutralised with acetic acid (using litmus as indicator). The cellulose ether remained in solution and was precipitated as a gelatinous mass by adding 1·5 litres of acetone. The product was filtered, and worked several times with acetone to remove the quaternary ammonium acetate; the ether was finally dried at 80° C. Analysis of this water-soluble cellulose ether for combined formaldehyde gave 5·2% CH_2O, corresponding to 0·33 groups per glucose residue. The ether was found to dissolve slowly in water, forming a viscous solution, which on evaporation gave a tough elastic film.

The formula for this ether is probably Cell.O.CH_2.CH_2.OCH_3.

The water-solubility is accounted for by the hydrophilic nature of the two oxygen atoms in proximity.

U.S.P. 2,084,125 deals with new ethers, such as lauryl cellulose methylene ether, Cell.O.CH_2.O$C_{12}H_{25}$, obtained by reacting chlormethyllauryl ether with bleached sulphite pulp dissolved in 40% trimethylbenzylammonium hydroxide solution. The reaction is allowed to proceed at room temperature for 5 hours, followed by a period of 2·5 hours at 45° C. The ether was found to contain one lauryloxymethyl group per glucose unit, and was soluble in toluene and in aliphatic hydrocarbons. Films from toluene solution were tough, transparent and more extensible than cellulose or cellulose ether films having a relatively small number of substituted groups. The patent specification claims the new ethers containing the group R.O.CH_2—in cellulose, where *R* is a radicle carrying more than 5 carbon atoms.

These two patents represent great progress in the preparation of well-defined alkylated hydroxymethyl ethers of cellulose which are soluble in water and common solvents; they also represent an interesting comparison of similar reactions carried out in solution and in the fibrous state (see page 310).

Alkyl Carboxy Ethers

The first member of this series would be represented by Cell.—O.COOH, but it is only known in the form of an ester obtained by the action of chloroformic ester on soda cellulose (see page 303).

Cellulose glycollic acid has been described by Sakurada, and is referred to on page 325; it is prepared by the action of monochloracetic acid on soda cellulose.

The methods of preparing the cellulose ethers of hydroxy carboxylic acids have been described in B.P. 343,521, by treatment of soda cellulose with the halogenated acids or their derivatives. The etherifying agents mentioned were chlorpropionic acid, chlormalonic acid and chlorsuccinic acid. The ethers are soluble in organic solvents and are also soluble in water. They are stated to give salts in the usual manne owing to the presence of the carboxyl group.

Unsaturated Ethers

The first member of the series, vinyl cellulose has not been isolated, but like most initial members of a series of aliphatic compounds might have been expected to show some anomaly.

B.P. 342,689 states that soda cellulose may be treated with allyl halides in liquid or vapour form under such conditions that the strength of the fibre is not impaired. The reaction with allyl bromide has been described in more detail by Sakurada (Bull. Inst. Phys. Chem. Research, 1929, *8*, 114). When filter paper was suspended in 40% NaOH (by volume), a single treatment with allyl bromide gave the di- or triether of cellulose. Estimation of the halogen absorption showed that the double bond remained intact and the tetrabromide of cellulose diallyl ether was obtained in an almost pure form. The higher allyl ethers were partially soluble in alcohol, benzene, carbon tetrachloride, etc., but the solubility was smaller than expected and no completely soluble ether was obtained. The purified ether was stable and showed no apparent change when heated to 210° C.

Crotyl cellulose and other unsaturated ethers have been prepared according to the methods of B.P. 391,171. Etherification was affected in presence of a base, either in an aqueous medium or in benzene, toluene, etc. These ethers are stated to undergo polymerisation very readily on exposure to light or heat and give insoluble products. Halogenation of the unsaturated ethers of cellulose is stated to give products of reduced inflammability.

Another method of preparing crotyl cellulose is given in U.S.P. 2,082,797. Cellulose is treated with crotyl chloride in presence of NaOH at 120 to 170° C. in a closed container. The product of this reaction is stated to be soluble in ethyl alcohol, benzene, ethyl acetate, and acetone. It also is capable of age-hardening.

Halogenated Ethers

Halogen-containing cellulose ethers are prepared by treating cellulose, or alkali cellulose, with an etherifying agent with at least one reactive halogen atom as part of the etherifying group. B.P. 277,721 disclosed the interesting information that it is preferable to utilise compounds which contain different halogen atoms, e.g. ethylene chlorbromide, 1-chlor-2-iodoethane, 2-chlor-1-brompropane, etc. Where compounds are employed which contain the same halogen atom it is more difficult to bring about reaction to produce a halogen-containing cellulose ether—reaction between cellulose and ethylene dichloride in presence of alkali gives products which do not contain chlorine combined with the cellulose.

The preparation of halogeno-alkyl ethers of cellulose has been described in B.P. 344,529 and 346,806. One method of preparation is by treatment of the hydroxyalkyl ethers with thionyl chloride, but, in addition, they have also been prepared by treatment of soda cellulose with a dihalogenated hydrocarbon such as $CH_2Br.CHCl_2$; $CH_2Cl.CH_2I$; or $CH_2Br.CH_2CH_2Cl$. The products of the reaction are monohalogenated alkyl cellulose ethers. They react further with ammonia or organic bases to give nitrogen containing derivatives of cellulose, or amino ethers of cellulose, some of which are described in the section on "Aminocellulose," etc.; some basic ethers of cellulose are also described in the same section.

Chlorhydroxypropyl cellulose has been prepared (B.P. 346,806) by treating cellulose which has been brought into a reactive state, with epichlorhydrin; the mixture was allowed to steep overnight and was then refluxed for from four to eight hours. About 6 to 10 parts by weight of epichlorhydrin is employed, and the final product may show a gain in weight of 100 to 170% estimated on the original cellulose. The higher substituted products are soluble in a mixture of chloroform and alcohol.

Benzyl, chlorbenzyl and chlordinitrophenyl ethers have been described by Niethammer and König (Cellulosechem., 1929, *10*, 201). They were prepared by the action on cellulose in presence of alkali, of benzyl chloride, p-chlorbenzyl chloride and 1 : 2 : 4 chlordinitrobenzene. Similar compounds had been prepared by Peacock (J.S.D.C., 1926, *42*, 53) by the use of nitrobenzylphenyldimethyl ammonium chloride, and are referred to in the section on Aminocellulose (page 417).

The higher p-chlorbenzyl celluloses were more difficult to prepare than the corresponding benzyl celluloses. The higher ethers were produced in the form of plastic masses, which were soluble in certain organic solvents. o-chlorbenzyl chloride behaved in an entirely different manner from the p-compound or benzyl chloride itself, for although the cellulose appeared to be attacked, the final product was soluble in cuprammonium hydrate solution and it contained only a small amount of chlorine.

The derivative formed by the action of 1 : 2 : 4-chlordinitrobenzene on alkali cellulose was brownish in colour, but may be prepared in an almost white state if ethyl alcohol is used as the solvent for the chlordinitrobenzene.

The formation of cellulose o-chlorobenzyl ethers by the

reaction of o-chlorobenzyl chloride on soda cellulose has been examined, in some detail, by Ball and Hibbert (Canadian J. Res., 1932, *7*, 481).

The products of reaction were separated into two fractions, depending on their solubility in chloroform. The soluble ethers had more than one hydroxyl group replaced by o-chlorbenzyl, whereas the insoluble ether consisted of mono-o-chlorbenzyl cellulose together with any lower ethers and unchanged cellulose. The ethers formed more rapidly and in greater yield when any excess of alkali was removed from the alkali cellulose before treatment with the etherifying agent. In addition to the differentiation on a basis of solubility in chloroform, the o-chlorbenzyl celluloses showed a break between the chlorine contents of the soluble and insoluble ethers. The most highly substituted insoluble ether prepared contained 12·37 % of chlorine, equivalent to mono-o-chlorbenzylcellulose, but the soluble ether of lowest substitution contained 15·25 % of chlorine, which is the calculated amount for the sesqui-o-chlorbenzylcellulose $C_{12}H_{17}O_{10}(C_7H_6Cl)_3$.

The effect of temperature was studied at one alkali concentration, and the effect of concentration at one definite temperature, and a combination of the data obtained led to the conclusion that the influence of each variable was specific so that these factors could be altered to lead to the formation of ethers of well-defined structure. Theoretical interpretation of the results assumed a shift of the equilibrium from mono-sodium cellulosate to the sesqui- and di-sodium cellulosates as the temperature and alkali concentration are raised.

CHAPTER SEVENTEEN

MIXED CELLULOSE ETHERS

THE mixed ethers of cellulose fall naturally into two classes, the first of which is merely a physical mixture. For example, it has been proposed in B.P. 252,176 to counteract the sensitivity to water of some of the methylcelluloses and the lower ethylcelluloses, more especially at 20° C. and lower, by mixing them with a relatively small proportion of a water-insoluble or more highly etherified ethylcellulose. Apparently only about 2% of the insoluble ether is necessary, and the mixing may be effected by a thorough kneading until the colloidal solution is complete. Films from this physical mixture are stated to be resistant to water.

The second type of mixed cellulose ether is that in which the cellulose derivative contains two or more different ether groups. The general procedure is either to use a mixture of alkylating agents, such as methyl and ethyl chlorides, or to adopt a two-stage process, in which an incompletely etherified compound is first formed and further substituted.

It is claimed that these mixed ethers possess an unusually low sensitivity to water, together with a high film strength, even in cases where only a low degree of etherification is found.

Alkyl Ethers

A typical method of preparation has been described in B.P. 326,865, where alkali cellulose is treated with a mixture of methyl or ethyl halide and an alkylating agent in which the alkyl group contains three or more carbon atoms. Ethylbutyl cellulose was made by first preparing alkali cellulose by means of the reaction between 40 parts of cellulose and 160 parts of 50% NaOH solution. The alkali cellulose was then treated with 80 to 100 parts of ethyl chloride and 60 parts of butyl chloride at 120° C. The excess alkylating agents were removed by distillation. The use of equal parts by weight (i.e. 20) of ethyl and butyl chlorides, on 10 parts of cellulose

with 60 parts of 50% NaOH solution, gave a mixed ether containing 32% ethoxyl and 14% butoxyl. The mixed cellulose ether was soluble in a mixture of alcohol and benzene, and possessed a very low capacity for stretching in the wet state when films were prepared and moistened with water.

Ethyl propyl cellulose has been prepared in a somewhat similar manner. Ten parts of cellulose were mixed with 50 parts by weight of a 50% solution of NaOH, and 10 parts each of ethyl chloride and propyl chloride. Examination of the resulting mixed ether gave an ethoxyl content of 33% and a propoxyl content of 12%. The product also showed a very high resistance to swelling in water, and was soluble in a mixture of one part of alcohol and nine parts of benzene. The resistance to swelling in water of ethylamylcellulose is still higher, whilst that of methylethylcellulose is lower.

The processes described in B.P. 6035 of 1913, and B.P. 184,825, for the production of the simpler mixed ethers of cellulose, such as methylethylcellulose, gave compounds which were stated to be insoluble in benzine, or in methyl, or ethyl alcohol.

A mixed methyl-methylene ether has been described by Wood (J.S.C.I., 1931, *50*, 411)—prepared by the action of chlormethyl-methyl sulphate on soda-cellulose.

Aryl Ethers

The resistance to swelling in water of the alkyl ethers of cellulose may also be improved by the incorporation of a small proportion of benzyl ether, either by the use of a mixed etherifying agent or by treatment of the alkyl ether with benzyl chloride. For instance, ethyl cellulose containing 0·5 to 1·5% ethoxyl possesses a very low resistance to swelling in water, but the introduction of 0·5 to 2% of benzyl cellulose counteracts this swelling power in the mixed derivative. B.P. 331,903 gives the following method of preparation. 100 parts of cotton or wood pulp are soaked in 30% NaOH solution and then pressed to 2·5 times the original weight of the cellulose. The alkali cellulose is then mixed with 100 parts of ethyl chloride and 14 parts of benzyl chloride, and heated for three hours at 110° C.

The product is washed and dried, yielding 115 parts of a mixed ether containing 1% benzyl.

Nitrobenzylchloride may also be utilised to give an ethyl-nitrobenzyl-cellulose. It is possible to esterify these products.

Ethylbenzylcellulose has also been prepared according to the methods described in B.P. 164,375. Cellulose was first converted into alkali cellulose by treatment with a 50% solution of NaOH, so that it contains about four molecular proportions of NaOH. The soda cellulose was then kneaded with two molecular proportions of benzyl chloride and afterwards with one molecular proportion of ethyl sulphate. The reaction with benzyl chloride takes place at 50 to 100° C., and with ethyl sulphate, at 50° C. or lower. After the reaction had been allowed to proceed for two to four hours, six molecular proportions of NaOH in powder form were added and the mass kneaded with a further three molecular proportions of benzyl chloride at 50 to 100° C., followed by two molecular proportions of ethyl sulphate at 50° C. or lower. The final additions were three molecular proportions of powdered NaOH and three molecular proportions of diethylsulphate. The ethylbenzylcellulose formed in this manner was readily soluble in organic liquids and was unaffected by water.

Austrian Patent 126586, also described the preparation of methylbenzylcellulose and two forms of ethylbenzylcellulose, one of which was soluble in aliphatic hydrocarbons and the other in a mixture of equal proportions of alcohol and benzene. The general method was to etherify the alkali cellulose at ordinary or increased pressures, with 10 to 30 molecular proportions of the alkylating agent and two molecular proportions of the aralkylating agent. Methylxylylcellulose is also mentioned, together with ethylxylyl-, propylxylylcellulose, etc. The temperature of the reaction is so controlled that any hydrolysis of the excess of alkylating agent is avoided.

The simultaneous use of methyl- or ethyl-chlorides with brombenzylchloride on alkali cellulose, results in the production of methyl- or ethylbrombenzylcellulose.

Benzylchlorbenzylcellulose has been made by the use of a mixture of benzylchloride and chlorbenzylchloride according to U.S.P. 1,451,330.

General Properties

The general properties of some of the simpler mixed ethers of cellulose have been compared by Hagedorn and Möller (Cellulosechem., 1931, *12*, 29).

MIXED ETHERS.

	Water.	Alcohol.	Ether.	Acetone.	Ethyl acetate.	Benzine.	Benzene.	Chlorinated hydro-carbons.
Ethyl butyl.	Very slight swelling.	sol.	strong swelling.	strong swelling.	sol.	swells.	sol.	sol.
Ethyl benzyl	insol.	sol.	slight swelling.	slight swelling.	strong swelling.	insol.	strong swelling.	sol.
Propyl benzyl	insol.	slight swelling.	strong swelling.	easily sol	sol.	insol.	sol.	sol.
Butyl benzyl	insol.	slight swelling.	strong swelling.	easily sol.	sol.	insol.	sol.	sol.

STRENGTH AND EXTENSION DATA.

Mixed ether.	Strength. Kg./sq.mm.	Extension. %
Ethyl-butyl .	6·0–6·5	30
Ethyl-benzyl	6·0–6·5	12
Propyl-benzyl	5·0	18
Butyl-benzyl	4·5	28

The above data refer to the properties of films. The solubilities of the mixed ethers in various solvents are shown in the table, on the previous page.

Multiple Ethers

Mixed ethers containing more than two different ether groupings have been prepared. A typical prescription is given in B.P. 346,426, where ethylbutylcellulose is first described as being prepared by treating 10 parts of filter paper with 20 parts of 50% NaOH solution to which 10·5 parts of powdered NaOH were added, followed by etherification with a mixture of 20 parts of ethyl chloride and 30 parts of butyl chloride. The reaction is conducted for two to three hours at 110° C., followed by the same length of time at 140° C. If the above method is followed in the use of 14 parts of methyl chloride, 16 of ethyl chloride and 24 of butyl chloride, then methylethylbutylcellulose results. Each alkyl radicle is present in the same proportion. Similarly, methylethylpropylcellulose may be formed by the use of 14 parts of methyl chloride, 16 of ethyl chloride and 21 of propyl chloride, and ethylpropylbutylcellulose from 16 parts of ethyl chloride, 21 of propyl chloride and 26 of butyl chloride. All these mixed ethers are stated to be soluble in benzene-alcohol mixture.

Another example of a mixed ether of cellulose is seen in U.S.P. 1,833,720, which describes the preparation of methylethylcellulose followed by treatment with benzylchloride to produce methylethylbenzylcellulose.

Hydroxy-ethers

The production of mixed cellulose ethers which contain glycolcellulose, by the addition of ethylene oxide or its homologues to the alkylating agent is accomplished by a reduction in time of reaction, or alternatively, a lowering of the temperature of reaction. This is disclosed in B.P. 345,028. Practically all the halogen containing agents may be utilised—simple and

substituted, saturated and unsaturated. Hydroxyethylbenzylcellulose was prepared by mixing one molecular proportion of alkali cellulose with six molecular proportions of benzyl chloride and one molecular proportion of ethylene oxide in an autoclave at 50° C., the temperature rising to 120° C. on account of the heat of reaction. The mixture was maintained at 100° C. for two to three hours after the initial reaction had subsided. The product was then cooled and extracted with ethyl alcohol. The excess of benzyl chloride was removed and the mixed ether washed with water. The hydroxyethylbenzylcellulose is soluble in chloroform and benzene, but is insoluble in benzine and in alcohol. Hydroxybutylbenzylcellulose and propylhydroxyethylcellulose may be prepared in a similar manner.

Mixed cellulose ethers may be prepared by the treatment of alkali-cellulose with an alkyl halide and ethylene oxide in presence of a diluent and a catalyst. According to F.P. 686,598, benzylhydroxyethylcellulose has been made by the action of benzyl chloride and ethylene oxide on alkali cellulose, whilst propylhydroxyethylcellulose has been made by a similar process involving the use of propyl chloride.

CHAPTER EIGHTEEN

CELLULOSE ETHER-ESTERS

THERE are three possible methods of forming the cellulose ether-esters :

(*a*) By the physical admixture of cellulose ether with a cellulose ester.
(*b*) By the esterification of cellulose ethers.
(*c*) By the etherification of cellulose esters.

The course considered under (*c*) cannot be realised in actual practice because of the poor resistance of cellulose esters to alkali, which is usually employed when etherification is desired.

The physically mixed ether-ester composition has not attracted great attention in the scientific literature, nor does it appear to have been utilised to a large extent in industry. A typical method has been described in U.S.P. 1,429,153, where equal parts by weight of cellulose nitrate, cellulose acetate and ethylcellulose, were dissolved in pyridine. The cellulose acetate employed was the acetone-soluble variety and the ethylcellulose was insoluble in water. Other examples include a mixture of equal parts of cellulose acetate and ethylcellulose in pyridine.

F.P. 660,510, has described the use of a mixture of ethylcellulose with cellulose trilaurate.

According to D.R.P. 540,872, where water-soluble cellulose ethers are mixed with the cellulose esters, the films and fibres from the mixed product are insoluble in water. In all the examples given, an aqueous solution of the ether is made into an emulsion with a solution of the ester generally in mixed solvents. Mixtures of methylcellulose and cellulose nitrate, hydroxyethylmethyl cellulose and cellulose nitrate, and cellulose acetate and ethylcellulose, have been prepared. Not only is the ether component of the mixture made insoluble in water, but the ester component is no longer affected by those solvents in which it originally dissolved.

Somewhat similar methods have been utilised in D.R.P. 534,852, for the preparation of a mixture of methyl cellulose and cellulose acetate, and methyl cellulose with cellulose nitrate.

This method of physical admixture is obviously capable of utilisation in the case of a fully etherified ether and a fully esterified ester, whereas the production of a true chemical ether-ester necessitates a starting product containing free hydroxyl groups which can be esterified.

Denham and Woodhouse (J.C.S., 1913, *103*, 1735) prepared methylated cellulose from cotton and then esterified the product with a mixture of acetic acid and acetic anhydride containing a little sulphuric acid. They obtained methylcellulose acetate, which was readily soluble in chloroform, but analysis showed that during acetylation some hydrolysis of the methoxyl group had taken place.

Hess and Wittelsbach (Ber., 1921, *54*, 3232) have examined the acetates of diethylcellulose, and isolated the diethylcellulose monoacetate, which was obtained after two hours treatment. It had a melting point of 196-205° C. The details of products obtained after various other times of reaction were also given.

Heuser and Neuenstein (Cellulosechemie., 1922, *7*, 89) carried out similar experiments to those of Hess, but using a smaller amount of sulphuric acid as the catalyst in order to avoid degradation. The main product of reaction was the monoacetate of dimethylcellulose. The crude product was extracted with acetone, yielding a compound which melted at 110° C., and contained 26% methoxyl and 17% acetic acid. The residue was extracted with ether and gave a small yield of a product melting at 140° C., and containing 23% methoxyl and 17% acetic acid. A fraction was also obtained from chloroform and this melted at 99° C., and contained 27% methoxyl and 16% acetic acid. The theoretical figures for dimethylcellulose acetate require 26·7% methoxyl and 18·6% acetic acid.

Heuser and Heimer (Cellulosechemie., 1925, *6*, 101) have shown that dimethylcellulose monoacetate may be methylated in one operation to give trimethylcellulose.

Most of the information concerning the preparation and properties of cellulose ether-esters is obtained from patent specifications, and it is generally found that the method is to esterify a diether of cellulose.

Alkyl Ether-Organic Ester

Dimethylcellulose formate and diethylcellulose formate have been prepared according to the methods of B.P. 347,651, where the di-ether of cellulose is dissolved in four to nine times its weight of 90% formic acid at room temperature. Methylcellulose takes considerably longer than ethylcellulose to dissolve, 24-30 hours compared with 6-7, but in both cases the product is isolated by pouring into cold water. The ether-ester is insoluble in water but soluble in organic solvents

A large number of cellulose ethers possess the property of swelling in water and some of them are readily soluble, but when these ethers are acetylated, they become unaffected by water and soluble in solvents, such as acetone, and ethyl and butyl acetate, etc., in which they were not soluble before esterification. D.R.P. 525,835 describes the acetylation of dimethylcellulose by treatment with acetic anhydride, acetic acid and a small trace of sulphuric acid until a sample is readily soluble in acetone.

The product was precipitated by pouring into water when the methylcellulose acetate separated in flakes, but if the esterification takes place in presence of a diluent which is not a solvent, then fibrous ether-esters are obtained. The same specification describes the preparation of ethylcellulose stearate by treatment of ethylcellulose with stearyl chloride in presence of benzene and pyridine. The mixture is heated for 6-8 hours under a reflux condenser. The purified product was found to be soluble in benzene and benzine.

Propyl cellulose oleate was prepared by the treatment of monopropyl cellulose with oleyl chloride in presence of toluene and dimethyl aniline, in a somewhat similar manner to that described above for ethylcellulose stearate. The propyl cellulose oleate is also soluble in benzine and benzene.

Monethylcellulose monobenzoate was prepared by treatment of monoethyl cellulose with sodium hydroxide solution and benzoyl chloride in benzene. The reaction is somewhat vigorous, but further heat is necessary after the initial heat of reaction has diminished. The ether-ester contains 35·5% benzoic acid and is soluble in acetone, benzene, pyridine and chlorinated hydrocarbons.

Where a methyl cellulose of a higher degree of etherification is used as the starting material, an ether-ester with 2·5 out of a possible 3 substituted hydroxyl groups was obtained,

containing 39% benzoic acid and this ethylcellulose benzoate was also soluble in benzene, acetone and chlorinated hydrocarbons.

The same patent specification, i.e. D.R.P. 525,835, gives examples of the use of p-toluene sulphochloride in the place of acetyl or benzoyl chloride.

The general method of esterifying di-ethers of cellulose is also described in B.P. 241,679, and the mono-ethers, in B.P. 268,552. Ethylcellulose acetate processes are the subject of B.P. 177,809 and 177,810.

Whilst a number of patent specifications deal with the esterification of a definite cellulose ether, it is not essential for the alkyl content to be well defined prior to esterification in order for the desired properties of resistance to water and solubility in organic solvents to be obtained. In other words, in addition to the esterification of mono- and di- ethers of cellulose, the process and its benefits apply to ethers in which 0·5 to 1·5 hydroxyl groups of the original $C_6H_{10}O_5$ have been etherified. In this manner, ether-esters have been prepared in which the proportion of ester grouping to ether grouping is 4 : 1, 3 : 2, and 2 : 3, all of which are insensitive to water and soluble in inert organic solvents. The methods of preparation have been described in D.R.P. 510,424. 100 parts of methylcellulose, containing 0·5 methoxyl groups per $C_6H_{10}O_5$, were kneaded with 200 parts of acetic anhydride, 250 parts of acetic acid and 0·25 parts of sulphuric acid for half an hour. The methylcellulose rapidly dissolved and the resulting methylcellulose acetate was precipitated by water. Analysis showed the ether-ester to contain 2·6 acetyl groups per $C_6H_{10}O_5$. A corresponding ethylcellulose acetate was obtained in a similar manner.

B.P. 334,897 describes an esterification of ethylcellulose by means of a mixture of the fatty acids contained in coconut oil. 40 parts of ethylcellulose, with 40% ethoxyl content were stirred for eight hours at 130–150° C., with 200 parts of the fatty acids from coconut oil. The reaction mass was then extracted with benzine which dissolved the excess fatty acid. In this manner, a mixture of ethylcellulose caprate, caprylate, caproate, myristate, laurate, palmitate and oleate was obtained. This mixture is thermoplastic.

Ethylcellulose stearate is described in B.P. 270,347.

The same specification describes the preparation of butyl cellulose linoleate by treatment of butyl cellulose with five

parts of linoleic acid and a trace of boric acid. The mixture was stirred for 8–10 hours at 150° C., and the free acid removed by methyl alcohol. The ether-ester is soluble in benzine, benzene and toluene. At ordinary temperatures its films are stated to be remarkably tough.

Ethylcellulose linoleate has been prepared by treatment of ethyl cellulose with linseed oil at 140° C., according to F.P. 660,510. Ethylcellulose oleate and stearate are described in the same specification.

Ethylcellulose benzoate has been described in B.P. 300,942. It is prepared by dissolving ethylcellulose, containing 2·5 ethoxyl groups per $C_6H_{10}O_5$, in molten benzamide. Another method of preparation is given in B.P. 334,897, when the ethylcellulose is heated with five parts of benzoic acid for three hours at 130–150° C. In either case the reaction product is purified by extraction with water or dilute sodium carbonate solution. The ethylcellulose benzoate is soluble in a mixture of benzene and alcohol. In the method described in B.P. 334,897, the benzoic acid may be replaced by salicylic acid, phenylacetic acid, undecylic acid, etc.

The preparation of ethylcellulose phthalate has been described by Malm and Fordyce (Ind. Eng. Chem., 1940, *32*, 405). Ethylcellulose (42 % ethoxyl) was treated with the dibasic acid anhydride in pyridine for 12 hours at 100° C., and the ether-ester precipitated by pouring into a large volume of dilute HCl.

Ethylcellulose naphthenate has been described in U.S.P. 1,867,942, and is stated to contain 40 to 43 % ethoxyl, and 20 to 25 % naphthenic acid.

F.P. 629,861, describes a general method for cellulose ether-ester preparation by the action of the acid anhydride on the cellulose ether and an example of ethylcellulose myristate is given.

The general process of U.S.P. 1,880,558, describes the treatment of cellulose ethers with organic acid to form mixed ether-esters, and in this case, ethylcellulose acetate was produced by treatment of 10 parts of ethylcellulose with 100 parts of glacial acetic acid at 100° C. for 41 hours. The ether-ester contained 7·3 % acetic acid and was soluble in benzene-alcohol, chloroform-alcohol, etc.

Ethylcellulose lactate was prepared by treating 80 parts of ethylcellulose with 85 % lactic acid in presence of 1 : 4 dioxan for 90 hours at 100° C. The combined lactic acid was found to be 4·7 %.

Alkyl Ether-Inorganic Ester

The resistance to water of the cellulose ethers has also been improved by transforming them into ether-esters, where the ester grouping comes from an inorganic acid. B.P. 347,423 demonstrates that the introduction of a small amount—some 2·5 %—of nitrogen into diethylcellulose increases the resistance to water, improves the solubility in organic solvents but does not render the ether-ester more inflammable. If the nitrogen content is increased to the stage which represents complete esterification of the one remaining hydroxyl group, the product is soluble in ether, hydrocarbons and turpentine.

It is not possible to employ nitric acid or the usual mixture of nitric and sulphuric acids, but the reaction readily proceeds with diacetyl-o-nitric acid. The temperature is not allowed to rise above 10° C. Solution occurs in about ten minutes and the ether-ester is precipitated by pouring into cold water. Diethyl cellulose nitrate is soluble in mixtures of benzene and alcohol, butyl alcohol and toluene, etc., whilst dimethyl cellulose nitrate is soluble in methyl, ethyl or butyl acetate, and in mixtures of these with ethyl alcohol, benzene, etc.

Another interesting specification which describes the esterification of cellulose ethers depends on the treatment of the ether in a dispersed state with acid chlorides in organic solvents. For example, ethylcellulose silicate has been prepared by dissolving 5 g. of silicon tetrachloride in 10 cc. of chloroform and 7·5 cc. of pyridine. The addition product is mixed with a solution of 20 g. of water-insoluble ethylcellulose in 200 cc. of xylene. On gentle heating, the reaction commences and the mass is transformed into a jelly. The solvents are removed by steam distillation and the dried product extracted with benzene. The ethylcellulose silicate contains 3·8 % SiO_2, and is soluble in benzene. (D.R.P. 511,208.)

Ethylcellulose phosphate has been prepared from water-insoluble ethylcellulose by dissolving it in methylene chloride. Urea is added and $POCl_3$ is slowly added with stirring, and the mixture shaken for three to four hours, after which it is poured into boiling water and heated until the methylene chloride is removed. The ethylcellulose phosphate contains 48 % ethoxyl and 2·7 % PO_4.

Ethylcellulose phosphate has also been described in B.P. 300,942. It is prepared by treatment of ethylcellulose, obtained by heating alkali cellulose at 120° C. with ethyl

chloride, benzene and NaOH, without isolation, with $POCl_3$ in further benzene. This product is stated to contain 5·5% PO_4, and be soluble in ethyl aclohol, ether, benzene, chloroform and ethyl acetate.

Aryl Ether-Inorganic Ester

Benzylcellulose nitrate has been prepared according to the methods of B.P. 319,691, either by the benzylation of cellulose nitrate or the nitration of benzylcellulose.

B.P. 334,897 refers to benzylcellulose linoleate, prepared by treatment of benzylcellulose with four parts of linoleic acid for nine hours at 130–150° C. in an atmosphere of nitrogen. Similar methods are employed in B.P. 330,957, for the production of benzylcellulose benzoate, salicylate, phenylacetate, laurate, stearate, oleate, etc.

