The Chemistry of
CELLULOSE

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BY

EMIL HEUSER

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PREFACE

The idea of writing a more comprehensive book on the chemistry of cellulose than the author's "Textbook" of 1924 was conceived a number of years ago but, because of many interruptions, it is only now that the result is presented to the public.

This volume is, first, a compendium and critical digest of the literature of the chemistry of cellulose with due consideration of the microscopic and submicroscopic structure of the cellulose fiber. Emphasis has been laid on the scientific aspect rather than on the practical application of cellulose chemistry. An attempt having been made to present the current knowledge of the subject from this viewpoint, it may be hoped that the book will be useful not only to the scholar who wishes to inform himself about a field which was hitherto unfamiliar to him or in which he intends to specialize, but also to those who practice the chemistry of cellulose in industrial and other research laboratories and who wish to acquire or renew their knowledge of the fundamental background of their specialized activities.

Secondly, the book may be regarded as a textbook, inasmuch as it has been written from the point of view of presenting the subject matter in a systematic and simple manner to the student who is looking for guidance in his studies and who expects to find an unbroken and coherent treatise, rather than a number of individual and loosely connected chapters.

Although an attempt has been made to consider all the essential literature up to the end of October, 1943, some difficulties have been encountered because war conditions either prevented access to some of the more recent European publications or delayed their availability to such an extent as to preclude the inclusion of such material except in the form of references.

The author is greatly indebted to Mr. Westbrook Steele, Executive Director of The Institute of Paper Chemistry, for permission to devote the necessary time for the completion and revision of the text and to make use of the various facilities of the Institute. The author is particularly grateful to Dr. C. J. West, Editor of the Institute, for reading the original manuscript and making valuable suggestions which resulted in manifold improvements, as well as for the substantial assistance rendered in the preparation of the author and subject indexes, in the location of buried literature, and in various other respects.

On several occasions, the author had the privilege of discussing various phases of the colloidal and physical aspects of cellulose chemistry with Dr. B. W. Rowland of The Institute of Paper Chemistry, and wishes gratefully to acknowledge the enlightenment which he derived from those discussions.

Thanks are also due to Mr. Clark G. Berry for assistance rendered in the preparation of drawings for part of the illustrations, as well as to Dr. I. W. Bailey, Professor of Plant Anatomy at Harvard University, and to Dr. D. B. Anderson, Professor of Botany at North Carolina State College, for having supplied certain photographs for reproduction. Many other illustrations, diagrams, and the like have been taken from various published sources; in each case credit is given where such figures appear in the text.

EMIL HEUSER

Appleton, Wisconsin
December, 1943

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CHAPTER I

INTRODUCTION

Viewed by the organic chemist, cellulose may be termed a natural high polymer, the building unit of which is an anhydride of glucose. Nature, it is now believed, produces this polysaccharide in the form of long-chain molecules, possibly by condensation and dehydration of glucose.

However, cellulose as it exists in plants, as well as in its isolated form, possesses a complex physical structure which manifests itself in various forms; for example, as hair in cotton, as bast in flax, and as fiber in wood.[1] The cellulosic substance in these and other plant materials is regarded as an aggregate of a great number of individual glucose anhydride chains, arranged more or less parallel to each other and stabilized in the lateral direction by secondary valences or by hydrogen bonds between opposite hydroxyl groups. In addition, the probability exists that cross linkages, also of primary valence nature, are operative between the individual chain molecules.

X-ray analysis, the primary means of elucidating the fine structure of natural polymers, has definitely shown cellulose to be of crystalline nature. The chain bundles are conceived as representing hypothetical, submicroscopic units, of varying length but of fixed breadth and thickness, which are termed crystallites or micelles. The micelles build up the fibrils, the first constituents of the fiber which may be detected under the microscope.

In defining the term cellulose, distinction must be made between cellulose as it exists in plants and cellulose in its isolated form, because in the plant it may be chemically combined with other plant constituents (noncellulosic carbohydrates or their acids) and not merely mechanically associated with these and other compounds as, for example, lignin in wood. On isolation and subsequent thorough purification, cellulose may be obtained practically free of noncellulosic substances. Thus, in isolated cellulose the nature of certain groups would be different from that of groups which were involved in a combination with noncellulosic plant constituents. Moreover, as yet, no means is

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[1] The term fiber is now used to designate all forms.

available which permits the isolation of cellulose from its various sources without breaking a greater or smaller number of the linkages which unite the glucose residues in the individual chains. As a result, isolated cellulose, no doubt, possesses a shorter average chain length than cellulose in the plant. Finally, on isolation and purification, oxidation may take place and thus give rise to a further change in certain groups of the isolated product. Since almost all cellulose reactions have been and are undertaken with isolated cellulose, a discussion of these reactions and their evaluation must necessarily refer to cellulose as the isolated substance unless otherwise stated.

In dealing with the chemistry of cellulose we cannot afford to neglect either its microscopic and submicroscopic morphological structure or, as a result of its high-polymeric character, its colloidal nature as it manifests itself in its solid form as well as in dispersions and solutions. Rather do these peculiarities call for close consideration, because they cause the reactions of cellulose to take a more or less heterogeneous course and, in most cases, to proceed at a relatively slow rate. On the other hand, its fibrous structure and its colloidal nature explain the enormous utility of cellulose for a great variety of purposes.

Cellulose may be obtained from any plant. The process of isolation, whether carried out in the laboratory or in commercial practice, is always the same in principle; that is, the raw materials are subjected to agents which are expected to dissolve or destroy the noncellulosic substances but to have as little effect as possible upon cellulose itself. The chief commercial raw materials are cotton, flax, and hemp for the textile industry and the various species of wood and, to a smaller extent, wheat straw and esparto grass (alfa) for the pulp and paper industry. Cotton, in the form of cotton linters,[2] is the most important source of cellulose for the manufacture of cuprammonium and acetate rayon as well as of most of the cellulose esters and ethers, but the viscose rayon industry uses wood pulp almost exclusively.

Whereas the small percentage of impurities present in the cotton fiber are removed relatively easily, the isolation of cellulose from lignified plant material requires a far more drastic treatment. The separation of cellulose from the lignin in wood may be accomplished by treatment either with a combination of calcium or sodium bisulfite and sulfurous acid (sulfite process) or with sodium hydroxide alone (soda process) or in combination with sodium sulfide (sulfate process).

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[2] The shorter fibers remaining attached to the seeds after delinting (ginning); see Matthews, "The Textile Fibres," John Wiley & Sons, Inc., New York (1924), p. 368.

These treatments are carried out under pressure and at elevated temperature and are followed by a process of bleaching with chlorine and alkali hypochlorite. The wood pulp thus obtained may be further purified by extraction with sodium hydroxide solution, whereby the percentage of noncellulosic carbohydrates, such as pentosans (xylan) and hexosans (mannan, galactan, etc.), and of short-chain cellulose material (*beta-* and *gamma*-cellulose) are further reduced and the long-chain cellulose material (*alpha*-cellulose, characterized by its resistance to 17 to 18 per cent sodium hydroxide solution) is correspondingly increased.[3]

The highest cellulose content, i.e., 97–99 per cent, is found in cotton, ramie, and flax,[4] whereas the cellulose content of the various wood species amounts to 41–53 per cent.[5] Cereal straws contain between 30 and 43 per cent.[6]

The purest cellulose which as "standard cellulose" [7] may be used for experimental studies is obtained from raw cotton. After fat, wax, and other soluble impurities have been removed by extraction with organic solvents, the residue is freed of other noncellulosic substances, particularly pectin, by careful treatment with dilute alkali; after washing, it is bleached slightly with hypochlorite or other bleaching agents.

Small amounts of cellulose occur in certain animal tissues, for example, in *Phallusia mammillaris,* from which tunicin, a type of animal cellulose, may be obtained.[8] This has been found to be identical with cotton cellulose.[9] As a material in which the chain molecules reveal particularly pronounced parallel orientation it has often been used in

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[3] For an account of the manufacture of wood, straw, esparto, and other types of pulp the reader is referred to Sutermeister, "Chemistry of Pulp and Paper Making," John Wiley & Sons, Inc., New York (1942), 3rd ed.; Witham, "Modern Pulp and Paper Making," Reinhold Publishing Corporation, New York (1942), 2nd ed.; "Manufacture of Pulp and Paper," New York, McGraw-Hill Book Co. (1937), 3rd ed., Vol. 3.

[4] See also Hall, "Cotton Cellulose," E. Benn, Ltd., London (1924), p. 1; Matthews, "The Textile Fibres," John Wiley & Sons, Inc., New York (1924).

[5] Schwalbe, "Die Chemie der Cellulose," Gebr. Borntraeger, Berlin (1938), 2nd ed., pp. 265, 281, 333. See also Jayme and Schorning, *Papier-Fabr.,* **36,** 235 (1938); Chen and Cameron, *Ind. Eng. Chem.,* **34,** 224 (1942).

[6] Hall, *loc. cit.,* p. 1. See also Heuser and Haug, *Z. angew. Chem.,* **31,** 99, 103, 166, 172 (1918).

[7] This is the American Chemical Society method. See Corey and Gray, *Ind. Eng. Chem.,* **16,** 853, 1130 (1924). See also Schwalbe, *Papier-Fabr.,* **24,** 769 (1926); Worner and Mease, *J. Research Natl. Bur. Standards,* **21,** 609 (1938).

[8] Winterstein, *Ber.,* **26,** 362 (1893); Abderhalden and Zemplén, *Z. physiol. Chem.,* **72,** 58 (1911); Zechmeister and Tóth, *ibid.,* **215,** 267 (1933).

[9] Zechmeister and Tóth, *loc. cit.*

comparative x-ray studies.[10] Small amounts of cellulose are found also in fungi and bacteria.[11]

The now generally accepted chemical constitution of the cellulose chain molecule (Fig. 1) is the result of more than one hundred years of research on the behavior of cellulose with most varied treatments. The reactions of cellulose resemble those which are observed to occur with the simple sugars. Since, however, all but one of the potential reducing groups of the glucose residues (the one terminating unit of the open chain) are involved in glycosidic linkages between individual members of the chain, cellulose lacks the pronounced reducing power of most of the sugars, and its chief reactions are those of its hydroxyl groups. As the formula shows, all glucose residues except one (the other terminating unit) possess three free hydroxyl groups, the one in the 1-position being of primary and those in the 2-position and the 3-position being of secondary nature. The terminating unit, which possesses four free hydroxyl groups, contains the additional hydroxyl group in the 4-position. The elementary composition of cellulose is expressed by the formula $C_6H_{10}O_5$. On the assumption that the chain is open, and thus possesses two terminating units which are different from the rest, the condensed formula should be written more correctly thus:

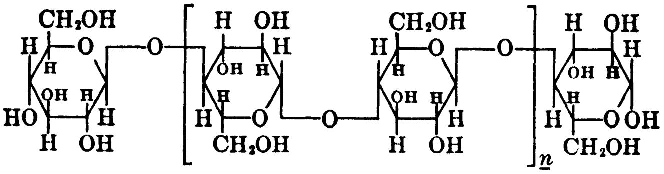

FIG. 1. Molecular chain formula of cellulose.

$$C_6H_{11}O_6—[C_6H_{10}O_5]_n—C_6H_{11}O_5$$

However, the length of the chains makes it impossible to detect the presence of terminating units by elementary analysis.

The free hydroxyl groups in cellulose react as in alcohols to form addition compounds with alkalies and certain complex salts. Under special conditions, they also react with sodium metal to form compounds comparable to the simple alcoholates (cellulosates). Furthermore, the hydroxyl groups of cellulose react to form esters and ethers and, on oxidation, are converted step-wise into aldehydic and car-

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[10] Herzog and Gonell, *Z. physiol. Chem.*, **141**, 63 (1914); Clark, "Applied X-Rays," McGraw-Hill Book Co., New York (1940), 3rd ed.

[11] See the review in Hess, "Die Chemie der Cellulose," Akad. Verlags-Ges., Leipzig (1928), pp. 5-8.

boxylic groups. In all these reactions cellulose behaves as an aliphatic polyalcohol.

Unless rigid precautions are taken, the introduction of new groups, as well as oxidation, is accompanied by hydrolytic attack of the glycosidic linkages which results in a shortening of the chain molecules. However, the chains obviously are long enough to endure frequent cleavage before they lose their polymeric and, hence, their cellulosic character.

The aggregate of chain molecules by which the cellulosic substance may be represented may not consist exclusively of glucose anhydride chains. Under certain conditions, cellulose reveals the presence of carboxylic groups; this may be interpreted to mean that nature has oxidized potential reducing groups or even primary alcoholic groups of some of the chains. Oxidation of the primary hydroxyl groups in a glucose anhydride chain would result in the formation of polyglucuronic acid. In a second phase, nature might convert polyglucuronic acid into xylan by way of decarboxylation.[12] The possible occurrence of such biochemical processes is suggested by the fact that both polyuronic acids and xylan are found to be associated with cellulose in many plants. It also might explain the difficulty of freeing cellulose prepared, for example, from wood and cereal straw, entirely of noncellulosic carbohydrates without breaking down the cellulosic constituent to a considerable extent.

Complete hydrolysis of cellulose yields glucose only. With the reservation that, under the influence of the hydrolyzing acid, some of the glucose is partly destroyed and partly subjected to reversion, the yield approaches the theoretical. On gradual and carefully controlled hydrolysis or acetolysis (hydrolysis with simultaneous acetylation of the products of hydrolysis), a number of oligosaccharides, consisting of six, four, and three glucose anhydride units, may be obtained before the chains break down to the disaccharide, cellobiose, and to the end product, glucose.