Ethylbenzylcellulose formate has been made by the treatment of ethylbenzylcellulose with 90% formic acid, when, according to B.P. 347,651, solution occurs after stirring for 10 hours at 20° C. The ether-ester is isolated by pouring into water and is washed until neutral and then dried. This product is soluble in methylene chloride.

Ethylbenzylcellulose acetate has been made by the acetylation of a mono-ethylcellulose containing about 1% benzyl, by means of acetic anhydride, acetic acid and a trace of sulphuric acid. The ether-ester is produced by slow heating for about two hours.

Hydroxyalkyl Ether-ester

Hydroxyethylcellulose benzoate has been described in U.S.P. 1,863,208. Alkali cellulose was first made into hydroxyethylcellulose by treatment with ethylene oxide and the ether was then treated with benzoyl chloride in presence of an excess of benzene. The excess of solvent was removed by means of a centrifuge, and the ether-ester dissolved in 4·75% NaOH, frozen and then thawed. The process may be reversed, so that the alkali cellulose can be esterified, and the cellulose benzoate produced may be treated with ethylene oxide with no difference to the final product.

Hydroxyethylcellulose acetate was described in B.P. 358,510. The ether was first made by means of an excess of ethylene oxide reacting with cotton in presence of diethylaniline under pressure. The mono-hydroxyethylcellulose produced was

then acetylated by acetic anhydride in presence of liquid sulphur dioxide and zinc chloride. The product is soluble in acetone. Another method of preparation is given in F.P. 717,623, where the hydroxyethylcellulose was acetylated by means of acetyl chloride in petroleum ether at room temperature. This reaction takes place without any apparent change in structure of the fibrous hydroxyethylcellulose which does not pass into solution. The ether-ester is soluble in acetone and in chlorinated hydrocarbons.

The use of acetic anhydride alone as a means of producing hydroxyethylcellulose acetate is described in B.P. 365,250.

Hydroxypropylcellulose butyrate has been prepared by the action of butyryl chloride on hydroxypropylcellulose, according to F.P. 717,623. Another method of preparation, involving the use of butyric anhydride, is given in B.P. 365,250. The ether-ester is soluble in chlorinated hydrocarbons, acetone and ethyl acetate. F.P. 708,538 refers to the preparation of the corresponding acetates of hydroxypropyl and hydroxybutyl cellulose.

The di-basic esters of hydroxyalkylcellulose have received attention in F.P. 705,816. The hydroxyethyl, or methyl cellulose, is caused to react with the anhydrides of acids such as malonic, succinic, malic, tartaric, etc., in the absence of catalysts and diluents, but at fairly high temperatures. Hydroxymethylcellulose malonate is one example out of eighteen ether-esters mentioned in this specification.

Hydroxypropyl-hydroxybutyl cellulose benzoate has been prepared by treatment of a mixed ether with benzoic anhydride at 130° C. The ether-ester is soluble in chlorinated hydrocarbons according to B.P. 365,250. The same specification refers to the preparation of dihydroxypropylcellulose acetate, which is soluble in acetone, and to hydroxyethylcellulose naphthenate, which is soluble in benzene, toluene and the chlorinated hydrocarbons.

F.P. 695,283 describes hydroxyethylcellulose acetobutyrate, prepared from the monohydroxyethylcellulose by treatment with acetic anhydride, butyric acid and glacial acetic acid containing a trace of sulphuric acid. The ether-ester is soluble in acetone.

The same specification describes the preparation of hydroxyethylcellulose phthalate and succinate.

Other Compounds

The basic cellulose ethers formed by the action of halogen alkylamines on cellulose, according to B.P. 318,255, may be esterified. For example, diethylaminoethylcelluloseacetate has been prepared by the acetylation of diethylaminoethylcellulose by means of acetic acid and acetic anhydride in presence of zinc chloride. Similar methods are mentioned in F.P. 680,956. Diethylaminocellulose formate is also described.

D.R.P. 521,721 describes the preparation of the halogen-containing ethers of cellulose, such as methyl- or ethyl-brombenzyl-cellulose, which have been acetylated to the corresponding methyl- and ethyl-brombenzyl-cellulose acetate.

The above descriptions represent a brief account of the cellulose ether-esters. In the present state of knowledge, it is not possible to express this on a very sound chemical basis; many of the ethers and esters are themselves ill-defined chemically and most research has been directed towards commercial rather than scientific ends. The position is further complicated by the fact that the technical investigations into cellulose ethers have latterly been pursued with a view to the reaction of less than one hydroxyl group per glucose residue.

CHAPTER NINETEEN

AMINO-CELLULOSE AND OTHER NITROGENOUS DERIVATIVES

ATTEMPTS were made many years ago to introduce basic nitrogen into the cellulose molecule. In 1861 both Thenard and Schutzenberger claimed to have produced an amidated cellulose by treatment with ammonia in an autoclave. It has also been claimed that similar results could be obtained by treating cellulose with calcium chloride-ammonia. In 1892, Vignon (Bull. Soc. Chim. Mulhouse, *62*, 563) claimed that he had produced amidated cellulose by treatment with ammonia at temperatures between 100 and 200° C., introducing as much as 3% of nitrogen into the cellulose which then possessed an affinity for the acid dyestuffs.

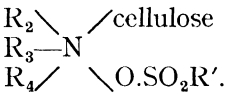
These results were not reproducible and it has been suggested that the product was merely cellulose in which the air spaces were filled with ammonia. Even this possibility is open to doubt. The matter was considered by Bernardy (Z. angew. Chem., 1925, *38*, 1195). There is also no chemical evidence for the formation of addition compounds of the type cellulose-NH_4OH, similar to soda-cellulose, and if such compounds were formed they would undergo hydrolysis in presence of water. Treatment of cellulose under vigorous conditions with ammonia leads to degradation and the formation of coloured decomposition products.

Direct introduction of the amino group into cellulose appeared hopeless, but Karrer (Helv. Chim. Acta, 1926, *9*, 592) produced amino-cellulose by an indirect method. He made use of the fact that whereas the esters of carboxylic acids are decomposed by ammonia and amines into acid amides and alcohols, the esters of the mono- and disulphonic acids react with ammonia to produce amines and the ammonium salt of the particular sulphonic acid. A satisfactory ester had just been produced on a commercial scale by means of p-toluene sulphochloride, which is a by-product in saccharin manufacture. This ester was found to react readily with ammonia, primary

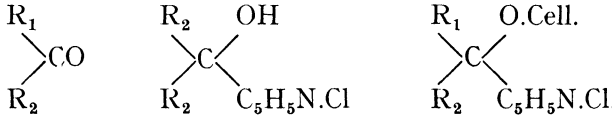
and secondary aliphatic amines, and hydrazine, etc. The reaction will take place in the cold if the ammonia is allowed to react for a period of weeks, but at 100° C. it is complete in an hour. The esterified cellulose contains 1·9% sulphur, but after the process the sulphur content is reduced to 1·3%, and a nitrogen value of 0·7 to 0·8% is obtained, indicating that one amino group to every 9 to 11 $C_7H_{10}O_5$ residues has entered into combination. This small amount of combined nitrogen is sufficient to impart characteristic dyeing properties to the fibre. The ester from which the amine was made resisted the direct dyes which colour ordinary cellulosic material, but had an affinity for the basic colouring matters. This affinity was less in the case of the amidated product and may even be destroyed by prolonged treatment with ammonia. Tests with acid dyestuffs showed that the amidated cellulose has a greater affinity for this class of colouring matter than wool itself.

The "amine yarns," as they were termed, are referred to in B.P. 249,842 and 263,169. A simplification of the process is seen in B.P. 284,358 where the product is obtained directly by the action of organic sulphochlorides on cellulose in presence of tertiary amines.

Tertiary amines can form addition compounds with the cellulose sulphonic acid esters and so produce quaternary ammonium compounds



Similar properties may be imparted to cellulose, according to B.P. 426,482 by treatment with ketones or aldehydes and pyridine bases. Formaldehyde is mentioned and also compounds such as butyl-chlormethyl ethyl ether.



This type of reaction should be considered in connection with those mentioned on pages 365 and 384.

According to Ichiro Sakurada (J. Soc. Chem. Ind., Japan, 1929, *32*, 11B) when the cellulose mono-ester of p-toluene sulphonic acid is heated with concentrated ammonia in a closed tube at 100° C., a preparation is obtained consisting

of two parts aminocellulose, two parts of cellulose and one part of ester. The concentration is the same even after heating for 60 hours, but better yields are obtained by heating for 20 hours with absolute alcohol saturated with ammonia; the amount of residual ester is then found to be one quarter of that of the amino cellulose. When the preparation is heated for 90 hours, the residual ester is reduced to one-sixth.

When the toluenesulphocellulose is heated with aniline in anhydrous glycerine on a water bath for 24 hours, the following preparation is obtained: two anilinocellulose + one cellulose + two ester, and after 100 hours: two anilinocellulose + $\frac{1}{2}$ cellulose + two ester. Methylaniline behaves in a similar manner.

When the unaltered ester is saponified and the cellulose dissolved away from the mixtures, aminocellulose $C_{12}H_{19}O_9NH_2$ and anilinocellulose $C_{12}H_{19}O_9NHC_6H_5$ are obtained.

These methods are successful not only for the introduction of substituted amines, but also for a large number of other basic substances with heterocyclic rings.

According to Karrer's process 100 parts of alkali cellulose were treated in suspension in benzene with benzene sulphonic chloride. After removal of the solvent and of the salt by washing with alcohol and water, the water is removed by means of acetic acid. It is important that not more than 90 parts of acetic acid should be present. After adding 0·3 parts of H_2SO_4 in 30 parts of CH_3COOH, the mixture is allowed to stand overnight and then 80 parts of acetic anhydride are added; after further addition of acetic acid and H_2SO_4, the mass is extracted with a mixture of methylene chloride and ethyl alcohol and freed from undissolved material. The dry ester is finally heated for three hours with 61 parts of aniline in an autoclave at 160° C. and the reaction product precipitated with dilute HCl. It is soluble in some organic solvents. In a similar manner cellulose toluene sulphonate can be heated on an oil bath with pyridine and benzyl chloride. The pyridine serves the two-fold purpose of entering the cellulose molecule and combining with the HCl formed. The amidated product is obtained by precipitation with water and has been found to be soluble in pyridine and in chlorinated hydrocarbons.

It will be realised that these methods, unlike those previously described, aim at the production of an amidated cellulose without attempting to retain the fibrous structure of the original cellulose.

Direct Amination

The greater part of the information concerning the nitrogen-containing derivatives of cellulose is to be found in the patent specifications. Vignon's early experiments are described in D.R.P. 57,846, according to which, cellulose is treated for six hours at 100° C. with ammonia or with calcium-chloride-ammonia. It is interesting to compare this old method with that described in B.P. 345,989, where the cellulose is first made more reactive by some moderate method of hydration and then treated with organic bases, e.g. primary and secondary alkylamines, organic ammonium bases, methylaniline and heterocyclic bases. In general, high temperatures are preferable, i.e. 150–250° C. The temperature varies with the reactivity of the starting material, with the pressure and with the organic base employed. Weak bases such as methylaniline require more vigorous conditions than do the stronger bases. Cellulose esters and incompletely etherified ethers may be treated in a similar manner as described in B.P. 344,480. Hydroxy-esters and ethers are preferably treated in two stages by first replacing the hydroxyl group with a halogen atom by means of thionyl chloride and then treating the resulting compound with the amine.

The treatment of unsaturated esters and ethers with ammonia is described in D.R.P. 542,004, and some of the examples are of interest in view of the information they contain regarding the amount of nitrogen in the final product. The method of Karrer, by treating a cellulosearylsulphonate with ammonia, gives a compound containing about 1 % of nitrogen. Cellulose-allylether reacts with ammonia at room temperature and after 48 hours gives a compound containing the grouping $-O-CH_2-CH_2NH_2$ or $-O-CH_2-CH(NH_2)-CH_3$, the compound containing some 2·75 % of nitrogen. At a temperature of 100° C. and at 35 atmospheres pressure, a period of 10 hours treatment gave a compound containing 2·02 % of nitrogen. Similar treatments of cellulosedicrotonate, hydroxyethylcelluloseundecylenate or hydroxypropylcellulosecrotonate give compounds containing about 2 % of combined nitrogen. When cellulose allyl ether was treated with liquid ammonia at room temperature, 5 g. of the ether gave 4·7 g. of the nitrogen-containing derivative.

The amino-compounds of cellulose produced by Karrer's method are insoluble in water or in organic solvents, but soluble derivatives of aminocellulose may be made by esterifying the

aminocellulose. The methods described in B.P. 279,801, include the treatment of cellulose esters of organically substituted inorganic acids with an acid chloride or anhydride in presence of tertiary aliphatic, aromatic or araliphatic amines, or the treatment may be to esterify the ester by acetylation and then boil the mixed product with aniline and alcohol.

One might expect aminocellulose to be soluble in dilute acid, but many of the earlier products did not possess this property. They were generally formed by treatment with ammonia on aryl sulphonates of cellulose of no high degree of substitution. U.S.P. 1,777,970 discloses the treatment of alkali cellulose with aliphatic monohalogen alkylamines but does not lead to products soluble in dilute acid. B.P. 346,806 refers to treatment with ethylenechlorbromide followed by ammonia or an amine, but again does not give a product soluble in acid. B.P. 344,480 mentions a product which is soluble in acetone and in acetic acid (concentration not stated) made by the treatment of hydroxyethyl cellulose with thionyl chloride followed by ammonia or an amine.

U.S.P. 2,136,296 discloses two methods of obtaining aminocellulose which is soluble in dilute acetic acid. The first is to prepare an alkali cellulose by means of an alkali metal in liquid ammonia and react the product with a monohalogen amine or its salt. The second method is to treat a hydroxyalkyl cellulose with an aromatic sulphonyl chloride in pyridine followed by reaction with a secondary amine. When soda-cellulose was treated for 20 hours at room temperature in a bomb with bromopropyldimethylamine hydrobromide, a dimethylaminopropyl cellulose was produced which contained 1·6% nitrogen and was soluble in 1·5% acetic acid and in 10% NaOH solution. Glycol cellulose may be treated with sodioammonia and then bromoethylamine hydrobromide to give a product containing 0·8% nitrogen. Again, glycol cellulose may be dissolved in pyridine and then treated with *p*-toluene sulphochloride. The ester, which is formed on warming, may be precipitated in ethyl alcohol and dissolved in benzyl alcohol where it is treated with dibutylamine; the aminocellulose (2·1% nitrogen) is precipitated with ether.

U.S.P. 2,136,299 refers to the formation of alkylaminocelluloses. Methyl cellulose was dispersed in NaOH and then treated with *p*-toluene sulphochloride in benzene, the resulting ester being isolated and dried. Reaction with *n*-amylamine for 12 days gave a product containing 5·1% nitrogen; it

dissolved in 2.5 % acetic acid to give 5 % solutions and in 5 % acetic acid to give 10 % solutions. The acetate, formate, lactate, propionate, butyrate, and benzoate of the alkylaminocellulose are soluble in water ; the hydrochloride is also soluble in water but is precipitated by excess of HCl, whereas the sulphate is insoluble.

It would appear that the early work on aminocellulose did not produce soluble products for several reasons. The fibrous cellulose sulphonates were unevenly esterified and insoluble, hence the reaction with these insoluble products was permutoid and led to surface effects. The use of ammonia instead of amines also tended to produce aminocelluloses which were not soluble in dilute acid.

A different method of making nitrogen-containing derivatives of cellulose is described in D.R.P. 550,760. The main principle is to treat alkali cellulose with a halogenalkylamine. For example, chlorethyldiethylamine may be applied in acetone solution in the cold or the hydrochloride may be used at a temperature of 50–60° C. The product is diethylaminoethylcellulose. Other amino-compounds, such as chlorethylethylaniline or chlorethylpiperidine may be used. The product may contain from 0·5 to 4 % of nitrogen according to the degree of alkylation.

A very interesting method of introducing nitrogen may be found in B.P. 322,556, which deals with the treatment of alkali cellulose by a basic sulphonic acid chloride, i.e. a compound of formula $X-SO_2-Cl$, in which X indicates a residue of an aromatic or heterocyclic base. Suitable compounds are the sulphochlorides of tertiary amines of the benzene or naphthalene series, quinoline-8-sulphochloride, amino-toluenesulphochloride, etc. It is rather surprising that such substances are capable of esterifying cellulose in view of the basic residue. The method of treatment is to effect reaction between the cotton yarn which has been transformed into the alkali compound, by means of treatment with alcoholic sodium hydroxide solution, and the basic sulphonic acid chloride in toluene or benzene at about 60° C. until the yarn no longer exhibits an alkaline reaction.

Nitrogen-containing cellulose derivatives are frequently prepared with a view to their utility as " effect threads."

It is interesting to note that according to Bredig and Gerstner (Biochem. Zeit., 1932, *250*, 414) diethylaminocellulose may be used as a catalyst for splitting CO_2 from β-ketocarboxylic acids

and the formation of mandelic acid nitrile from HCN and benzaldehyde.

The nitrogen content of cellulose may be increased by the means employed in B.P. 393,254, where cellulose is treated with amino acids or anhydrides, chlorides salts or esters, particularly in the case of those amino acids having a polypeptide structure obtained by the decomposition of albumen. These amino acids may be replaced by chlor-carboxylic acids in admixture with ammonium derivatives.

B.P. 393,242 deals with the treatment of cellulose with acetic acid, acetic anhydride, sulphuric and nitric acids and an amino compound, e.g. urea, biuret, aniline, phenyl glycine, aminophenolene, methyl aniline or glycocoll: The nitrogen of the resultant product will be present partly as $-NO_2$ and partly as $-NH_2$ directly bound to the carbon atom of cellulose, the proportions being at least 1% of $-NH_2$ and less of $-NO_2$. Undesirable side reactions and acetolysis are avoided by selecting amino compounds which give off NH_3, or by the addition of ammonium sulphite, formate, or acetate.

A comprehensive specification, B.P. 394,722, describes treatment of unsaturated esters or ethers of cellulose with an organic base particularly one containing replaceable hydrogen attached to nitrogen. In the case of esters, saponification must be avoided. Suitable cellulosic starting products include allyl, vinyl, crotonyl and styryl ethers and the following esters: crotonate, undecylenate, oleate, linoleate, ricinoleate and maleate. The basic substances with which these esters and ethers, including also ester-ethers, are made to react at an elevated temperature and under increased pressure comprise methyl, ethyl, propyl, amyl hexylamines, the mono- and di-ethanolamines, propanolamine, etc. Aniline, toluidine, urea, benzamide, and alcoholic amines from reduced cyanhydrins may be used and also amino-fatty acids and methyl and ethyl glycerine. In a modification of this process the unsaturated derivative of cellulose is first treated with a halogenating agent or hydrogen halide, and then with the desired base, in presence or an organic base without a replaceable hydrogen atom or in presence of an inorganic base. The purpose of this is to neutralise any free acid which may be produced.

The chemists of the I.G. have succeeded in condensing cellulose with ethylene imine. In an example of B.P. 460,590 air dry viscose staple fibre is heated above 100° C. with ethylene imine vapour. The resulting nitrogenous cellulose

derivative dyes with the acid colours. The reaction is probably as follows :

$$\text{Cell.OH} + (CH_2)_2NH \longrightarrow \underset{\text{aminoethylcellulose.}}{\text{Cell.O.}CH_2CH_2.NH_2}$$

If this reaction is carried out on viscose which has been coagulated but still contains xanthates, a woollenised viscose fibre is produced (B.P. 476,431) containing both sulphur and nitrogen.

Use of Nitro Groups

Another means of introducing nitrogen into cellulose derivatives is by forming nitro-derivatives which may be reduced. It will be remembered that " nitrocellulose " cannot be reduced in this manner, the effect of reducing agents being to remove the ester group. A slight residue of nitrogen, however, gives cellulose regenerated from " nitrocellulose," some affinity for the acid colours. There may be between 1 and 2% of nitrogen in " denitrated " cellulose nitrate.

Briggs (Z. angew. Chem., 1913, *26*, 256) nitrated benzoylated cellulose and then reduced the product. Peacock (J.S.D.C., 1926, *42*, 53) treated cotton cellulose with a solution of nitro-benzylphenyldimethylammonium chloride (nitro-Leukotrope) in presence of sodium carbonate. The nature of the product varies with the time of boiling and the proportions of the reactants. The treated material may be reduced with hydro-sulphite solution in the usual manner and the well-washed product diazotised and coupled by standard methods used for dyeing, giving coloured cellulose derivatives.

With a similar object in view, Riesz (Bull. Soc. Ind. Mulhouse, 1933, *99*, 349) described experiments with the trichloride of amino-benzene-trisulphonic acid. Reaction with soda cellulose in CCl_4 showed that one equivalent of the acid chloride possessing three active groups can esterify three times as many $C_6H_{10}O_5$ residues. The cotton esterified in this manner can be diazotised and coupled in a variety of ways.

B.P. 322,556 (page 415) covered esterification of cotton by amino sulphonic acid chlorides and according to this process the esterification can be conducted equally well by means of the chlorides of nitroaryl sulphonic acids with subsequent reduction of the nitro group on the fibre. The material produced in this manner, with free aromatic amino groups is also susceptible to diazotisation and coupling. Similar results

may be obtained by esterifying cellulose with isatoic anhydride (D.R.P. 433,147).

F.P. 687,298 describes the treatment of alkali cellulose with aromatic compounds containing NO_2 groups capable of reduction to NH_2, and a substituent capable of double decomposition in presence of an acid binding agent having no caustic action. The product may then be reduced. 1-chloro 2 : 4 dinitrobenzene is mentioned.

Paranitrobenzyl chloride is referred to in B.P. 344,420. This is made to react with cellulose in the general manner for this class of compound, and the product subsequently reduced in presence of a base. 2-aminomethylbenzyl chloride may also be brought into reaction with cellulose to form an aminoaralkyl ether.

B.P. 346,385, 347,263 and 347,117 describe the formation of cellulose derivatives containing diazotisable amino groups by reduction on the fibre of the NO_2 groups introduced by treating alkali cellulose with compounds of the type of nitrobenzyl chloride, nitrobenzoyl chloride and chlornitrobenzenes with mobile halogens, e.g. nitroxylyl chloride, ortho- and para-nitrochlorobenzene and chlorodinitrobenzene derivatives (but not the ortho dinitro).

Another method of obtaining an aminocellulose via the nitro-group is contained in F.P. 659,929, which utilises such compounds as metanitrobenzenesulphochloride, 4-nitrotoluene-2-sulphochloride, etc. The nitroarylsulphochloride reacts with alkali-cellulose, as previously described, and the resulting nitro group in the derivative may be reduced by means of stannous chloride in acetic acid solution, formaldehyde, hydrazine, alkali polysulphides, etc.

Use of Halogens

Halogen-containing compounds have been utilised as a means of producing nitrogen-containing cellulose derivatives, as already described, but the Swiss Patent 147,791, and D.R.P. 553,069, contain a reference to the somewhat unusual compound phosphonitrilchloride, or the corresponding halide. An example mentions the treatment of 100 g. of dry cotton linters with 30 g. of phosphonitril-chloride $P_3N_3Cl_6$ in 500 cc. of pyridine for about four hours on the water bath. The product was then well squeezed and washed with cold water.

The new cellulose derivative also contains halogen.

A number of instances are recorded where halogen-containing cellulose derivatives are treated with ammonia or amines in

order to produce nitrogen-containing cellulose derivatives. For instance, in B.P. 346,806, cellulose is treated, in presence of caustic alkali, with an aliphatic etherifying agent containing halogen in addition to the etherifying group, e.g. epichlorhydrin, or with an agent containing halogen, atoms of different reactivity, so that one halogen is retained in the product, e.g. C_2H_4ClBr. The cellulose derivative is then treated with ammonia or an amine to yield an amino ether. In a broadly similar manner B.P. 360,742 states that chlorohydroxypropyl ethers of cellulose, obtained from cellulose and epichlorhydrin, are converted into nitrogen-containing cellulose derivatives by treatment with tertiary amines, e.g. pyridine or trimethylamine. Ammonia or an amine may be caused to react with a halogen substituted fatty acid ester of cellulose according to B.P. 320,482, whilst the action of trimethylamine on chloracetylcellulose and on acetylchloracetylcellulose is mentioned in the Swiss Patents 148,491 and 150,790.

The method of B.P. 344,480 has already been mentioned, but this specification also mentions that where acid amide derivatives of cellulose have been prepared, for instance, from cellulose glycollic acid ester, these may be turned into the simple amine by means of treatment with hypochlorite or hypobromite. The process involves the substitution of the hydroxyl group in a cellulose derivative, such as a hydroxy ester, or ether, or in a derivative containing a carboxyl group, with halogen by means of, say, thionyl chloride. The halogen is converted to amino by treatment with an amine and in the case of the initial carboxyl containing derivative, this results in an amide.

The original fibrous structure may be retained and a satisfactory tensile strength of the final product obtained according to B.P. 341,237, where alkali cellulose is treated at low temperatures with CS_2 and an alkyl or aralkyl halide. The material is then washed with water and warmed with organic bases such as piperazine and dimethylethylenediamine,

B.P. 320,842 states that the cellulose may be acylated by means of chlor- or brom-acetic anhydride and then the halogen groups replaced by amino or alkylamino groups.

The treatment of cellulose with halogenometh
long chain fatty acids, referred to on page 384
very rapidly in recent years and produced a
patent specifications.

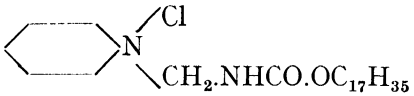
The general method of preparing these re

HCl into a solution of the fatty alcohol (with more than ten carbon atoms) in presence of trioxymethylene. Usually a pyridinium salt is then formed for application to the textile material and is decomposed on heating on the yarn or cloth which combines with the halogenoalkyl ether. Anions other than halogen may be utilised as mentioned on page 385; B.P. 495,025 mentions $C_{18}H_{37}O.CH_2.C_5H_5N.NO_3$ and also compounds of the general formula $C_{16}H_{33}O.CH_2.C_5H_5N$ X, where X may be SO_3H, SO_4H, or CO.COOH. B.P. 466,853 utilises sulphur dioxide instead of hydrogen chloride.

The reaction with hydrogen chloride, trioxymethylene and a fatty alcohol may also be applied to fatty acid amides, urethanes (carbamic esters), hydrazides and so on. Quaternary ammonium salts may be formed and when these react with the cellulose, a hydrophobic effect is obtained and the new derivative is nitrogenous.

The amide of general formula $R.CONH_2$ gives a compound $R.CONHR'.CH_2X$ such as N-methylstearamidomethyl chloride $C_{17}H_{35}.CO.N(CH_3).CH_2Cl$, and the carbamic ester $RO.CO.NH_2$ gives a product $RO.CO.NR'.CH_2X$ such as N-carbomethoxyheptadecylaminomethyl chloride $CH_3O.CO.N(C_{17}H_{35}).CH_2Cl$. (B.P. 471,130.)

The commercial product sold as Velan P.F. (Zelan in the U.S.A.) appears to consist, in all probability, of a stearyl compound



mixed with about 40% of common salt which has a definite effect in promoting better surface action.

Quaternary ammonium salts of the halogenomethyl ethers of urethanes ($RO.CONH_2$), hydrazides ($R.CO.NH.NH_2$) and ...tly acetylated ureas ($R.CO.NH.CO.NH_2$) are mentioned in ...508,173, $C_{17}H_{35}.CO.NH.CO.NH_2$ being a specific instance ... urea type which may be treated with trioxymethylene ...l, followed by pyridine.

...ne of tertiary aliphatic or heterocyclic amine may be ...l in the reagent according to B.P. 493,920, which ...aramidomethylpyridinium salts, cetoxymethyl-tetrammonium bromide and benzyloctadecoxy-...um bromide. These reagents are particularly ...tment of wool and silk.

The range of reagents is extended still further by B.P. 494,761 which discloses the use of the methyliminoether quaternary ammonium halides. The chlormethyl ethers are formed by the usual method with trioxymethylene and HCl. Halogen methyl imino-ethers of general formula R.C : (NH). $O.CH_2.\ddot{N}.X$ are mentioned, together with halogen methyl ethers of general formula $R.CONH.CH_2.OCH_2.\ddot{N}.X$ derived from fatty acid methylol amides. Cyanhydrins are capable of producing halogen methyl ethers of general formula R.CHOHC : (NH).$OCH_2.\ddot{N}.X$. *R* represents an aliphatic radical of more than ten carbon atoms.

Another method of making the reagents which later combine with the cellulose is seen in B.P. 475,170. Stearohydroxymethylamide may be prepared by warming stearamide, paraform and potassium carbonate in presence of benzene. The stearohydroxymethylamide is warmed with pyridine hydrochloride and pyridine until a test sample dissolves in water ; the new quaternary salt may be precipitated by acetone and corresponds to the formula $C_{17}H_{35}CONH.CH_2.N(C_5H_5)Cl$, stearamidomethylpyridinium chloride. Alternatively, the quaternary salts may be made by heating the amide with formaldehyde and a tertiary amine salt in presence of a tertiary amine. B.P. 477,991 discloses hydrophobic effects by treating cellulose with stearamidomethylpyridinium chloride ; the treated material is dried and then heated at 105 to 120° C. for 10 to 20 mins.

An ingenious development has recently been disclosed in B.P. 517,474 which refers to the use of quaternary salts of halogenomethyl compounds of the general formula

$$\begin{array}{c} R.CO.N.CH_2.X \\ \dot{C}H_2 \\ R.CO.\dot{N}.CH_2.X \end{array}$$

where *R* is an aliphatic hydrocarbon radicle containing not less than seven carbon atoms and *X* is a halogen. The starting material in one case is distearyldiaminomethane (methylene distearamide), which may be treated with paraformaldehyde and hydrogen chloride to give a product with the following formula

$$\begin{array}{c} C_{17}H_{35}.CO.N.CH_2.Cl \\ \dot{C}H_2 \\ C_{17}H_{35}.CO.\dot{N}.CH_2.Cl \end{array}$$

This forms a quaternary ammonium salt, soluble in water, in the usual manner. Excellent waterproof effects are obtained by following the " Velan " technique.

The condensation product of a halogenomethyl ether of an aliphatic alcohol of not less than C_{17} with a thiourea derivative has been described in B.P. 527,012. When a compound of this type, as for example $C_{18}H_{37}.O.CH_2.S.C.(:NH).NH_2.HCl$ is applied to cotton at 75° C. a waterproof effect is obtained according to B.P. 526,738.

Although the application of many compounds of high molecular weight, such as the halogenomethyl ethers, carbimides, etc., has been discussed under the heading of cellulose ethers, it is also quite conceivable that long chain fatty methylene compounds become entangled in the cellulose structure and are not readily removed except by acid hydrolysis.

Long chain fatty compounds have also been " fixed " to cellulose by synthetic resins in order to produce waterproof effects. In this manner it is possible to produce crease-resistance and waterproofing in one operation, as for example according to B.P. 506,721 ; 495,645 ; 495,714 ; 495,829 and numerous other specifications which do not strictly fall within the scope of cellulose chemistry.

Use of — CN Group

There are two instances in patent specifications of obtaining amino-derivatives of cellulose from cyano-derivatives. B.P. 344,488 refers to the reduction of cellulose esters, or ethers containing the — CN group, by means of sodium amalgam in alcohol or aqueous alcohol at the boil. F.P. 714,061 introduces the — CN group by means of hydrogen cyanide, and the nitrile group may be converted to amino by means of reducing agents, such as sodium amalgam in alcohol, or by hydrogen in presence of the usual catalysts, such as nickel, copper and their oxides, platinum, palladium, etc.

The — CN group may also be introduced into cellulose in a manner similar to that used for introducing alkylamines.

F.P. 714,061 states that it is possible to introduce the — CN group by means of hydrogen cyanide reacting on cellulose, hydrocellulose or oxycellulose. Cellulose esters and ethers may be treated in solution or suspension.

B.P. 370,355 mentions the treatment of cellulose with alkali to ensure swelling, followed by removal of the alkali by washing. The reactive cellulose is then treated with a solution of

potassium cyanide and the excess removed by centrifuging and squeezing. The product is then treated with chlorine or bromine in CCl_4 at O° C. The reaction is probably due to the controlled formation of cyanogen halide but the amount of combined nitrogen is small, i.e. 1 % or less.

B.P. 343,748 states that alkali cellulose may be treated with CS_2, and subsequently, or simultaneously, with a solution of a cyanogen halide in benzene. Treatment of cellulose with alcoholic KOH, followed by cyanogen chloride in xylene in presence of chalk is covered by F.P. 687,310. Cyanogen bromide may also be used.

The reaction with cyanogen chloride is apt to be vigorous, according to Malowan (Kunststoffe, 1934, *24*, 53), but if the treatment is carefully applied the cotton shows no apparent change other than a slight increase in weight and a nitrogen content of about 1·7 %.

Cellulose esters and ethers containing —CN may be prepared, according to B.P. 344,488, where cellulose or a derivative containing a free OH group is treated with an esterifying or etherifying agent containing —CN, e.g. chloracetonitrile, cyanoacetylchloride, α or β-chlorpropionitrile. The product may then be subjected to reduction, etc., to give nitrogen-containing derivatives.

Alkali cellulose may be converted into products of the type under review by treatment with those heterocyclic compounds which contain cyanohalide groups, such as those mentioned in B.P. 342,166, e.g. cyanuric chloride and cyanuric bromide, or by compounds of the triazine series, with at least one labile halogen atom, e.g. chloroquinazoline, and tribromo-pyrimidines. These new cellulosic derivatives may be further treated with compounds containing —NH, —OH or —SH, according to B.P. 347,167, or alternatively, by a salt of such a compound. As the result of such a treatment, the affinity for the basic colouring matters is replaced by an affinity for the acid dyes. B.P. 393,914 extends the treatment with substances like cyanuric chloride to partially esterified or etherified cellulose, condensation taking place in presence of a tertiary base. Soluble products may thus be obtained by treating 10 parts of acetone soluble cellulose acetate with five parts of tetrachloropyrimidine, and five parts of dimethyl aniline in 50 parts of chloroform. The mixture should be warmed to 50° C., and 10 to 20 parts of acetone added, and the whole mass stirred until it thickens to a gelatinous mass.

After an hour the product may be precipitated with alcohol, washed and dried. It dissolves in acetone and pyridine but has only a nitrogen content of 0·5 %.

About 1·7 % of nitrogen may be combined with cellulose after the procedure of U.S.P. 1,813,619, which entails the treatment of 10 parts of cotton with 33 % NaOH solution, followed by squeezing, in order to form the alkali cellulose which is then cooled and stirred, into 150 parts by volume of a 2 % solution of cyanogen chloride in ether at −10° C. An exothermic reaction takes place, and when this is complete the cotton is washed, soaped, washed and dried. Provided the reaction is carefully carried out, the cotton shows no apparent change other than a slight increase in weight. It dyes with the acid colours.

According to another process (D.R.P. 574,002) 50 parts of cotton linters were impregnated with 18 % solution of NaOH, the excess of caustic soda removed, and the alkali cellulose added to a solution of 30 to 50 parts of cyanuric chloride in 1000 parts of carbon tetrachloride, at 25 to 30° C. The temperature rose to 60 65° C., and after two hours the product was filtered by suction, washed and dried. A double repetition of this process produced a white product which had increased 100 % in weight from the original cellulose. It contained 11·7 % of nitrogen and 4·5 % of chlorine. It no longer showed signs of swelling in the usual solvents and swelling agents for cellulose, and as it did not reduce Fehling's solution, is stated to be an undegraded cyano-cellulose.

G. R. Levi (Boll. Assoc. Ital. Chim. e. Col., 1930, *6*, 80) states that mixed acetic and cyanacetic esters of cellulose can be prepared, that spin like cellulose triacetate and can be mixed in all proportions with its acetic solution. The —CN groups may be transformed into $-CONH_2$ by treatment at 40–50° C., with alkali and hydrogen peroxide, under conditions in which the triacetate is not altered. The hydrolysis results in products containing free carboxylic groups without any saponification of the cellulose esters which retain all the physical properties of the cellulose triacetate.

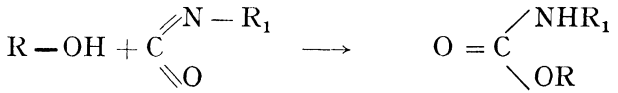
Heterocyclic Bases

The production of a nitrogen-containing derivative of cellulose includes the introduction of a heterocyclic basic group. This is accomplished by some of the methods which have previously been described, for example, by the treatment of the arylsulphonic ester of cellulose, according to Karrer's

method B.P. 249,842 and 263,169, where pyridine, quinoline or piperidine are employed. The methods of B.P. 322,556, where esterification with basic aromatic sulphonic acid chlorides are employed, also include esterification with basic heterocyclic sulphonic acid chlorides, such as quinoline-8-sulphochloride. In Swiss Patent 145,053, there is reference to the treatmcnt of alkali cellulose with chlorethylpiperidine whilst in the three Swiss Patents 150,789, 150,791 and 152,480 is described the treatment by pyridine of chloracetylcellulose and acetylchloracetylcellulose and also the further treatment of the product from the reaction between epichlorhydrin and cellulose, with pyridine.

Urethanes and Thio-urethanes

A very interesting reaction in cellulose chemistry is that of phenyl isocyanate on cellulose, as outlined in B.P. 130,277 and 317,019, and D.R.P. 544,777. Alcohols or phenols act on the aliphatic or aromatic isocyanates and produce esters of the alkyl or aryl carbamic acids.



This reaction can be applied to cellulose and to its derivatives which contain hydroxyl groups. One part of dry cotton cellulose was treated with three parts of phenyl isocyanate, diluted with about six parts of pyridine for 12 to 24 hours at 120° C. with stirring. The cotton fibres gradually disappeared and a colloidal solution was obtained from which the cellulose phenyl urethane was isolated by pouring the mass into water. The insoluble ester was thus precipitated and isolated. A small amount of diphenylurea was formed at the same time and removed by means of petroleum ether. A surface action with retention of the fibre structure is obtained by a modification of the method.

Cellulose alkyl urethanes with hydrophobic properties permanent to washing and dry cleaning have been recently produced from isocyanates (carbimides) or isothiocyanates (thiocarbimides) carrying long chain fatty radicles. B.P. 461,179 contains a comprehensive account of these reactions in which the structure of the material is maintained and includes the use of the simple derivatives of carbimides, e.g. $C_{18}H_{37}$.NH.CO.Cl.

In one example, cotton twill is treated in a solution of 10 g. stearyl isocyanate per litre of carbon tetrachloride, the goods hydroextracted and dried at 100° C. during one hour.

Other reagents exemplified include octadecyl thiocyanate, the cetyl ether of hydroxyethyl thiocyanate, octa-decyl mustard oil ($C_{18}H_{37}NCS$), and octadecyl urea chloride.

B.P. 474,403 by different inventors contains similar ideas, but in treatment with $C_{18}H_{37}.NCO$, viscose is only heated for one minute at 100° C. or two minutes at 140° C. In addition such derivatives as alkyl-CO-NCO and the azide $C_{27}H_{45}.O.CO(CH_2)_4.CON_3$ are specified. The addition of stearyl isocyanate (800 g.) to 100 litres of 20% acetyl cellulose in acetone affords water-repellent filaments when spun.

B.P. 494,833 refers to the treatment of cellulose with thiocyanic methyl ethers of high molecular weight, such as $R.O.CH_2S.C:N$ where R has at least 10 carbon atoms. Octadecylchlormethyl ether may be converted to the thiocyanic methyl ether by treatment with potassium thiocyanate. If necessary these ethers may be converted to soluble quaternary ammonium salts before reaction with cellulose.

The reaction between cellulose and phenyl isocyanate has already received mention in the chapter on cellulose esters (see page 340).

Alcohols and isocyanates react to give urethanes, the typical example being urethane itself or ethyl carbamate $NH_2CO.OC_2H_5$.

The reaction between alcohols and isocyanates proceeds as follows:

$$O:C:NCH_3 + C_2H_5OH \longrightarrow O:C\begin{matrix}\diagup NHCH_3 \\ \diagdown OC_2H_5\end{matrix}$$

so that with cellulose

$$O:C:NR + Cell.OH \longrightarrow O:C\begin{matrix}\diagup NHR \\ \diagdown O.Cell.\end{matrix}$$

In addition to the method already described by Goissedet, in B.P. 130,277, there is a patent by the Society of Chemical Industry in Basle (B.P. 317,019) for a surface reaction in which the cellulose does not pass into solution if treated with 90 parts of phenyl isocyanate and 10 parts of pyridine.

Reactions of this type have also been utilised in the production of resist effects illuminated with vat dyes, by printing

with vat dye pastes containing organic carbimides (B.P. 489,235).

Another class of nitrogen-containing cellulose derivatives is the cellulose thiourethanes of Lilienfeld, who describes their preparation in B.P. 231,801. Viscose solution is neutralised with acetic acid and then treated with the sodium salt of monochloracetic acid. After standing for some 6 to 48 hours the mixture is again carefully neutralised and then treated with 60 to 120 parts of aniline per 100 parts of cellulose. The product begins to separate after several hours and precipitation is complete in three days. The new product is cellulose phenylthiourethane, formed by the action of aniline on the sodium salt of cellulose xanthoacetic acid—sodium thiogylcollate is split off in the reaction and remains in the mother liquor. By the use of any primary or secondary amine, the corresponding thiourethane of cellulose may be obtained, e.g. ethyl or methyl thiourethanes.

The product is very resistant to water but is soluble in dilute sodium hydroxide solution (1–10%) or in aqueous 70–90% pyridine. The solutions may be caused to deposit clear films or threads of good elasticity by evaporation, or by coagulation with acids or ammonium salts.

Later work (B.P. 248,246) shows that instead of the cellulose xantho fatty acid derivatives, other compounds of cellulose, containing the CSS-group, may be brought into reaction with a primary or secondary amine to form new compounds of N-substituted thiourethane type. Cellulose xanthate (i.e. viscose) or cellulose xanthic acid, or the products obtainable from them by the action of oxidising agents, or the products obtained by esterifying cellulose xanthic acid, may be treated with primary or secondary amines or hydroxy amines. The products of reaction between esters of chlorcarbonic acid and cellulose xanthate, or cellulose xanthic acid, may also be condensed with suitable amines in a similar manner.

(The patents of Lilienfeld on this subject are, perhaps, most conveniently consulted in the American specifications, U.S.P. 1,674,401-5.)

Cellulose xanthic or xanthogenic acid may be represented by

$$\begin{matrix} \diagup\text{O.Cell.} \\ \text{C : S} \\ \diagdown\text{SH} \end{matrix}$$

, xanthogenic acid being

$$\begin{matrix} \diagup\text{OR} \\ \text{C : S} \\ \diagdown\text{SH} \end{matrix}$$

(compare

$$\begin{matrix} \diagup\text{OR} \\ \text{C : O} \\ \diagdown\text{OH} \end{matrix}$$

)

so that sodium cellulose xanthacetate Cell.O.CSSCH$_2$COONa, reacts with aniline to form $C_6H_5NH.CS.OCell$, which may be termed either cellulose phenylthiourethane or cellulose xanthanilide.

U.S.P. 1,674,405, refers to the action of ammonia on cellulose xantho-fatty acids with the formation of cellulose xanthamide, i.e. a thiourethane in which neither of the amido hydrogens is replaced by an organic radical $\begin{matrix} \diagup \text{O.Cell.} \\ \text{C : S} \\ \diagdown \text{NH}_2 \end{matrix}$

Lilienfeld, in B.P. 390,518, has prepared cellulose derivatives from the xanthate by treatment with the halogen derivatives of nitro- or amino- derivatives of oxy- or oxo- compounds, e.g. epichloramine (3 : chloro-1 : amino-propano 1 : 2), N-methyl N-chloracetyl urea, chloracetylaminoacetic-acid-ethylether, chloracetyldiglycine amide, etc.

Derivatives of cellulose containing sulphur, selenium or tellurium, have been obtained in a manner similar to the above (B.P. 385,979). Lilienfeld has also shown (B.P. 357,526) that cellulose xanthate may be treated with halogen alkyl-amines, halogen derivatives of the ethers of aminophenols, halogen derivatives of cyanogen, nitrobenzene, etc.

The treatment of cellulose xanthate, in presence of mild oxidising agents, with ammonia or its organic or inorganic substitution products, has been observed by Harrison also (B.P. 286,331). The reaction is probably :

$$\begin{matrix} \diagup \text{OC}_6\text{H}_9\text{O}_4 \\ \text{C : S} \\ \diagdown \text{SNa} \\ \diagup \text{SNa} \\ \text{C : S} \\ \diagdown \text{OC}_6\text{H}_9\text{O}_4 \end{matrix} + 2\ \text{NH}_2\text{C}_6\text{H}_5 + (\text{oxidation}) \qquad \begin{matrix} \diagup \text{OC}_6\text{H}_9\text{O}_4 \\ \text{C : NC}_6\text{H}_5 \\ \diagdown \text{S} \\ \diagup \text{S} \\ \text{C : NC}_6\text{H}_5 \\ \diagdown \text{OC}_6\text{H}_9\text{O}_4 \end{matrix}$$

The treatment of cellulose thiourethanes with inorganic acid esters has been described by Lilienfeld in B.P. 241,149, the reaction probably proceeding in the following manner :

$$\begin{matrix} \diagup \text{OC}_6\text{H}_9\text{O}_4 \\ \text{C : NR} \\ \diagdown \text{SNa} \end{matrix} + \text{C}_2\text{H}_5\text{I} \qquad \begin{matrix} \diagup \text{OC}_6\text{H}_9\text{O}_4 \\ \text{C : NR} \\ \diagdown \text{SC}_2\text{H}_5 \end{matrix}$$

The product is reported to be soluble in alkali and in organic solvents.

The Society of Chemical Industry in Basle has also worked on the treatment of cellulose xanthate with a mild oxidising agent, a sulphur containing compound such as sulphur chloride or thiophosgene, followed by treatment with an aliphatic diamine, such as piperazine, ethylenediamine or diethylenediamine, to produce compounds containing both nitrogen and sulphur (D.R.P. 551,679).

The reaction described by Lilienfeld in B.P. 231,801 (see above) may be represented as follows :

$$\begin{array}{l} /OC_6H_9O_4 \\ C:S \\ \backslash SCH_2COONa \end{array} + NH_2R \longrightarrow \begin{array}{l} /OC_6H_9O_4 \\ C:S \\ \backslash NHR \end{array} + CH_2(SH)COONa$$

but in this connection it is interesting to note the cellulose, thiourethane and cellulose xanthogenamide show tautomerism, so that the following type of reaction is possible :

$$\begin{array}{l} /OC_6H_9O_4 \\ C:S \\ \backslash SH \end{array} + NH_2R \longrightarrow \begin{array}{l} /OC_6H_9O_4 \\ C:S \\ \backslash NHR \end{array} \quad \text{or} \quad \begin{array}{l} /OC_6H_9O_4 \\ C:NHR \\ \backslash SH \end{array}$$

Lilienfeld giving the two cases in U.S.P. 1,674,401, of RNH.CS.OCell., and RN : C(SH).OCell.

In B.P. 357,080, Lilienfeld has described the formation of alkyl thiourethanes of cellulose without making use of the xanthate, by means of alkyl isothiocyanates. The mustard oils, or isothiocyanates RN : C : S, have properties analogous to those of the isocyanates and combine with alcohols to give thiourethanes.

Alkali cellulose from 100 parts of cotton or wood pulp is kneaded with 100 parts of methylisothiocyanate for three hours and allowed to stand for 24 to 48 hours. The mass is dissolved in 5–8% NaOH solution, filtered and precipitated with H_2SO_4, of 12 to 20% strength. The precipitate when finely ground, is insoluble in water and in organic solvents, but is soluble in 5–8% NaOH solution.

A solution of 5 to 10% of cellulose methyl thiourethane can be precipitated to form clear films by means of 10–16% H_2SO_4, whilst stronger acid (30–70%) exerts a plasticising effect on the newly coagulated material.

Ethyl thiourethanes of cellulose may be formed in a similar manner, and allyl isothiocyanate (the compound from which mustard oils derive their name) may also be used.

CHAPTER TWENTY

SODA CELLULOSE

A GREAT deal of experimental work has been done on the vexed question of whether cellulose forms a compound with sodium hydroxide. It still remains undecided, but it is difficult to account for some of the reactions of cellulose—the viscose reaction in particular—without assuming compound formation. The behaviour of other simple and polyhydric alcohols must also be considered; Karrer (Cellulosechem., 1921, *2*, 124) has shown that the evidence of chemical analogy is very strong. There is a large range of complex compounds formed by glycerol with the alkaline hydroxides, the alkaline earths and the heavy metals. The same power of complex formation with alkali is shown by the sugars and the crystalline amyloses. Investigation of the system sugar-lime-water has shown that several complex compounds probably occur and the equilibria are attained so slowly that even partial elucidation of the relations is a highly involved problem. The case of cellulose is complicated by the further factors which arise, i.e. the colloidal properties and characteristic absorption effects.

The original view of the mercerising process was that there was chemical combination between cellulose and the sodium hydroxide followed by decomposition of the soda cellulose by the action of water in a manner similar to sodium ethoxide formation and hydrolysis. The resulting mercerised cellulose was termed cellulose hydrate or hydrated cellulose and was held to be chemically distinct from cellulose. The evidence was mainly based on the higher moisture content of the mercerised material, but the work of Miller (Ber., 1910, *43*, 3430; 1911, *44*, 728) and Ost and Westhof (Chem. Zeit., 1909, *33*, 197) showed the identity of chemical composition of mercerised and unmercerised cellulose. The matter is also discussed in considering the dispersed forms of cellulose (see page 187) and the moisture relations (see page 34). Increased moisture content is a matter of increased absorptive capacity and does not indicate hydrate formation in the sense of the hydrates of inorganic salts.

Mercer's original observation that when cotton was placed in concentrated solutions of sodium hydroxide, there was a fall in concentration of the alkali caused him to come to the conclusion that a chemical combination took place, the compound being destroyed on treatment with water. Gladstone (J.C.S., 1852, *5*, 17) investigated the possible reaction by removing the uncombined alkali from the system by washing with alcohol. The composition of the alkali cellulose was then examined by conversion of alkali into the corresponding sulphate, and the opinion put forward that compounds were formed $(C_6H_{10}O_5)_2NaOH$ and $(C_6H_{10}O_5)_2KOH$. Hübner and Teltscher (J.S.C.I., 1909, *28*, 641), however, were able to wash all the sodium hydroxide from the cotton by means of hot absolute alcohol.

Absorption Measurements

The first quantitative measurements of the relation between the compositions of the solid and liquid phases of the system were made by Vieweg (Ber., 1907, *40*, 3876), who shook known weights of dry cotton with known volumes of NaOH solutions in predetermined and increasing concentration. The mixture was shaken for one hour and then allowed to stand for two hours. When equilibrium had been attained, the concentration of the alkali was determined in the various solutions. A diminution in the alkali concentration was observed in all cases and in this manner Vieweg made a calculation of the alkali absorbed. This method of procedure involved two assumptions, firstly, that no water had been absorbed and secondly, that the volume of the liquid phase remained constant. Two definite steps appeared in the curve corresponding to the compounds $(C_6H_{10}O_5)_2NaOH$ and $(C_6H_{10}O_5)_2\ 2NaOH$.

Vieweg also showed that the alkali cellulose reacted with benzoyl chloride to form cellulose benzoates (see page 229).

Vieweg's calculations were given in volume concentrations and not in weight calculations, but Clibbens (J.T.I., 1923, *14*, 217) in his excellent review of the literature on the mercerisation of cotton has recalculated the analyses in order to make comparisons with later work on the subject; the essential nature of the curve as given (fig. 141), does not differ from Vieweg's own curve.

It will be seen that the absorption, within the liquid concentration range of 16 to 24% NaOH, remains approximately constant.

Miller (Ber., 1907, *40*, 4903) carried out his experiments at a temperature of 25° C. and found that the percentage of sodium hydroxide in the alkali cellulose increased with the concentration of the alkaline solution; he was, therefore, unable to subscribe to the view that the compound $(C_6H_{10}O_5)_2NaOH$ was formed.

The later work of Joyner (J.C.S., 1922, *121*, 2395) also gave a smooth curve showing that sorption takes place rather than compound formation. Vieweg took known volumes of solution

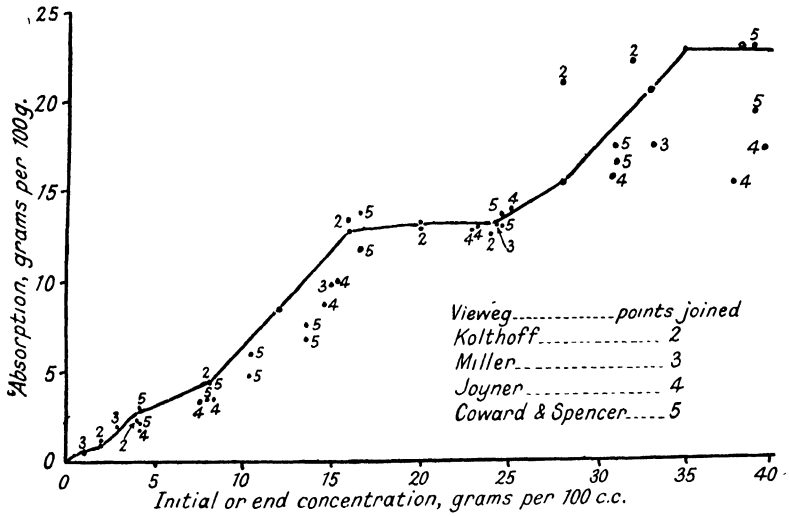


FIG. 141.—The absorption of NaOH (composite graph by Clibbens).

before and after the addition of the cotton, but Joyner carried out his analyses on definite weights of the solutions with a view to obtaining more accurate results. Known weights of sodium hydroxide and cellulose were mixed at room temperature and a definite weight of solution titrated.

The analyses of the sodium hydroxide solutions expressed in grams per 100 grams of solution by Joyner and also by Coward and Spencer (see later) are better than in grams per 100 cc. of solution, but these have been recalculated by Clibbens, as previously stated, for purposes of comparison as shown in the graph above.

The heat of reaction between sodium hydroxide solutions of varying concentration and cellulose has been examined by Barratt and Lewis (J.T.I., 1922, *13*, 113), who found an abrupt

change in direction of the curve where the concentration of alkali lay between 10 and 15% NaOH indicating a rapid increase in the heat evolved over this range.

Use of Centrifuge

The centrifugal method of examining the problem was undertaken by Leighton (J. Phys. Chem., 1916, *20*, 32), who offered two criticisms of Vieweg's results, firstly, that the calculations were based on small difference figures with a high experimental error, and secondly, that Vieweg had assumed that no water is adsorbed from the solution. Vieweg was, therefore, measuring absorption and not adsorption, because of the liquid taken up by the capillaries. Leighton's own work, however, was based on the following method. Cotton was immersed in solutions of NaOH of various concentrations and after equilibrium had been reached, the liquid phase was separated as completely as possible by centrifuging for one hour in a machine running at 4,000 r.p.m. The alkali content of the resulting solid was determined by analysis, and the water content by the figure thus obtained in conjunction with the difference between initial and equilibrium concentrations. The composition of the adsorbed solution was calculated from the water and alkali contents of the centrifuged cotton, and when this was plotted against the composition of the equilibrium solution a smooth curve was obtained. Hence Leighton concluded that there was no compound formation between cotton and sodium hydroxide, the alkali merely being adsorbed.

The inaccuracies of this work were pointed out by Coward and Spencer (J.T.I., 1923, *14*, 32), who used a centrifuge giving 8,000 r.p.m., obtaining results of much greater value, for they first examined the performance of the machine with other liquids, and made the first direct determinations of both water and sodium hydroxide present in the alkali-saturated fibre, thereby eliminating errors occurring in Leighton's work.

In the case of water, they came to the conclusion that after centrifuging, the liquid is held in the cellulose itself and not between the hairs, as the result of experiments with other and non-aqueous liquids. In addition, results where the cotton was replaced with glass wool were considered. When the water was replaced by solutions of sodium hydroxide, the weight of liquid retained after centrifuging was found to be greater than when water was used. The greater weight

was not due to the higher viscosity of the alkaline solution, for in the case of castor oil, which has a viscosity sixteen times that of the most concentrated alkali solution, it was only adsorbed to one-sixth of the extent. Coward and Spencer, therefore, concluded that most of the mass of the adsorbed alkali solution must be held in the substance of the cotton hairs. Cotton was therefore immersed in solutions of sodium hydroxide of varying concentration, the external liquor removed in the centrifuge and the absorbed sodium hydroxide was determined by titration of the alkali in the centrifuged mass.

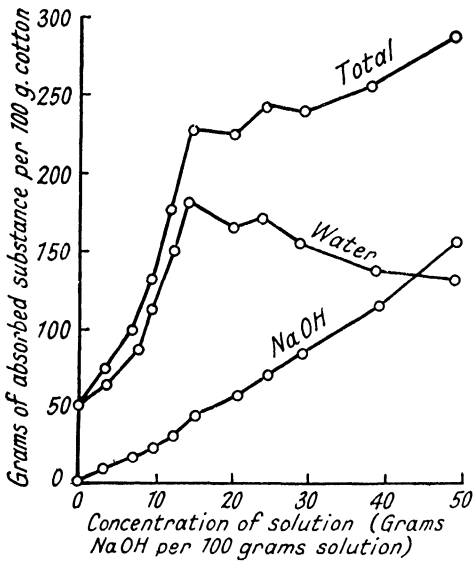


FIG. 142.—Absorption of sodium hydroxide by cotton.

The absorbed water was determined as the difference between the weights of absorbed solution and absorbed caustic soda.

The total weight of absorbed solution rapidly increased with increase in alkali concentration up to 14% NaOH, but above that figure the increase was very slow. Coward and Spencer concluded that, although the shape of the curves (fig. 142) is not inconsistent with compound formation, the results yield no definite evidence for it.

Other Investigations

A number of investigators—Heuser and Niethammer (Cellulosechem., 1925, *6*, 13), Heuser and Bartunek (*ibid.*, 19),

König and Dehnert (*ibid.*, 1924, *5*, 107; 1925, *6*, 1), and D'Ans and Jager (*ibid.*, 1925, *6*, 137)—worked in the same manner as Vieweg, and came to the same conclusion, i.e. that the compound $(C_6H_{10}O_5)_2NaOH$ was formed in mass. On the other hand Leighton (J. Phys. Chem., 1916, *20*, 32), Miller (Ber., 1907, *40*, 4903) and Joyner (J.C.S., 1922, *121*, 2395) held the mercerising process to be one of adsorption.

Neale's view of the mercerising process (see page 147) is that cellulose behaves as a weak monobasic acid which forms a sodium salt according to the law of mass action, in increasing amount with the alkali concentration. He put forward (J.S.C.I. 1931, *50*, 177) his view of the results which led to the Vieweg type of hypothesis, on the basis that if the concentration of free alkali in the cellulose phase is not equal to that of the external solution, but is determined by the Donnan equation of membrane equilibrium, then it follows algebraically, that the amount of salt formation is not equal to the preferential absorption of alkali from the solution, but at high concentrations is, approximately, twice that amount. On this account the evidence for the supposed formation of $C_{12}H_{19}O_{10}Na$, is rather to be interpreted as pointing to a substance in which one molecule of alkali reacts with each glucose residue, i.e. $C_6H_9O_5Na$.

The work of Champetier, in connection with the possible formation of soda-cellulose, has proceeded along two lines which yielded similar results In his first paper (Compt. rend., 1931, *192*, 1593) experiments were described of the following type. Five g. of dry cotton linters were treated for 24 hours at a temperature of 18 to 20° C. with 200 cc. of an aqueous solution of sodium hydroxide of known concentration. The alkali cellulose formed was then submitted to progressive pressure, during which samples were taken. For each sample, the total weight, alkali, weight of cellulose after washing and drying at 100 to 105° C., and by difference the weight of water in the sample were determined, from which the amount of sodium hydroxide, fixed by the cellulose, was calculated for various initial concentrations. The number of molecules of NaOH fixed by each $C_6H_{10}O_5$ unit was plotted against the concentration of the initial sodium hydroxide solution, and the resulting curve showed four breaks, indicating that the fixation proceeds in a discontinuous series of definite molecular combinations. The alkali celluloses indicated were $2C_6H_{10}O_5.NaOH$; $3C_6H_{10}O_5.2NaOH$; $4C_6H_{10}O_5.3NaOH$ and $C_6H_{10}O_5NaOH$.

Similar conclusions were reached in a later publication (*ibid.*, 1932, *195*, 499). Cellulose was immersed in a solution of the alkali and then pressed. Samples were taken at intervals during the pressing operation and analysed. The variation of the sodium hydroxide content of the samples, expressed as a function of the water content, gave a straight line, and when these lines were drawn for different concentrations of the original solution, the composition of the addition compounds was determined by the points of intersection of the lines. The same series of alkali celluloses was detected as those described above.

In addition to the centrifuge method of removing the excess liquor, blotting paper has been employed by Beadle and Stevens (8th Inter. Cong. Appl. Chem., 1912, *13*, 25), in using hanks of viscose yarn, whilst Neale (J.T.I., 1929, *20*, 373; 1930, *21*, 225) has used the blotting paper method for cellophane.