Whereas it has not yet been possible to unite by common laboratory methods glucose anhydride molecules to chains containing more than three members, long glucose anhydride chains result from bacterial synthesis from simple sugars. The product of reaction, bacterial cellulose (B-cellulose), has been found to possess the molecular and submicroscopic structure of natural plant cellulose.

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[12] See Mahood and Cable, *Ind. Eng. Chem.*, **14**, 727 (1922); Lewis, *Paper Trade J.*, **95**, No. 21, 29 (1939).

Cellulose possesses a high molecular weight. On the assumption that it is represented by a system of polymeric molecules without side chains, the molecular weight corresponds to the number of glucose anhydride units of the chain molecules multiplied by the molecular weight of the unit (162). The number of units, that is, how often the "building unit" repeats itself in the chain, is termed the degree of polymerization (D.P.), i.e., the molecular weight divided by the molecular weight of the glucose residue.

The molecular weight of cellulose may be determined in various ways. It varies largely with the plant material and the method of isolation. Thus, cotton cellulose possesses a molecular weight which is 3 to 4 times that of cellulose isolated from wood, and cellulose regenerated from its solution (as represented in the various rayon types) has retained only a fraction of the molecular weight of the original cellulosic material.

A simple and approximate assessment of the degree of polymerization of cellulosic materials may be made by determining their solution viscosity. The viscosity decreases with decreasing degree of polymerization and may thus be used for recognizing and controlling the extent to which cellulosic materials undergo degradation during the various steps of isolation, purification, conversion into derivatives, and during other reactions.

It is very probable that in the various plants and even in the same plant, nature produces chains of different lengths, because the isolated cellulose may be fractionated into numerous portions, each of which possesses a different degree of polymerization. The molecular weight of a cellulose preparation thus represents an average value.

CHAPTER II

MORPHOLOGY OF THE FIBER AND COMPOSITION OF THE CELL WALLS

Microscopic Structure

Cellulose [1] is the chief constituent of the cells—the small units which compose the plant tissue. The cells may be seen when cross sections of plant material are observed under the microscope; they appear in various forms, such as spheres, polygons, cylinders, prisms, tubes, etc. The interior of the young plant cells consists of protoplasm and cell sap; it is surrounded by a colorless, transparent skin (the cell membrane) which consists chiefly of cellulose. Millions of such cells compose the organs of the plant and thus become visible to the unaided eye.

In some cases, however, the single cell may be seen without the aid of a microscope. For example, cotton hairs represent single cells; they vary considerably in size, ranging from 1 to 5 cm. in length, and from 12 to 42 μ in thickness. ($1\ \mu = 1/1000$ mm.) Bast fibers, as, for example, flax and ramie, also represent single cells. The flax fiber measures 4.3 to 5.3 cm. in length and 12 to 26 μ in width. Still longer is the ramie fiber, for which lengths up to 26 cm. have been reported; its thickness measures from 40 to 100 μ.[2] On the average, softwood fibers have a length of 3 mm. and hardwood fibers, of 1.2 mm., the width being 0.03–0.04 and 0.015–0.025 mm.

The morphological arrangement of the cellulose fiber may be studied by means of cross sections of fibrous tissue, for instance, of a wood species.[3] In Fig. 2, *A* represents an entire fiber surrounded by seven others. The individual fibers are separated by the intercellular substance (*a* in *B*, representing a section of adjacent cell walls), also termed middle lamella. Adjacent to the intercellular substance is the

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[1] Cellulose derives its name from the Latin word *cellula*, the diminutive of *cella*, meaning chamber.

[2] von Wiesner, "Die Rohstoffe des Pflanzenreichs," W. Engelmann, Leipzig (1927), 4th ed., Vol. II, p. 493; Matthews, "The Textile Fibres," John Wiley & Sons, Inc., New York (1924).

[3] I. W. Bailey, *Ind. Eng. Chem.*, **30**, 40 (1938).

primary wall (*b*); then follow the outer layer of the secondary wall (*c*), the central layer of the secondary wall (*d*), and the inner layer of the secondary wall (*e*) which surrounds the lumen (*A*).

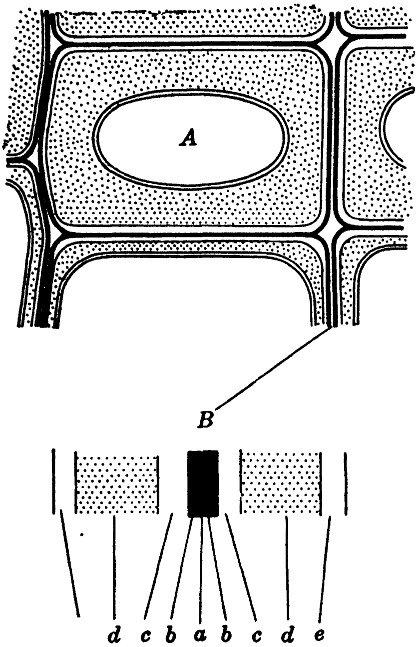

FIG. 2. Transverse section of wood fiber. I. W. Bailey.

Both primary and secondary wall consist chiefly of cellulose but in addition contain varying amounts of hemicelluloses.

The term hemicellulose was first suggested by Schulze[4] for a group of "carbohydrates similar to cellulose," characterized by their behavior with dilute mineral acids by which they are more easily hydrolyzed to sugars than is cellulose. The use of the term hemicellulose has changed frequently and is still being used with different meanings. Some investigators wish to confine the term to the noncellulosic carbohydrates and to define hemicelluloses as being composed of (1) pentosans, chiefly xylan and araban, yielding on hydrolysis the pentoses xylose and arabinose; (2) hexosans, chiefly mannan and galactan, capable of being hydrolyzed to the hexoses mannose and galactose; and (3) polyuronides, mostly in the form of polyuronic acids.[5]

The wood and cellulose chemists, however, have been accustomed to define the term hemicelluloses as that portion of a plant material which is soluble in cold sodium hydroxide solution of 17–18 per cent (by weight). This agent, as has been seen, is a solvent not only for the noncellulosic carbohydrates but also for the short-chain cellulose material which is either originally present in the plant or which has been subsequently produced during its isolation and purification. Both groups of constituents are also included under the term *beta-* and *gamma*-cellulose, whereas the alkali-resistant part of the fiber is called *alpha*-cellulose. *Beta-* and *gamma*-cellulose are distinguished by their behavior with dilute acids: *Beta*-cellulose precipitates on acidification of the alkaline solution but *gamma*-cellulose remains in solution. This classification, originally suggested by Cross

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[4] Schulze, *Z. physiol. Chem.*, **16**, 387 (1892); *Ber.*, **24**, 2285 (1891).

[5] For a general account of the chemistry of the noncellulosic carbohydrates, see Norman, "The Biochemistry of Cellulose, etc.," Clarendon Press, Oxford (1937); Tollens-Elsner, "Handbuch der Kohlenhydrate," Barth, Leipzig (1935); Micheel, "Chemie der Zucker und Polysaccharide," Akad. Verlags-Ges., Leipzig (1939), pp. 305, 316; as well as the numerous publications by Ernest Anderson in *Journal of Biological Chemistry*.

and Bevan,[6] English pioneers in the field of cellulose chemistry, is based on purely arbitrary conditions but is conveniently used in analytical cellulose chemistry.[7]

By the action of chlorine dioxide on plant material such as wood, a fraction is obtained which is composed practically of the entire cellulose and the noncellulosic carbohydrates and which has been termed *Skelettsubstanz* (plant skeleton material). The lignin constituent is oxidized by the chlorine dioxide to water- and alkali-soluble compounds.[8] On replacing the chlorine dioxide by chlorine and removing the oxidized lignin by treatment of the chlorinated wood with an alcoholic solution of ethanolamine, a fraction practically identical with the "skeleton material" is obtained. Since it contains all the cellulose in addition to all the hemicellulose, it has been given the name holocellulose.[9]

The intercellular substance which separates the cells (Fig. 2) consists chiefly of lignin. Although most of it is deposited in the middle lamella, it is not confined to this part of the tissue. Bailey and Kerr have shown that lignin is also contained in the primary and secondary cell walls. These investigators regard cellulose and lignin as representing two interpenetrating systems.[10] In spruce wood, the lignin deposited in the secondary wall seems to be more concentrated in the outer layer of this wall than in that adjacent to the lumen.[11]

Besides lignin, wood tissue, depending upon the species, contains numerous other noncellulosic compounds such as tannins, phlobaphenes, and resins.[12]

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[6] Cross and Bevan, "Cellulose," Longmans, Green and Co., London (1918), p. 93.

[7] Dorée, "The Methods of Cellulose Chemistry," Van Nostrand Company, New York (1933), p. 340.

[8] Schmidt and co-workers, *Ber.*, **54**, 1860 (1921); *Cellulosechem.*, **11**, 49, 73 (1930); **12**, 201 (1931); *Ber.*, **70**, 2345 (1937); see also Heuser and Merlau, *Cellulosechem.*, **3**, 101 (1923); Heuser, *Ber.*, **59**, 598 (1926).

[9] Ritter and co-workers, *Ind. Eng. Chem.*, **25**, 1250 (1933); *Paper Trade J.*, **104**, No. 19, 49 (1937); **105**, No. 18, 127 (1937); *J. Am. Chem. Soc.*, **59**, 802 (1937); *Paper Trade J.*, **108**, No. 7, 27 (1939); **109**, No. 22, 107 (1939); **113**, No. 13, 83 (1941).

[10] Bailey and Kerr, *J. Arnold Arboretum*, **16**, 273 (1935); **18**, 261 (1937); Bailey, *Ind. Eng. Chem.*, **30**, 40 (1938); see also Harlow, *Paper Trade J.*, **109**, No. 18, 38 (1939), and previous papers; also *ibid.*, **112**, No. 23, 35 (1941). See also the results of recent experiments by M. Staudinger, *Holz*, **5**, 193 (1942).

[11] Bixler, *Paper Trade J.*, **107**, No. 15, 29 (1938).

[12] For detailed accounts of the occurrence and chemistry of these compounds, the reader is referred to the books on wood chemistry as, for example, Hawley and Wise, "The Chemistry of Wood," The Chemical Catalog Co., New York (1926) (second edition in preparation); Shorger, "The Chemistry of Cellulose and Wood," McGraw-Hill Book Co., New York (1926); Hägglund, "Holzchemie," Akad. Verlags-Ges., Leipzig (1939), 2nd ed.; Schwalbe, "Die Chemie der Cellulose," Part 1: "Die Chemie der Hölzer," Gebr. Borntraeger, Berlin (1938), 2nd ed., Vol. I. See also von Wiesner, "Die Rohstoffe des Pflanzenreichs," 4th ed.

The cotton hair is composed of a rather thin primary wall, a thicker secondary wall, and the lumen.

The primary wall is also called the cuticle.[13] It is about 0.5 μ thick and contains, besides cellulose, certain amounts of pectin and waxes. Pectin[14] may be defined as representing chains of polygalacturonic acids combined with varying numbers of molecules of *l*-arabinose and *d*-galactose, whereas cotton wax represents a mixture of liquid hydrocarbons with higher alcohols and acids (esters).[15] Pectin and waxes amount to 0.5–1.0 per cent each of the raw cotton fiber. In the older literature, the term cutin is frequently used for the waxy substance. It is likely that both terms are equivalent.[16]

It is generally believed that common coniferous woods contain no pectin. However, Wurz and Haider[17] claim to have identified this substance in spruce wood. Anderson and co-workers[18] have found pectin in some less common wood species, such as black locust wood and lemon wood, but small amounts have also been found in white pine and in white spruce wood. With regard to the amount of pectin in cotton, the reader is referred to the recent studies of Harris and co-workers[19] and of Nickerson and Leape.[20]

Thus far, investigators have regarded the waxes as forming a definite layer covering the outer surface of the primary wall.[21] However, no justification for this concept can be found from studies on cutinized

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[13] Haller, *Textile Forschung,* **3,** 20 (1921); Sakoschnikoff and Korscheniovsky, *ibid.,* **9,** 249 (1931/32); Schneider, *Faserforschung,* **13,** 121 (1938).

[14] Anderson and co-workers, *J. Biol. Chem.,* **112,** 531 (1936); **121,** 165 (1937); see also Schneider, *Ber.,* **69,** 2530 (1936); Schneider and Bock, *ibid.,* **71,** 1353 (1938); Lampitt and Money, *J. Soc. Chem. Ind.,* **59,** 29 (1939); Luckett and Smith, *J. Chem. Soc.,* 1106, 1479 (1940); Hirst, *ibid.,* 70 (1942).

[15] Fargher and Probert, *J. Textile Inst.,* **14,** T49 (1923); Tschilikin, Paper, Kongress der Chemiker-Koloristen, Karlsbad (1927); Hess, Gundermann, and Wergin, *Ber.,* **70,** 517 (1937); Chibnall, Piper, *et al., Biochem. J.,* **28,** 2175, 2189 (1934); Kollmann, *Melliand Textilber.,* **18,** 994 (1937).

[16] See, however, Frey-Wyssling, "Die Stoffausscheidung der höheren Pflanzen," Springer, Berlin (1935), p. 82, and "Submikroskopische Morphologie des Protoplasmas und seiner Derivate," Gebr. Borntraeger, Berlin (1938), pp. 228, 230, 234.

[17] Wurz and Haider, *Papier-Fabr.,* **36,** 302 (1938).

[18] Anderson, *loc. cit.*

[19] Whistler, Martin, and Harris, *J. Research Natl. Bur. Standards,* **24,** 13 (1940); Whistler, Martin, and Conrad, *Textile Research,* **10,** 449 (1940).

[20] Nickerson and Leape, *Ind. Eng. Chem.,* **33,** 83 (1941).

[21] Balls, "Studies on the Quality of Cotton," Macmillan and Co., London (1928), p. 18; Schneider, *Faserforschung,* **13,** 121 (1938). See also Frey-Wyssling, "Submikroskopische Morphologie des Protoplasmas und seiner Derivate," Gebr. Borntraeger, Berlin (1938), p. 225.

walls in general. It is likely that the waxes are distributed more or less uniformly[22] within the primary wall of cutinized cells along with the pectin. The waxes make the cotton fiber water-repellent[23] and only after they have been extracted by means of organic solvents does the fiber become water-absorbent.

The primary wall or cuticle of the raw cotton fiber may be made visible under the microscope by allowing the fiber to swell in suitable swelling agents, such as cuprammonium hydroxide solution[24] (also called Schweizer's reagent[25]) or sodium hydroxide solution of 17–18 per cent (by weight), in combination with carbon disulfide (this treatment represents the procedure by which cellulose is converted into viscose).[26] In these agents, the primary wall, probably because of lack of elasticity, does not swell, whereas the secondary wall swells considerably. This difference causes the primary wall to be torn to ribbon-like pieces which form ring-like bands around the fiber and prevent those parts of the fiber which lie beneath the bands from swelling. In this way the fiber appears to be divided into beads, balls, or balloons[27] (Figs. 3 and 4).

The swelling effect of cuprammonium solution on cellulose increases with increasing copper content of the solution; it is further increased by addition of aqueous alkali. Under these conditions a swelling effect, measured by the method suggested by Heuser and Bartunek,[28] of 1800 per cent has been observed.[29] On longer treatment, the secondary wall dissolves in the cuprammonium solution, whereas the cuticle remains undissolved.[30]

Anderson[31] believes that the pectin in the primary wall causes the constrictions during swelling in cuprammonium solution. When fibers

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[22] Anderson, *Ohio State J. Science,* **34** (Jan. 1934); Meyer, *Protoplasma,* **29,** 552 (1938).

[23] Frey-Wyssling, *loc. cit.,* p. 235.

[24] O'Neil, "Calico Printing, Bleaching and Drying," London (1863); quoted in Bowman, "The Cotton Fiber," Macmillan and Co., London (1908), p. 106; Hess and Trogus, *Z. physik. Chem.,* **A145,** 415 (1929).

[25] Schweizer, *J. prakt. Chem.,* 109 (1857).

[26] Hooper, *Contrib. Boyce Thompson Inst.,* **10,** 267 (1939); Kühnel, *Cellulosechem.,* **19,** 58 (1941).

[27] Balls, *Proc. Royal Soc.,* London, **B90,** 542 (1918); Herzog, "Mikrophotographischer Atlas, etc.," Part I, I. B. Obernetter, Munich (1908).

[28] Heuser and Bartunek, *Cellulosechem.,* **6,** 22 (1926).

[29] Hess and Trogus, *Z. physik. Chem.,* **A145,** 448 (1929); *ibid.,* **B11,** 381 (1931).

[30] Hock and Harris, *J. Research Natl. Bur. Standards,* **24,** 743 (1940); Hock, Ramsay, and Harris, *ibid.,* **26,** 95 (1941).

[31] Private communication from D. B. Anderson; see also Haller, *Melliand Textilber.,* **22,** 153 (1941).

are freed completely of their pectin constituents, the constrictions fail to develop. Moreover, the band or string-like residues give the staining and solubility tests of pectic compounds.[32] From these studies it would appear that the waxes, provided they remained in the fiber after treatment with pectin-removing agents, are not responsible for the constriction phenomenon. However, further studies in this direction will have to be made.

Fig. 3. Sea Island cotton hair in polarized light. A. Herzog.

Fig. 4. Cotton hair swollen in cuprammonium hydroxide solution. Polarized light. A. Herzog.

In this connection results may be mentioned which indicate that an artificial cuticle on a rayon fiber (an originally cuticle-free fiber) may be obtained by superficial esterification with stearic anhydride. Fibers thus treated are water-repellent and on treatment with cuprammonium solution show a swelling phenomenon similar to that observed with the raw cotton fiber. The artificial

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[32] See also Nickerson and Leape, *loc. cit.;* Whistler, Martin, and Harris, *loc. cit.*

cuticle, consisting of esterified cellulose, separates from the fiber and winds itself around it in rings and spirals.[33]

If a comparison is permissible, Schneider's results would indicate that the waxes in the primary wall might play at least a part equal to that of the pectin. Moreover, it is not improbable that, in the natural primary wall, the waxes are in chemical (ester) combination with cellulose as is the stearic acid in the rayon fiber.

It is generally believed that the primary wall may be removed from the cotton fiber by boiling with dilute caustic soda solution; this is illustrated by the process of kier boiling, a normal pretreatment given to cotton or cotton linters in order to remove pectin and waxes and prepare the material for subsequent bleaching. However, if we accept Anderson's explanation of the ballooning phenomenon, we may assume that the primary wall is not actually removed, but merely that its chemical composition is changed and that this change endows it with the elastic properties possessed by the secondary wall. In cuprammonium solution, both walls would swell to the same extent, and ballooning would no longer occur. Similar views have been expressed by Haller [34] with regard to the process of mercerization (see later), during which the cotton fiber is treated with strong caustic soda solution.

Wood fibers also show the phenomenon of ballooning in cuprammonium solution, even after the lignin and other noncellulosic substances have been removed; for example, by the sulfite process, followed by bleaching. However, the more severely the fibers have been treated, the less pronounced is the phenomenon.[35] Possibly, in wood fibers also, the primary wall is maintained but the removal of the noncellulosic substances makes it swell to the same extent as does the secondary wall.

Chemical investigation seems to indicate that the carbohydrate portion of the primary wall of the spruce cellulose fiber consists of about half cellulose and half pentosans and some noncellulosic hexosans.[36] Since wood cellulose fiber contains no waxes, it is likely that in this case other noncellulosic substances are responsible for the ballooning effect—possibly lignin and small amounts of pectin.

It has been observed that no ballooning occurs with cotton fibers after treatment with chlorine dioxide,[37] after steaming at high pressure,[38] and after heating to 150°.[39]

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[33] Schneider, *Faserforschung,* **13,** 121 (1938).

[34] Haller, *Textile Forschung,* **3,** 20 (1921).

[35] Carpenter and Lewis, *Paper Trade J.,* **99,** No. 3, 37 (1934).

[36] Brauns and Lewis, *Paper Trade J.,* **105,** No. 10, 35 (1934); Howells and Lewis, *Paper Trade J.,* **105,** No. 27, 37 (1937); Lewis, *Paper Trade J.,* **106,** No. 16, 36 (1938).

[37] Schlotmann, *Planta,* **19,** 313 (1933).

[38] Haller, in Herzog, "Technologie der Textilfasern," Springer, Berlin (1928), Vol. IV, Part 3.

[39] Schneider, *loc. cit.,* p. 123.

It has also been observed that the primary wall resists the action of certain cellulose-decomposing bacteria,[40] whereas other observations seem to indicate that the primary wall may be removed by bacterial action.[41]

The cell walls, as a result of mechanical or chemical treatment or a combination of both, may be subdivided into elements of various shapes and dimensions which are described in the literature under various terms. Usually they are called fibrillae or fibrils, and we may speak of the cellulose fiber as exhibiting a fibrillar structure. Such a structure is shown in Fig. 5.

As may be seen from the picture, the direction of the fibrils reverses at certain distances. Balls[42] has directed attention to the relationship existing between the fibrillar structure and the spiral twists or convolutions which, in contrast to the wood fiber, are characteristic of the cotton hair. These spiral convolutions are shown in Fig. 3. They occur when the hair, after having ceased growing, dries and collapses. Balls found the reversal points of the convolutions to be coincident with, and determined by, the reversals of the spiral fibrillar structure of the cell wall as shown in Fig. 5.

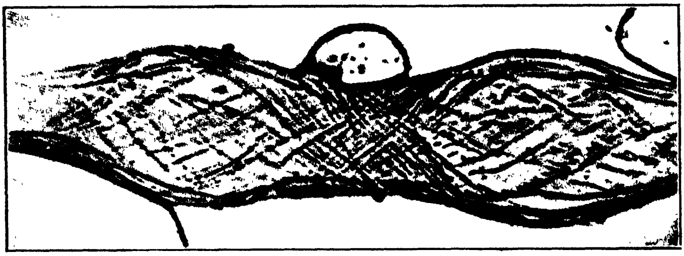

FIG. 5. Cotton hair which has been crushed to show the fibrillar structure of its wall. Balls.

The question whether or not the fiber elements, which may be made microscopically visible by various treatments, are to be regarded as fundamental structural units has frequently been, and still is, the object of considerable controversy. At the present time, there seem to be two chief schools of thought.

The one, led by I. W. Bailey,[43] D. Anderson,[44] and T. Kerr,[43] postu-

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[40] Gulati, *Ind. J. Agr. Soc.*, **6**, 861 (1936).

[41] Hooper, *loc cit.*

[42] Balls, "Studies of Quality in Cotton," Macmillan and Co., London (1928), p. 20; Clegg and Harland, *J. Textile Inst.*, **15**, T14 (1924); Schwarz and Shapiro, *Rayon Textile Monthly*, **12**, 371 (1938).

[43] Bailey and Kerr, *J. Arnold Arboretum*, **16**, 273 (1935); **18**, 261 (1937); Bailey, *Ind. Eng. Chem.*, **30**, 40 (1938).

[44] Anderson, *Ind. Eng. Chem.*, **30**, 48 (1938); Kerr, *Protoplasma*, **27**, 229 (1937).

lates that the fiber elements which may be liberated from the cell wall upon mechanical or chemical treatment are rather heterogeneous fragments, which are shredded or disrupted from an originally continuous and coherent cellulose matrix.

This definition, then, would have to be applied to the various elements described in the literature under manifold terms,[45] i.e., to the fibrillae or fibrils and to the smaller segments described as "dermatosomes" (von Wiesner, 1886),[46] "fusiform bodies" and "spherical units" (Ritter, 1928),[47] cellulose "crystals" (Hess, 1927),[48] or "cellulose particles" (Farr, 1934, and Wergin, 1939).[49]

Obviously the form and size of these fragments are dependent upon (1) the structural pattern of the cellulose matrix and (2) the type and severity of the chemical and mechanical treatments to which the material is subjected. The secondary wall exhibits planes of structural weakness due to differences in density and porosity of the individual layers.[50] These planes occur parallel to the long axis of the fiber and, thus, elongated aggregates and, after chemical treatment, smaller segments may be dissected from the cell wall.[51]

In addition, splits and cracks in the cell wall and submicroscopic, transverse, or oblique planes of cleavage [so-called "slip planes" (von Höhnel, Schwendener [52])], as well as planes of definite angularity, made visible by the enzymatic activity of certain wood-destroying fungi,[53] facilitate the dissection of the fiber as well as of the elongated complexes into shorter segments. It is thus not surprising that the variously termed units are found to be of widely varying dimensions in length and thickness. Fibrils, the larger elements which may be seen under the microscope and may be dissected from the wall even without chemical treatment, may, for example, have a length of 100 μ and even reach 230 μ and more.[54] The data on the diameter or thickness of the fibrils also vary, although not to the same extent, 0.3–0.5

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[45] Lüdtke, *Biochem. Z.*, **233**, 1 (1931).

[46] von Wiesner, "Die Rohstoffe des Pflanzenreichs," 4th ed., Vol. I, p. 396.

[47] Ritter and Chidester, *Paper Trade J.*, **87**, No. 17, 131 (1928); Ritter and Seborg, *Ind. Eng. Chem.*, **22**, 1329 (1930).

[48] Hess and Schultze, *Ann.*, **456**, 55 (1927).

[49] Farr and Eckerson, *Contrib. Boyce Thompson Inst.*, **6**, 189 (1934); Wergin, *Protoplasma*, **32**, 116 (1939).

[50] Bailey, *loc. cit.*

[51] See the pictures in Carpenter and Lewis, *loc. cit.*

[52] Quoted by Bailey and Kerr, *J. Arnold Arboretum*, **16**, 291 (1935).

[53] Bailey and Vestal, *J. Arnold Arboretum*, **18**, 196 (1937).

[54] Ritter, *Paper Ind.*, **16**, 178 (1934).

μ[55] and 0.4 μ[56] being reported. By microdissection with the aid of the Zeiss-Peterfi micromanipulator, Seifriz and Hock[57] separated wood pulp fibers into fibrils, 1.4 μ thick. These fibrils, however, are bundles of finer threads, estimated to be of the order of 0.1–0.3 μ in diameter. It is significant that by this technique wood pulp which has been beaten may be separated into fibrils much more easily than the unbeaten material.

The smaller segments into which the finer fibrils may be subdivided by mechanical or chemical treatment likewise show considerable variations. Thus, von Wiesner's dermatosomes, obtained by treatment of fibers with dilute hydrochloric acid at 50–60° have dimensions of 0.4 by 0.4 by 0.5 μ.[58] Farr's ellipsoidal particles, also obtained on chemical treatment from the cotton fiber, show dimensions of 1.0 by 1.1 by 1.5 μ. Wergin's particles, obtained by subjecting the fiber to swelling in alkali and observing the result microscopically under illumination with ultraviolet light, measure only 0.25 by 0.2 by 0.2 μ.

Lüdtke[59] has claimed that the fibrils are subdivided by regularly spaced, transverse plates (*Querelemente*) consisting of very thin membranes of noncellulosic material. The segments are claimed to measure 0.3–0.5 μ in length. The observation of transverse elements gave rise to the postulate that a special reticulate membrane system (*Hautsystem*) traverses the whole fiber.[60] However, such claims seem to lack foundation.[61]

The other school is represented particularly by Farr and co-operators.[62] These investigators claimed that the cellulose particles which may be obtained from the cell wall under chemical treatments of various kinds are not just incidental fragments. Rather are they consid-

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[55] Herzog and Jancke, *Papier-Fabr.*, **23**, 121 (1925).