The inherent error in the Vieweg " change in titre " method is caused by the fact that cellulose takes up water in addition to the sodium hydroxide. The amount of water taken up passes through a maximum, as shown by the work of Beadle and Stevens, Coward and Spencer, and Neale (supra), but investigations based on the " change in titre " method assume that the water in the supernatant liquor is constant. This point was strongly emphasised by Bancroft and Calkin, in their detailed and critical review of the action of sodium hydroxide on cellulose (Textile Research, 1934, *4*, 119 and 159). Where centrifuging or blotting paper is used, however, the absolute amount of sodium hydroxide taken up is measured. From a consideration of the difference between the two methods, Bancroft and Calkin deduced an equation by means of which the Vieweg " change in titre " data could be calculated from the total adsorption data of Coward and Spencer, Pfeffer, Neale and their own data. This review of all the available information showed that the part of the curves indicating constant composition, as obtained by the Vieweg method, was the result of a balance between the increased sodium hydroxide and water taken up. They also pointed out that the well-established data relating to the effect of temperature on the amount of sodium hydroxide taken up by cellulose was difficult to reconcile with the compound theory. For instance, the curve of D'Ans and Jager (Cellulosechemie, 1925, *6*, 137) at 23° C. contained a flat portion which was

held to show the formation of a definite chemical compound, but their curve at 2° C. was not as flat nor had it a flat portion at 0·5 mol. of NaOH per mol. of cellulose. Bancroft and Calkin concluded that there was no definite proof of the formation in mass of a compound of cellulose and sodium hydroxide, but that the mercerising process should be considered one of adsorption. Their work is also described in a later publication (J. Phys. Chem., 1935, *39*, 1), reiterating that the method of estimation, depending on the change in concentration of the alkali before and after the addition of the cellulose, is inaccurate as it only measures the NaOH taken up in excess of the adsorbed solution. The curve for the " true " adsorption of NaOH by cellulose is smooth. They also pointed out that even if the " change in titre " method gave true adsorptions, the data would not justify the conclusion that chemical compounds were formed. Where the concentration of alkali is plotted along the abscissa, the presence of two solid phases would show itself by a vertical portion, of which there is no evidence in the various published results.

They also showed that when curves were drawn by plotting the amount of NaOH taken up, against initial concentration, there was no passing back along the same curve when the sodium hydroxide was washed out, except at very low concentrations, so that the apparent adsorption of sodium hydroxide by cotton is a partially irreversible process. The curves for estimations with increasing concentration of NaOH in the initial solution came together at 14% NaOH where X ray analysis shows the change from one lattice to another with consequent change in the degree of adsorption as this is the region of maximum swelling. The previous conclusion that there was no evidence for the existence in mass of a stoichiometric compound, was repeated.

Bancroft and Calkin's Work

To appreciate Bancroft and Calkin's work, some details are necessary. Their centrifugal machine was a Foerst machine rated at 15,000 r.p.m. and had a cup 2·5 cm. radius giving a centrifugal force 6,300 times gravity. With this machine they found that water may be removed from a cotton water system down to 12%, i.e. less than the moisture content at 100% R.H.

Applying this machine to water-NaOH-Cotton systems, they obtained changes in the ratio of NaOH to water in the

solid phase and the centrifuged liquid after a certain time of centrifugal action such as the following :

Time of centrifuging.	NaOH per gram of water in the centrifuged liquid.
0 min.	0·18832
¼ ,,	0·18838
½ ,,	0·1883
1 ,,	0·18819
3 ,,	0·1880

After the half minute interval truly adsorbed liquor is evidently being thrown off from the solid. The break in this time curve is made sharper by centrifuging a system containing much less supernatant liquor as is shown by the further set of figures :

Time of centrifuging.	Gm NaOH per gram water in the centrifuged liquid.
0 min.	0·18832
¼ ,,	0·1893
½ ,,	0·1879
1 ,,	0·1860
3 ,,	0·1833

Here the break is at the ¼ minute.

From these very accurate analyses, the exact point may be established, where all the supernatant liquor is removed.

The argument for the calculations is based on the following considerations :

Let G = Grams of solvent in the NaOH outside solution at start.
X_0 = Mols. NaOH per 1 g. solvent in outside solution at start.
X = Mols. NaOH per 1 g. solvent in outside solution at end.
A = Mols. NaOH taken up by the sample of cellulose.
B = Grams of solvent taken up by the sample.

Now total NaOH initially = NaOH taken up by the solid phase, + NaOH in liquid phase at the end,

$$\text{i.e.} \quad GX_0 = A + (G - B)X$$
$$\text{or} \quad GX_0 - GX + BX = A$$

If s = grams of cellulose taken

then $\frac{A}{s} = \frac{XB}{s} + \frac{G(X_0 - X)}{s}$ mols of NaOH per gram of cellulose.

The second term on the right hand side is the change in titre value used by a host of workers who have neglected $\frac{XB}{s}$

$\frac{G(X_0 - X)}{s}$ may be called excess solute and

$\frac{XB}{s}$ is adsorbed solution.

If no water were taken up then B would = O. If on the other hand the solution was adsorbed without change, then $\frac{G(X_0 - X)}{s}$ would = o.

Whenever water is absorbed then the problem is to determine $\frac{XB}{s}$ and the authors intimate that they believe their method may be used to investigate other similar systems.

It should be emphasised that the key to the results given by Bancroft and Calkin lies in the extremely high centrifugal action to which the system was subjected, when the ratio NaOH/water in the centrifuged liquid is actually found to fall. Neale (J. Phys. Chem., 1935, *39*, 1245) emphasised the importance of the fact that the concentration of the *adsorbed solution removed* by powerful centrifuging falls steadily as centrifuging proceeds, which would be explicable if the concentration of free hydroxyl ion in the adsorbed solution is determined by the Donnan equation.

The following table gives results on Standard Cotton Cellulose using 0·5 g. of cotton in the centrifuge.

TRUE ADSORPTION OF NaOH AND WATER BY COTTON CELLULOSE.

End molality.	Adsorption per gram of cellulose. NaOH	Water.
1·741	0·0767 g.	0·701 g.
3·421	0·3573	1·914
4·040	0·4938	2·290
4·708	0·5315	2·099
5·923	0·5923	1·894

From the curves it will be seen that the maximum water taken up occurs at about the 4 molality point, while the adsorption of NaOH progressively increases and exhibits no evidence of chemical compound formation up to 20% NaOH.

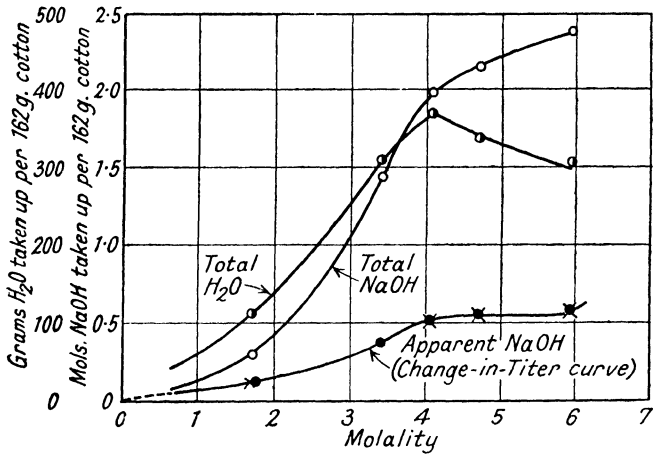


FIG. 143.—Absorption of NaOH.

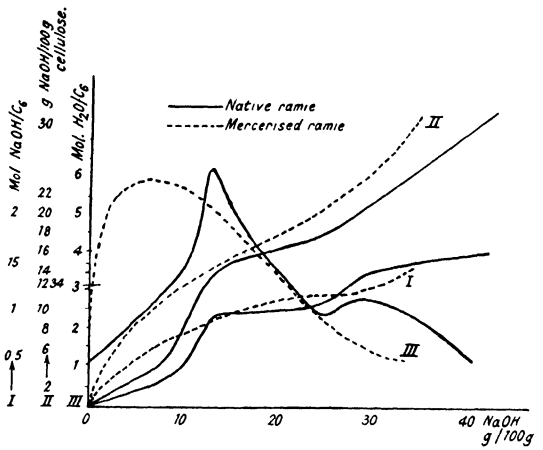


FIG. 144.—Absorption of NaOH and H_2O.

The method of experimentation in which the cellulose sample after immersion in the caustic alkali solution is taken out and centrifuged and then blotted between filter paper is similar in principle to work by Beadle and Stevens in 1912 (loc. cit.) on artificial silk yarns and later by Neale with

cellophane sheet. Some results of this method on Standard Cotton have been given by Bancroft and Calkin (Textile Research, 1934, *4*, 138).

In addition to the work of Coward and Spencer (see Fig. 142) and of Bancroft and Calkin (see Fig. 143), it has also been shown by Schwarzkopf (Z. Elektrochem., 1932, *38*, 353) that, whereas the amount of alkali taken up increases continuously with the concentration, the water taken up reaches a sharp maximum. Schwarzkopf employed "pressure methods" for his work, the main results of which are shown in Fig. 144. It will be noticed that the behaviour of mercerised ramie is different from that of native ramie.

Sodio-ammonia

Investigation of the action of metallic sodium in liquid ammonia on cellulose has produced a definite compound—sodium cellulosate, $C_6H_7O_2(ONa)_3$. Kraus and White (J.A.C.S., 1923, *45*, 768) had shown that when an alcohol is treated with sodium in liquid ammonia, a sodium alcoholate is formed and an atom of hydrogen is liberated according to the general reaction

$$R.OH + Na = R.ONa + \tfrac{1}{2}H_2.$$

Scherer and Hussey (*ibid.*, 1931, *53*, 2344) applied this reaction to cellulose. The amount of hydrogen obtained from a definite amount of sodium and cellulose was carefully determined and found to agree with the above reaction. The final product was examined and found to possess in full, the property of normally prepared soda cellulose, e.g. of reacting with carbon disulphide to form xanthates. One atom of sodium entered the cellulose molecule rapidly, but the second and third entered very slowly. As there was no appreciable amount of sodium amide formed, the hydrogen can only come from reaction between the cellulose and sodium. A maximum of three atoms of sodium per glucose residue entered into combination with the cellulose.

Similar experiments by Schorigin and Makarowa-Semljanskaja (Ber., 1936, *69*, 1713) failed to reveal special reactivity of any one hydroxyl group, but the reaction became sluggish towards the end. However, the three sodium atoms were found to be combined with varying strength.

Dry mercerised ramie has been treated with thallous ethylate in benzene or ether to give a thallium cellulose in which the

hydrogen of the hydroxyl group is replaced by thallium. Harris and Purves (Paper Trade J., 1940, *110*, *T.A.P.P.I.*, 63) find that the reagent does not penetrate into the interior of the micelle; methylation of the product showed that only one hydroxyl group in forty had been affected. These experiments were in connection with estimates of the internal surface of cellulose (see page 29) and suggest areas of $3{\cdot}7 \times 10^4$ sq. cm. per gramme for unmercerised ramie and $2{\cdot}9 \times 10^6$ sq. cm. per gramme for mercerised ramie.

X-Ray Contributions

Some of the conflicting evidence concerning the action of sodium hydroxide on cellulose has been partially explained by the data obtained from X-ray examination of the phenomena. There appears to be no change in the X-ray lattice where alkali concentrations of 10% and less are employed so that any effect is more likely due to surface adsorption or reaction rather than stoichiometric combination as the interior of the micelle is not accessible to the alkali. With increasing concentration, however, the changes in the lattice show that an intramicellar change has taken place whereby it must be supposed that the interior surface of the micelles becomes more accessible so that there is a greater adsorption. It is only when all the internal surface is available, that is under conditions of optimum swelling, that the addition of alkali could be regarded as a true stoichiometric chemical reaction.

A great deal of the investigations have been made by Hess and Trogus (Z. physik. Chem., 1929, *4*, 321; 1930, *11*, 381), who examined the X-ray diagrams obtained when caustic soda and other alkalis are left in ramie. When the fibres were treated with 16% NaOH, and the solution allowed to remain in the fibres a new diagram resulted of the so-called Soda-cellulose I, and when this was dried a further diagram was obtained of so-called Soda-cellulose III. The latter in presence of water reverted to Soda-cellulose I. Where about 21% of NaOH was used another diagram termed Soda-cellulose II was obtained and this did not change on dehydration, but the addition of sufficient water caused the formation of Soda-cellulose I.

The transition from one diagram to another did not occur sharply and mixed diagrams were obtained; for instance in the change from the native fibre to Soda-cellulose I, mixed diagrams were obtained over a 3% range.

Susich and Wolff (Z. physik. Chem., 1930, *8*, 221) examined the effect of treating ramie with NaOH and the subsequent effect of removing the alkali by washing. They found that the washed product gave yet another diagram—the mercerised or "hydrated" lattice, and when cellulose with this lattice was treated with NaOH it gave the same diagram with the NaOH in the sample as did the native fibre containing NaOH of the same concentration.

Calkin (J. Phys. Chem., 1936, *40*, 27) re-examined the effect of alkali concentration on cotton and found that the X-ray pattern of native cellulose began to change at a concentration of 12·8% NaOH and was changed completely between 14·3 and 14·4% NaOH (the samples examined were washed free from NaOH and dried). This concentration coincides with the point of maximum water adsorption and the point where the change in direction of Vieweg's curve occurs. When the NaOH was allowed to remain in the fibre, the diagram of Soda-cellulose I was obtained where concentrations of from 13·4 to 14·1% NaOH were employed. In the case of mercerised cotton the change occurred with concentrations of NaOH between 10·8 and 11·85%. Trogus had also claimed the formation of Soda-cellulose III, at low concentrations of NaOH —some 2·65% NaOH in the case of mercerised cellulose, but Calkin was unable to confirm this diagram.

Hess and Trogus (loc. cit.) also obtained interesting results by treating ramie with 20% solutions of NaOH in methyl alcohol. If the ramie was steeped in the alcoholic alkali for one day there was no change, but after more than a week the fibre diagram of Soda-cellulose III or II gradually appeared. Calkin (supra) treated cotton with caustic soda in ethyl alcohol for 24 hours, but although there was a change in concentration, the washed product gave the spacings for native cellulose—the diagram being unchanged.

There is also some evidence to show that the greater the swelling the quicker and greater is the penetration of the alkali into the cellulose. This is in agreement with the observation of Kress and Bialkowsky (Paper Trade J., 1931, *93*, 35), who showed that water is a better swelling agent than alkali. Hess and Trogus (loc. cit.) showed that when ramie was treated under tension with alkali, a greater concentration of alkali (30 to 35% compared with 12·5% in the case of the unstretched fibre) was necessary to obtain the new diagram. If a sufficient degree of tension was applied the application of 45% NaOH

for a week followed by washing under tension gave the diagram of native cellulose. Hess and Trogus emphasise that water is necessary for the formation of Soda-cellulose I, and for the re-arrangement of Soda-cellulose II to Soda-cellulose I.

Hess (Z. physik. Chem., 1932, *162a*, 187) has considered that there are two solid phases in the system and these are cellulose and sodium cellulosate, but Calkin prefers to regard the position as showing only one solid phase consisting of sodium cellulosate adsorbed by the cellulose. The simple adsorption of NaOH is ruled out as the diagrams obtained are not those of NaOH, whilst the fact that the diagram does not change continuously disposes of the possibility of solid solution formation, but the simple formation of sodium cellulosate does not account for the changes in the diagram.

Recent Conclusions

Bancroft (J. Phys. Chem., 1936, *40*, 43) in a paper on the phase rule in colloid chemistry, emphasised the fact that the phase rule method only shows the number of solid phases and does not show the form in which the dissolved or peptised substance is adsorbed. The X-ray method shows the form in which the adsorbed substance is taken up, but gives no evidence as to the number of solid phases. X–ray investigators had assumed that a mixed diagram means two solid phases, but there was no supporting evidence.

Their assumption rests on two other assumptions, that the adsorption layer is only one molecule thick, and that a layer of that thickness cannot give an X-ray diagram.

Elimination of the change in X-ray pattern of the cellulose itself, by starting with mercerised cotton, allows a smooth adsorption curve to be obtained with no sign of two solid phases. On the other hand, an X-ray study of cellulose containing sodium hydroxide shows the existence of sodium cellulosates which are definite chemical compounds. Bancroft pointed out that the results of X-ray and phase rule methods of study are complementary and not contradictory. From a combination of the results of the two methods it appears that mercerised cotton adsorbs NaOH as such from dilute solutions, one definite sodium cellulosate from stronger solutions, and another definite sodium cellulosate from still stronger solutions without there being two solid phases present at any time. The modifications of cellulose adsorb each other and do not occur as two solid phases.

According to the modern idea of the structure of cellulose, the lower concentrations of alkali cannot effect stoichiometric combination as the interior of the micelles is not available. With increasing concentration of alkali the lattice expands and the interior surface of the micelles becomes more and more available, but it is only under conditions of optimum swelling, when all the internal surface is available, that the taking up of alkali can be considered as a stoichiometric reaction.

CHAPTER TWENTY-ONE

VISCOSE

Cellulose Xanthates and the Viscose Reaction

EXCEPT in considering the triacetate, it will have been noticed in the preceding sections that very seldom is the tri-derivative of cellulose formed easily. The xanthation of cellulose is no exception.

The action of carbon disulphide on alcohols in the presence of sodium hydroxide has been known for a long time, and we may assume that when Cross, Bevan and Beadle discovered the " Viscose Reaction " they consciously applied this knowledge to cellulose which was known to be of an alcoholic nature. The general nature of the method of linkage in uniting carbon disulphide to an alcohol is seen by the equation :

R. ONa	+	CS_2	=	R.O.CS.SNa
sodium salt of the alcohol.				organic sodium dithiocarbonate.

The copper salts of the alkyl dithiocarbonates are yellow, whence the name *xanthate* was derived. When these compounds are acidified the free dithiocarbonic acid derivative which is liberated, being unstable, breaks up again into the alcohol and carbon disulphide.

$$R.O.CS.SH \longrightarrow CS_2 + R.OH.$$

Turning now to the reaction with cellulose as the alcohol, there is a difference between the processes which take place when inorganic bases are used and those which result from the use of organic bases causing swelling only on the one hand and dissolution on the other hand (*vide* page 156).

The chemistry of this reaction has been clarified in such a remarkable way during the last few years that it is better to consider these most recent investigations first, since an appreciation of them will enable the reader to understand the colloidal chemical nature of the " Viscose " solution discovered in 1892.

Lieser has shown that if cellulose is dispersed in tetraethyl

ammonium hydroxide it reacts with carbon disulphide to give the tetraethyl ammonium salt of cellulose trixanthic acid according to the equation :

$$C_6H_7O_2(OH)_3 + 3\,NEt_4OH + 3CS_2$$
$$= C_6H_7O_2(O.CS.SNEt_4)_3 + 3H_2O$$

The product which Lieser isolated gave analytical figures corresponding to the formula given $\left[C_6H_7O_2(OCS.SNEt_4)_3\right]_n$ which should give 49·7% sulphur, whilst 48% was actually estimated (Chem. Zeit., 1936, *40*, 387-9). Lieser found that tetra*methyl* ammonium hydroxide only swells cellulose, but does not dissolve it and a trixanthate could not be obtained with it.

The same author with Leckzyck (Ann., 1936, *522*, 56-65) has found that cellulose acts rapidly with a mixture of carbon disulphide in 3·7 normal tetraethyl ammonium hydroxide at 0° to give the trixanthate.

In order to obtain solutions or dispersions of cellulose before xanthation these workers have found that the following limits are applicable :

2·27 to 4	Normal	tetraethyl ammonium hydroxide
2·1 to 3·6	,,	paratolyl trimethyl amm. hydroxide
1·7 to 2·4	,,	Ethyl tributyl ammonium hydroxide

the minimum concentration for complete solubility thus decreasing as the molecular weight of the base increases (cf. Röhm and Haas, B.P. 439,806, and see page 158).

The trixanthate obtained above can be oxidised in N/10 iodine in methyl alcohol, giving a nearly pure trixanthogen $\left[C_6H_7O_5(CS_2)_3\right]_2$. The trixanthate is soluble in methyl but not in ethyl alcohol, and is also precipitated by ether and acetone.

From certain concentrations of tetrapropyl, ethyltributyl, or paratolyltrimethyl ammonium hydroxides and CS_2 on cellulose followed by oxidation the main product is the dixanthogen $\left[C_6H_8O_5(CS_2)_2\right]_2$.

The facts reported by Lieser (cf. also Koll. Zeit., 1937, *81*, 234) support his contention that molecular solutions, i.e. isolated thread molecules at low temperatures or complete dispersions of cellulose, exist in organic bases (and incidentally

in inorganic acids), whilst solutions of viscose and cuprammonium-cellulose have a micellar character.

With this introduction to the complete reaction between CS_2 and completely dispersed cellulose, it is now proposed to describe the reaction between *swollen* cellulose and carbon disulphide, the so-called "Viscose Reaction" which is of far greater technical importance than those reactions producing the well-defined compounds described in outline above.

When Cross, Bevan and Beadle discovered that alkalised cellulose reacted with carbon disulphide to give a product soluble in dilute caustic soda, they regarded the reaction as a means for the dispersion and manipulation of the cellulose into any desired form. It was, however, more than a decade before the potentialites of viscose for the manufacture of artificial fibres were realised. Cellulose sodium xanthate is not so much important in itself, therefore, as in its application as a cheap means of preparing a dispersion of a cellulose derivative in colloidal solution which may be coagulated and regenerated as cellulose by suitable simple treatment.

Laboratory Preparation

Acquaintance with the viscose reaction is best made by an immediate description of a laboratory method whereby the solution may be obtained. Foster D. Snell gave the following directions (Ind. Eng. Chem., 1925, *17*, 197). Surgical Cotton (37 g.) is immersed in 558 cc. of 17·5% sodium hydroxide solution at 20° C. for 1½ hours in a tightly stoppered bottle. The mass is shaken out and pressed to 160 g. and disintegrated by tweezers and allowed to mature for 96 hours at 18° C. This matured alkali cellulose is treated with 30 cc. of CS_2 in a revolving vessel for over two hours. Unmatured alkali cellulose at this stage gives a faint yellow colour, but the matured product gives a deep orange colour. This is stirred with a small quantity of sodium hydroxide solution and diluted rapidly with 120 cc. of 4% sodium hydroxide solution and 25 cc. of a 10% sodium sulphite solution. The viscosity is determined at intervals by the fall-ball method (3 mm. steel ball should fall about 20 mm. in 30 secs.). Further addition of 4% caustic solution is made till a correct viscosity of 40 to 50 secs. is obtained. It is now filtered under pressure and kept at 20 mm. for four hours at 18° C. to remove the gas bubble, and is ripened 90 to 150 hours in stoppered bottles at 18°.

Unripe viscose gives a fluffy film having very little lustre.

Morse's laboratory production of viscose solution (Ind. Eng. Chem., 1926, *18*, 400) is stated to give grades comparable with commercial grades and in this he uses the following method:

(1) 20 to 21% NaOH in the first stage.
(2) Presses in a letter press.
(3) The fluffy soda cellulose is matured 24 hours at 18° to 23° C.
(4) CS_2 to the extent of more than one-third of the weight of the cellulose is added in four portions.
(5) The ripening process takes place at room temperature.
(6) The filtration process is carried out after keeping the solution for 24 hours.

The suitable viscosity is given as 15 secs. for a 3 mm. ball to fall 100 mm. which viscosity may be altered by small additions of clear 15% NaOH solution.

The present authors make use of the following method with sulphite cellulose. Two lots of 30 g. sulphite cellulose (air dry) are torn up into small pieces and put into 32 ounce bottles (wide neck). 450 cc. of 40° Tw caustic soda solution are added to each and shaken up and allowed to stand 1½ hours. The contents of the bottles are then put in cloth bags and centrifuged so that the 30 g. has increased to 105 g. The product is now shredded thoroughly and allowed to age for four days. To prepare the xanthate the bottle containing the cellulose is placed on revolving rubber rollers and 26 cc. of CS_2 added over a period of one hour (about 5 cc. at a time). The total time required for completion of this sulphiding action is about three hours, when an orange coloured crumbly mass is produced whose particles begin to stick together. The excess of CS_2 is removed by suction and the xanthate dissolved by the addition of dilute caustic soda solution, and the mass is stirred and allowed to stand and ripen.

The viscose is spun or made into films when the ammonium chloride ripening number (q.v.) is 8 to 10. For spinning into threads 140 g. of this viscose solution, 6 cc. of 63° Tw NaOH, 50 cc. water are mixed. The day before it is to be spun, when the ripening number is say 15, the viscose is filtered through a pad of a thin layer of cotton wool between two pieces of muslin and supported by a piece of wire gauze in the pot. A pressure of 3 to 4 atms. is required. The spinning solutions are then filtered into glass bottles, which are then evacuated to

remove air bubbles. A standard spinning bath is made up containing 200 g. glucose in 600 cc. water, 280 g. sodium sulphate and 200 g. commercial sulphuric acid in 700 cc. water at temperature of 40° to 50° C. The rate of spinning is 100 feet per minute at 30 to 40 lbs. per sq. inch, and the thread is collected on a perforated bobbin from which it is twisted off after desulphurising with 50 g. sodium sulphide in 1700 cc. water at 50° to 60° C., washed, bleached with 6 cc. NaOCl in 1700 cc. water for 10 minutes and scoured in half Twaddle HCl. After the twisting operation it is dried under tension.

Manufacture

A typical commercial preparation of viscose is given by Wheeler (Manufacture of Artificial Silk, Chapman and Hall), and may be outlined as follows :

100 kg. of sulphite cellulose pulp in sheets are immersed edgewise in a tank with 160 litres of 17 to 18·5 % NaOH at 15° to 20° C., room being allowed for swelling. The solution is drained off and the sheets pressed to between 300 and 350 kg. The waste liquor from this operation may be used again to a certain extent. The alkali cellulose is shredded into crumbs in a machine which exerts a tearing, rubbing, and kneading action to produce a light fluffy material which should only weigh not more than 225 to 235 gs. per litre. These " crumbs " are put in covered bins at 20° to 25° for 48 to 72 hours, during which period oxygen is absorbed and a depoly-merisation of the cellulose takes place. The sulphiding next takes place by churning the crumbs with CS_2 in an iron double jacketed cylindrical vessel, which is slowly rotated. The space between the two jackets allows for the passage of cooling water. 325 kg. of alkali cellulose occupies 920 litres and the churn has a capacity of 2,000 litres. 30 to 32 kg. CS_2 are slowly added to the charge and the operation takes two hours at a temperature not above 30° C. The quantity of CS_2 corresponds to 1 mol. CS_2 to 1·25 to 1·5 mols. $C_6H_{10}O_5$.

The yellow colour of the mixture gradually changes to orange red and thence to a brown red. When a sticky elastic state has been attained churning is stopped and the unchanged CS_2 removed by suction and sufficient water and NaOH solution added to produce a 7 to 8 % cellulose and 6·5 to 7 % NaOH content. This mixing may take three to six hours and the temperature is kept at 15° to 17° C. The dark coloured solution is then ripened at 15° to 20° C. for four to five days.

During this period tests of combined sulphur, viscosity, and ripening number are made. Then filtration through cotton wool and fabric is carried out and the solution stored in vacuum for 24 hours to eliminate bubbles of gas before coagulation.

Before proceeding to a discussion of the variations and researches on the viscose process, the process may be broadly described in terms of colloid chemistry and physics.

The formation of alkali cellulose is discussed elsewhere (Chapter 20). The ageing process seems to result in a depolymerisation of the cellulose, in other words, a hydrolysis combined also with a small amount of oxidation (see page 260).

After sulphiding, the xanthate absorbs a large quantity of water and since the viscosity is high, much of the water must be present as envelope-water of the internal disperse phase. When aqueous sodium-hydroxide is added, the osmotic pressure of the external water is raised and water is attracted from the disperse phase into the external phase—thus reducing the viscosity. During ripening, the sodium cellulose xanthate gradually decomposes and its internal water passes to the external phase with further reduction in viscosity till spinnable. Any regenerated cellulose is emulsified or dispersed in the presence of undecomposed xanthate.

C. J. J. Fox (J.S.C.I., 1930, *49*, 85) represents these changes as

$$\text{NaCell.} + CS_2 \longrightarrow \text{NaCell. Xan} \longrightarrow \text{Na}^{\cdot} + \text{(micelle. ion)}'.$$

$$\text{Micelle ion, i.e.} \left(\begin{array}{l}\text{Cell. Xan.}\\ \text{Na Cell. Xan.}\\ \text{Water imbibed}\\ \text{Cell. reverted.}\end{array}\right) \longrightarrow \begin{array}{l}\text{Cellulose}\\ + \text{NaOH}\\ + H_2O, \text{ etc.}\end{array}$$

A cellulose xanthate ripened solution contains crystallites — rod shaped particles dispersed without order. If in extrusion these crystallites were solidified in completely parallel formation—a fibre of maximum strength might be attained with a low extensibility, but in actual practice the filaments consist of a non-parallel arrangement of the crystallites, and this probably accounts for the elasticity and extensibility. (Schorger. J.S.C.I., 1930, *49*, 157.)

Just prior to the spinning operation there is present dispersed cellulose protected by the cellulose xanthate which remains undecomposed during the ripening process. The colloidal particle is regenerated cellulose together with associated areas of xanthate. The acid bath causes coagulation and decom-

position of the remaining cellulose xanthate. In addition to this major function of the liquor the sulphur compounds formed as by-products during the ripening are also decomposed by the acid. These compounds are sodium thiocarbonate, carbonate and sodium sulphide. The H_2S which is produced during the action is prevented from being evolved by the addition of sodium sulphite to the viscose. The sulphite generates SO_2 which gives colloidal sulphur with the H_2S. The main chemical changes in the spinning bath are (1) the neutralisation of the alkali, (2) Decomposition of the xanthate salts (3) Regeneration of the cellulose from the free xanthic acid.

$$2(C_6H_9O_5)_n\ CSS\ Na + H_2SO_4$$
$$\longrightarrow 2(C_6H_9O_5)_n\ CSS\ H \longrightarrow 2\ (C_6H_{10}O_5)_n + CS_2$$

In the coagulating bath sulphuric acid alone does not give the best results. Soluble sulphates are usually added such as sodium or zinc and a carbohydrate which protects the surface of the newly formed thread and prevents the crystallisation of salts on the filament surface. The presence of glucose also assists the solution of the gases produced.

The various factors in each division of the viscose process may be described separately.

Raw Materials

Wood pulp from spruce, fir or hemlock, cotton linters, ramie and cotton waste have been used, but sulphite wood pulp is used most often. As pure a product as possible is obtained by boiling wood chips with calcium bisulphite followed by a bleaching process. The viscose manufacturer obtains this in the form of sheets which are immediately ready for the alkalising process. The essential properties of the cellulose for viscose manufacture have been described in detail by Goldsmith (Rayon and Melliand Textile Monthly, 1935, *16*, 513), and in a paper given at a Textile Institute Conference (J.T.I., 1936, *27*, Conference Number 169-180 P.) Hebbs gives an account of methods of assessing cellulose quality in a pulp in which the ratio of the cuprammonium viscosity to the viscose viscosity is considered. The cuprammonium viscosity is taken of a 1% cellulose solution and expressed in centipoises ; the viscose viscosity is taken of a 7% cellulose solution in 7·8% caustic soda solution and expressed in poises. For any one type of pulp the ratio of the two viscosities should be constant. The

reader should consult this valuable paper for an interesting account of raw materials and for the discussion which followed the meeting.

Other workers previous to Hebbs have maintained that even after the elementary analyses of alpha cellulose (85 to 89%) moisture (8 to 12%), resin, copper number, ash, etc., are passed as satisfactory, the chief test in the technical characterisation involves the isothermal treatment of a large sample through the complete process. (Weingard and Acker, Kunstseide, 1929, *11*, 419–424 and Viviani, Chimica e Industria, 1935, *17*, 10–14).

The usefulness of the method detailed by the first two authors has also been confirmed by Fabel (Kunstseide, 1935, *17*, 42–46), who gives further information on viscosity and the preparation of films whose mechanical properties can be quickly determined.

The use of cotton waste or cotton linters undoubtedly possesses many advantages in the direction of increased wet and dry strength, total extensibility, elasticity and resistance to creasing according to Ohl (Silk and Rayon, 1935, *9*, 18, 50). These better mechanical properties are explained by the higher molecular chain length of cotton compared with wood cellulose (see section on Constitution).

Similar reports emanate from Golowa (Kunstseide, 1935, *17*, 302–307), who states that the short cotton fibre from the waste from oil mills gives a high quality viscose rayon resembling cuprammonium in handle and appearance. The preparation of viscose from the remnants of cotton textiles or waste is the subject of a patent of Fasoli, B.P. 424,925.

The other raw materials—caustic soda and carbon disulphide —are obtained in a high state of purity. As regards the caustic soda, sodium carbonate has been shown to produce a reduction in strength and extensibility when present in greater amounts than about 3%, but up to this amount no noticeable effect is traceable either in the properties of the threads or the ripening or viscosity. (Jimbo, Riko, Takada, J.S.C.I. Jap., 1935, *38*, 123B.) The effect of the presence of hemicelluloses in addition to the alpha cellulose has been recently restudied and shown to be detrimental. (Soyer RUSTA, 1935, *10*, 499 and Monden and Kizu, J.S.C.I., Jap., 1935, *38*, 123–124B.)

Caustic soda contains traces of iron oxide and Davidson has shown that this impurity catalyses positively the absorption of oxygen by soda cellulose (J.T.I., 1932, *23*, 107), thereby

producing modified cellulose to the detriment of the final product. This has been mentioned on page 260.

The Preparation of Alkali Cellulose

There are a great number of considerations entering into a thoroughgoing discussion of the alkalising process and the maturing operation before combination with carbon disulphide is allowed to take place and only the most important will be discussed.

In the steeping treatment, variations in the initial alkali concentration and temperature of the solution have been studied at great length—the lower the temperature, the less concentration of alkali and the less CS_2 is required (Lilienfeld, B.P. 212,865), but it has also been proposed to lower the temperature in the normal treatment with 17–18·5% NaOH solution in order to effect a quicker and more even penetration and less swelling of the cellulose. Dreaper, B.P. 178,152, steeped cellulose in vacuo below 5° C. for this purpose.

The pressing factor (i.e. the ratio alkali cellulose to wood pulp) has been studied many times and recently by Soyer (RUSTA, 1937, *12*, 79–83). If T = the pressing factor, y = % cellulose, and x = % alkali cellulose, then $\frac{y}{x} = \text{Tb}$, where b is a constant, and Soyer shows that $\text{T} = \frac{\alpha}{x}$ where α = % of alpha cellulose. In usual practice 100 kg. wood pulp are pressed to 325–355 kg.

If this weight is increased to 350–370 kg. the filtration of the viscose becomes difficult owing to the inefficient removal of the hemicellulose. If pressing is put down to 290 kg. difficulties are experienced in dissolving the xanthate, but the strength of the thread increases with diminution in weight of alkali cellulose. When cotton cellulose is used the product can be compressed much further without such difficulties, but improvements in strength and elasticity are not produced.

An improved mercerising press has been described in which automatic regulation of pressure is made to control the alkali content of the alkali cellulose (Hydraulic Press Corp., U.S.P. 2,053,570).

Alkali cellulose has been made by a continuous counter-current process by impregnation in 25 minutes (Fischer, Rayon Text. Monthly, 1937, *18*, 227–228). Plauson (B.P. 184,533)

made a dispersion of cellulose in the theoretical amount of aqueous alkali by grinding 32 parts of cotton, eight parts of sodium hydroxide, and 600 to 800 parts of water in a colloid mill for half an hour, and then adding 7–8 parts of CS_2. In ten minutes the reaction is complete and no ageing is required. In conformity with this disclosure Rogowin (Kunstseide, 1933, *15*, 374) shows that grinding cellulose at 32–36° C. produces the same result as ageing.

Another variation of the alkalising operation consists in the elimination of the steeping process by spraying. By this method 100 kg. of bleached linters are placed in a shredder and sprayed with the alkali solution 260 g. per litre. 210 litres of this solution are used in half an hour. Prepared in this way, the alkali cellulose ripens very quickly, according to RUSTA, 1929, *4*, 843–5. The increased cost of the linters over wood pulp cancels the cost of the caustic soda saved. This same method for sulphite wood pulp is the subject of B.P. 434540/1934, by the I.G., in which moist pulp containing 25 to 75% cellulose is treated, but it is difficult to see what becomes of the hemicellulose.

The alkalising of ramie fibre has been studied by Kita and co-workers (J.S.C.I., Japan, 1934, 765–768).

The presence of 2% salt in the steeping liquor has a beneficial effect on the strength and extensibility. (Jimbo and others, J.S.C.I., Japan, 1934, *37*, 395B.)

In the ordinary steeping process, 0·1 to 0·6% of methyl cyclohexanol, borneol, or terpineol added to the mercerising liquor facilitates the operation and with this method, maturation may be dispensed with. (B.P. 426,553.)

Undegraded cellulose with a high alkali content for xanthation may be obtained by taking ordinary alkali-cellulose and suspending it in liquid ammonia containing metallic sodium (B.P. 463,056).

Replacement of caustic alkali by organic bases in the steeping process has been described in B.P. 281,117 ; trialkyl sulphonium hydroxide is given as an example.

Ageing of Alkali Cellulose

Although many patent specifications concern processes for dispensing with the " ageing " of alkali cellulose, they do not appear to have attained commercial eminence.

The alkali cellulose is generally shredded mechanically in two or three hours, and as the temperature would otherwise

rise, cooling is carried out with water or brine below 25° C. Air is excluded during the shredding operation.

The ageing process consists in keeping the shredded alkali cellulose for two to three days in closed iron drums at 24–27° C. Depolymerisation of the cellulose may occur and/or oxidation —and the question is still being debated. The presence of excess of oxygen is generally considered to be detrimental to the quality of the thread and may be obviated by the use of sodium sulphite in the impregnating lye (D.R.P. 422,179). During the ageing the amount of cellulose material, soluble in alkali, increases but the " oxy-cellulose " content only slightly increases. Cotton alkali cellulose requires a larger ageing time than wood pulp alkali cellulose. (c.f. Waentig. Papier Fabrikant, 1928, *26*. Fest und Auslandsheft, 64 66, and Cellulosechemie, 1929, *10*, 81–85.)

Indication of the degree of ageing may be obtained by nitrating the washed coagulated product, dissolving the ester in acetone and determining the degree of diffusion and relative viscosity against a standard sample. Diffusion experiments of this kind show that ageing is accompanied by a decrease in the size of the cellulose aggregate. (Krueger, Cellulosechemie, 1927, *8*, 1.)

The chief interest in varying the conditions of ageing has centred round the result produced in the quality of the thread, but there have also been a large number of attempts to ascertain the chemical changes taking place.

Alkali cellulose aged in absence of air (Waentig, Papier Fabrikant, 1928, *26*, 64–70), or in presence of hydrogen (Kita and co-workers, Chem. Zentr., 1929, i, 589) gives a viscose solution more viscous than when aged in air, and furthermore, it is easier to spin. Kita also reported that a long steeping in alkali with short ageing gives similar filament strength to that obtained after ageing in hydrogen. (Chem. Zentr., 1929, i, 590.) For example, steeping for five days was followed by ageing 6–12 hours.

No advantage seems to be gained by ageing in hydrogen, however, for viscose prepared from alkali cellulose aged for a short time in air gives filaments as fine as those from alkali cellulose aged in hydrogen or steeped for a long time and aged a short time. (Kita and co-workers, Chem. Zentr., 1929, i, 1289.)

The change of structure in ageing has been described by Waentig in Cellulosechemie, 1929, *10*, 81–5, who suggests that the regular arrangement of anisotropic micelles of the purified

cellulose changes in the regenerated cellulose to an irregular micellar arrangement, and in alkali-soluble cellulose the micelles have been broken up into smaller units.

Cellulose decomposition products are produced in these changes in the molecular structure. The caustic soda alone produces no decrease in the size of the micelles. The observed depolymerisation is due to oxidation. Faust, however (Cellulosechemie, 1931, *12*, 125–6), showed that the hydrolysis number and copper number are not affected by the ageing process, and concludes that in the process a shortening of the chain occurs and a reduction in micellar size, but no further loosening of the structure.

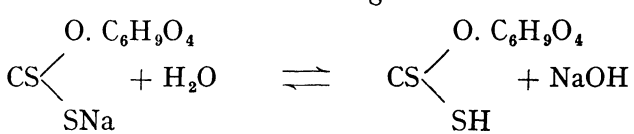
Investigation of these matters is extremely difficult and it is not surprising that contradictory conclusions have been reached at times.

Xanthation and Ripening

A study of the xanthation and ripening process by Berl, Bitter and Lange (Cellulosechemie, 1926, *7*, 137–147) started with an examination of the xanthate formation with glycol and glycerol, and here they found that only one hydroxyl group was xanthated.

Cellulose was next methylated to various degrees and it was shown that two hydroxyl groups were necessary before xanthation can take place.

During the formation of xanthate groups, a disintegration of the cellulose to a high degree of dispersion occurs, since through the introduction of the xanthate groups the cellulose micelles are displaced so far out of their natural spheres of influence that the fibre cohesion is lost. Ripening of the xanthate takes place by the action of the water present by hydrolysis of the salt of a weak acid and a strong base :



The free xanthic acid breaks down to CS_2 and free cellulose, whereupon further free xanthic acid is formed, and so on. (cf. Liepatoff, Kolloid Zeit., 1929, *49*, 441–50.)

The CS_2 formed is in a fine state of division and reacts with the alkali, giving trithiocarbonate and finally sulphide.

The colloidally dispersed degraded cellulose particles become

aggregated to particles which gradually grow larger until finally, on keeping, a mass of coagulated gel of hydrated cellulose is produced.

This theory affirms that the ripening process is not a polymerisation of cellulose, but a cementation of small micellar aggregates and is confirmed by viscosity measurements of products (after nitrating and dissolving in acetone). There is a minimum viscosity in the initial stages of ripening.

The viscosity changes taking place during ripening and their interpretation are given in full in a paper on " The Scientific Basis of the Viscose Process," by Heuser and Schuster (Cellulosechemie, 1926, *7*, 44–46).

Analysis during Ripening

During this period determinations are usually carried out which, in the main, estimate its suitability for spinning. They are, therefore, in the majority of cases, empirical tests designed solely for this practical end.

Some of these tests are dealt with in the following statement:

(1) *The Salt Point.* This gives the concentration of common salt, which just suffices to coagulate a drop of viscose when allowed to fall in it. 0·1 cc. viscose is allowed to drop into 20 cc. of the salt solution with stirring. There are many ways of carrying out the test—seven modifications being described by D'Ans and Jäger, and the reader is referred to the original paper in Cellulosechemie, 1935, *16*, 33–34, where these may be found. When the salt point is about 3·5, the viscose is suitable for spinning.

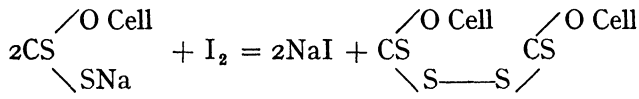
(2) *The Ammonium Chloride ripeness test* (Hottenroth) is the volume of 10% ammonium chloride solution required to coagulate the viscose under given conditions (20 g. viscose dilute with 30 cc. water). Ammonium chloride ripeness depends on the degree of degradation of the cellulose, the number of xanthate groups still retained and the electrolytes in the solution, and temperature. The sodium hydroxide content is important in this test. (D'Ans and Jäger, Kunstseide 1926, *8*, 17, 43, 57, 82, 110.)

(3) Viscosity changes.

(4) Jentgen's method in which sulphur bodies are titrated with iodine.

(5) Leuch's method in which CS_2 and H_2S are estimated.

Jentgen's test determines combined alkali after purification of the xanthate by precipitating the cellulose xanthate which is then redissolved in alkali. Free caustic soda is neutralised with acetic acid and the solution titrated with iodine before the acid has had time to decompose the xanthate, when the following reaction takes place :



Xanthate. *Dioxythiocarbonate.*

The iodine method shows that there is a clear relationship between the number of xanthate groups and the properties of the viscose solution.

Critical reviews of the methods of determining the degree of ripening and the theories of it have been given by Lotze (Kunstseide, 1934, *16*, 290–296), and later by D'Ans and Jäger (Cellulosechemie, 1935, *16*, 22–36).

These latter authors state that with the film method the solution should contain a little excess of acetic acid before titration with iodine.

They found that a connection between the iodine number and salt point is given by

$$N = (30 \text{ to } 35) - 24S\,(1{\cdot}2 + S),$$

where N = iodine number,
S = salt point.

D'Ans and Jäger's paper gives extensive tables of figures.

Voskressenski (Jl. App. Chem. Russ., 1934, *7*, 967 ; Chim. et Ind., 1935, 655) found a relationship between temperature and time for ripening by studying the process at 15, 18, 25 and 30° C., and he gives the relationship as $a/A = (T/t)^x$, where a and A are times required at t and T, and x is a constant (2·4 approx.). Pitter (J.S.D.C., 1935, *51*, 23) finds a linear relation between reciprocal log. viscosity and maturing time at constant temperature ; 1/log. $\eta = At + C$, where η is in poises, t is time, A and C are constants.

A *chemical ripeness test* which gives the degree of esterification of viscose has been described by Fink, Stahn and Mathes (Angew. Chem., 1934, *47*, 602) by precipitation of it with chloracetdiethylamide, which gives Cell — O.CSS.CH_2.CO.

NEt_2. A nitrogen determination is made on the precipitate. The highest ratio of CS_2 per 100 $C_6H_{10}O_5$ was 171.

The ripening of soda cellulose-carbon disulphide mixtures has been followed by X-rays and viscosity measurements by Centola (Atti X Congr. Internaz. Chim., 1938, IV, 722, 728).

The *viscosity standard test* now recommended by the Faserstoffe Analysenkomm. des Vereins der Zellstoffe u. Papier Chem. u. Ing. (Papier Fabr., V.Z.I., 1936, *34*, 57–9) for xanthate viscosity is carried out as follows:

Five g. dry disintegrated pulp are allowed to remain with 25 cc. 17·5% NaOH for one hour at 20°. The product is filtered and aged in a stoppered bottle at 30° C. for 22 hours. The pulp is kept at room temperature for five minutes and allowed to react at 15° with 3·6 cc. CS_2 for 4·75 hours with frequent shaking. Excess of CS_2 is removed and the pulp dissolved in 17·5% NaOH at 15°, a volume being taken which is 2 cc. greater than the volume of the first caustic alkali filtrate.

The solution is now made up to 500 cc. with water and its viscosity determined in an Ost-Ostwald viscometer. The method gives values which may be repeated within 3% if the technique is strictly followed.

A laboratory scheme for the complete examination of viscose must include:

(1) Determination of alkali as NaOH by acidimetry (normal H_2SO_4).
(2) Cellulose—as film regenerated by salt solution.
(3) Total sulphur—by hypochlorite oxidation and estimation as barium sulphate.
(4) Xanthate soda, i.e: the weight of NaOH combined as xanthate with 100 g. cellulose. (Dorée, Methods of Cellulose Chemistry, 1933, page 249.)

The Spinning Bath and Coagulation

An enormous amount of work has been done on the variation in the spinning or coagulating bath. A brief account of the development of viscose spinning baths from 1903–1930 has been given by Steimmig (Kunstseide, 1930, *12*, 242–243.)

Publications from Japan indicate that the subject is undergoing examination anew. The connection between denier, extensibility, strength per denier, and cross sectional area,

has been ascertained, and correlated with the kind and concentration of acid used. Acid alone produces a circular cross section. Concentrated acid coagulates strongly and rapidly. (Kami and Nozaki, from Brit. Chem. Abstr., B. 1929, 553).

The physical and chemical changes involved in the coagulation of viscose are a dehydration causing gelling, followed by the decomposition of the remaining cellulose xanthate. In the spinning operation, stability of the thread is only reached after some time—the highly swollen filament is initially actually soluble in water. The effect of salts is to reduce the speed of this coagulation and increase the complexity of the cross section of the filament—zinc sulphate having the most pronounced effect. (C. L. Moore, Silk and Rayon, 1935, *9*, 19, 20, *et seq.* to 182.) The degree of complexity is expressed by the relation Complexity $\lambda = \frac{L}{L'}$ according to Hase (J.S.C.I., Japan [Suppl.], 1932, *35*, 367B).

where L = circumference of the section of the fibre.
L′ = circumference of the circle having the same area (A) as that of the section.

or $\lambda = \frac{0{\cdot}28\,L}{\sqrt{A}}$

Moore (loc. cit.) also details methods of analysis of the bath for free acid, sodium sulphate, magnesium and zinc (oxine method) and glucose (decinormal iodine).

The properties of the yarn (cross section, handle, lustre, and dye affinity) vary systematically with the concentration of sodium sulphate when the concentration of sulphuric acid is fixed. The change in pH (which rises with increasing sodium sulphate concentration) is responsible for the variation in yarn properties. With too low pH, gelation, regeneration and gas evolution are too rapid. If the pH is too high the yarn has too poor affinity for direct dyes. The optimum pH value is 0·6. (Tanemura, J. Cell. Inst. Tokyo, 1935, *11*, 12, 100–105.)

The coagulating bath in the *Lilienfeld Process* (B.P. 274,521; 274,690) is 40–85 % H_2SO_4, in which case, a higher viscosity viscose is used with little or no ripening. The filaments are apparently parchmentised immediately they are formed. The increased tensile strength is to be accounted for partly by the large micelle condition, but this superior strength is attained at the expense of other desirable properties such as extensibility and softness.

It is believed that considerable technical difficulties were encountered in the working of this process. Strong rayons of regenerated cellulose from the acetate by stretching and hydrolysis are described under " Fortisan." (See page 322.)

Desulphurising and Bleaching

The removal of free sulphur from the coagulated fibre, which has been washed, reeled, twisted and dried under tension, is accomplished by treating with 1 % sodium sulphide at 40–50° C. The chemical action is apparently simple—polysulphides being formed in solution. The accumulation of polysulphides is undesirable so in practice caustic soda and glucose are continually added so that the polysulphide content is kept low. (Wheeler, Manufacture of Artificial Silk, 2nd Edition, 1931, p. 64.)

Scherer, however, believes (Ind. Eng. Chem., 1933, *25*, 1319-21) that there are two types of sulphur present in the sulphurised viscose. One is removed by water, even in the cold, but the other requires hydrolysis of some kind between sulphur and another radicle before removal. Ordinary reagents such as caustic soda, glycerol or acetic acid remove about one half of the total sulphur.

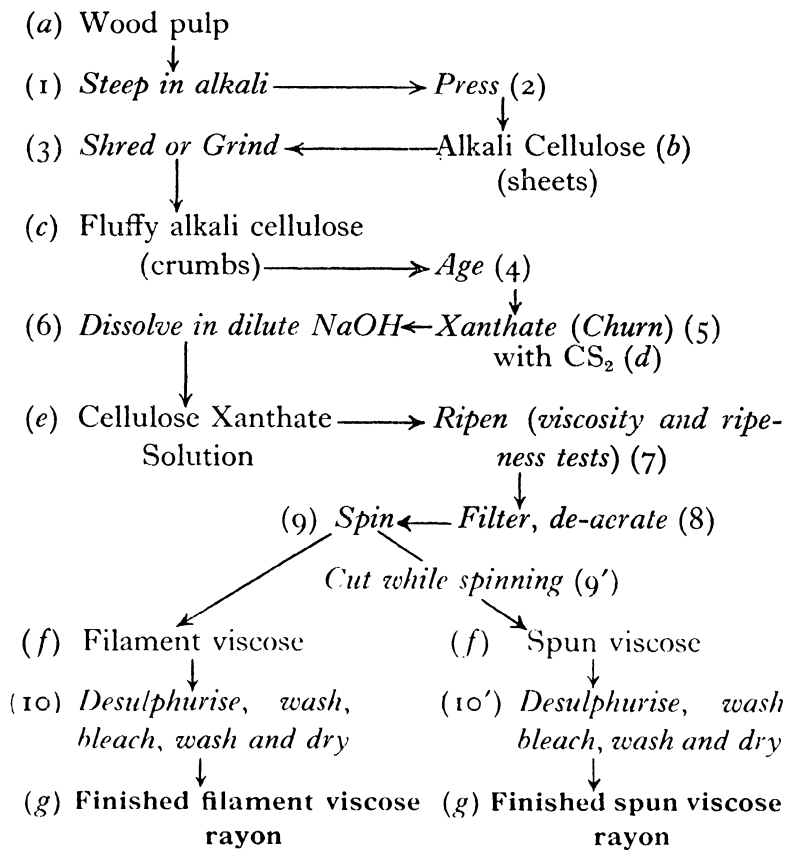
It has been proposed to use desulphurising agents which do not swell the viscose thread, e.g. phenol, pyridine, glycerine, and dextrose, or sodium sulphide, or cane sugar in acetone. The thread in these cases has a more subdued lustre and the dry and wet strengths 50 % higher than the usual. (Hermighaus & Co., F.P., 655,729/1929.)

Stein (B.P. 428,955/1934) desulphurises for, say, one to two hours at 80–90° C. with 1·5 to 2 % aqueous fatty alkyl sulphates such as Gardinol, Igepon A. The disadvantages of alkaline swelling of the fibre and attack on the bobbins and vats, etc., are thereby avoided.

B.P. 429,165/1934, by the same inventor, accomplishes simultaneous desulphurising and scrooping with a neutral salt of a fatty acid amide of an unsymmetrical dialkyl diaminoethane. Other compounds previously proposed as desulphurising agents were sodium sulphoricinoleate (I.G. B.P. 279,437) and dilute sodium hydroxide containing a fractional per cent. of sodium cyanide. The last addition also dissolves metallic compounds from the fibre (Du. Pont U.S.P. 1,655,097).

OPERATIONAL STEPS IN THE VISCOSE PROCESS

Numerals are processes.
Letters are products.



The removal of sulphur is also effected or faciliated by addition to the spinning or other bath of a quaternary phosphonium or tertiary sulphonium salt with at least one radicle of not less than eight carbon atoms, e.g. dodecyl triethyl phosphonium bromide (I.C.I. B.P. 464,116).

Finally, bleaching is carried out with a solution of a hypochlorite containing 0·05 to 0·1% available chloride.

Washing, soaping or oiling and drying at 40° to 60° completes the treatment. This final drying is carried out at low temperature and without tension.

Physical Deformation of Hydrate Cellulose Gels

Some attempts have been made to give regenerated cellulose some of the properties of the animal fibres in the direction of crimp, and this may conveniently be mentioned here as an illustration of the kind of fundamental physicochemical considerations which is even invading commercial textile patent specifications. According to one invention by Ubbelohde (B.P. 477,428) a strong and permanent crimped effect may be obtained by rearranging the micelles in the hydrate cellulose gel by procedures in such a way that they do not follow a straight line but the curved line of a crimped thread. For this purpose the thread bundle *whilst still loaded with precipitating agents* must be drawn and stretched into the crimped form—that is—must be strained during the shaping operation beyond its limit of elasticity, preferably at a moment when the threads are only solidified to such a degree that the micelles can still arrange themselves in accordance with the curled or crimped shape to be imparted to the threads. The threads thereby assume the crimped form as their natural form and become particularly resistant to pull and moisture if the micelles are allowed to grow together quietly and to completion in their new position. The crimped threads are left without tension for a certain time to the action of the precipitating agent, and must therefore not be soaked in water immediately after the crimping operation. Special toothed rollers are employed to effect this drawing and stretching beyond the elastic limit.

The mechanism of deformation and swelling anisotropy in hydrous cellulose gels has been studied by Hermans and de Leeuw (Koll. Zeit. 1938, *82*, 58-67).

They find that stretching of swollen isotropic filaments results in almost complete orientation of the particles in the

direction of extension and that scarcely any orientation takes place with air dry filaments although both show about equal extensibility. Stretching in the dry state causes tearing of the inner structure producing a matt turbid gel.

The water of strongly swollen cellulose has been displaced by organic solvents and organogels produced which only contain 50 % cellulose by volume. Evaporation of the solvent gives dull white aerogels with a specific gravity less than unity. For example, the water in a hydrogel may be successively displaced by ethyl alcohol, then by xylene, and finally by ethyl ether. This ether organogel still retains 60 % of its weight of ether even after heating at 105° C. for 3 hours.

The reader will remember that the reverse operation has been used in analysis of cellulose acetate wherein the acetate is swollen in acetone-water and the acetone in the highly swollen gel displaced by water (Knoevenagel).

General Considerations

Lieser (Chem. Zeit., 1936, *60*, 387-389) concludes that xanthation of cellulose in the viscose reaction on cellulose swollen in caustic alkalis is a micellar surface reaction. The reacting ratio 2 $C_6H_{10}O_5$ to 1 CS_2 found in practice is due to half the cellulose being in the surface and xanthation occurs at random along the superficial chain molecule.

The final product (yarn) obtained for the textile industry or as a film may be described correctly as a regenerated hydrate cellulose. It is a hydrate cellulose and not a cellulose hydrate. (See " Dispersed Cellulose.")

In commercial viscose solution (of comparatively high viscosity) the cellulose is in the form of a micellar dispersion. To obtain a fundamental dispersion of the individual long chains of the cellulose would require a much more dilute solution (cf. Staudinger's work).

The skin effect of viscose filaments is probably due to orientation of the micelles on the surface caused by the frictional effect in the streaming of the viscous solution past the edges of the holes in the spinneret. (cf. strength increase by friction. Kita and co-workers. Brit. Chem. Abstr., 1929, 772-773.)

Turning from the technical aspects of the viscose reaction, a few comments must be made regarding the purification and reactions of sodium cellulose xanthate.

Purification of Cellulose Xanthate

Weak acids such as formic, acetic, carbonic and other substances such as salts and alcohols precipitate the xanthate unchanged. By this means it may be purified ; for example, a mixture of an acid and a salt may be employed. The by-products can then be washed out and the yellowish brown coloured mass re-dissolved in dilute caustic soda. Numerous patents deal with variations in the method of precipitation (*vide* Hottenroth. Die Kunstseide ; Hirzel ; Leipzig ; 1926, page 327).

Heavy metal salts give variously coloured precipitates. Iron—red brown ; lead—carmine red ; mercury—yellow ; bismuth—red brown ; copper—chocolate brown ; nickel—cherry red ; cobalt—brown black ; silver—rose brown ; cadmium—yellow ; antimony—red yellow ; zinc—whitish.

The reaction with iodine has already been dealt with.

Further Reactions

Analyses of commercial cellulose xanthate show that only about one or less CS_2 group is present per C_6 unit. This indicates that further reactions should take place not only on the —CSSNa group, but on the remaining hydroxyl groups. Alkylation of the xanthate sodium was accomplished by Lilienfield.

Etherification and esterification and other reactions on viscose have been patented in a very large number of specifications of Lilienfeld. A few only can be mentioned.

Cellulose Xanthate Acid Esters are described in B.P. 252,654 by treating a cellulose xanthic acid or xanthate with inorganic esters (dimethyl or diethyl sulphate ; methyl or ethyl iodide) under faintly acid or alkaline or neutral conditions. For example, crude viscose diluted with water and rendered faintly alkaline, neutral or acid by addition of acetic acid is treated with dimethylsulphate in the cold.

The products are carefully washed. They are soluble in alkali and in organic solvents such as pyridine.

Presumably, the reaction occurs as follows :

$$\text{Cell.O.CSSNa} + CH_3I \longrightarrow \text{Cell.O.CSSCH}_3.$$

Halogen derivatives of di- or polyvalent alcohols may be reacted with viscose according to B.P. 335,906, 335,993, 335,994. B.P. 356,286, modifies 335,906, in which halogen

derivatives of di- and polyvalent alcohols are allowed to act on cellulose xanthate.

Viscose solution is treated with a halogen fatty acid, salt or ester and the products when coagulated have high wet and dry strengths according to B.P. 341,843. (Lilienfeld.)

$$\text{Cell.O.CSSNa} + \text{Cl.CH}_2\text{.COOR.} \rightarrow \text{Cell.O.CSS.CH}_2\text{.COOR.}$$

B.P. 357,154, a modification of B.P. 335,906, uses di- and polyhalogen paraffins such as ethylidene dichloride, tetrachlorethone and methylene chloride on cellulose xanthate. B.P. 257,167 uses alkali soluble alkyl celluloses, or alkali soluble or alkali insoluble aralkyl celluloses, or alkali soluble or insoluble cellulose ether of oxyalkyl carboxylic acid and reacts these with CS_2 and alkali.

B.P. 357,526, 357,527, 357,549, 357,551, and 357,595 detail reactions in which the free OH groups of viscose or xanthated cellulose derivatives are made to react with, for example, alkyl halides, such as the chlorethylenes, vinyl or allyl chlorides, dichloracetaldehyde, mono and dichloracetone.