[56] I. W. Bailey and Kerr, *J. Arnold Arboretum*, **16**, 290 (1935); see also A. I. Bailey and Brown, *Ind. Eng. Chem.*, **32**, 57 (1940).

[57] Seifriz and Hock, *Paper Trade J.*, **102**, No. 19, 36 (1936).

[58] Bailey and Kerr, *J. Arnold Arboretum*, **16**, 290 (1935).

[59] Lüdtke, *Ann.*, **466**, 27 (1928); *Cellulosechem.*, **13**, 169, 191 (1932); **14**, 1 (1933); see also Wergin, *Protoplasma*, **32**, 116 (1939).

[60] Hess, *Ann.*, **450**, 59 (1926); **466**, 73 (1928); Hess and Sakurada, *Ber.*, **64**, 408 (1931); Sakurada and Lee, *Kolloid-Z.*, **61**, 50 (1932); Sakurada, *ibid.*, **63**, 311 (1933); **66**, 62 (1934); **67**, 1045 (1934); **68**, 300 (1934). See also Lüdtke, *Papier-Fabr.*, **36**, 214 (1938).

[61] Frey-Wyssling, *Protoplasma*, **25**, 261 (1936); *Papier-Fabr.*, **36**, 214 (1938); I. W. Bailey, *loc. cit.;* see also Staudinger, *Ber.*, **68**, 1234 (1935).

[62] Farr and Eckerson, *loc. cit.;* Farr, *J. Phys. Chem.*, **42**, 1113 (1938); Farr and Sisson, *Contrib. Boyce Thompson Inst.*, **6**, 315 (1934); **10**, 127 (1939); Barrows, *ibid.*, **11**, 61 (1940); Farr, *ibid.*, **12**, 18 (1941); see also *Rayon Textile Monthly*, **22**, 519 (1941).

ered as being of invariable dimensions (see above) and thus as being fundamental structural units of the fiber. Farr believes her hypothesis to be largely supported by her observation that, while the fiber develops, the cell wall is being built up of cellulose particles of the same dimensions as those which may be liberated from the mature cell wall. These particles are seen to be present in the interior of the young (still undeveloped) cotton fiber, scattered throughout the viscous protoplasm. During the cell wall development, these particles aggregate to bead-like rows, which represent the fibrils, which unite to form the layers of the cell membrane.

Farr's hypothesis of the formation of the cell wall from uniform particles has met with objections. Thus, Preston[63] has criticized Farr's optical arrangement and has stated that such images as Farr's may be produced synthetically by a defective optical arrangement. Anderson and Kerr[64] have expressed the opinion that the particles observed in the protoplasm consist not of cellulose but of starch.

Farr believes, further, to have proved that in the mature cotton fiber the particles are embedded in a colloidal material. The nature of this colloidal "cementing" material is unknown. At first it was regarded as essentially pectic in nature, but more detailed analysis made it seem improbable that the material contained any pectin.

The cementing material concept is derived from the observation that the mature raw cotton fiber, upon treatment with pectin-removing agents (such as dilute aqueous ammonium oxalate solution) or with dilute or strong hydrochloric acid, was found to separate into cellulose particles and an amorphous colloidal substance.

However, the effect of these two very different agents obviously cannot be the same. There is no doubt that, under the action of the hydrochloric acid for many hours, the cellulose fiber suffers hydrolysis, i.e., conversion into hydrocellulose, consisting of small fiber fragments. Indeed, the molecular weight of the particles, deduced from ultracentrifugal data, was found to be only 40,000,[65] which is less than one-twelfth that usually found with the ultracentrifugal method for raw cotton (which Farr used for the isolation of the particles).

It appears improbable, then, that treatment with such a neutral agent as ammonium oxalate should lead to the same result, unless the assumption is made that, under the conditions employed, oxidizing and hydrolyzing effects result. In fact, no disintegration of the cotton fiber on treatment with ammonium oxalate solution has been observed by other investigators.[66] Obviously, this agent re-

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[63] Preston in "Annual Report on Progress of Applied Chemistry," **23**, 198 (1938); Barnes and Burton, *Ind. Eng. Chem.*, **35**, 120 (1943).

[64] Anderson and Kerr, *Ind. Eng. Chem.*, **30**, 54 (1938).

[65] Kraemer, *Ind. Eng. Chem.*, **30**, 1201 (1938).

[66] Nickerson and Leape, *Ind. Eng. Chem.*, **33**, 83 (1941); Heuser and Green, *ibid.*, **33**, 868 (1941); see also Leger and Larose, *Can. J. Research*, **B19**, 61 (1941).

moves only the pectin present in the raw fiber, and a pectin-free fiber, subjected to the treatment with ammonium oxalate solution, yields no cementing substance and remains undisintegrated. Hence, the pectin does not seem to contribute to the continuity of the structure of the fiber, and no other material is removed which would be essential in maintaining structural continuity.

Apart from the fact that the experimental evidence does not favor the cementing substance concept, it would appear to be unnecessary to resort to a cementing material as an essential structural constituent of the cellulose fiber when the botanists' view on the growth and microstructure of the cell wall is taken into consideration.

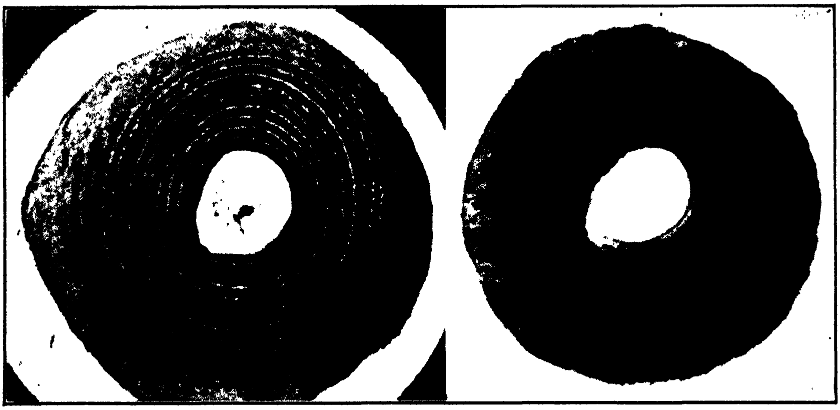

FIG. 6. Cross sections of cotton hairs with and without growth rings. Anderson and Kerr.

On the basis of the early observations by Balls [67] and the more recent confirmation of Balls's results by Anderson and Kerr and others,[68] the cell wall is viewed as being formed by the deposition of coherent cellulose layers or lamellae, i.e., not of single particles. This process is influenced by conditions of temperature and light.

Balls has directed attention to the fact that the depositing process is commonly discontinuous; i.e., the growth of the cotton plant is arrested during the night and continues during the day. As a result, the secondary wall appears to be built up of concentric shells or lamellae. By subjecting cross sections of the cotton hair to a swelling procedure, Balls was able to make the deposited layers visible as "growth rings." Anderson and Kerr confirmed Balls's results. In fact, no growth rings

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[67] Balls, "Quality in Cotton," p. 18.

[68] Anderson and Moore, *Am. J. Bot.*, **24**, 503 (1937); Anderson and Kerr, *Ind. Eng. Chem.*, **30**, 48 (1938).

were observed when the cotton plant was grown under continuous illumination and at uniform temperature (Fig. 6).[68]

In view of such observations it would be surprising if the growth rings were only artifacts, due merely to mechanical pressure exerted upon the thin cross sections under the coverglass as has been claimed by Farr and by Barrows.[69]

Likewise, in the wood of trees, the thickening of the secondary wall seems to occur by way of discontinuous layering, because transverse sections through the wood tissue reveal a similar picture (Fig. 7).[70] Besides concentric lamellation, one also observes radial orientation of the lamella. An example is given in Fig. 8.[71] A combination of both concentric and radial lamellation is shown in Fig. 9.[71]

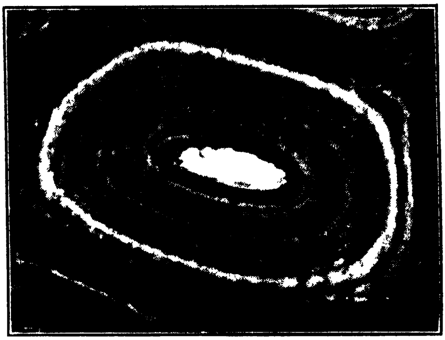

FIG. 7. Transverse section through wood fiber showing concentric layering of cellulose (light) and lignin (dark). I. W. Bailey.

In the fibers of both soft woods (pine, spruce, fir, hemlock, larch, cedar, etc.) and hard woods (poplar, birch, maple, elm, oak, etc.) a wide range of variability of structural patterns, i.e., all transitions from typically concentric to radiocentric and dominantly radial patterns, was observed.[72]

As a result, the cellulose matrix of both the primary and the secondary wall, in single hairs as well as in fibrous tissues, appears to be composed of aggregations of threads or fibrils held together by branching and lateral interconnections. According to Bailey, such an anastomosing and coalescing system seems to be sufficiently stable in itself and would not require a foreign material of cementing properties as a means of holding the fibrils together.

Another argument against Farr's concept, namely, that the smaller segments which may be liberated from the fibrils are fundamental structural units of the cell wall, is derived from the following consideration. A comparison of the dimensions of the various smaller units

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[69] Farr, *Contrib. Boyce Thompson Inst.*, **10,** 103 (1938); Barrows, *ibid.*, **11,** 161 (1940).

[70] Bailey, *Ind. Eng. Chem.*, **30,** 43 (1938).

[71] Bailey and Kerr, *J. Arnold Arboretum,* **16,** 273 (1935).

[72] Bailey, *loc. cit.*, p. 45.

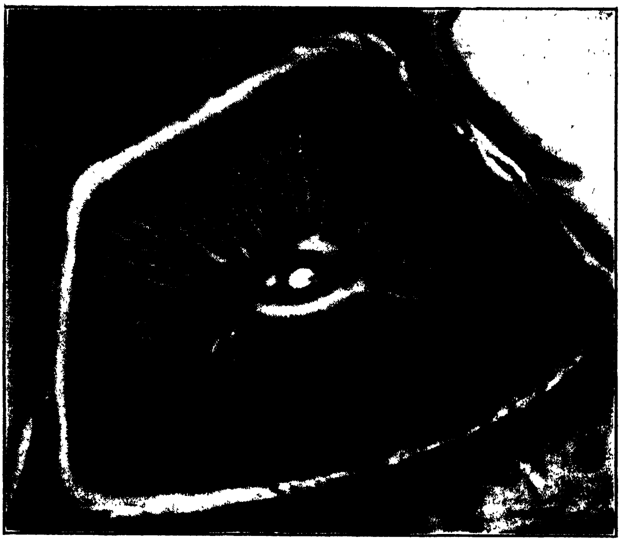

Fig. 8. Unswollen transverse section of radially striated wood fiber. I. W. Bailey.

Fig. 9. Transverse section through wood fiber after treatment with 72 per cent sulfuric acid and staining, showing concentric and radial lamination. (Dark zones heavily lignified, light zones less intensely lignified.) I. W. Bailey.

with the thickness of a lamella shows that the dimensions of the former are all much larger than those of the latter. Although the thickness of the individual lamella also varies, Bailey[73] finds it to be, on an average, only 0.1 μ or less. This observation would indicate that the plant, in building up the cell wall, uses much smaller entities than the units which Farr and others claim compose the fibrils, entities which are of submicroscopic dimensions. This is illustrated in Fig. 10, in which the circle at (*a*) indicates the size of an ellipsoidal particle as postulated by Farr. It is seen that such a particle, assumed to have a diameter of 1.0 μ, would cover more than two lamellae.

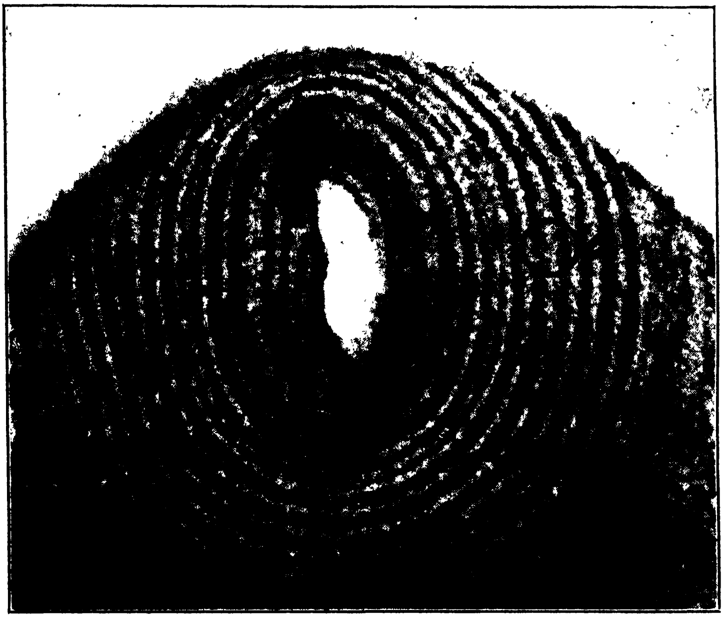

FIG. 10. Transverse section through cotton hair after swelling in cuprammonium hydroxide solution and staining, showing alternating lamellae. Bailey and Kerr.

Likewise, it is difficult to conceive, as Preston[74] puts it, how particles having dimensions of 1.0 by 1.0 by 1.5 μ can exist in fibrils with lateral dimensions of only 0.4 μ or less. Finally, the results of studies with the electron microscope have been interpreted to show that Farr's cellulose particles, obtained by the action of hydrochloric acid on the

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[73] Bailey and Kerr, *loc. cit.*, p. 290.