In B.P. 368,288 a list of reactions on cellulose with ethylene dichloride, acetylene dichloride, chloracetone, chlormethyl-ether, bromostearic acid, $COCl_2$, CNBr, $C_6H_3CH_2Cl$, etc., is given and the products after xanthation are described. This document contains 75 examples. In B.P. 367,920 Lilienfeld xanthates a product obtained from cellulose and a halogen alkylamine or aralkylamine, e.g.,

$$\text{CH}_3\text{. CHCl. CH}_2\text{. NH}_2\text{. HCl.}$$
$$\text{or } \text{CH}_2\text{. Cl. CH}_2\text{. CH}_2\text{. NMe}_2\text{. HCl.}$$

Lilienfeld's B.P. 389,518/9 reacts cellulose xanthate or xantho-fatty acid or cellulose dixanthate, etc., with an organic substance containing at least one nitrogen, one oxygen and one halogen atom each attached to its own carbon atom,

$$\text{e.g. NH}_2\text{ CH}_2\text{. CHCl. CH}_2\text{ OH.}$$

B.P. 390,519 uses the same organic compounds on cellulose and then xanthates the products.

Viscose reacts with benzoyl chloride to give a thioanhydride of a cellulose xanthic acid. The metal-free compound reacts with acids to give CS_2 and with alkalies to give xanthates (Chem. Zentr., 1936, i, 777).

None of these compounds appears to have been investigated scientifically nor has any of them yet attained commercial significance.

An interesting chronology of the rayon industry (not confined to viscose) has been given by Jackson (Textile Mercury, Jubilee Number, 1939, p. 162).

CHAPTER TWENTY-TWO

SOME GENERAL CONSIDERATIONS

DURING the past twenty years (1920-1940) the observations and methods of textile technology have gradually become grouped into an organised system, so that one may now speak and write of *textile science.* This may not, as yet, be highly developed, but nevertheless its roots are firmly established. Critical examination of the somewhat empirical work of the early pioneers has yielded important results from the scientific standpoint, and has led to a fuller knowledge and deeper understanding of many fundamental textile operations; it has sometimes led to striking advances. Most of this work has been concerned with the structure of cellulose, with dispersed cellulose and with modified cellulose. The same critical examination of cellulose derivatives does not appear to be attracting as much attention in Europe, as in Japan, the U.S.S.R., and the U.S.A. The source material is mainly confined to patent specifications, which are apt to be full of ambiguities and peculiar phraseology, and certainly constitute the most difficult part of the "literature" of textile science, but nevertheless provide a rich field for exploration, and possibly exploitation, by the more academic textile scientists.

Any attempted classification of the reactions of cellulose suffers from the fact that neither the parent substance nor its derivatives are well characterised from the strictly scientific point of view.

In the case of the derivatives which have been examined in solution, the length of the chain molecule may vary within wide limits and some of the glucose units may have been modified by oxidation. The reactions which lead to degradation are numerous, but may be divided into three main classes, (*a*) oxidation, (*b*) acid hydrolysis, (*c*) decomposition by dehydration through heat or chemical reagents. The section on Modified Cellulose is mainly devoted to this type of effect, but it must be remembered that it plays an important part in the

production of cellulose derivatives as well as in our understanding of the constitution and structure of cellulose. The physical properties of cellulose and its derivatives are largely determined by chain length so that the degrading action of *any* reagent must be kept in mind. Hydrolysis in the initial stages of a reaction may be a determining factor in the later stages, and where a low viscosity product is required it is often possible to bring about the necessary hydrolysis during the reaction. On the other hand, some of the derivatives of cellulose are more resistant to hydrolysis than the parent substance, e.g., cellulose ethers.

In some cases, particularly with acid chlorides, a certain amount of degradation seems to be an inevitable accompaniment to the reaction. For instance, Bernoulli and Satuffer (Helv. Chim. Acta, 1940, *23*, 627) have shown a connection between the degree of degradation and the capacity of cellulose for esterification to the *p*-toluenesulphonic ester. Cellulose is not esterified by the anhydride and the chloride is only effective in great excess and in presence of pyridine. The presence of magnesium oxide, which hinders degradation, prevents esterification, but previously degraded cellulose can be esterified in presence of magnesium oxide. It is not clear, however, whether the reduction in chain-length is a necessary condition for esterification or an accompanying effect of the proper conditions of reaction.

Degradation takes place during the formation of many cellulose derivatives, cellulose nitrate being a notable exception (see page 293). The case of the viscose reaction for the production of regenerated cellulose is interesting in that degradation must take place for technical reasons as low viscosities are essential for spinning; this type of regenerated cellulose combines the features of modified cellulose and dispersed cellulose.

Before leaving the subject of hydrolysis, it may be pointed out that the terms hydrocellulose and hydrate cellulose seem sufficiently alike to occasion confusion, particularly for chemists who have no intimate knowledge of cellulose chemistry. Hydrocellulose is a modified cellulose sufficiently degraded by acid hydrolysis to acquire *new* chemical properties, whereas hydrate cellulose is dispersed cellulose which has been activated by swelling. A comparison of these two types has been made by Neale (Trans. Farad. Soc., 1933, *29*, 228) as shown in the tables on pages 472 and 473.

Substitution

In the organic chemistry of cellulose, the chief feature is the presence of three functional groups which are alcoholic in nature; those hydroxyls in the *2* and *3* positions belong to secondary alcohols and that in the *6* position to a primary alcohol.

The general formation of cellulose derivatives is a matter of the substitution of these groups, and it is now becoming common to show this more clearly by using the formula $C_6H_7O_2(OH)_3$ in place of $C_6H_{10}O_5$. Thus cellulose trinitrate may be written $C_6H_7O_2(ONO_2)_3$; similarly cellulose triacetate $C_6H_7O_2(OCOCH_3)_3$ and the trimethyl ether of cellulose as $C_6H_7O_2(OCH_3)_3$.

The chemical reactions of cellulose are complicated by several factors, one of which is the degree of orientation of the material and this also exerts a great influence on the physical properties as shown on page 113. The extent of orientation controls the rate of penetration of the reactant into the interior of the fibre and so influences not only the simpler process of dyeing, but also the mechanism of chemical reaction; for instance, Elöd and Schmid-Bielenberg (Z. phys. Chem., 1934, *B25*, 27) found that the velocity of acetylation of cellulose increased in the order of decreasing orientation of the structural units in flax, ramie and cotton.

The early views on the nature of the lower derivatives of cellulose supposed these to be mixtures of cellulose and the tri-substitution product, but this idea has given way to the more complex conception of heterogeneous micellar reactions. In the case of purified fibres, it is assumed that the reagent penetrates the fibre, and first attacks the surface of the micelle which is transformed into the tri-derivative. The reagent then penetrates into the micelle and produces a partially reacted area in which only some of the hydroxyl groups are substituted and which lies between the fully-substituted surface and the untreated interior. It has been estimated that the molecules which make up the surfaces of cellulose comprise 70% of the fibre, so that in the case of cellulose acetate, for example, 70% acetylation is required to produce a monomolecular layer of tri-acetate on the micellar surfaces. This layer is not detected by X-ray analysis, according to Hess and Trogus (Z. phys. Chem., 1932, *B15*, 157) whereas the unreacted residue in the centre of the micelle is sufficient to give the characteristic pattern of native cellulose. This has been suggested as an

PROPERTIES WHICH CHANGE WITH "DEGRADATION" OF CELLULOSE.

		Tensile strength, dynes/cm²	Fluidity in 0·5% Solution	Copper No (Braidy) Gms. Cu. reduced by 100 g. of Cellulose	Absorption of Methylene Blue (Basic dye)
Natural cotton cellulose scoured with 1–2% NaOH under 10–40 lb/sq in. pressure		$4·9 \times 10^9$	1·5	0·02	0·3 to 0·8
"Degraded" cotton cellulose.	Treated HCl 200 g./1 for 24 hrs at 20° C.	$1·5 \times 10^9$	34·5	2·44	"
	Oxidised by alkaline hypobromite 0·32 g.	...	...	...	...
	O_2 consumed by 100 g. cellulose	$2·4 \times 10^9$	31	0·5	3·0
	Oxidised by hypochlorous acid 0·32% O_2 consumed	...	29	3·4	1·1
"Activated" cotton cellulose.	Treated 25% NaOH without restraint on swelling or shrinkage, washed, air dried	These properties are unaffected by swelling or activation of cellulose.			
	As above, but without allowing shrinkage	...	...	...	...
	Treated without shrinkage, but dried at 110° C.	...	...	...	...
	Swollen in 65–70% H_2SO_4 without restraint (Time of action—5 mins)	...	...	...	...
		See refs. (20, 6, 12, 7, 8, 3.)			
Cellulose both "degraded" and "activated"	Viscose rayon	About 4×10^9	40	1·1	...
	Cupra rayon (Bemberg)		28	0·5	...
REF. Nos.		19, 12, 6	9, 4, 12, 21	4, 6, 21	3, 4

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Absn of water gms./gm. at 50% Relative Humidity.	Absn of NaOH from N/2 soln.	Absn. Ba $(OH)_2$ from N/5 soln.	Rise in Cu. No. (Schwalbe) after 15 mins. in boiling 5% H_2SO_4	Cu. No. (Braidy) after 2 hrs. in N/10 KOH, N/10 KBrO at 18° C.	Absn. Sky Blue FF (Direct dye) at 100° C.
	Milli-Equivalents per Glucose Unit.				
0·055 Ratios.	42·5	71	2·2	1·5	0·15%
0·97	Unaffected by hydrolysis or oxidation of the cellulose. (See refs. 17 and 18)		Tests obviously invalidated by great degradation of cellulose, but unaffected by mild degradation. (See ref. 2)		
0·97	...	...	...	...	...
	Expressed as Ratios Relative to Scoured Cotton.				
1·50	2·55	2·70	1·7	1·6	1·8
1·35	1·96	2·05	...	1·45	1·6
1·2	1·89	1·99	...	1·45	...
1·83 (max.)	3·20	3·20	...	2·54 (max.)	...
2·0	3·6	4·0	5	...	0·9
1·84	3·4	3·8	5	...	2·9
7,25,2,26,28	17	18	22	2	29

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28. Urquhart and Eckersall . . . . J.T.I., 1932, *23*, 163.
29. Neale.

explanation of the fact that cellulose tri-acetate is not detected by these methods until 50% of the cellulose has reacted (Textilber., 1934, *15*, 29). For a purely surface reaction of the fibre, there should be a X-ray evidence at about 6% transformation. This explanation, however, does not allow for a sufficient residue of unchanged cellulose to give a diffraction pattern. It would appear that in many cases the heterogeneous nature of reactions with cellulose is due to both micellar structure and fibre structure. The less organised parts of the structure would tend to react before the crystalline regions, and this may produce a random arrangement of substituted groups along the cellulose chains. The outer sections of the fibre and the external chains of the crystallites probably tend to be more highly substituted than the interior. Recent work on the cellulose acetates by Sakurada (J.S.C.I., Japan, 1938, *41*, 381) indicates that chemical reaction first takes place in the non-crystalline fringes which unite the micelles and then spreads along the chain molecules to the micelles.

Not only does the *arrangement* of the chain molecules permit of variation in any one particular sample of cellulose, but the *length* of the molecular chain may also vary within fairly wide limits. The complexity of the factors which affect the reactions of cellulose is increased by the morphology of the native fibres, and this aspect is apt to be overlooked on account of the more recent and striking developments concerning their molecular architecture.

Some attempts have been made to prepare the mono-derivatives of cellulose, as for instance described on page 319, and it is often assumed that the primary hydroxyl group esterifies more readily than the secondary hydroxyl. The work of Hatch and Adkins (J.A.C.S., 1937, *59*, 1694) leads to the conclusion that esterification equilibria are not greatly different for primary and secondary hydroxyl groups. The direct production of a pure primary monoester appears to be impossible as yet. This seems to be confirmed by the work of Sakurada (J.S.C.I., Japan, 1934, *37*, 604) who determined that the ratio of primary to total free hydroxyl groups in cellulose acetate, whose degree of substitution was 2·3, was about one-third.

The triphenylmethyl ether might be expected to be exclusively and completely substituted in the primary hydroxyls (see page 372) as the result of treatment with a specific reagent for a particular hydroxyl group. Similarly, the

CuO-NaOH addition product of cellulose might be reacted in such a way that the remaining hydroxyls are substituted and the blocking group then removed; the work of Piwonka (Ber., 1936, *69*, 1965) on these lines indicates a methylated cellulose substituted in the *3* position, but the more recent work of Heddle and Percival (J.C.S., 1938, p. 1690) tends to show that both secondary hydroxyls react but not the primary hydroxyl group. Determinations of unesterified primary and secondary hydroxyl groups in secondary cellulose acetate have been made by Cramer and Purves (J.A.C.S., 1939, *61*, 3458). Kobe and Montanna (J.A.C.S., 1931, *53*, 1889) in their work with cellulose furoate, found that one acyl residue was much more firmly bound than the other two—probably to the primary alcohol group.

Lieser (Papier Fabrikant, 1938, *36*, 272) has abandoned his original contention (Ann., 1929, *470*, 104) that cellulose xanthate is exclusively substituted in the *2* position.

According to Spurlin (J.A.C.S., 1939, *61*, 2224) the substituents in a cellulose derivative are distributed among the hydroxyl groups according to the laws of chance. The three hydroxyls are relatively substituted according to their reactivity and the nature of the reaction. The latter point has been dealt with in greater detail by the same author (Electrochem. Soc., Preprint, 1938, *73*, 411). The reaction of the cellulose in the fibrous state is governed by the rate of diffusion of the reagent to the individual hydroxyl groups, and this in turn is determined by the peculiarities of fibre structure and the degree of swelling. The reaction proceeds more rapidly with great swelling and more uniformly with uniform swelling.

The fact that some reactions of cellulose or its derivatives when in solution proceed very smoothly, and uniformly may be regarded as important evidence for molecular dispersion in these cases. Examples are the partial saponification of primary acetate to secondary acetate, esterification of cellulose dissolved in organic bases and the chlorination of cellulose acetate to the trichloracetate. The corresponding reaction on the swollen fibre shows an essential difference between the molecular arrangement in the fibre and in solution.

The structure of the cellulose has an important influence on the nature of reaction and in this connection the morphology of the native fibres must not be overlooked as may easily happen with the intense modern emphasis on molecular architecture.

It is usual to visualise many reactions taking place through initial loose addition compounds between the cellulose and the reagent, followed by swelling and then more complete reaction. Alternatively, the reaction proceeds from the outside of the micelle, inside which is a region which still maintains its original structure. The chief difference appears to lie in the swelling power of the reagent. In the second case, as pointed out by Spurlin (loc. cit.), it may be that the structure

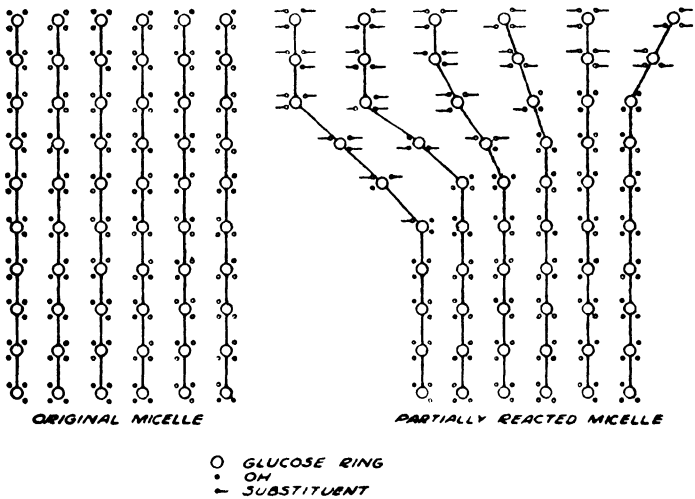


FIG. 145.—Diagram representing a reaction of cellulose with retention of fibre structure, showing a comparison of the unchanged micelle with that in which the reaction is proceeding from one corner. At various stages in the reaction the unreacted and reacted portions hold the structure together.

of the micelle is altered at one corner, but not at the opposite end, and within the intermediate zone the chain molecules are more or less loose. The hypothesis of attack from " spots " is supported by the fact that, when a reaction giving a product insoluble in the reagent is terminated before reaching its conclusion, the product is soluble in all solvents. This is due to the unreacted portion holding the chains together. From Fig. 145 it is apparent that the hydroxyl groups which escape reaction, and becomes enclosed in the new structure, have little chance of ever reacting unless the new structure is swollen.

In cases where the derivative is soluble in the reaction mixture, it is impossible to determine whether the reaction

has proceeded from the outside of the micelle towards the interior, or has proceeded uniformly throughout the micelle at the same time. Where intramicellar swelling is rapid and the reaction slow, it is possible to stop the reaction and obtain a fairly uniform product, as with some forms of etherification, but if swelling is absent or slow, as in fibrous acetylation, it is not possible to arrest the reaction and secure a uniform product.

Micellar heterogeneous reactions are generally associated with intermicellar swelling ; the small amount of the reagent which penetrates between the micelles produces sufficient swelling to permit access of the reagent to the inside of the fibre. This may be seen with fibres pre-treated with acetic acid and a catalyst in a medium of acetic anhydride and acetic acid. Intermicellar swelling may be prevented by the addition of benzene, an anti-solvent. In the first case, penetration of the acetic acid produces local reaction and further swelling. In the second case, the reaction is initially restricted to a few spots on the outside of the fibre, when the distortion produced allows further penetration and the reaction proceeds throughout the fibre in bands. This microscopically non-uniform type of reaction has been studied by Kanamaru (Helv. Chim. Acta, 1934, *17*, 1429) who produced bands of completely acetylated cellulose separated by unaltered material.

Highly swollen material may produce further complications. This has been shown by Frey-Wyssling (Protoplasma, 1936, *26*, 45) in the denitration of cellulose nitrate. If the reduction takes place by aqueous ammonium sulphide solution, the cellulose is greatly swollen and the reaction proceeds in a uniform layer from the outside towards the centre ; with an alcoholic solution of ammonium sulphide, however, the reaction begins in spots and continuous from these as with fibrous acetylation. Similar observations have been made by Lorand (J.A.C.S., 1937, *59*, 1166) for the later stages of the benzylation of cellulose.

Many reactions are not influenced by the structure of the fibre ; these include hydrolysis and degradation by heat and acid, a number of nitrations, and the permutoid reactions in which the chain-molecules have been made readily accessible by swelling or solution.

Spurlin (loc. cit.) has summarised the factors which determine the course of a given reaction as follows :

(*a*) the state of the cellulose (dissolved, intramicellar swelling, intermicellar swelling, no swelling).

(*b*) The solubility of the product in the reaction mixture.

(*c*) The number of reagents which must be available at one point before reaction occurs (e.g. two-phase reagents for etherification, etc.).

Although it appears that the distribution of groups in partly substituted cellulose derivatives is determined by the laws of chance, the distribution of substituents is modified by the tendency for some groups to react before others. This may be due to a different degree of reactivity of the three hydroxyl groups or to the arrangement of the cellulose. There can be little doubt that fibre structure is the most important single factor determining the nature of the chemical reactions of cellulose.

Solubility of Derivatives

For technical reasons, it is usually undesirable to prepare the fully substituted derivatives of cellulose ; they are also more difficult to prepare, in general, than the lower derivatives. The solubility of these partly substituted products has received considerable attention on account of their technical value, although few broad theoretical hypotheses for solubility have been advanced as yet.

It will be recalled that there is an essential difference in the solubility of crystalloids and colloids. When crystals of a salt dissolve, the salt passes into the solvent from the surface of the crystals which are not penetrated by the solvent. The crystals diminish in volume as they dissolve ; dissolution continues until the solution is saturated or completely inactive towards the crystals.

Macromolecular colloids, however, undergo swelling as a primary phenomenon ; instead of passing into the solvent, the solid absorbs the liquid, and its particles gelatinise as they increase in bulk, finally becoming completely miscible with the solvent. The solid and the solvent are mutually miscible in all proportions to an apparently homogeneous mass, which may be gelatinous, viscous or mobile according to the concentration. In some cases there is only a limited swelling, as the swollen particles do not form an apparently homogeneous solution with the remainder of the solvent. As these polymeric substances are generally heterogeneous with regard to micellar size, part of the swollen material will pass into solution, but

this limited solubility is quite different from that of a salt in water for instance, where the solubility is limited by saturation. In this case there is a simple linear relation between the amount of the solid added to a definite quantity of the solvent, and the amount which passes into solution. With polymeric substances this relation is much more complicated, and the term percentage solubility as applied to the weight of solution has no real significance ; it must be applied to the weight of the solid when it denotes the extent of complete dissolution under the particular conditions (see page 159).

The characteristic properties of the polymeric substances are partly due to their micellar structure which enables them to swell, that is to say, to absorb a liquid without immediately losing their internal coherence. For complete dissolution, however, a dispersion, or splitting up, of the structure must take place. In some cases, it seems possible to dissolve and precipitate the material without attacking the micelles, provided highly reactive solvents and excessive temperatures are avoided. When dissolution is complete, the extent of dispersion may vary with the nature of the solvent, its concentration and temperature.

In considering the specific influence of solvent towards definite polymers, Coltof (J.S.C.I., 1937, *56*, 363) has put forward the view that the atom groupings of the solvents may be classified according to their action. A group may exhibit a strong or weak swelling action, or a dispersing action ; it may cause both effects to take place simultaneously or it may be inactive. The action of the solvent molecule as a whole is determined by the combined effect of the atomic groups, hence if both dispersion and swelling take place, then the polymer will be dissolved. The groups which exert no influence are termed " ballast " and tend to counteract dispersion in particular.

An extension of this view is that the groups which co-operate to give the necessary swelling and dispersion need not all be parts of the same molecule but may very well be incorporated in different molecules, the mixture of which comprises the solvent.

Coltof points out that in many of the high molecular products or polymers, two groupings may be found, one of which repeats frequently (such as the acetyl group in cellulose acetate) and the other repeats less frequently (e.g. the hydroxyl groups) ; these are termed *A* and *B* groups respectively.

The mutual influence of the solvent groups and the *A* and *B* groups may be seen from the following table :

INFLUENCES OF SOLVENT GROUPS.

Solvent Group.	Cellulose Acetate.	Ethyl Cellulose.
$.C_2H_3$	Ballast.	Chiefly swelling.
.C : C.	Swelling.	Swelling and dispersion.
.Cl	Chiefly ballast.	Chiefly ballast.
.C : O	Swelling and dispersion.	Dispersion.
.OH	Dispersion.	Dispersion.

There seems to be a strong relation between the swelling action of the solvent groups and the *A* groups of the polymer, whereas the *B* groups appear to be primarily affected by dispersion. If the *B* groups are entirely absent, hardly any dispersion takes place ; for instance completely acetylated cellulose resists the action of practically all solvents. If, on the other hand, the proportion of *B* groups exceeds certain limits, then the solubility of the product is restricted to strong dispersing liquids and finally disappears, as for example when cellulose esters are hydrolysed to an increasing extent.

The solubility of a polymer, therefore, is determined partly by the ratio between the *A* and *B* groups and partly by the ratio of the swelling and dispersing groupings in the solvent.

Comparison of ethyl cellulose with cellulose acetate shows that on account of the swelling action of the ethyl group towards the ether, this is soluble in a much larger number of liquids than the ester.

Coltof has examined the effect of some 120 different liquids on cellulose acetate and the results confirm the views previously expressed. The alkyl group is quite inactive and merely acts as ballast. The double linking has a swelling action and as such is unable to bring the cellulose acetate into solution, but it succeeds when combined with dispersing groups. The benzene nucleus, on account of its unsaturated and cyclic nature has a strong swelling action.

The hydroxyl group exerts a strong dispersing action and little swelling ; hence combination with swelling groups will produce a solvent except in the case of excessive ballast, such as in the case of alkyl alcohol. Substances such as cyclohexanol, phenol, benzyl, alcohol, diacetone alcohol and so on, are further solvents.

The carbonyl group of the aldehydes and ketones causes swelling as well as dispersion so that the simple compounds can

be solvents. The higher members of the series, however, are non-solvents on account of the ballast action.

Acid anhydrides which combine two carbonyl groups with an ether linkage are good solvents. The action of the esters is similar to that of the ketones as an additional ether linking is the only structural difference, but the solvent action is reduced by the ballast effect when the molecule contains 4 carbon atoms or more.

Amino-groups cause both swelling and dispersion, but many of the amines cannot carry much ballast and remain solvents. When the nitrogen atom forms part of a nucleus, the dispersing effect is greatly increased. Pyridine forms a good combination of strong dispersion and strong swelling in a compact molecule with little ballast and is therefore the most universal solvent for all types of cellulose acetate.

The effect of increasing chlorine substitution in methyl or methylene groups is remarkable. The grouping CH_2Cl not only causes swelling, but a dispersing action also appears at higher temperatures. The groupings $CHCl_2$ cause less swelling but more dispersion whereas the grouping CCl_3 has swelling action but produces little dispersion. Completely chlorinated hydrocarbons such as carbon tetrachloride and tetrachlorethylene are inactive.

The influence of the acetyl content was also examined by Coltof. The conditions of preparation were varied to obtain a series of secondary acetates with decreasing acetyl content; these amount to 62·5% for the triacetate and 48·8% for the diacetate, calculated on the basis of weight per cent. acetic acid.

CELLULOSE ACETATE.

Solubility at room temperature in

Acetic acid %	Chloroform.	Acetone.	Ethyl Acetate.
60·0	5	0	0
58·9	5	2	–
58·5	5	3	–
57·2	5	4	2
56·8	5	5	–
56·0	5	5	–
55·5	4	5	4
54·5	3–4	5	–
54·0	3–4	5	3
52·8	3	5	2
46·0	0	2	–

The figure 5 denotes complete dissolution, the figure zero complete insolubility. It is evident that the ratio between the dispersing and swelling action must increase with decreasing acetyl content. Solvents with small ballast, such as chloroform, acetone, etc., will dissolve acetates over a fairly wide range of acetyl content, but those with a large ballast, such as ethyl acetate, only work within a very narrow range. All the cellulose acetates in the above table were soluble in pyridine which has the smallest ballast and the strongest dispersing and swelling action ; consequently it is capable of dissolving a wide range of cellulose acetates, even down to those containing only 30-35 % acetic acid. However, the true triacetate containing 62·5 % acetic acid and prepared from undegraded material which has suffered attack during the preparation, is insoluble in chloroform and acetic acid and is only soluble with difficulty in pyridine. Apparently the dissolution of the cellulose acetates becomes impossible when their B groups are absent. This means that on account of the combined action of swelling and dispersing groups towards the *A* and *B* groups, the partly esterified products are much more readily soluble than either the completely acetylated cellulose or the acetate which has been hydrolysed too far. The technical value of the secondary acetates is based on this argument.

Consideration of ethyl cellulose containing 45·8 % ethoxyl, which is a degree of substitution corresponding to that of the acetate, gave further interesting data. Hydroxyl, aldehyde, keto-, nitro-, amino- and cyano-groups have a dispersing action ; the benzene ring and the ester group also cause swelling. Examination of a number of solvents revealed a remarkable difference between ethyl and methyl groups ; the former is a swelling group but the latter is only ballast.

Comparison of the results with ethyl cellulose and cellulose acetate shows that in many cases the same atomic groupings may serve as dispersion groups in the liquid under examination but there is a great difference in the swelling groups. The ethyl group has a swelling effect on the ether but not on the ester ; the former is soluble in a larger number of liquids and is less affected by ballast action. These relations support the assumption that dispersion groups act specially on the hydroxyl or *B* groups of the cellulose esters or ethers, but the *A* groups (acetyl or ethoxyl) are particularly influenced by the swelling groups in the liquid.

Coltof finds that it is not possible to express the solvent

power of a liquid towards these highly polymeric substances by means of some function of the physical constants of the liquid.

It appears, therefore, that the physical and chemical properties of cellulose derivatives may vary profoundly according to the degree of substitution as well as with the substituent group. Similar considerations apply with the mixed esters, the mixed ethers, and the ether-esters; the possible scope appears enormous. In view of the large number of derivatives, as witness the volumes of Worden, it is with amused interest that one recalls the time when cellulose was described as a non-reactive or inert substance.

Cellulose is not only " the structural basis of the vegetable world," but has been adapted to form an integral and ever-growing part of our daily lives, and its use will be extended still further by future generations of textile scientists and technologists, to whom we hope our work may be of some assistance.

APPENDIX

DENSITY TABLES

Baumé.	Twaddell.	Sp. Gr.	H_2SO_4.	HCl.	HNO_3.	NaOH.	KOH.
			%	%	%	%	%
0	0	1·00	0·09	0·16	0·10	0	0
1·4	2	1·01	1·57	2·14	1·9	0·86	1·18
2·7	4	1·02	3·03	4·13	3·7	1·69	2·28
4·1	6	1·03	4·49	6·15	5·5	2·60	3·36
5·4	8	1·04	5·96	8·16	7·26	3·50	4·44
6·7	10	1·05	7·36	10·17	8·99	4·34	5·53
8·0	12	1·06	8·77	12·19	10·68	5·20	6·6
9·4	14	1·07	10·19	14·17	12·33	6·13	7·68
10·6	16	1·08	11·60	16·15	13·95	7·05	8·76
11·9	18	1·09	12·99	18·11	15·53	7·95	9·82
14·2	20	1·10	14·35	21·92	18·67	8·78	10·87
15·4	24	1·12	17·01	23·82	20·33	10·56	12·96
17·7	28	1·14	19·61	27·66	23·31	12·49	15·04
19·8	32	1·16	22·19	31·52	26·36	14·19	17·13
22·0	36	1·18	24·76	35·59	29·38	16·00	19·15
24·0	40	1·20	27·32	39·11	32·36	17·81	21·17
26·0	44	1·22	29·84		35·28	19·65	23·15
27·9	48	1·24	32·28		38·29	21·47	25·13
29·7	52	1·26	34·57		41·34	23·23	27·07
31·5	56	1·28	36·87		44·41	25·04	29·0
33·3	60	1·30	39·19		47·49	26·85	30·91
35·0	64	1·32	41·50		50·71	28·83	32·78
36·6	68	1·34	43·74		54·07	30·74	34·63
38·2	72	1·36	45·88		57·57	32·79	36·46
39·8	76	1·38	48·0		61·27	34·71	38·28
41·2	80	1·40	50·11		65·30	36·67	40·09
42·7	84	1·42	52·15		69·80	38·67	41·89
44·1	88	1·44	54·07		74·68	40·68	43·63
45·4	92	1·46	55·97		79·98	42·75	48·37
46·8	96	1·48	57·83		86·05	44·33	47 09
48·1	100	1·50	59·70		94·09	46·94	48·78
49·4	104	1·52	61·59		99·67	49·05	50·48
50·6	108	1·54	63·43				52·15
51·8	112	1·56	65·08				
53·0	116	1·58	66·71				
54·1	120	1·60	68·51				
55·2	124	1·62	70·32				
56·3	128	1·64	71·99				
57·4	132	1·66	73·64				
58·4	136	1·68	75·42				
59·5	140	1·70	77·17				
60·4	144	1·72	78·92				
61·4	148	1·74	80·68				
62·3	152	1·76	82·44				
63·2	156	1·78	84·50				
64·2	160	1·80	86·90				
65·0	164	1·82	90·50				
65·9	168	1·84	95·60				
		1·841	97·0				
		1·8415	97·7				
		1·841	98·2				
		1·840	99·2				
		1·839	99·7				

The acid and alkali percentages are by weight—for grams per 100 ccs., multiply the percentage figure by the specific gravity.

AUTHOR INDEX

ADAM, 381
Agardh, 12
Ambronn, 44, 100, 101
Anderson and Kerr, 7, 8, 10
Andress, 59, 109, 117
Armstead and Harland, 22
Astbury, 48, 94, 95, 109, 125
Astbury, Bailey and Chibnall, 96
Astbury and Woods, 121
Atsuki and Ishiwara, 111
Atsuki and Kagawa, 377
Atsuki and Shimoyama, 343

BALL and Hibbert, 394
Balls, 7, 8, 10, 11, 171, 186
Bancroft, 25, 444
Bancroft and Calkin, 36, 37, 192, 436, 437
Barnett, 52, 312, 323
Barratt, 137
Barratt and Lewis, 432
Barrett, 366
Barrett and Foulds, 168, 366
Barry, Peterson and King, 161, 193
Bartell and Carpenter, 43
Barwick, 30
Bateman and Belinger, 32
Battergay and Penche, 323
Beadle and Stevens, 146, 148, 436
Bechamp, 167
Bechhold, 43, 44
Beil, 170
Belinger, 32
Beltzer, 152, 216, 365
Bemberg, 184
v. Bemmelen, 32
Benoist, 85
Bergmann and Machemer, 64, 65
Berl, Bitter and Lange, 457
Berl and Klaye, 216, 243
Berl, Rueff and Wahlig, 323
Berl and Rueff, 292
Berl and Schupp, 371, 373
Bernal, 116
Bernardy, 161, 410
Bernoulli and Satuffer, 470
Berthelot, 364
Bertrand and Benoist, 85
Birtwell, Clibbens and Geake, 122, 208, 209, 211, 214, 215, 217, 220, 264, 265
Birtwell, Clibbens, Geake and Ridge, 152, 196, 261, 472
Birtwell, Clibbens and Ridge, 21, 244, 249, 251, 261, 265, 472
Bitter, 457
Bitz, 35
Blondeau de Carolles, 298
Bock, 383
Bonniksen, 88
Boulton, Delph, Fothergill and Morton, 128
Boulton and Morton, 26, 131, 201
Bowman, 16
Bragg (W. H.) and Bragg (W. L.), 104, 109
Bragg, W. H., 105, 111
Braconnot, 298
Braidy, 240
Bredig and Gerstner, 415
Briggs, 47, 48, 214, 337, 417
Brownsett and Clibbens, 159, 182, 270, 280
Brownsett and Davidson, 267, 280
Brownsett, Farrow and Neale, 173, 174
Bruckhaus, 365
Buchner and Samwell, 63, 68
Buchner and Stentel, 63
Buckley, 125
Budnikoff, 169
Bull, 239
Bumcke and Wolffenstein, 236, 238
Buttner and Neuman, 234

CAILLE, 35, 299
Calkin, 36, 37, 192, 436, 437, 443
Calvert, 145, 207
Calvert and Summers, 139
Cameron, 28
Caro, 338
Carothers and Hill, 77
Carpenter (*see* Bartell)
Centola, 313, 460
Champetier, 24, 40, 41, 84, 119, 301, 435

Chardonnet, 291, 295
Cherissey, 276
Chippindale, 320, 348
Clark, 84, 109
Clark and Farr, 111
Clark and Malm, 343
Clayton and Peirce, 39
Clegg, 144
Clément and Rivière, 304
Clibbens, 431, 432, 472
Clibbens and Geake, 175, 180, 240, 472
Clibbens, Geake and Ridge, 218, 263
Clibbens and Little, 180
Clibbens and Ridge, 219, 253, 271, 276
Clifford, 234
Clifford and Fargher, 242, 243
Collins, 30, 42, 144
Collins and Williams, 138, 143
Coltof, 310, 479, 481, 482
Corey and Gray, 19
Councler, 167
Coward and Spencer, 26, 36, 141, 148, 191, 432, 433
Coward, Spencer and Wood, 27
Coward and Wigley, 28
Coward, Wood and Barrett, 208
Craig and Miles, 121
Cramer, 171
Cramer and Purves, 475
Cross, 164
Cross and Bevan, 3, 5, 23, 166, 172, 208, 235, 309, 319, 322, 342
Cross, Bevan and Beadle, 243, 446
Cross and Briggs, 319
Cross and Dorée, 22
Cunliffe, 21
Cunliffe and Farrow, 21
Cunningham and Dorée, 236, 238

D'ANS and Jager, 153, 435, 436, 458, 459
Davey, 125
David, 202
Davidson, 29, 37, 64, 87, 153, 182, 189, 226, 228, 256, 261, 262, 266, 268, 275, 276, 453
Debye and Scherrer, 101
Dehnert and König, 156
Deming, 162, 170
Denham and Woodhouse, 52, 60, 367, 370, 402
Deripasko, 315
Dietz, 233, 236, 241
Dobry, 62, 63, 167
Donnan, 435
Dorée, 5, 22, 42, 48, 239, 281, 295, 460
Dorée (*see* Cunningham)
Dorée and Dyer, 236, 238
Dorée and Healey, 236, 257
Dorr, 381
Dreaper, 454
Dreyfus, 311, 320, 326, 327, 364, 367, 368, 375
Dubosc, 163
Duclaux, 24
Duclaux and Errera, 43
Duclaux and Nodzu, 63
Duclaux and Woolman, 63
Du Pont, 79, 90, 462
Duyk, 172

EBERSTADT, 322
Eichengrun, 310
Ekenstam, 182
Elford, 43
Elöd and Schmid-Bielenberg, 113, 471
Elöd and Frey, 304
Ermen, 202, 241
Errera (*see* Duclaux)
Eschalier, 364, 365
Evans and others, 256
Everest and Hall, 243

FABEL, 453
Faber and Tollens, 236, 239
Fabrics Coordinating Research Committee, 175, 180
Fargher and Probert, 15
Farr, 123
Farr and Eckerson, 12
Farrow and Neale, 174, 181, 472
Fasoli, 453
Faust, 349, 457
Fenton and Barry, 323
Fenton and Gosling, 41
Fehling, 298
Fermazin, 322
Ferretti, 96
Filby and Maass, 38
Fink, Stahn and Mathes, 459
Fischer, 364, 454
Fischer, Emil, 92
Flechsig, 51
Fleming and Thaysen, 22
Fleury, 276
Fleury and Lange, 276
Foltzer, 152
Fordyce and Meyer, 356
Fort, 284
Foster, Kaji and Venkatarman, 241
Foulds, 365, 366
Foulds, Marsh and Wood, 365

Fox, 451
Franchimont, 53
Franke, 166
Frank and Caro, 338
Frank and Cohn, 328
Frank and Mendrzyk, 345
Franz, 71
Freiberger, 243
Fremy, 3, 4
Freudenberg, 54, 61, 65, 86
Freudenberg and Boppel, 372
Freudenberg and Braun, 60
Freudenberg, Friedrich and Bumann, 86
Freudenberg and Nagai, 86
Freudenberg and Weber, 323
Frey, 45
Frey and Elöd, 304
Frey-Wyssling, 126, 130, 131, 132, 477
Friederich and Rapoport, 323
Fuchs and Katscher, 366

GARDNER and Carter, 27
Garrett and Howitt, 91
Gault and Ehrmann, 329, 330
Gault and Urban, 329
Gavoret, 28
Geake, 215, 371
Geake (*see* Clibbens)
Gebauer-Fulnegg, Stevens and Dingler, 300
Gerritsen, 162
Gerstner (*see* Bredig)
Gibson, 174, 296
Gilson, 100
Girard, 167, 207, 208, 233
Gladstone, 431
Glanzstoffe, A. G., 183, 184, 304
Goissedet, 426
Gohda, 88
Goldsmith, 452
Golowa, 453
Gomberg and Buchler, 376
Götze, 241
Grace and Maass, 29
Grandmougin, 166
Grard, 63
Gray (*see* Corey)
Green and Perkin, 322
Grun and Wittka, 330

HAGEDORN and Möller, 332, 333, 341, 355, 379, 397
Hall, 153, 156
Haller, 27, 143, 284
Hanson, Neale and Stringfellow, 282
Harland, (*see* Armstead, Clegg)
Harris and Purves, 442
Harrison, 28, 48, 202, 214, 241
Hartley, 28, 44
Hartshorne, 30
Hase, 461
Hatch and Adkins, 474
Haussermann, 169, 208
Haven, 48
Haworth, 55, 59, 106, 117
Haworth and Hirst, 53, 54
Haworth, Hirst and Thomas, 86, 369
Haworth and Leitch, 54
Haworth, Long and Plant, 56
Haworth and Machemer, 60, 64, 65, 68
Hebbs, 452
Heberlein, Co., 136, 168, 295
Heddle and Percival, 475
Helferich and Koster, 372
Hengstenberg, 59, 109
Hengstenberg and Mark, 62, 109, 112
Hermans and Kratky, 129
Hermans and de Leeuw, 464
Herminghaus and Co., 462
Herz, 63
Herzog, 45, 62, 102, 111, 120
Herzog and Beck, 162, 163
Herzog and Deripasko, 63, 318
Herzog and Gonell, 113
Herzog and Herz, 63
Herzog and Jancke, 101, 113, 118
Herzog and Londberg, 342
Herzog and Spurlin, 63
Hess, 24, 44, 61, 87, 119, 311, 444
Hess, Grigorescu, Steurer and Frahm, 64
Hess and Gundermann, 194, 195
Hess and Katona, 236
Hess and Ljubitsch, 311
Hess and Mesmer, 171
Hess and Muller, 373
Hess, Schultz and Messmer, 317
Hess, Weltzien and Messmer, 313
Hess and Trogus, 119, 120, 161, 173, 194, 442, 471
Hess and Wittlesbach, 402
Heuser and Bartunek, 144
Heuser and Herzfeld, 216
Heuser and Hiemer, 370, 402
Heuser and Neuenstein, 216, 402
Heuser and Niethammer, 434
Heuser and Schneider, 303
Heuser and Schott, 41
Heuser and Stöckigt, 233, 242
Heuser and Schuster, 458
Heyes, 241

Hibbert, 54, 83, 84
Hibbert (*see* Ball)
Hibbert and Hill, 42
Higgins, 21, 28, 187
Hill (*see* Carothers)
Hirst, Jones and Jones, 87
Hirst and Young, 97
Hitchcock, 43
Hönig and Schubert, 298
Hottenroth, 458, 466
Houwink, 48
Huebner, 15, 202
Huebner and Pope, 136, 144, 145, 167, 168, 169, 190
Huebner and Telscher, 431
Hull, 101
Humbert, 385
Hydraulic Press Corp., 454

I.C.I., 420, 464
I.G., 416, 455, 462
Irvine and Hirst, 52, 53, 55, 60, 322
Irvine and Soutar, 52
Irvine and Robertson, 85
Iwasaka, 318

JACKSON, 468
Jackson and Hudson, 255, 276
Jandrier, 243
Jeanmaire, 235
Jentgen, 208
Jimbo, 455
Jimbo, Riko and Takada, 453
Johnson, 100
Joly, 276
Joyner, 174, 181, 432
Judd Lewis, 44
Justin Muller, 214

KAGAWA (*see* Atsuki)
Kami and Nozaki, 461
Kanamaru, 477
Karrer, 348, 410, 412, 430
Karrer and Widmer, 54
Katz, 24, 25, 102, 103, 104, 118
Katz and Dirksen, 119
Katz and Hess, 170
Katz and Mark, 103
Katz and Vieweg, 103
Katz and Weidinger, 119
Kami and Nozaki, 461
Kerr, 11
Khouvine, 84
Kita, 330, 331, 342, 455, 456, 465
Kita, Mazume, Nakashmi and Sakurada, 344
Klason, 167
Knaggs, 202
Knecht, 15, 27, 42, 169, 190, 202, 236, 241, 243, 337
Knecht and Hall, 21
Knecht and Harrison, 156
Knecht and Thompson, 236, 237, 239, 240
Knoevenagel, 41, 465
Knoevenagel and Busch, 308
Knoevenagel and König, 323
Kobe and Montanna, 343, 475
Kodak Ltd., 353
Kolb, 235, 236
Kollman, 233
Konig and Dehnert, 435
Kraemer and Lansing, 61, 67
Kratky and Mark, 126
Kraus and White, 441
Krauz and Blechta, 292
Kress and Bialkowski, 443
Kreuger and Tschirch, 308
Krueger, 322, 456
Kruger, 349, 350
Kuhn, 86
Kullgren, 290
Kunike, 90

LADENBERG, 181
Lange (*see* Berl)
Langer, 144
v. Laue, 100
Lawrie, Reynolds and Ward, 387
Leighton, 433
Lenze and Rubens, 293
Lester, 30, 31
Leuchs, 364, 367, 375
Levene and Walti, 83
Levey, 345
Levi, 424
Lewis (*see* Barratt)
Liechti and Suida, 27
Liepatoff, 457
Lieser, 156, 158, 371, 446, 465, 475
Lieser and Leckzyck, 156, 447
Lilienfeld, 152, 156, 166, 186, 194, 364, 367, 385, 427, 454, 467
Lindemann, 144
Little, 328
Lomax, 48
Lorand, 381, 477
Lötze, 459
Lowe, 135, 145
Ludtke, 283
Lunde, Heen and Oy, 88
Lunge and Bebie, 289

MACHEMER (*see* Bergmann, also Haworth)
Makarowa-Semljanskaja, 441
Malm and Clarke, 307, 328
Malm and Fordyce, 339, 353
Malowan, 423
Maquenne and Goodwin, 53
Marchand, 298
Mardles, 318
Marsh, 25, 199, 365
Masson and Richards, 30, 32
Masters, 28
Mark, 24, 64, 65, 68, 98, 111, 113, 114
Mark and Susich, 119
Matthews, 14, 26, 48
McBain and Whistler, 43
McNally and Godbout, 317
Medvedev, 63
Mennell, 202
Mercer, 135, 142, 162, 166, 171, 190, 431
Meunier and Guyot, 35, 365
Meyen, 12
Meyer, 59, 95, 194, 195
Meyer and Bodenhuisen, 194
Meyer, Hopff and Mark, 86
Meyer and Mark, 59, 108, 109, 110, 114
Meyer and Misch, 114
Meyer and Wehrli, 90
Michaelis, 27
Midgley, 48
Miles, 121, 309
Miller, 40, 430, 432
Mills and Takamine, 27
Mitra and Venkataraman, 31
Moehring, 323
Monden and Kizu, 453
Monier Williams, 52
Moore, 461
Morey, 112
Morse, 449
Morton, 43, 44
Murphy and Walker, 46
Murray, Staud and Gray, 44, 323
Murumow, Sack and Tollens, 233

NABAR, Scholefield and Turner, 253, 271, 283
Nageli, 12, 100
Nageli and Schwendener, 100
Nakashima, 377
Nastukoff, 167, 236, 239
Neale, 39, 121, 147, 154, 171, 192, 198
Neale and Stringfellow (*see* also Brownsett, Farrow), 2, 42, 174, 282, 435, 439, 470, 472
Nef, 83
Neumann, 234
Nierenstein, 371
Niethammer and Konig, 393
Nihon Kaisan Kogyo Kabushiki Kaisha, 88
Nilssen, 96
Nisizawa, 319
Nishikawa and Ono, 100
Nitikin and Orlova, 373
Nitikin and Rudneva, 374
Nodder, 222
Nodder and Kinkhead, 142
Nowakowski, 331, 376

OBOGI and Broda, 63
Oertel, 236
Ohl, 317, 318, 327, 453
Okada and Hayakawa, 181
Okamura, 63, 374
Omeliansky, 22
Osborne, 14
Ost, 85, 174, 214, 253, 308, 323, 460
Ost and Katayama, 214, 323
Ost and Klein, 342
Ost and Westhof, 40, 430
Ost and Wilkening, 51
Ostwald, 24, 460

PARIS, 276
Parsons, 323
Peacock, 393, 417
Peirce, 40, 42, 48, 62, 120, 473
Peirce (*see* Clayton)
Peirce and Lord, 42
Penche (*see* Battergay)
Perkin, 323
Permetier, 244
Peterson (*see* Barry)
Pfeffer, 436
Philana, A. G., 169
Piest, 201
Pitter, 459
Piwonka, 475
Plauson, 302, 454
Polanyi, 59, 102, 107, 115
Pope and Huebner, 165, 166
Pregl and Soltys, 323
Preston, 45, 113
Prindle, 22
Pringsheim, 53, 61
Pringsheim and Ward, 331
Purdie and Irvine, 364

REEVES and Thompson, 371
Reinthaler, 319
Rheiner, 320
Rideal, 97

Ridge, 15
Ridge (*see* Birtwell)
Ridge, Parsons and Corner, 183, 185, 195, 200, 473
Riesz, 348, 417
Ristenpart, 143, 144
Ritter, 12
Rocha, 317
Rogowin, 455
Röhm and Haas, 447
Ross and Payne, 186
Rudy, 324
Rueff (*see* Berl)
Russell and Woodberry, 182
Rowe (*see* Reinthaler)

SAEGUSA, 366
Sakurada, 317, 325, 391, 392, 411, 474
Sakurada and Hutino, 192
Sakurada and Nakashima, 347
Sakurada and Taniguchi, 318
Sakurada and Hess, 319
Samec and Ferjancec, 384
Schaposchnikoff and Minajeff, 190
Schenk, 367
Scheidegger, 315
Scherer, 462
Scherer and Hussey, 441
Scherrer (*see* Debye)
Scheurer, 30
S.C.I.B.A., 426, 429
Schloesing, 30, 34
Schmidt, 64, 65, 68, 283
Schneider, 166
Scholefield, 253, 271, 283
Scholl, 242
Schoemaker, 387
Schonbein, 289
Schorger, 387, 389, 451
Schramek, 204
Schramek and Schubert, 119
Schubert, 144
Schulze, 4
Schulze and Hess, 322
Schultz-Tiemann, 294
Schunk, 15
Schupp (*see* Berl)
Schutzenberger, 307
Schwalbe, 23, 195, 217, 240, 242, 322, 473
Schwalbe and Becker, 243
Schwartz, 170
Schwarzkopf, 440
Schweizer, 171
Sheppard, 36, 38
Sheppard and Newsome, 29, 35, 38, 336
Schorigin, 441
Shimoyama (*see* Atsuki)
Sisson, 118, 120, 123, 124, 126
Sisson and Saner, 158
Skinkle, 48
Skraup, 53
Skraup and Koenig, 53
Snell, 448
Sookne and Harris, 28
Soyer, 453, 454
Speakman, 88, 95
Spencer (*see* Coward)
Spietel and Schenk, 366
Sponsler, 105, 110, 111, 113
Sponsler and Dore, 57, 58, 104, 105, 106
Spurlin, 294, 475
Stamm, 24, 45, 61, 68
Stamm and Cohen, 182
Staudinger, 65, 66, 68, 70, 85, 95, 122, 292
Staudinger and Feuerstein, 168
Staudinger and Daumiller, 70
Staudinger and Jurisch, 74
Staudinger and Schulz, 63
Steimmig, 460
Stein, 216, 462
Steinberger, 111
Stern, 208, 298
Stevens (*see* Beadle)
Stevens and Dingle (*see* Gebauer)
Stringfellow (*see* Neale)
Sudborough and Thomas, 323
Suida, 364
Susich and Wolff, 443
Susich, 113
Svedberg, 61
Swan, 295

TANKARD, 41
Tankard and Graham, 181
Tanner, 302
Tanemura, 461
Tagliani, 347
Terreil, 207
Thaysen, 22
Thenard, 291
Thiele, 184
Thomas, 284
Thor and Henderson, 90
Tocco, 306
Tocco and Nyssens, 305, 306
Todtenhaupt, 96
Tollens, 4, 54, 236, 244, 364
Tootal Broadhurst Lee Company, 365
Tomonari, Trogus and Hess, 294
Traill, 378, 388

Traube, 171, 173, 383
Traube, Blaser and Grunnert, 299
Traube, Blaser and Lindemann, 300
Trillat, 119, 332
Truog, 28
Trogus, 293
Trogus and Hess, 118
Trotman and Bell, 91
Turner, Nabar and Scholefield, 271, 283
Tweedie, 91

UBBELOHDE, 464
Ullmann, 291
Ure, 16
Urquhart, 30, 33, 34, 36, 39, 188
Urquhart, Bostock and Eckersall, 35, 473
Urquhart and Eckersall, 35, 189, 473
Urquhart and Williams, 31, 33, 34, 151, 187, 473
Uschakov and Schneer, 374
Uyeda, 305, 306
Uyeda and Fujiwara, 305
Uyeda and Hata, 304
Uyeda and Kato, 305

VALKO, 24, 26
Van Natta, 78
Venkatarama, 31, 241
Vereinigte Glansztoff, A. G., 183, 304
Victoroff, 145
Viviani, 453
Vieweg, 198, 201, 431, 433
Vignon, 233, 236, 239, 243, 410, 413
Viking Corp, 90
Voskressenski, 459

WAENTIG, 456
Wahlig (*see* Berl)
Walker, 38, 39, 46
Weingard and Acker, 453
von Weimarn, 162
Werner, 318
Wheeler, 450
Wiesner, 12
Wigley (*see* Coward)
Williams, H. E., 163, 164
Williams, A. M. (*see* Collins)
Willows, 28, 139
Willows and Alexander, 137
Willows, Barratt, Parker, 137, 139, 150
Willstätter and Zechmeister, 51, 52, 85, 170
Wilson and Fuwa, 30, 35, 36
Witt, 23
Witz, 219, 235, 236, 243, 244
Wohl, 342
Wolf, 348
Wolffenstein (*see* Bumcke)
Wood, 27, 208, 215, 365, 366, 396
Woods (*see* Astbury)
Woodhouse (*see* Denham)
Worden, 291, 327

YARSLEY, 311, 312
Young, 375

ZANKER and Schnabel, 27
Zdanowich, 314
Zechmaster and Toth, 85
Zetsche and Rosenthal, 4
Zwicky, 124

SUBJECT INDEX

ABSORPTION, Effect of heat on, 191
—— of moisture, 29
—— —— Effect of temperature on, 33
—— —— Effects of mercerising on, 34
—— ratio, 152, 188, 195, 198
—— of water and caustic alkali, 146
Acetic acid, 208
Acetolysis of cellulose, 53
Acetylation of cellulose without solution, 310
—— —— without mineral acid, 311
Acetyl chloride, 313
—— groups determination, 322
Acetate-sulphate, 307
Acid dyes, 29
—— formaldehyde, 168, 216, 365
—— combined, 218
—— estimation, 28
Acids, Action on cellulose, 207
Acid steep, 20
Activation of cellulose, 473
—— —— by mercerising, 195, 200
Activation ratio of cotton, 199, 201
—— —— of rayon, 201
Addition compounds of cellulose with acids, alkalis, water, 119
Adhesive properties of esters, 339
Adipocelluloses, 4
Adsorption of dye by cellulose, 190
Aerogels, 465
Ageing of alkali cellulose, 455
Alcohols, Absorption by cellulose, 29
Aldehydes, Action on cellulose, 365-7
Alginates, 87, 88
Alginic acid, 87, 89
—— beryllium, 88
Alkali estimation, 28
—— cellulose oxidation, 260
—— —— ageing, 260, 455
—— —— Chloracetic acid on, 323
—— —— for viscose, 454
—— action and molecular chain theory, 273
Alkaline hydroxides, 135
Alkylene oxide, 372, 385
Alkyl ammonium bases, 156
—— ethers, 375
Allyl cellulose, 392, 413
—— Ammonia on, 413
Alpha-cellulose, 5
Amination of cellulose, 413
Amine-yarns, 411
Amino-benzene trisulphonyl chloride, 348, 417
—— —— action on soda cellulose, 417
Aminocellulose, 410
Aminoethyl cellulose, 417
Ammonia, 29
—— $CaCl_2$ on cellulose, 413
—— -cellulose, 194
Ammonium chloride. Ripeness of viscose, 458
Analyses, of acetates, 322
—— of formates, 306
—— of viscose, 458
Angle of orientation, 45
Animal fibres, 90
Anisotropy, 44
Anticrease processes, 365
Aromatic Esters, 359
Arsenic acid, 170
Ash alkalinity, 249
Arsonium bases, 156
A–T Cellulose BS and B, 381

BACTERIUM xylinium in cellulose synthesis, 84
Barium hydroxide. Preferential absorption, 198
Bases. Strong, 156
—— Solubility of modified cellulose in, 229
Basic Cellulose Ethers, 409
—— Dyes, 29
Beetling, 30
Benzene sulphonic acid, 331

Benzoyl chloride, 342
Benzoylation of cellulose, 201, 342
Benzopurpurin 4B, 190
Benzyl cellulose, 376, 383
—— quaternary ammonium bases, 157, 389
Beryllium alginate rayon, 88
Beryllium perchlorate as solvent, 167
Beta-cellulose, 5
Bleaching, 19, 20, 21
Breaking load, 144, 145
Bromine, 236
Butyl Alcohol vapour. Absorption by cellulose, 29
Butyl Cellulose, 376
—— chlormethyl ether. Action on cellulose, 384
Butyryl chloride. Action on cellulose, 329
B.Z. Cellulose, 381

CÆSIUM hydroxide, 144
calcium chloride-ammonia on Cellulose, 410
—— —— -formaldehyde on cellulose, 165
—— thiocyanate, 165
Caproate ester of cellulose, 333
Caramelisation, 214
Carbamates of cellulose, 340
Carbon bisulphide, 185
—— dioxide from Oxycellulose, 242
Carbonates, Cellulose alkyl-, 302
Casein, 306
Caustic soda, Centrifuge experiments with cotton, 141
—— swelling of cellulose in, 26
—— 10N–2N treatment, 220
Cellobiose and octacetate, 53, 54, 55, 56, 57
—— Model, Plate XII
—— Synthesis, 86
Cellofas (I.C.I.), 388
Cellophane, 154, 306
—— Absorption of dyes, 43
—— Swelling of, 146, 149
Cellotriose, 85
Cellotetraose, 85
Celluloid, 291
α, β, γ-Cellulose, 5
Cellulose, Absorption of alkali, 431, 432
—— —— of water, 24
—— —— of dilute acids, 27
—— —— of dilute solutions, 27
Cellulose, Absorptive properties, 25
—— Acetate, solubility, 481
—— Action of fungi mildew and bacteria, 21, 22
—— Action of light, 21
—— Action of heat, 42
—— Alkaline hydroxides on, 135
—— Colloidal aspects, 23
—— Electrical properties, 46
—— Heavy water on, 41
—— Mechanical properties, 48
—— Model (Haworth), Plate XIII
—— Model (Meyer), Plates XV, XVI, XVII
—— Moisture relations, 29
—— Native, 5
—— Occurrence, 3
—— Optical properties, 44
—— Refractive index, 45
—— Sodium zincate on, 136
Cellulose, Sorption of vapours, 29
—— Swelling of, 25, 135
—— Standard, 17
—— Water systems. Pressure experiments, 40, 41
Cellulose Acetate, 307
—— Absorption of water, 35, 36
—— Analysis, 322
—— Chlorination of, 324
—— Crystalline, 317
—— deacetylation and methylation, 369
—— fibrous, 310
—— fluorescence, 44
—— fractionation, 317, 318
—— hydrolysis and stretching, 321
—— rayon, 320
—— viscosity, 318
Cellulose Benzoate, 342
—— Butyrate, 327
—— Carbamates, 340
—— Chloracetate, 323, 326
—— Chlorbenzoate, 343
—— Cinnamate, 345
—— Dextrin, 167
—— Diacetate, 313
—— Dicarboxylates, 337
—— Elaidate, 341
—— Esters. *See* under Esters
—— Esters, Absorption of water, 36
—— Ethers. *See* under Ethers
—— Formate, 304 *et seq.*
—— Formate Analysis, 306
—— Furoate, 343
—— Glycollic acid, 391
—— Higher fatty esters, 329
—— Hydrate, 136

Cellulose Maleate, 341
—— Methylene Ether, 364
—— Modified, 207
—— Modified solubility in alkali, 220 *et seq.*, 226
—— Monoacetate, 319
—— Naphthenate, 344
—— Nitrate from Cellulose and Hydrocellulose, 216
—— Nitrate, 289
—— Nitrate, Absorption of water, 36
—— Nitrate, Denitrated, 295
—— Nitrate rayon, 295
—— Oleate, 341
—— Peroxide, 238
—— Phenyl Acetate, 346
—— Phosphate, 301, 302
—— Phthalate, 344
—— Propionates, 326
—— Soda cellulose, 430
—— Standard cotton, 17
—— Sulphacetate, 307, 310
—— Sulphides, 302
—— Thallium, 441
—— Thiourethanes, 425
Cellulose Toluenesulphonate, Action of ammonia, 410
—— Triacetate, Action of PCl_5, 324
—— Urethanes, 425
—— Xanthamide, 428
—— Xanthate, 447, 475
—— Xanthogenic acid, 427, 457
Cementing material "Kittsubstanz," 120
Centrifuge method of swelling and absorption estimations, 26, 36, 141, 433, 437
Cetoxymethyl cellulose ether, 385, 389
Cetyl ketene, 314
Chain molecule length and fluidity, 228
Chemic, 20
Chemical ripeness test for viscose, 459
China grass, 14
Chitin, 90
—— Deacetylated, 89
Chloral on cellulose, 186
Chloracetic acids, 323, 325
—— anhydride, 325, 339, 346, 353, 360
Chloracetonitrile, 423
Chlorbenzyl ethers of cellulsoe, 393-4
Chlorination of cellulose acetate, 3[illegible]
Chlorine-sulphur dioxide catalyst in acetylation, 312
Chlormalonic acid on soda cellulose, 391
Chlormethyl ethers, 385
—— lauryl ether, 391
—— methy sulphate on soda cellulose, 396
Chlormethoxysulphonic chloride on soda cellulose, 366
Chloroformic ester on soda cellulose, 303, 391
Chlorproprionic acid on soda cellulose, 391
Chlorsuccinic acid on soda cellulose, 391
Chlorsulphonic acid-pyridine on cellulose, 301
Chromic acid, 237
Chromium, Catalytic effect of, 253
—— oxychloride, 352
—— sulphate, 315
Collodion, 291
Colloid mill, 302, 455
—— systems classification, 122
Colloidal double salts, 23
Colloresin, 369
Compound celluloses, 3
Convolutions. Removal by mercerisation, 137-8
Copper-ethylene diamine, 173
Copper number, 239
—— and solubility numbers, 224
—— micro method, 241
Cordite, 291
Cork, 4
Cotton, Alkalinity of ash, 21
—— Analysis of, 19
—— American, 7
—— Ash, 16
—— Bleached, 6
—— Cellulose, physical props, 42
—— Characteristics of typical, 7
—— Derivatives, solubility, 478
—— Drying of, 31
—— Egyptian, 7
—— Electrical properties, 46
—— Fine structure, 7
—— Goods, Purification, 19
—— Growth rings, 10
—— Impurities, 15
—— Indian, 7
—— Isoelectric point, 28
—— Nitrogen content, 15
—— Phosphorous content, 16
—— Primary wall, 8
—— Pigment, 16
—— Pore size, 43