[74] Preston in "Annual Reports on Progress of Applied Chemistry," **23**, 198 (1938).

cotton fiber, cannot be regarded as preformed fundamental units of the fiber structure.[75]

Thus, there does not seem to be sufficient evidence, either in untreated or in carefully swollen fibers, of discrete entities of cellulose, such as ellipsoidal particles or the like, which may be liberated simply by dissolving a (hypothetical) noncellulosic constituent. Furthermore, in view of the extremely complex and varying structure of the cell membrane, Bailey considers it misleading and quite fruitless to attempt to homologize all types of fibers in a single structural model.

It remains to be seen whether Farr's concept of cell wall formation from cellulose particles can be confirmed by other investigators. But even if this concept were accepted eventually, nothing seems to be gained by insisting on the belief that the original particles have retained their shape and size in the *mature* cell wall. No serious objection should arise against the postulate that the particles grow into a continuous anastomosing structure and thus lose their original individuality. It would seem that portions of such a structure can be separated from the cell wall only by mechanical or chemical disrupture resulting in fragments which have no connection with the original units except that both consist of cellulose.

SUBMICROSCOPIC ARRANGEMENT OF FIBER ELEMENTS AS REVEALED BY X-RAY ANALYSIS

In advancing from the visible to the invisible region of fiber structure, we find that, as early as 1858, von Nägeli [76] expressed the belief that the fiber elements which are visible under the microscope are further subdivided into smaller, now microscopically invisible, particles which he regarded as crystals and for which he coined the term micellae (diminutive from the Latin mica, meaning "crumb"). von Nägeli's ideas were forgotten for a long time until Ambronn's findings [77] (namely, that the cellulose fiber shows the phenomenon of double refraction, the latter being an essential characteristic of crystalline substances) seemed to lend strong support to von Nägeli's concept.

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[75] Ruska and Kretschmer, *Kolloid-Z.*, **93**, 163 (1940).

[76] Nägeli, "Die Stärkekörner, Pflanzenphysiologische Untersuchungen," No. 2 (1858); Nägeli and Schwendener, "Das Mikroskop," Engelmann, Leipzig (1877), 2nd ed., p. 422. See also Frey, "Die Micellar-Theorie von Carl Nägeli," Akad. Verlags-Ges., Leipzig (1928). For predecessors of von Nägeli, see Strachan's article on the early history of fiber structure, *Paper-Maker*, **91**, TS33 (1936).

[77] Ambronn, *Ber. Verhandl. sächs. Akad. Wiss. Leipzig*, **63**, 249 (1911); Möhring in "Ambronn-Festschrift," *Kolloidchem. Beihefte*, **23**, 162 (1926).

However, Ambronn[78] met with relatively little success in his endeavors to convince his contemporaries of the feasibility of von Nägeli's ideas.

It was one of the rare but gratifying coincidences that a short time after Ambronn's findings, a new tool became available to science in the form of Röntgen rays or x-rays, a tool which soon proved to be eminently suitable for elucidating the fine structure of high molecular substances and textile fibers. The results of x-ray analysis furnish definite proof of the crystalline nature of cellulose and, hence, may be regarded as an excellent confirmation of Ambronn's findings and, consequently, of von Nägeli's concept.

It seems to be fairly safe to state that the development which resulted in the establishment of the crystalline structure of cellulose and other textile fibers by x-ray analysis began with von Laue's[79] fundamental discovery that a crystal behaves as a three-dimensional diffraction grating to x-radiation, a discovery which indicated regularity of interatomic distances and, hence, of internal structure. von Laue's discovery was followed by the application of x-radiation to cellulose and starch by Debye and Scherrer[80] and by Hull.[81]

The Debye-Scherrer method permits an investigation of cellulose fibers pressed into a small rod and surrounded by a photographic film on which the effect of x-radiation is reflected. The diagram of a ramie fiber thus obtained by Scherrer revealed a regularity of internal structure similar to that obtained with macrocrystals. The geometric spacing of the smallest crystals (crystallites or micelles) may thus be established.

Systematic x-ray studies on textile fibers and particularly on cellulose began with the work of R. O. Herzog and co-workers, Jancke, Polanyi, Weissenberg, and many others. In 1920, Herzog and Jancke,[82] using a technique which differed in various ways from that used before, published the first monochromatic cellulose fiber diagram. The rapid development which followed and which is particularly characterized

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[78] Steinbrinck in "Ambronn-Festschrift," p. 6.

[79] Friedrich, Knipping, and von Laue, *Sitzungsber. Bayer. Akad. Wiss.*, **5**, 303 (1912).

[80] Debye and Scherrer, *Physik. Z.*, **17**, 277 (1916); Scherrer, *Göttinger Nachrichten*, p. 98 (1918).

[81] Hull, *Phys. Rev.*, **10**, 661 (1917).

[82] Herzog and Jancke, *Ber.*, **63**, 2162 (1920). The first x-ray fiber diagrams of hemp and of natural silk were published by Nashikawa and Ono in 1913 (*Phys.-Math. Soc. Tokyo*, Sept. 1913) and the diffraction effect was regarded as indicative of small crystals arranged parallel to the fiber axis. This publication remained hidden for a long time.

by the contributions made by Polanyi[83] and by Weissenberg[84] furnished the fundamental data according to which the cellulose fiber may be regarded as representing a crystal lattice in which rows of crystals are arranged essentially in a position parallel to the fiber axis.

At the same time, the first attempt was made by Polanyi[83] to determine the dimensions of the "unit or basic cell," i.e., the smallest unit which still possesses the geometric characteristics of the whole crystal lattice. The dimensions stated by Polanyi underwent only small changes as the result of later investigations.[85] It appears that the lattice on which the cellulose crystal is built may be ascribed to the monoclinic system with dimensions of the basic cell expressed in Ångström units (1 Å = 10^{-8} cm. = 0.1 mμ) as follows[86]:

a	(horizontal)	8.35 Å
b	(vertical, representing the length of the basic cell, parallel to the fiber axis)	10.3 Å
c	(forming the angle with a)	7.95 Å
$\beta = 84°$		

These dimensions being known, the volume of the unit cell may be calculated. From the volume and the mass of the anhydroglucose formula unit and the density of cellulose, it was found that four cellobiose residues form the edges of the unit cell and one passes through the center. However, it must be kept in mind that the four cellobiose residues are shared by neighboring unit cells.

Making use of the work of W. H. Bragg and his numerous collaborators on the radii of atoms and the distances between atoms of homopolar compounds, Sponsler and Dore[87] devised a picture of the possible structural arrangement of the glucose units in the basic cell.

It is most interesting to note that a decision with regard to the glucose structure to be selected for the arrangement within the unit cell could be made from three-dimensional models carefully constructed to a scale based upon the atomic radii of carbon and oxygen and the distances C—C and C—O. It was found that the amylene oxide ring structure which, as a result of chemical evidence, had been suggested by the Haworth school, fitted best into Sponsler's lattice spacing as

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[83] Polanyi, *Naturwissenschaften*, **9**, 288 (1921); *Z. Physik.*, **7**, 149 (1921).

[84] Polanyi and Weissenberg, *Z. Physik.*, **9**, 123 (1922).

[85] Mark, "Physik und Chemie der Cellulose," p. 138.

[86] Meyer and Misch, *Helv. Chim. Acta*, **20**, 232 (1937); Gross and Clark, *Z. Krist.*, **99**, 357 (1938).

[87] Sponsler and Dore, "Colloid Symposium Monographs," (1926), [IV], p. 174; see also Sponsler, *Am. J. Botany*, **9**, 471 (1922).

derived from x-ray data. For reasons of symmetry, the *beta*-structure was given preference over the *alpha*-structure.

Regarding the mode of linking between neighboring glucose units of the chain, Sponsler and Dore erroneously chose alternating glucosidic and ether linkages instead of glucosidic linkages only. However, this has practically no bearing as far as their concept of the arrangement of the glucose units within the basic cell is concerned. The most essential result was that the investigators recognized the recurrency period (*b*) of 10.25 Å along the fiber axis, as evidenced by x-ray investigations, to be a figure dependent upon the chemical structure of the cellulose. The diameter of one glucose unit, using Haworth's pyranose ring structure, was calculated to be 5.13 Å; that is, just half of the recurrency period. This means that in the unit cell, within the spacing of 10.25 Å on each chain, there occur two glucose units or one cellobiose unit (Fig. 11). This finding suggested that the constituent units are arranged in continuous chains which run parallel to the fiber axis through the unit cell. The position of the chains with respect to each other, stabilized by secondary valence forces, is shown in Fig. 12.

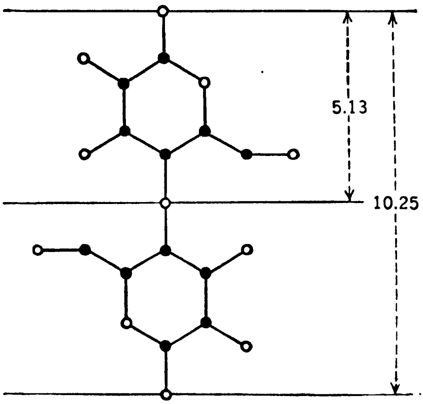

FIG. 11. Cellobiose unit. From Sponsler and Dore in "Colloid Symposium Monograph IV," The Chemical Catalog Co., 1926.

Sponsler and Dore's work gave great impetus to the studies in the years which followed, notably to those of K. H. Meyer[88] and Meyer and Mark.[89] Their work was facilitated by the accumulation of chemical evidence on questions of molecular structure, particularly by the establishment of the structure of cellobiose by Haworth and co-workers and by the abundance of x-ray data gathered from the studies of numerous organic compounds.

Meyer and Mark, following Sponsler and Dore's procedure, constructed three-dimensional models of the constituent units from balls

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[88] Meyer, *Z. angew. Chem.*, **41**, 935 (1928).

[89] Meyer and Mark, *Ber.*, **61**, 593 (1928); Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akad. Verlags-Ges., Leipzig (1930), pp. 93, 113.

having multiples of the atomic radii and distances that had been established for other compounds. They also gave consideration to the tendency of the carbon atom to arrange neighboring carbon atoms tetrahedrally around itself.

In their attempts to accommodate the glucose units in a basic cell, Meyer and Mark chose the dimensions as established in 1921 by Polanyi and made use of the β-form of Haworth's cellobiose model as represented in Fig. 13. For the construction of this model, 1.54 Å was chosen as the distance between carbon and oxygen atoms.

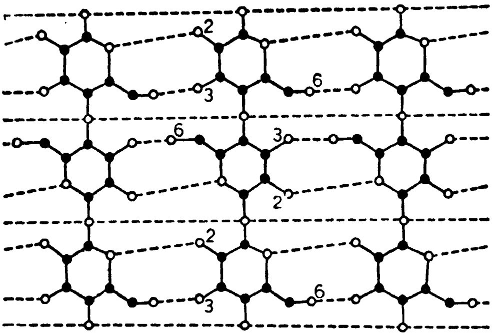

FIG. 12. Position of anhydroglucose chains in cellulose. (From Sponsler and Dore in "Colloid Symposium Monograph IV," The Chemical Catalog Co., 1926.

By turning the lower part of the model through 180° and shifting it upward it will cover exactly the upper part of the model. Thus, the cellobiose configuration reveals the principle of a diagonal screw arrangement. X-ray analysis has shown that the same principle prevails parallel to the fiber axis and that the screw component equals half the recurrency pattern, that is, 5.13 Å. Since the length of the cellobiose model is 10.25 Å, it is evident that this length is almost identical with that of the recurrency pattern. Combining the various pieces of evidence, Meyer and Mark concluded that, in the basic cell, the cellobiose residues lie parallel to the *b* axis. Meyer and Mark's arrangement of the basic cell, recently modified in accordance with Meyer and Misch's[90] suggestion, namely, with the glucose residues pointing alternately in opposite directions, is shown in Fig. 14.[91]

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[90] Meyer and Misch, *Helv. Chim. Acta,* **20,** 232 (1937).

[91] W. H. Bragg [*Nature,* **125,** 634 (1930)] pointed out that Meyer and Mark's cell and that of Sponsler and Dore are mathematically identical, the side of one cell being the diagonal of the other, and *vice versa.*

Recently Sauter has proposed a unit cell for cellulose which deviates materially in some dimensions from that represented in Fig. 14. However, the controversy which arose between Meyer and Mark and Sauter seems to be closed by the results of investigations which Gross and Clark[92] undertook with the object of arriving at a definite decision. These authors showed that the x-ray patterns which they obtained from very different types of cellulose were all consistent with the Meyer and Mark unit cell.

An approximate idea of the size and form of the micelles or crystallites has been derived from the breadth of the hyperbolas (layer lines) of the diagram. Accordingly, the micelle of the ramie fiber is calculated to be a rhombus which measures at least 600 Å along the fiber axis and about 50 by 60 Å across this direction.[93] One micelle would thus accommodate 100–170 individual chain molecules.

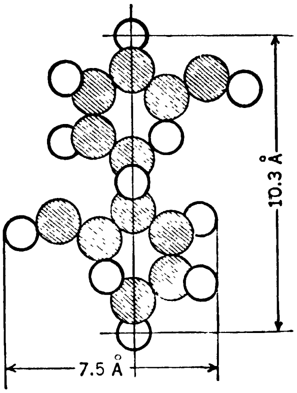

FIG. 13. Cellobiose model. The shaded circles indicate the carbon atoms; oxygen atoms are represented by the other circles; hydrogen atoms are omitted. Haworth. From Meyer and Mark.