Cotton, Raw, Analysis, 19
—— Sea Island, 7
—— Secondary layers, 9
—— Standard cellulose from, 17
—— Swelling with CS_2 and NaOH, Figs. 21 and 22 and p. 185
—— Wax in, 15
—— Hairs, Action of KOH, 143
—— Hairs, Changes in mercerisation, 137-41
—— Hairs, Tensile strength of, 144
Cotton-rayon mixtures and mercerising, 150
Cuprammonium hydroxide, 6, 171
—— Absorption by cotton, 27
—— Cellulose, 184
Cuprammonium Rayon, 183
——, Fluidity, 174, 185
——, Sodium hydroxide, 173, 174
Crease resistance, 98, 365, 366, 453
—— and orientation, 113
—— and waterproofing, 422
Cross section of rayon, 461
—— complexity, 461
Crotonic anhydride, 340
Crotyl cellulose, 392
Crystal unit of cellulose, 115
Cutin, 4
Cuticle, 6
Cutocellulose, 4
Cyanacetic esters of cellulose, 424
Cyanocellulose, 422
Cyanogen chloride, 422
Cyanuric chloride, 423
Cyclic fatty acid chlorides, 346

DAILY growth rings in cotton, 171, 186
De-convolution of cotton hairs, 137
Degradation products of cellulose, 41
Degree of complexity of cross section of viscose, 461
—— of polymerisation, 65, 67, 69, 70
—— of ripening of viscose, 458
De-nitration of cellulose nitrate, 297
Derivatives of cellulose, X-ray analysis, 118
Desulphurising agents for viscose, 462
Deuterium oxide, 41
Diacetyl o-nitric acid, 406
Diazomethane, 371
Dibenzyl cellulose, 377
Dicarboxylic acids, Esters with cellulose, 337
Dichlordimethylsulphate, 366
Diethylaminocellulose, 415
Diethylamino ethyl cellulose, 409
Diethyl sulphate, 373
Dimethyl dibenzyl ammonium hydroxide (also called Triton F q.v.), 158
Dimethyl sulphate, 52, 367
Dioxane, 360, 362
Dispersed cellulose, 135
Donnan membrane equilibrium, 435, 439
Double refraction of textile fibres, 44, 100
——, Test for mercerisation, 202
Dye affinity of mercerised cellulose, 190

EFFECT threads, 415
Elasticity, 6
—— and plasticity of cellulose esters, 333
Electrical conductivity, 46
Electrification of dry cotton, 30
Electrokinetic phenomenon, 47
End groups, Determination in cellulose, 62
Esters of cellulose :—
Acetates, 307-323
Benzoates, 342
Butyrates, 327, 336
Carbonates, 303
Carbamates, 340
Chloresters, 323
Cinnamates, 345
Crotonates, 340
Dicarboxylates, 337
Formates, 304
Furoates, 343
Glycollates, 337
Hydroxy esters, 336
Linoleate, 341
Maleates, 341
Mixed, 349
Naphthenates, 336, 344
Nitrates, 289
Oleates, 341
Oxalates, 338
Palmitates, 330
Phosphates, 301
Propionates, 326
Solubility (table), 334
Stearates, 330
Succinates, 339
Sulphacetates, 307

Esters of cellulose :—
Sulphates, 298
Undecylenates, 329
Unsaturated, 340
Ester Ethers of cellulose, 401
Ethers of cellulose :—
Alkoxy alkyl, 384
Alkyl, 375
Alkyl carboxy, 391
Allyl, 413
Aryl, 376
Basic, 409
Benzyl, 376
Chlorbenzyl, 393
Crotyl, 392
Ethyl, 372
Glycol, 384
Halogenated, 392
Hydroxylalkyl, 384, 388
Methyl, 367
Methylene, 364, 391
Methyl-methylene, 396
Mixed, 395
Multiple, 399
Triphenyl methyl, 372
Unsaturated, 391
Properties, 379
Solubility, 380
Strength and extension, 379
Ethylation of cellulose, 372
—— by ethyl sodium sulphate, 374
—— by ethyl chloride, 374
Ethylene chlorhydrin, 387
—— diamine, 161, 172
—— imine on cellulose, 416
—— oxide derivatives, 83
—— oxide on cellulose, 385
Extension and strength of fatty esters of cellulose, 336

FALLING sphere viscosity method, 181
Fatty acid anhydride impeller in esterification, 353
Finishing processes, 30
Flax, 13
——, Action of caustic soda, 142
——, Nitric acid on, 170
Fluidity measurements, 174
——, Tendering relation, 180
Formates of cellulose, 304
—— analysis, 306
Formaldehyde, 164
—— -acid on cellulose, 364
—— -acid pyridine, 384
—— sulphuric acid on cellulose, 168, 202
Formic acid, 208
Formamide, 194, 195
" Fortisan," 322
Fractionation of cellulose acetate, 317
—— of hydrocellulose with caustic soda, 228
Furoyl chloride on soda cellulose, 343

GAMMA-CELLULOSE, 5
Gases. Sorption by cellulose, 29
Gardinol, 462
β-Glucosan, 42
Glucose, 4, 51, 55, 56, 84, 233
Glutoline, 369
Glycerol chlorhydrin, 389
Glycol cellulose, 385
(*see also* Cellofas)
Glycollicester of cellulose, 337
Glycide, 386
Glycidol, 83
Gossypyl alcohol in cotton wax, 15
Guanidine, 157
Guncotton, 6, 290, 291

HACKLING (or Heckling), 13
Hairs of cotton :—
—— Breaking load and copper number, 211
—— Breaking load and viscosity, 210
—— Ripe and unripe, 186
Halogenated esters, 323
—— ethers, 392
Heat. Action on cellulose, 42
—— Effect on absorption capacity of cellulose, 191
—— of adsorption of water by cellulose, 38
—— of adsorption of caustic soda by cellulose, 146, 431
Heavy water (D_2O), 41
—— Hydrogen, 41
Helium. Use in specific volume measurements, 37
Hemicellulose, 4
Hemp, 3
Higher fatty esters of cellulose, 329
Holocellulose, 5
Hydral cellulose, 238
Hydracrylic esters of cellulose, 337
Hydrate cellulose gel deformation, 464

Hydrate cellulose, X-ray work, 202
Hydrated cellulose, 136, 192
Hydrazine, 161
Hydrocellulose, 207
—— Absorption of formaldehyde, 216
—— and chain molecule, 230
—— Acetylation of, 216
—— Dimethylether, 216
—— Esterification, 216
—— Methylene blue absorption, 215
—— properties, 214
—— Reducing properties, 236
—— Solubility in caustic alkalies, 216
—— Test for, 212
—— Trisulphuric acid, 301
—— Velocity constant of formation, 212
—— Viscose, 217
Hydrobromic acid, 170
Hydrochloric acid, 51, 168, 207
Hydrofluoric acid, 16, 170
Hydriodic acid, 170
Hydrogen bromide, 207
—— chloride, 29, 207, 208
—— -ion concentration, *see* pH
—— peroxide, 21, 236
—— from cellulose by sodioammonia, 440
Hydrophobic esters of cellulose alkylurethanes, 420-5
Hydrolysis number, 196
Hydroxyacids. Cellulose esters of, 336
Hydroxyalkyl ethers, 384
Hydroxyesters of cellulose, mixed, 358
Hydroxyethyl cellulose, 385, 388, 389
Hydroxymethyl furfuraldehyde, 41, 233
Hydroxypropyl cellulose, 389
Hyprobromite, 196
Hypochlorous acid, 265
Hysteresis in moisture relations of cotton, 32, 36

IGEPON. Desulphurising agent, 462
Immunisation of cotton to dyestuffs, 347
" Impellers " in esterification, *see* Chloracetic anhydride
Inorganic hydroxide, 135
—— Salts as solvents, 162
Insulation resistance, 38, 46
Internal surface, 29, 39
Iodides. Solvent power, 165
Iodine absorption, 202
—— Action on cellulose xanthate, 459
—— Number, 64, 459
Iron. Catalyst in oxidation of soda cellulose by oxygen, 261
Isocyanic esters. Action on cellulose, 340, 425
Isothiocyanic esters. Action on cellulose, 429
Isonitrile test in chlorination of cellulose acetate, 325

JUTE, 4
—— Nitric acid on, 170

KETEN, 314, 353
Ketonic esters. Mixed, 359
Kier boil, 20

LACTIC acid cellulose ester, 336
Lactose (formula), 57
Lauric chloride, 351
Lauryl methylene ether of cellulose, 391
Lead chromate and acetate. Test for oxycellulose, 284
Lignin, 3
Lignocelluloses, 4
Lilienfeld rayon, 194, 461
Limited viscose reaction, 186
Linters, 5
Liquid ammonia in mercerising action, 161
—— in methylation, 372
—— Use of, 455
Lithium hydroxide, 144, 229, 270
—— thiocyanate, 165
Linear polymers, 78
Lumen, 6
Lustre, 7
Lye boil, 20

MAGNESIUM perchlorate, 393, 343, 346, 353
Maleic anhydride, 341
Maltose, 56, 57
Mechanical Properties of cellulose, 48
Membrane equilibrium equation, Donnan, 435

Mercerisation :—
Action of liquified ammonia, 161
Under tension, 135
Cotton-rayon mixtures, 150
Effect of temperature, 136, 152
Effect on chemical properties, 195
Effect on tensile strength, 195
Single hairs, etc., 137-145
X-ray diagrams, 202-204
X-ray work, 117
Tests, 201
Mercerised cotton. Effect of boiling water, 191
Methane sulphonic acid, 170
Methylation by diazomethane, 371
Methylene Blue, 21
—— Blue absorption, 195, 215
—— Cellulose, 364
—— Cellulose acetate, 253
—— Disteara mide, 421
—— Iodide, Plate II
—— Methyl ether, 396
—— Sulphate. Action on soda cellulose, 366
Methyl Cellulose, 367
—— chloride and sulphate, 367
—— chloroformate. Action on soda cellulose, 303
—— Glucoside, 52
—— Isothiocyanate, 429
Micelle theory, 100
—— size, 106-111
Microchemical Solubility Number method, 222
Mineral acids. Action on cellulose, 207
Mixed Ethers, 395
—— Esters, 349
Modified cellulose, 205 *et seq.*
Molecular weight of cellulose, 61
Moisture determination, 31
—— relations of cotton, 29
—— —— of cellulose derivatives, 35
—— —— of mercerised cotton, 189
—— —— of rayon, 35
Monochloracetic acid. Action on soda cellulose, 391
Montanyl alcohol, 15
Mordants, 27
Mucocelluloses, 4
Mustard oils (Isothiocyanates), 429

NAPHTHENIC acid esters, 344
Native cellulose, 5
Neutral salts. Action on cellulose, 27, 162
Nickel ammonium hydroxide, 173
Nitrate-Acetates, 349
Nitration of cellulose. Influence of water, 290
Nitric acid, 169, 207, 236
Nitroacetate, 350
Nitrobenzyl phenyl dimethyl ammonium chloride, 417
Nitrocellulose. Compounds with ketones, 294
Nitrogen in cellulose nitrate. Estimation, 294
Nitroleukotrope, 417
Nitrous acid in cuprammonium, 176
Non-aqueous vapours. Absorption by cellulose, 29
Nylon, 77

OCTADECYL chloromethyl ether, 384
—— thiocyanate, 426
—— oxymethyl pyridinium chloride, 384
Oligosaccharides, 86
Omega esters, *see* Polyesters
Optical properties, 44
Orientation, 151
—— by stretching, 113
—— and crease-resisting properties, 113
—— and velocity of acetylation, 113
Osmosis, 150
Osmotic pressure and swelling, 151
—— —— and molecular weight determinations, 62
Oxalic acid, 208
—— esters of cellulose, 337
Oxalyl chloride, 338
Oxidation. Electrolytic, 236
—— by ozone, 236, 238
—— by chromic acid, 237
—— by permanganate, 257
—— at varying pH, 249
Oxycellulose, 218, 219, 235
—— affinity for basic dyes, 243
—— alkaline hydrolysis, 244
—— and hydrocellulose tests, 283
—— ash alkalinity, 249
—— baryta absorption, 242
—— carbon dioxide from, 242
—— carboxyl groups in, 242
—— chain molecule and, 272
—— chromic acid, 237
—— colour reactions, 242
—— copper number of, 239, 245
—— esters, 243
—— fluidity, 252

Oxycellulose, furfuraldehyde from, 242
—— hot alkali on, 263
—— methylene blue absorption, 246
—— periodic acid, 255
—— permanganate, 257
—— preparation by heat, 236
—— properties, 237
—— rate of formation, 253
—— reactions, 239
—— reactions with phenyl hydrazine, 238
—— reducing action, 241
—— solubility at low temperature, 266
—— solubility, copper number and fluidity, 262
—— two types, 246
—— viscosity, 251
Oxygen. Absorption by soda cellulose, 260

PALMITYL chloride, 330
Parchmentised cellulose, Water held by, 192
Parchmentising effects, 164, 166, 168
Particle theory, 123
Pectocelluloses, 4
Perchlorates. Solvent power, 167
Perchloric acid, 308
See also magnesium salt
Permeability of cellulose, 43
Persulphates, 236
pH, copper number and methylene blue absorption, 249
Phenyl acetyl chloride, 346
—— hydrazine, 214
—— isocyanate, 340, 425
—— phosphate, 351
Philanising process, 170
Phosphate acetate of cellulose, 351
—— cellulose, 301
Phosphonium bases, 156
Phosphorus oxychloride on cellulose, 302, 351, 406
Phosphorus pentachloride on cellulose acetate, 324
Phosphoryl chloride, 302
Phosphoric acid, 169
—— Action on cellulose, 207, 209, 302
—— Combined, 215
Phosphonitrilic chloride on soda cellulose, 418
Photographic film, 291
Phthalic anhydride, 345
Physical properties of cotton cellulose, 43
Plasticity and elasticity of cellulose esters, 333
Polar solvents, 338
Polyamides, 78, 81
Polyesters, 66, 77
Polymers, synthetic, 83
Polyoxymethylenes, 66, 83
Polystyrenes, 66
Polyvinyl acetate, 66
Pore size in cellulose materials, 43
Potassium cellulose trisulphate, 300
—— hydroxide. Action on cotton, 143
—— —— Action on rayon, 152, 154, 156
—— —— Solubility of modified cellulose in, 229, 268
—— hydrocellulose trisulphate, 301
—— iodide, 165
—— mercuric iodide, 166
—— permanganate, 236
ζ-Potential, 48
Pressure experiments on cellulose-water systems, 40, 41
Propyl cellulose, 375, 379
Propylene oxide, 386
Proteins, regenerated, 96

QUATERNARY ammonium salts, 411, 417
See also Nitroleukotrope, 417
—— ammonium hydroxides, 156, 447
—— compounds. Swelling and dissolution of cellulose with, 156

RAMIE, 3, 14
—— Action of caustic soda, 142
—— Double refraction, 44
—— Liquid ammonia on, 193
—— Molecular weight, 69
—— Nitric acid on, 170
—— Thallous ethylate on, 441
—— X-ray diagram, 57
Rayon. Acetate, 320
—— —— stretching and hydrolysis, 321
—— Depolymerisation in, 69
—— Glycol cellulose as, 388
—— Lilienfeld, 194, 461
—— Manufacture of viscose, 450
—— Moisture absorption, 35, 189
—— Solubility in alkali, 153

Reactivity ratio, 152, 188, 195
Refractive index of celluloses, 45, 46, 113
Regenerated cellulose. Swelling of, 146
Relative humidity, 30
Retting, 7
Relative humidity and moisture absorption, 189
—— viscosity ηr (= η substance / η solvent), 66
Rigidity of cotton hairs, 48
Ripening of cellulose xanthate, 457
Ripeness tests for xanthate, 458
Rolling sphere viscometry, 180
Rosin, 18
R.O.X. mounting medium, Plates I to VII
Rubidium hydroxide, 144

SALT point. Ripeness test for viscose, 458
Selenic acid, 170
Selenium cellulose compounds, 428
Selenonium bases, 156
Shrinkage by alkali, 137, 143
Silicon tetrachloride. Action on cellulose acetate, 352
—— tetrachloride. In ether esters, 406
Silk, 7
—— chain molecule, 90
Silver number, 241
Soda boil for cotton goods, 20
Soda cellulose, 430
—— I, II, III, 442
—— Phase rule application, 444
Sodio ammonia on cellulose, 440
Sodium chloride. Action on cellulose, 28
—— ethyl sulphate. Ethylation by, 374
—— ethoxide, 136
—— hydroxide. Action on cotton, 136
—— —— Preferential absorption by cotton, 198, 431, 433
—— sulphide as swelling agent, 166
—— zincate, 136
Solid solution, 40
Solubility and copper number, 224
—— and fluidity, 225
—— at low temperatures, 226
—— number, 221
Sorption of dry gases by cellulose, 29
Sorption of moisture by cellulose, 187
Sour, 20
Specific viscosity (η_{sp}), Staudinger, 66
—— volume of cellulose, 29, 37, 190
Spinning bath for viscose, 460
Stabilisation of gun cotton, 290
—— of nitrocellulose, 296
Starch, 56
Stretch-spinning process, 185
See also "Fortisan," 322
Stearate ester of cellulose, 330
Stearyl aldehyde, 367
—— isocyanate, 340, 426
Stearoyl chloride, 330
Stoichiometric hydrates, 40
Straw, 3
Strength of fatty esters, 336
—— of materials compared, 114
Sulphate of cellulose and its salts, 298
Sulphide of cellulose, 302
Sulphoacetate of cellulose, 307
Sulphonium bases, 156
Sulphonic acids. Esterification of cellulose with, 346
Sulphur dioxide, 208
—— liquid—in acetylation, 313
Sulphuric acid, 207
—— combined, 215
—— -formaldehyde, 168, 202
—— swelling with, 167, 192
Sulphur trioxide—pyridine on cellulose, 301
Sulphobenzyl ethers of cellulose, 379
Sulphonium bases, 156
Sunlight, Effect of—in oxycellulose formation, 235
Superpolyamides, 79
Superpolymers, 77
Sulphuryl chloride on soda cellulose, 303, 352
Surface conductivity, 47
—— tension and pore size, 43
Swelling capacity of acid and alkali treated cellulose, 192
Swelling of cellulose—
—— by acids, 167, 192
—— by caustic alkalis, 141, 192
—— temperature effect, 152
—— by cuprammonium hydroxide, 171
—— Neale's theory, 146
—— X-ray work, 102
Synthetic cellulose, 69, 84
Synthetic resins, 48, 75
Synthetic rubbers, 75

TANNIC acid. Absorption by cellulose, 27
Tellurium compounds of cellulose, 428
Tendering, 175, 207
Tendering estimation by fluidity, 219
Tensile strength, 30, 77
—— comparisons, 77, 78
—— and copper number, 211
—— effect of mercerisation, 144
—— and fluidity, 219
—— of hairs and yarns, 144
Ternary systems. Cellulose-water-pyridine, etc., 40, 41
Tertiary amine oxides, 160
Tetraethyl ammonium hydroxide, 156, 447
Tetramethyl ammonium hydroxide, 156, 229, 268, 447
—— glucose, 60
Textiles. Fireproofing by sulphobenzylation, 379
—— Water-repellent, 314, 367, 384
Thermal expansion of cellulose, 107
Thallium cellulose, 441
Thallous ethylate, 441
Thiocyanates. Solvent power, 163
Thionyl chloride, 303, 414
Thiorethanes of cellulose, 425
Threads and hairs. Breaking load, copper number and viscosity, 210, 211
Thread molecules, 447
p-Toluene sulphocellulose, 411
p-Toluene sulphonic chlorides, 346, 404, 410
Transient swelling, 149
Triacetate of cellulose. Deacetulation and methylation, 369
Trialkyl sulphonium hydroxide, 455
Triethyl cellulose, 374
Trimethyl cellulose, 369
—— benzyl ammonium hydroxide (Triton B), 157
—— glucose from cellulose, 54
Triphenyl methyl cellulose, 372
Tri monochloracetate of cellulose, 324
Triton F, 280, 281
Tri-trichloracetates of cellulose, 324
Tylose, 369

ULTRA violet light. Oxycellulose formation, 236, 238
—— centrifuge method for molecular weight determinations, 61
Ultrafiltration in pore size measurements, 43
Undecylenate of cellulose, 329
Unsaturated esters mixed, 356
—— ethers, 391
—— fatty esters of cellulose, 340
Urea, 406, 416
Ureas, acetylated, 420
Urethanes, 340, 425
See also Carbamates

VALERATE ester of cellulose, 333, 336
Valonia ventricosa X-ray examination, 110
Vasculose, 3
Vat dyes. Reduction by oxycellulose, 241-242
—— Oxidation of cellulose in presence of, 271
" Velan," 422
Vinyon, 76
Viscometer, 174, 180
Viscose. Analysis, 458
—— Alkali cellulose for, 454
—— Desulphurising and bleaching, 462
—— Flow chart, 463
—— Laboratory preparations, 448
—— Manufacture, 450
—— Raw materials, 452
—— Rayon, molecular weight, 200
—— —— mercerisation, 151
—— Reaction, 446
—— Reactions of, 466
—— Ripening of, 457
—— Specific volume, 190
—— Spinning bath, 460
—— Viscosity standard test, 460
Viscosity, 174
—— of cellulose via nitrate, 181
—— and copper number relation, 212
—— of cellulose, 175
—— changes in viscose ripening, 458
—— falling sphere method, 181
—— specific (Staudinger), 66
—— and molecular weight, 66

" WATER-CELLULOSE," 193
—— -ternary systems, 40, 41
—— pressure experiments, 40, 41
Water held after centrifuging, 192
Waterproof and crease-resistance, 422

Waterproof effects, 314, 367, 384
Water removal by centrifuge, 26, 36
—— -resistance of cellulose ethers, 381
Wool, 91

XANTHACETATE of cellulose, 428
Xanthanilide of cellulose, 428
Xanthate of cellulose, 446
—— analysis, 458
—— metallic salts, 466
—— methylation of, 466
—— purification, 466
—— reactions, 466
—— ripening, 457
Xanthation of alkali cellulose, 457
Xylyl cellulose, 379
X-ray examination. Alkali cellulose, 442
—— Cellulose, 62, 100

YARNS. Shrinkage in mercerisation of cotton, 145

ZELAN. *See* Velan
Zeta potential, 48
Zinc ammonium hydroxide, 172
Zincate test for tendered cotton, 136
Zinc hydroxide, 135
—— chloride, 165, 166, 202, 308, 314, 345, 409

LIST OF PATENT SPECIFICATIONS

BRITISH

13,296/1850 . . 135, 166
20,314/1889 . . . 135
4,452/1890 135
19,428/1896 . . . 166
19,330/1905 . . . 309
5,016/1907 319
8,647/1910 351
12,854/1912 . . 367, 368
6,035/1913 396
6,036/1913 368
108,671 136
130,277 . . 340, 425, 426
139,232 315
149,320 368
156,735 368
163,016 to 8 . . . 368
164,374 368
164,375 . . . 375, 397
164,377 . . . 368, 375
164,379 368
166,767 385
167,143 328
176,420 368
177,809 to 10 . . 368, 404
178,152 454
181,391 to 5 . . . 368
182,820 328
183,908 302
184,533 454
184,825 . . . 375, 396
187,639 368
190,732 315
191,203 136
192,173 303
192,227 136
195,619 347
196,641 315
200,186 315
200,815 to 6 . . . 368
200,827 368
200,834 368
200,881 . . . 168, 366
203,346 to 7 . . . 368
212,864 152
212,865 454
216,476 186
216,477 186
217,166 156
219,926 352
227,134 315
230,530 168
231,801 . . . 427, 429
231,807 385
237,573 314
237,591 314
239,726 314
240,624 315
241,149 428
241,679 404
244,148 315
248,246 427
249,842 . . . 411, 425
252,176 395
252,654 466
257,167 467
260,650 306
262,477 295
263,169 . . . 411, 425
265,267 315
265,491 378
266,300 352
268,552 404
269,531 368
270,347 404
274,521 461
274,690 461
277,111 378
277,317 379
277,721 . . . 389, 392
279,437 462
279,796 302
279,801 414
280,493 320
281,117 455
281,473 160
284,358 411
286,331 428
287,880 362
289,582 . . . 353, 357
290,570 . . . 356, 357
291,473 to 4 . . . 365
295,062 150
295,488 156
300,058 361
301,036 313
300,207 355
300,942 . . 351, 405, 406
304,279 326
305,096 315
305,947 . . 344, 346, 355

306,531 313
308,322 315
312,095 315
312,098 315
313,408 346
314,913 320
314,918 337
314,919 358
315,434 341
316,160 . . 335, 337, 358
317,019 . . . 425, 426
318,255 409
319,691 407
320,482 419
320,842 . . 326, 337, 419
322,556 . 348, 415, 417, 425
323,174 166
323,307 150
323,500 320
323,515 320
323,548 320
323,869 328
324,780 320
326,865 . . . 376, 395
328,259 328
328,492 340
329,704 341
330,957 407
331,903 396
333,902 379
334,897 . . 404, 405 407
335,906 . . . 467, 466
335,993 466
335,994 466
338,201 . . . 358, 362
338,202 . . . 359, 362
338,210 358
341,147 350
341,237 419
341,843 467
342,166 423
342,391 378
342,689 392
343,104 332
343,521 391
343,748 423
343,873 389
344,420 418
344,480 . . 413, 414, 419
344,488 . . . 422, 423
344,529 393
345,028 399
345,408 318
345,989 413
346,385 418
346,426 399
346,806 . . 393, 414, 419
347,117 418
347,167 423
347,263 418
347,423 406
347,451 346
347,651 . . . 403, 407
355,172 361
356,286 466
356,665 353
357,080 429
357,154 467
357,526 . . . 428, 467
357,527 467
357,549 467
357,551 467
357,595 467
357,781 318
358,510 407
359,249 372
359,618 386
360,409 377
360,417 362
360,742 419
365,250 408
367,920 467
368,288 467
370,355 422
374,791 161
385,979 428
389,518 467
389,519 467
390,518 428
390,519 467
390,553 385
391,171 392
392,242 416
393,254 416
393,914 423
394,196 385
394,722 416
410,118 . . . 339, 345
410,125 339
410,126 339
415,042 88
417,220 322
417,222 88
424,925 453
426,482 411
426,553 455
428,955 462
429,103 322
429,165 462
434,540 455
437,361 145
438,584 to 7 321
438,588 to 91 321
438,656 321
438,786 321
439,806 . . . 160 447

439,880 145
443,564 316
443,707 321
443,773 321
445,243 365
447,651 365
449,183 327
450,620 365
452,150 365
452,506 . . . 369, 374
453,155 321
454,580 321
455,472 365
460,201 365
460,590 416
461,179 424
461,236 79
461,237 79
462,005 365
463,056 455
464,116 464
464,843 311
466,817 385
466,853 420
469,391 369
469,476 384
470,994 374
471,130 . . . 385, 420
474,403 426
474,999 80
475,906 386
475,119 385
475,170 . . . 385, 421
476,431 417
477,029 367
477,084 365
477,428 464
477,991 421
478,127 341
480,408 160
481,191 386
482,942 386
487,734 82
489,235 427
492,264 88
493,920 420
494,761 421
494,833 426
495,025 420
495,645 422
495,714 422
495,829 422
501,768 322
502,482 88
506,721 422
508,173 420
517,474 421
522,033 314
522,204 314
526,738 422
527,012 422

UNITED STATES

763,473 170
1,384,677 170
1,429,153 401
1,451,330 397
1,504,178 375
1,655,097 462
1,674,401 . . . 427, 429
1,674,402 427
1,674,403 427
1,674,404 427
1,674,405 . . . 427, 428
1,698,048 359
1,698,049 357
1,704,283 . . . 343, 360
1,704,305 345
1,704,306 359
1,734,516 365
1,777,970 44
1,785,466 360
1,813,619 424
1,824,877 327
1,833,720 399
1,861,200 360
1,863,208 407
1,867,942 405
1,880,420 306
1,880,558 405
1,896,725 302
1,941,276 to 8 . . . 387
1,969,741 to 3 . . . 355
1,984,094 363
1,990,483 353
1,991,107 353
1,998,267 316
2,000,596 363
2,000,621 327
2,009,015 160
2,036,382 311
2,040,065 160
2,040,093 355
2,051,217 353
2,053,570 454
2,066,571 311
2,069,892 83
2,080,043 365
2,082,797 392
2,082,804 355
2,083,554 385
2,084,125 . . . 385, 389
2,108,455 355
2,130,947 to 8 . . . 83
2,136,296 414

2,136,299 414
2,217,823 90

GERMAN

57,846 413
184,201 310
239,701 358
254,385 310
322,586 367
363,192 385
384,007 379
408,821 186
411,208 359
422,179 456
433,147 418
498,157 306
510,424 404
511,208 406
521,721 409
525,835 . . . 403, 404
534,852 402
540,872 401
542,004 413
544,777 425
547,812 307
550,260 357
550,760 415
551,679 429
553,069 418
556,590 302
556,951 352
574,002 424

FRENCH

286,906 329
347,724 365
348,122 365
349,904 365
349,905 365
310,760 365
435,507 359
462,274 367
478,023 311
530,891 368
615,349 378
629,099 389
629,861 405
655,729 462
659,929 418
660,510 . . . 401, 405
664,932 . . . 329, 376
680,956 409
684,320 170
686,598 400
687,298 418
687,310 423
695,283 408
702,116 357
705,816 408
708,538 408
714,061 422
717,623 . . . 352, 408
723,600 160

SWISS

145,053 425
147,791 418
148,491 419
150,789 425
150,790 419
150,791 425
152,480 425

AUSTRIAN

126,586 397

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Ann.	Liebig's Annalen der Chemie.
Ann. Chim. Phys. . .	Annales de Chimie et de Physique.
Angew. Chem. . . .	Angewandte Chemie (changed from Z. angew. Chem. in 1932).
Bot. Gaz. . . .	Botanical Gazette.
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