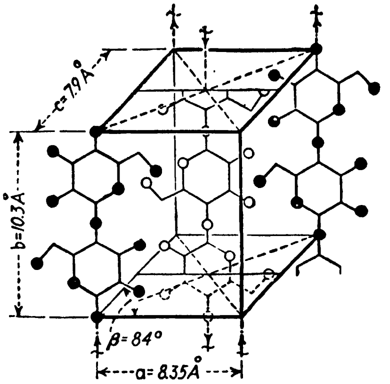

FIG. 14. The unit cell of cellulose. Meyer and Misch. From Clark, "Applied X-Rays," McGraw-Hill Book Co., New York, 1940, 3rd ed., p. 607. For the sake of clarity the chains forming the second front edge and the fourth back edge of the crystal have been omitted.

A possible arrangement of the micelles in the fiber according to Seifriz[94] is shown in Fig. 15. Here (*a*) indicates primary valences

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[92] Gross and Clark, *Z. Krist.*, **A99**, 357 (1938); *Textile Research*, **9**, 7 (1938); see also Kiessig, *Z. physik. Chem.* **B43**, 79 (1939).

[93] Herzog, *J. Phys. Chem.*, **30**, 457 (1926); Hengstenberg, *Z. Krist.*, **69**, 271 (1928); Clark, *Ind. Eng. Chem.*, **22**, 474 (1930).

[94] Seifriz, *Am. Naturalist*, **63**, 410 (1929); "Protoplasm," McGraw-Hill Book Co., New York (1936), p. 252; see also Meyer and Mark, *Kolloid-Z.*, **53**, 10 (1930); Hawley and Wise, "Chemistry of Wood," p. 26.

between glucose residues, (*b*) secondary valence forces holding the chains in bundles, and (*c*) tertiary or micellar forces between the micelles. This figure bears a certain similarity to the arrangement published by von Nägeli in 1877 [95] (Fig. 16).

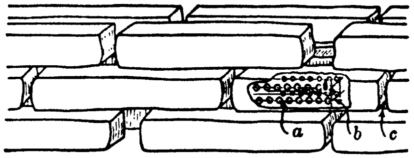

Fig. 15. Arrangement of micelles. Seifriz; Meyer and Mark.

At the present time the brick-like arrangement of the fiber structure is undergoing some significant changes leading to a less rigid and more flexible arrangement. These changes are essentially the result of the two following considerations. (1) X-ray analysis shows a considerable portion of the fibrous system not to be crystalline.[96] (2) Although it had been expressly stated by Hengstenberg and Mark [96] that the length of the chain molecules as calculated from x-ray data amounts to *at least* 600 Å, viscosity determinations according to Staudinger and co-workers [97] indicate that cellulose contains chains which are considerably longer (10^4 Å and longer) than the minimum value of 600 Å would suggest. Moreover, the length measurements of very long cellulose chains by means of x-ray analysis have been criticized as being rather inexact.[98]

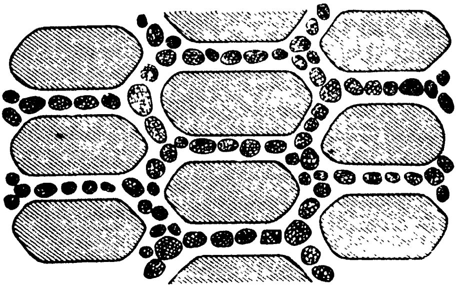

Fig. 16. von Nägeli's concept of the micelles. Nägeli and Schwendener.

Taking these two points into consideration a substantial part of the fibrous system must be ascribed to amorphous portions, and the chain

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[95] Nägeli and Schwendener, *loc. cit.*, p. 425.

[96] Herzog, *J. Phys. Chem.*, **30**, 457 (1926); Hengstenberg and Mark, *Z. Krist.*, **69**, 271 (1928); Mark, "Physik und Chemie der Cellulose," p. 156.

[97] Staudinger and Signer, *Z. Krist.*, **70**, 193 (1929); Staudinger and Sauter, *Melliand Textilber.*, **18**, 849 (1937).

[98] Frey-Wyssling, *Kolloid-Z.*, **86**, 148 (1938).

molecules must be given an indefinite length. With such changes, the micelles lose much of their previous individuality. The fiber may thus be regarded as a two-phase system, consisting of the same chemical material which, however, is arranged in two different types of physical aggregation, with a mesomorphous portion as the region of transition. Whereas in the crystalline portions or regions the chain molecules are arranged strictly parallel, they are less parallel in the mesomorphous and still less so in the amorphous regions. If the chains are long enough they extend through the whole system; i.e., they pass through crystalline, mesomorphous, and amorphous regions. On the other hand, there is obviously no reason to doubt that the crystalline portions possess a certain thickness which, as has been seen, has been calculated from x-ray data to measure 50–60 Å. Thus, the chains or parts thereof which are located within the crystalline regions constitute chain bundles of a definite thickness. For the crystalline regions the term micelle may be retained. An arrangement based upon the above-mentioned considerations is shown in Fig. 17.[99] Frey-Wyssling's suggestion is shown in Fig. 18.[100] To account for the penetrability of the fibrous system for liquids, dyestuffs, etc., the chain bundles are thought to be separated by intermicellar spaces of widely varying width and to communicate with each other. As pictured in Fig. 17, the ends of the chains of varying length may lie within the crystalline regions but they may also project from the crystalline into the amorphous region and thus appear as "fringes" of the crystalline regions (mi-

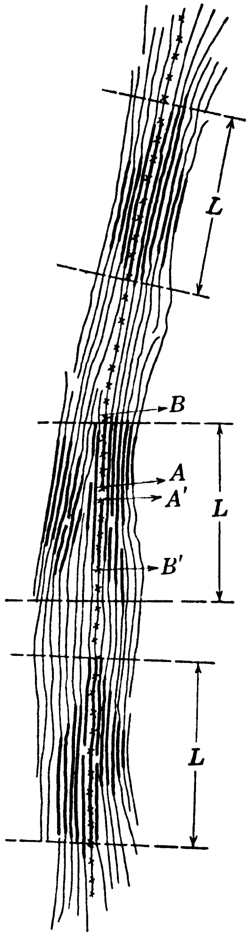

FIG. 17. Arrangement of chain molecules in cellulose. Heavy lines constitute the crystalline regions. The chains pass through crystalline and amorphous regions. Mark.

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[99] Mark, *J. Phys. Chem.*, **44**, 779 (1940); see also Kratky and Mark, *Z. phys. Chem.*, **B36**, 129 (1937).

[100] Frey-Wyssling, *Kolloid-Z.*, **85**, 148 (1938); *Papier-Fabr.*, **36**, 213 (1938); see also Frey-Wyssling's earlier suggestion, *Protoplasma*, **25**, 261 (1936).

celles). This comparison was first suggested in connection with the structure of gelatin.[101]

Another arrangement is shown in Fig. 19.[102] Here, the crystalline portions appear as rigid rods, whereas the amorphous portions may be regarded as flexible joints between the former. Both portions constitute a reticulate system, i.e., a network of chain molecules. Such a network may be likened to a textile fabric "cut on the bias," i.e., cut

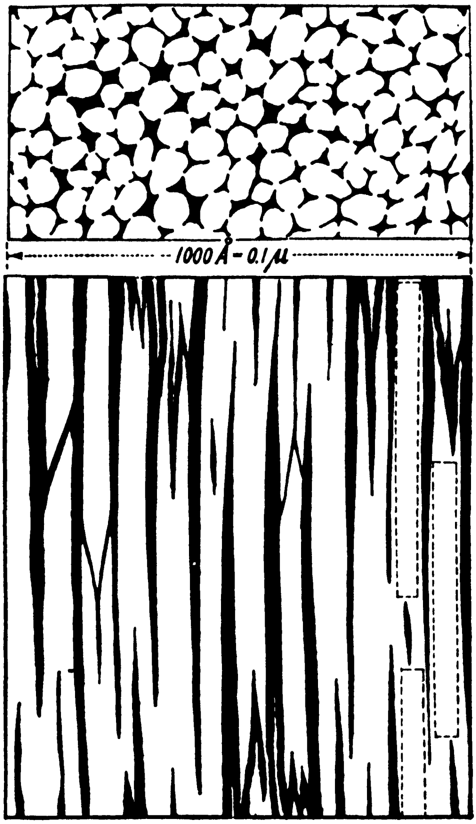

FIG. 18. Micellar structure. Frey-Wyssling. The upper part is a transverse section, the lower a longitudinal view. (The longitudinal view is greatly reduced in size, the crystalline regions being actually much more than ten times as long as wide.) The dotted lines signify the crystalline regions through which the long-chain molecules pass and the black lines signify the intermicellar spaces.

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[101] Gerngross, Hermann, and Abitz, *Z. physik. Chem.*, **B10**, 371 (1930); *Kolloid-Z.*, **60**, 276 (1932). Regarding cellulose, see Thiessen, *Angew. Chem.*, **51**, 170 (1938); Staudinger and Signer, *ibid.*, **42**, 71 (1929).

[102] Mark, *loc. cit.*, p. 784.

with the edges at a certain angle with the direction of the threads. If such a fabric is extended in one direction, it is contracted in the other. The action may also be likened to that of the well-known "lazy tongue" or "Nüremberg scissors," in which an extension of the device involves the rotation of the members above the points of linkage. The points of linkage correspond to the points of contact which are produced when the chain molecules cross each other.[103]

The assumption that such an arrangement is interposed with a system of holospaces (intermicellar spaces) seems to be well supported by the result of a technique which allows crystals of gold, silver, or silver amalgam to grow in the interstices.[104] Subsequent observation under the ultramicroscope and under x-radiation and evaluation of the data thus obtained have furnished an idea of the order of magnitude of the width of the intermicellar spaces.[105] The results may be interpreted to reveal a system of holospaces consisting of canals of largely varying width, ranging from 1000 to 100 or 50 Å, and probably even as little as 10 Å. Since all holospaces may be assumed to be in mutual communication, they would represent a heterocapillary system. Frey-Wyssling[106] has illustrated this concept as shown in Fig. 20. The chain bundles ("microfibrils," micelles) are shown to be fissured by small cracks (order of magnitude 10 Å) and to be surrounded by wider holospaces (order of magnitude 100 Å).

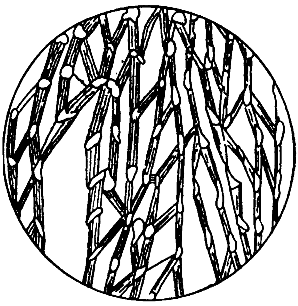

FIG. 19. Arrangement of chain molecules in cellulose. The crystalline regions are represented by lines and the amorphous regions by deformed circles. Kratky.

Further support of the existence of submicroscopic units surrounded by holospaces is derived from observations with the electron microscope of fine cross sections through cotton fibers.[107] A great portion

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[103] Ostwald, *Kolloid-Z.*, **69**, 340 (1934); see also Valkó, "Kolloidchemische Grundlagen der Textilveredelung," p. 204.

[104] Berkmann, Böhm, and Zocher, *Z. physik. Chem.*, **A124**, 83 (1926).

[105] Frey-Wyssling, *Protoplasma*, **26**, 261 (1936); **27**, 372 (1937); Kratky and Schlossberger, *Z. physik. Chem.*, **B39**, 145 (1938); Kratky, *Angew. Chem.*, **53**, 153, 158 (1940).

[106] Frey-Wyssling, *Protoplasma*, **27**, 372 (1937); *Kolloid-Z.*, **85**, 152 (1938).

[107] Ruska, *Kolloid-Z.*, **92**, 276 (1940); Ruska and Kretschmer, *ibid.*, **93**, 163 (1940); see also Kuhn, *Melliand Textilber.*, **22**, 249 (1941); Barnes and Burton, *Am. Dyestuff Reporter*, **31**, P254 (1942); Wergin, *Kolloid-Z.*, **98**, 131 (1942); Wallner and Schiebold, *ibid.*, **97**, 36 (1941); Marquette, *Rayon Textile Monthly*, **23**, 518 (1942).

of the capillary system and the micelles fall within the resolving power of this device (3–4 mμ). By special arrangement it was possible to detect transmissible regions, at least in places where the capillaries were relatively large in proportion to the thickness of the cross section. A cross section of a single cotton hair shows a system of coarse holospaces (200–800 mμ wide) in the center. In addition, a number of separating walls is seen in the center which may be attributed to a system of fine tubes (Fig. 21).

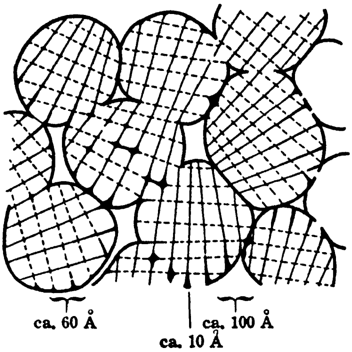

FIG. 20. Cross section showing bundles of chain molecules and holospaces. Frey-Wyssling.

The modern concept of the submicroscopic structure of the cellulose fiber would more satisfactorily account for its physical properties than the previous brick-like arrangement of the individual micelles. Obviously, the physical strength of a fiber (both natural and artificial or synthetic) is governed by the ratio of the crystalline to the amorphous portion. The tensile strength of a fiber may be improved by treatments (for example, the stretching of a swollen rayon fiber) which increase the crystalline portion. It would appear fairly safe to state that "crystallization" which manifests itself in the interference lines of the x-ray diffraction picture is preceded by orientation of the chains and chain bundles. When, through stretching, the optimum degree of orientation has been reached, crystalline structure results.

In natural fibers, also, the physical strength properties vary with the degree of orientation.[108] In most of these fibers the micelles appear to be more or less oriented parallel to the fiber axis. In cotton they are turned spirally around the axis.[109] The highest orientation is shown by the flax fiber.[110]

The micellar system as depicted above would explain also the ability of the fiber to become elongated on stretching and to return to its original position, unless the stretching is overdone. It would also account for the fact that the

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[108] Astbury, "Fundamentals of Fibre Structure," Oxford University Press, London (1933).

[109] Farr and Clark, *Contrib. Boyce Thompson Inst.*, **4**, 273 (1932); Steinberger, *Textile Research*, **4**, 495, 531 (1934).

[110] Morey, *ibid.*, **4**, 491 (1934). As to orientation in wood fibers, see Caldwell and Lark-Horovitz, *Bull. Am. Phys. Soc.*, **12**, 6 (1937); *Physical Rev.*, [2] **51**, 998 (1937); Schulze, Theden, and Vaupel, *Holz*, **1**, 75 (1937); Nagasawa, *ibid.*, **1**, 107 (1937); Krüger, *Zellstoff und Papier*, **17**, 9 (1937).

physical strength of the fiber is very great in the longitudinal but much smaller in the lateral direction, as well as for the ability of the fiber to swell very little in the direction of the fiber axis but considerably in the rectangular direction (anisotropy of swelling).

Generally speaking, it would appear that the crystalline parts of the fiber are responsible mainly for its tenacity, its high modulus of elasticity,[111] and its resistance toward bending, whereas the amorphous portions cause softness and long-range elasticity, and are concerned with swelling, dyeing, and similar phenomena.[112]

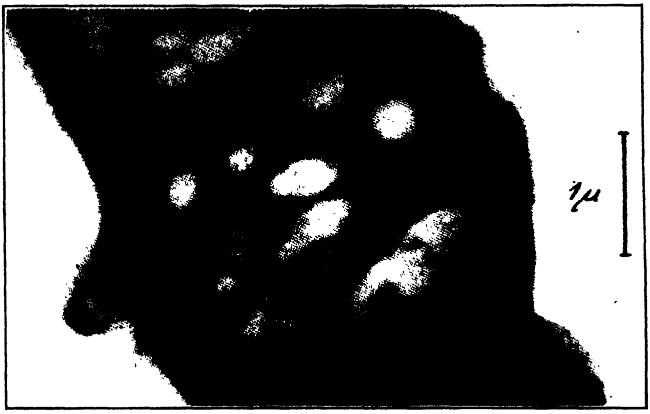

FIG. 21. Cross section through cotton fiber observed under the electron microscope (16,000 : 1). Ruska.

THE FORMATION OF CELLULOSE IN PLANTS

It seems to be an established fact that the plant synthesizes carbohydrates from carbon dioxide and water by a photochemical reaction (photosynthesis). The plant, under the influence of light, takes up the carbon dioxide from the air, whereas, in the absence of light, it liberates oxygen. Shortly after illumination has begun, the ratio of carbon dioxide to oxygen (the "photosynthetic quotient") approaches a constant value which has been accepted as evidence that the process is one of quantitative reduction of carbon dioxide to carbohydrates. Very little, however, is known about the intermediate reactions, although many hypotheses have been suggested.

One of the oldest and most popular hypotheses originates from von Baeyer.[113] It postulates that carbon dioxide, under the influence of

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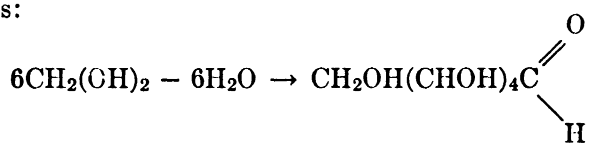
[111] Meyer and Lothmar, *Helv. Chim. Acta,* **19**, 68 (1935).

[112] Mark, *loc. cit.;* Freund and Mark, *Rayon Textile Monthly,* **23**, 515 (1942).

[113] von Baeyer, *Ber.*, **3**, 63 (1864).

light and in the presence of the chlorophyll of the plant leaves, is first decomposed to form carbon monoxide and that the latter, under the action of hydrogen (possibly resulting from the dissociation of water), is reduced to formaldehyde. In a third phase, the formaldehyde, under the action of the cell sap, is transformed into sugar. On the assumption that the formaldehyde in the presence of water exists in the form of its methylene glycol derivative, $CH_2(OH)_2$, the formation of sugar is interpreted as being the result of condensation with the loss of water, thus:



$$6CH_2(OH)_2 - 6H_2O \rightarrow CH_2OH(CHOH)_4C\overset{\displaystyle O}{\underset{\displaystyle H}{}}$$

The assumption that formaldehyde is the intermediate in the reactions which eventually result in the formation of sugar was based upon Butlerow's [114] observation that trioxymethylene (the condensation product of formaldehyde) actually polymerizes under the influence of alkali to sugar.

von Baeyer's hypothesis, appealing as it is, involves a number of weak points. Apart from the difficulty of accounting for the alkali which obviously is essential for the conversion of formaldehyde to sugar *in vitro,* formaldehyde as such exerts a poisoning effect upon plant life (although some plants were found able to assimilate it [115]). For this reason its presence in the plant for any length of time appears to be improbable. As a matter of fact, the attempts to identify formaldehyde as an intermediate of the photochemical reaction have not been very successful. Thus, the assumption would have to be made that the formaldehyde, if it were the intermediate, either undergoes polymerization immediately or is present in the form of a nonpoisonous derivative.

Willstätter and Stoll's [116] hypothesis ascribes an integral part of the photochemical reaction to the chlorophyll and particularly to its magnesium constituent. That chlorophyll plays an essential part in the photosynthesis of the carbohydrates in the plant has been known since the classical investigations of von Mohl and of Sachs.[117] Willstätter and Stoll's hypothesis postulates that the magnesium constituent of

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[114] Butlerow, *Ann.,* **111,** 242 (1859); *Compt. rend.,* **53,** 145 (1861).

[115] Jacoby, *Biochem. Z.,* **128,** 119 (1922).

[116] Willstätter and Stoll, "Untersuchungen über die Assimilation der Kohlensäure," Springer, Berlin (1918).

[117] See Spoehr, "Photosynthesis," The Chemical Catalog Co., New York (1926), p. 280.

the chlorophyll combines with carbon dioxide and water to form chlorophyll carbonate which, under the influence of light, rearranges itself to form chlorophyll formaldehyde peroxide. This compound decomposes, probably as a result of the action of enzymes, to regenerate chlorophyll and to emit oxygen and an "active" form of formaldehyde which immediately, i.e., without passing through the aldehydic form, polymerizes to carbohydrate.

That formaldehyde is produced from carbon dioxide and water under the action of both ultraviolet and white light has been known for a long time,[118] as has the fact that formaldehyde formation is stimulated by the presence of colored substances which are capable of forming labile addition compounds with carbonic acid.[119] More recently, Baur and co-workers[120] found that the carbonic acid esters of chlorophyll, as well as those of other dyestuffs of the fluorescing type, yield formaldehyde under certain conditions, obviously as a result of a reduction of the esterified carboxyl groups.

Although such and similar observations seem to support Willstätter and Stoll's hypothesis, the results of more recent studies indicate photosynthesis to take a different course. Particularly the investigations of Ruben and co-workers,[121] in which short-lived radioactive carbon was used as an indicator of the mechanism involved, seem to render the occurrence of formaldehyde as an intermediate quite improbable. Instead, carboxyl (RCOOH) seems to be the chief first product of the reduction of carbon dioxide. This reduction, representing an equilibrium reaction, takes place in the absence of light and is probably catalyzed by enzymes. It may be regarded as a step prior to actual photosynthesis and thus be expressed by the equation

$$\mathrm{RH} + \mathrm{CO_2} \rightleftarrows \mathrm{RCOOH}$$

Considering that cellulose is synthesized by bacterial action from simple sugars and, inversely, that it is broken down by the activity of bacteria and fungi to simple sugars, it would seem probable that such sugars are intermediates in the photosynthesis which leads eventually to polysaccharides in the plants.

In spite of the abundance of experimental data which has accumulated during many years of research, the nature of the first sugar to be

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[118] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1690 (1910); Stoklasa, *Biochem. Z.*, **41**, 333 (1912).

[119] Baly, Heilbronn, and Barker, *J. Chem. Soc.*, **119**, 1025 (1921).

[120] Baur and Gloor, *Helv. Chim. Acta,* **20**, 970 (1937); Fricker, doctoral dissertation, Zürich (1937).

[121] Ruben and co-workers, *J. Am. Chem. Soc.*, **61**, 661 (1939).

produced by photosynthesis is still unknown. Many reasons favor the assumption that it is glucose, i.e., the sugar most commonly found in plants. But experimental evidence, which would support this assumption unequivocally, is very small. In fact, the results of Ruben and co-workers[122] seem to indicate that simple sugars are not intermediates, but that, instead, the reaction leads directly to the long-chain molecules of the polysaccharides. Actual photosynthesis, being regarded, as mentioned above, as the second step in plant synthesis, could then be expressed by the equation

$$\mathrm{RCOOH} + \mathrm{H_2O} \xrightarrow{\text{Chorophyll}} \mathrm{RCH_2OH} + \mathrm{O_2}$$

RCH_2OH adds another carbon dioxide molecule, and the cycle is repeated to build up long carbohydrate chains. This view appears to be supported by the fact that the molecular weight of the first product of photosynthesis, detectable by its radioactivity in *Chlorella pyrenoidosa,* an alga, was found to be as high as 1000.

The large-molecule mechanism is regarded as advantageous not only thermodynamically but also kinetically, since it does not require polymerization of small molecules present in extremely low concentrations. The large-molecule hypothesis suggests that the simple sugars present in the plants are formed by cleavage of the long-chain molecules. In the light of this hypothesis, starch and cellulose may have to be regarded as the precursors rather than the products of the simple sugars.

In this connection, the results recently reported by Bois and Chubb[123] appear most enlightening. They found that the sap of the birch tree contained cellobiose and glucose as the only simple sugars and that these could be produced *in vitro* from starch by adding a sample of the dialyzed sap to an aqueous solution of soluble starch and allowing the mixture, buffered to a *p*H of about 6, to stand at a temperature of 50°. This result seems to indicate that starch is the primary product in the sap and that it is subsequently converted into the simple sugars by the action of enzymes. Indications are that two enzymes operate separately, a cellobiogenic and a glucogenic amylase. Indeed, it could be shown that the enzymes cellobiase and invertase were absent in the sap, indicating that the formation of glucose was not a result of the enzymatic cleavage of previously formed cellobiose or sucrose.

Cellobiose (together with sucrose) was found in the sap of the sugar maple tree (*Acer saccharum*)[124] and seems to be the result of the action of a sucrogenic amylase upon starch.

Since the yield of cellobiose (and sucrose) is considerable, the enzymatic hydrolysis of starch is possibly a more convenient method of preparing cellobiose than the acetolytic degradation of cellulose (see later).

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[122] Ruben, Kamen, and Hassid, *J. Am. Chem. Soc.,* **62,** 3443, 3450, 3451 (1940)

[123] Bois and Chubb, *Can. J. Research,* **20,** B114 (1942).

[124] Bois and Nadeau, *Can. J. Research,* **16,** B114, 121 (1938).

The formation of cellobiose and sucrose from starch should lead to a revision of the molecular structure of starch,[125] unless this formation is the result of a rearrangement of primarily formed maltose under the action of the specific enzymes.

Ruben's hypothesis seems to be supported further by the following interesting observation of Baly.[126] When a surface of nickel oxide (containing a certain amount of thallium oxide) adsorbed on kieselguhr was irradiated with white light in the presence of hydrated carbon dioxide, a substance was obtained which, gradually at room temperature but rapidly at 60°, changed into a stable colorless compound which could be hydrolyzed to a reducing sugar and therefore was probably a type of starch. This process seems to duplicate nature's method of producing carbohydrates from carbon dioxide, with the exception that metal oxide surfaces are used instead of chlorophyll.

On the other hand, Ruben's postulate that the carbohydrates are formed without simple sugars occurring as intermediates is difficult to reconcile with Compton and Haven's observation[127] that, in the developing cotton fiber, the content of reducing sugars is high during the period of rapid cell wall elongation (from the first to the twentieth day) but progressively decreases during cell wall thickening (i.e., when most of the cellulose is being formed) until maturity is reached.

As to the origin of the oxygen evolved in photosynthesis, Ruben and co-workers[128] believe to have evidence that it comes from water rather than from carbon dioxide.

The conclusions drawn from recent studies of the chemical kinetics of photosynthesis by Franck and Herzfeld[129] seem to demonstrate that this process is far more complex than would appear from the elucidating work of Ruben and co-workers. These investigators assume eight or more different photochemical reactions, with at least seven intermediates, to be involved in the reduction of one carbon dioxide molecule. As to the hydrogen needed for the reduction of the carbon dioxide, it is assumed (in agreement with the view of previous investigators) that the chlorophyll, having an abundant number of hydrogen atoms, is the source.

On the assumption that photosynthesis results in the formation of long-chain molecules directly, it would be these and not simple sugars

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[125] Haworth, *Chemistry and Industry,* **58,** 917 (1939); Freudenberg, *Ann. Rev. Biochem.,* **8,** 81 (1939).

[126] Baly, *Proc. Royal Soc., London,* **A172,** 445 (1939).

[127] Compton and Haven, *Contrib. Boyce Thompson Inst.,* **11,** 281 (1940).

[128] Ruben, Randall, Kamen, and Hyde, *J. Am. Chem. Soc.,* **63,** 877 (1941).

[129] Franck and Herzfeld, *J. Phys. Chem.,* **45,** 978, 1268 (1941).

which enter the cell sap and are transported to the places in the plant where they are eventually deposited in the form of solid compounds. It must be assumed further that the preformed long-chain molecules undergo further polymerization into their final stages, unless they reach this stage during the photosynthesis. Indications are that this might be so in the case of starch, whereas cellulose, which even in the highly swollen state is insoluble in water and, thus, could hardly be transported in this form, is probably formed at a later time. However, nothing seems to be known about the mechanisms involved.[130]

Hibbert[131] has advanced the idea that the plant might synthesize its carbohydrates from simple sugars in accordance with the principle which is operative in the polymerization of ethylene glycol and similar compounds to long-chain molecules. These ideas, however, have not yet been subjected to experimental test.

It is probable that enzymes play an essential part in the transformation of simple sugars or of other primary products of photosynthesis into the polysaccharides. Such transformations have been observed both *in vitro* and in the presence of living bacteria. Thus, according to Nishimura,[132] the enzyme amylosynthease is capable of converting the low molecular starch dextrins into higher polymerized products and, indeed, Hanes[133] synthesized starch itself by the action of potato-phosphorylase upon glucose-1-phosphate. Haworth, Heath, and Peat[134] have just reported that the synthetic starch is identical with the natural product. The fact that, thus far, it has not been possible to synthesize the higher oligosaccharides or cellulose itself from glucose or cellobiose by means of enzymes *in vitro* is, of course, no argument against the concept which postulates the participation of such enzymes in the production of cellulose. As has been mentioned before, certain living bacteria, such as *Acetobacter xylinum*, are capable of synthesizing from simple sugars cellulose which, chemically

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[130] Spoehr, *J. Chem. Education,* **19,** 20 (1942); Luck *et al.*, "Annual Review of Biochemistry," Vol. X, Ann. Reviews, Inc., Stanford University, California (1941).

[131] Hibbert and Perry, *Can. J. Research,* **8,** 102 (1933); Jahn and Hibbert, *ibid.*, **8,** 199 (1933); Lowell and Hibbert, paper presented before the American Chemical Society, Cellulose Division, Baltimore, Maryland, April 1939; Hibbert, *Ind. Eng. Chem.*, **32,** 984 (1940).

[132] Nishimura, *Biochem. Z.*, **223,** 161 (1930); **232,** 156 (1931).

[133] Hanes, *Nature,* **145,** 348 (1940); see also Astbury, Bull, and Hanes, *ibid.*, **146,** 558 (1940).

[134] Haworth, Heath, and Peat, *J. Chem. Soc.*, 55 (1942); see also Wolfrom, Smith, and Brown, *J. Am. Chem. Soc.*, **65,** 255 (1943).

and in most of its physical properties, appears to be identical with plant cellulose.[135]

Until recently opinions as to the first appearance of cellulose in the young cotton fiber were more or less divided. Microscopic and microchemical data seemed to indicate that cellulose does not appear until after the sixteenth day of fiber development, whereas x-ray data failed to produce evidence of the presence of cellulose until 30–35 days had elapsed, that is, at about the time when the process of cell elongation (the result of which is the outer layer of the primary wall) ceases and the thickening of the primary wall begins.[136] However, Sisson [137] has shown that the x-ray pattern of cellulose in early fiber development is masked by a crystalline pattern ascribable to wax and by an amorphous pattern belonging to pectin. When these two plant constituents were removed—the wax by extraction with an organic solvent and the pectin by treatment with dilute alkali and subsequent mild bleaching—the cellulose diagram was evident after 5 days of development.

During the development of the cotton fiber, the chain molecules become oriented. X-ray investigation has shown the chains or chain bundles in fibers younger than 25 days to be arranged at random but to develop orientation with reference to the fiber axis between the twenty-fifth and the thirty-fifth days.[138] However, the degree of orientation thus reached did not change appreciably with further thickening of the cell wall. On the other hand, the degree of orientation may be improved by drying the fiber under tension.

The x-ray findings obtained with the cotton fiber seems to be in agreement with the results produced with other fibers. For example, white fir wood fibers [139] reached their maximum orientation after about 10 days and beech wood fibers [140] after 14 days of development.

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[135] Hibbert and Barsha, *Can. J. Research,* **5,** 580 (1931); Barsha and Hibbert, *ibid.,* **8,** 170 (1934); Khouvine, *Compt. rend.,* **196,** 1144 (1933); **198,** 1544 (1934); "Cellulose et Bactéries," Hermann et Cie, Paris (1934), p. 24; Champetier, *Ann. Chim.,* **20,** 5 (1933); Schmidt and Schnegg, *Cellulosechem.,* **12,** 241 (1931); Sisson, *J. Phys. Chem.,* **40,** 343 (1936). Regarding solution viscosity of bacterial cellulose, see Fickentscher, *Cellulosechem.,* **13,** 58 (1932). See also Eggert, *Z. physik. Chem.,* **7,** 468 (1930); Lüdtke, *Biochem. Z.,* **268,** 383 (1934).

[136] Hess, Trogus, and Wergin, *Planta,* **25,** 419 (1936); Wergin, *Angew. Chem.,* **49,** 843 (1936).

[137] Sisson, *Contrib. Boyce Thompson Inst.,* **8,** 389 (1937).

[138] Sisson, *Contrib. Boyce Thompson Inst.,* **9,** 239 (1938); see, however, Berkley, *Textile Research,* **9,** 355 (1939).

[139] Ritter and Stillwell, *Paper Trade J.,* **98,** No. 22, 37 (1934).

[140] Hess, Lüdtke, and Rein, *Ann.,* **466,** 58 (1928).

It is interesting to note that fibers from a 385-year-old beech tree showed the same degree of orientation as the young, 14-day-old fiber, an observation which seems to reveal the great stability of cellulose in plants once it has reached maturity.

THE CHEMICAL REACTIONS OF CELLULOSE

The discussions in the previous sections on the morphological and histological arrangements of the various fiber elements, both as seen under the microscope and as revealed by x-ray analysis, will serve to direct attention to the influence that is to be expected from these structural peculiarities upon the course of the chemical reactions of the cellulose fiber.

As has been indicated, the reactions of cellulose are chiefly those which are characteristic of organic compounds having an abundance of hydroxyl groups. As is seen from the cellulose formula (Fig. 1) the hydroxyl groups, of which three are free to react in each glucose residue, have, by virtue of their position in the residue, different functional values. It may be anticipated that this difference will be evident under certain chemical treatments; examples of this will be found in succeeding chapters.

In addition the glycosidic linkages, which unite the individual glucose residues and characterize cellulose as a polysaccharide, are most responsive to certain treatments. Under the action of acids and certain oxidizing agents, these linkages suffer cleavage, and shorter-chain molecules result. The reducing power of cellulose, originally small, increases on such treatments, and the degradation of cellulose may thus be followed by determining the reducing power of samples removed from the reaction mixture at intervals.

The reducing power of cellulose is usually expressed as "copper number" (a term introduced by Schwalbe[141]) which represents the amount of reduced copper obtainable from 100 grams of cellulose by the action of Fehling solution. The original method has been frequently modified.[142] Instead of Fehling solution, alkaline hypoiodite solution[143] ("iodine number") or silver nitrate solution ("silver number")[144] may be used.

The copper number of cotton cellulose (standard cellulose) ranges from 0.05 to 0.08. Higher copper numbers indicate degradation. Ordinary bleached sul-

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[141] Schwalbe, *Ber.*, **40**, 1347 (1907); see also Schwalbe, "Die Chemie der Cellulose," 1st ed., p. 625.

[142] See, for example, Dorée, "The Methods of Cellulose Chemistry," p. 31.

[143] Willstätter and Schudel, *Ber.*, **51**, 780 (1918).

[144] Harrison, *J. Soc. Dyers and Col.*, **28**, 359 (1912); Dorée, *loc. cit.*, p. 125; Goetze, *Melliand Textilber.*, **8**, 624 (1927).

fite wood pulps have a copper number between 1.5 and 2.5, the latter figure being considered as rather high. The values for sulfite pulps bleached under alkaline conditions range between 0.5 and 1.0 and those for refined pulps (alkaline purified) may approach that usually found for cotton linters (0.05 or less).

The alcoholic and polysaccharidic nature of cellulose suggests that cellulose may undergo the following reactions:

1. Reactions characteristic of the polyhydric alcohol.
    - *a.* Formation of addition compounds, simple and more complex in nature; for example, with water, alkalies, cuprammonium hydroxide, other metal and organic bases and neutral metal salts.
    - *b.* Formation of compounds comparable with alcoholates.
    - *c.* Formation of esters and ethers.
    - *d.* Oxidation of hydroxyl groups to aldehyde and to carboxyl groups.
2. Reactions characteristic of the polysaccharide.
    - *a.* Hydrolysis and acetolysis, resulting in degradation to shorter chains; i.e., oligosaccharides, cellobiose, and the end product glucose, and their acetates.
    - *b.* Oxidation, causing cleavage of glycosidic linkages and resulting in shorter chains.

CHAPTER III

REACTIONS OF CELLULOSE WITH WATER

Considering the abundance of hydroxyl groups, cellulose may be expected to possess great attraction for water and aqueous solutions. Whether this attraction leads to chemical combination between the water molecules and the hydroxyls of the cellulose and to chemical combination in stoichiometric proportions is still a matter of discussion. The amount of water taken up by the individual cellulose fiber after the system has reached equilibrium is much smaller than it would be if all hydroxyl groups of the cellulose had reacted. Hence, chemical combination, if any, must be confined to selected hydroxyl groups. Such preference may be governed, first of all, by the degree of contact which the water molecules are capable of establishing with the hydroxyl groups of the cellulose; in other words, by the accessibility of these groups.

From the viewpoint of the morphological arrangement of the fiber, (i.e., its microscopic and submicroscopic structure) water may be expected to enter the fiber in different ways. The first contact will be with the surface of the fiber, then, through the capillaries (intermicellar spaces), with the surface of the micelles. X-ray analysis of the cellulose-water system is interpreted to show that this is as far as water is able to penetrate the micellar system. This penetration is accompanied by swelling, which sets in as soon as the water enters the intermicellar spaces. Further penetration of water, namely, into the spaces between individual chains (intramicellar spaces), occurs only if the crystalline structure is essentially loosened and widened; this occurs when the fiber is treated with strong swelling agents, such as strong alkalies, organic bases, or strong acids, or on esterification and etherification.

Consequently, the accessibility of the hydroxyl groups of cellulose for water molecules appears to be limited to those on the surface of the chain bundles. Meyer[1] has calculated from x-ray data that 30–50

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[1] Meyer, *Z. physik. Chem.*, **2**, 136 (1929); see also Mark, "Die Physik und Chemie der Cellulose," p. 187.

per cent of the total hydroxyl groups of cellulose are on the surface of the micelles, the rest being located within the spaces between the individual chains where they are inaccessible to water.

Opinions vary as to the nature of the forces by which the water molecules are held to the hydroxyl groups of cellulose. Urquhart[2] and Mark,[3] for example, have attributed the attraction for water to the residual affinity (secondary valences) of the hydroxyl groups of cellulose. Other investigators have made the polarity of the hydroxyl groups responsible[4] or have ascribed the water-binding ability to the capacity of the hydroxyl groups to form hydrogen bridges.[5] These concepts are discussed later.

That the hydroxyl groups are responsible for the water-binding ability of cellulose is seen from the fact that cellulose derivatives (for example, cellulose acetate in which all or part of the hydroxyl groups are occupied) take up considerably less water when brought into equilibrium with a humid atmosphere. Sheppard[6] found that the hygroscopicity of cotton (16 per cent at the saturation point) decreased to 9 per cent in fibrous cellulose triacetate (44.5 per cent acetyl content) and, as would be expected, this decrease proceeded linearly with the acetyl content.

However, even complete acetylation (or other types of substitution) does not reduce the ability of the derivative to take up water to the extent anticipated from the fact that water sorption of completely acetylated sugars (for example, cellobiose octaacetate and glucose pentaacetate, i.e., substances representing individual molecules) was reduced to less than 1 per cent (at the saturation point).[7]

This fact seems to indicate that a considerable part of the hygroscopicity of the cellulose derivatives and, for that matter, of cellulose itself, is independent of the presence of the hydroxyl groups and must be due to the peculiar arrangement of the cellulose molecules within the fiber. It appears safe to assume that, within the intermicellar spaces, a corresponding amount of water is being held mechanically,[8]

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[2] Urquhart, *J. Textile Inst.*, **20**, T125 (1929); Sheppard and Newsome, *Ind. Eng. Chem.*, **26**, 285 (1934).

[3] Mark, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Britain & Ireland*, **14**, 1 (1933).

[4] Koets and Kruyt, *Kolloid-Z.*, **82**, 315 (1938).

[5] Huggins, *J. Org. Chem.*, **1**, 407 (1936); Rideal, *J. Textile Inst.*, **30**, 242 (1939).

[6] Sheppard, *Trans. Faraday Soc.*, **29**, 81 (1933); see also Mardsen and Urquhart, *J. Textile Inst.*, **23**, T105 (1942).

[7] Sheppard and Newsome, *J. Phys. Chem.*, **33**, 1828 (1929).

[8] See also Mardsen and Urquhart, *loc. cit.*

possibly by capillary condensation.[9] In other words, even if all hydroxyl groups of cellulose are covered, the resulting cellulose derivative will still hold a certain amount of water.

This amount decreases as the groups being introduced into cellulose become longer; thus, the hygroscopicity was found to decrease with various derivatives as follows:

Triacetate	10%
Tripropionate	2–3%
Tributyrate	1.8%
Trivalerate	1.6%
Tristearate	1.0%

Sheppard believes that this result may be explained by the assumption that the substituting groups displace the water molecules from the intermicellar spaces, and the more so the longer the group.

When cellulose is exposed to water vapor and the vapor pressure is plotted against the moisture content of the sample, a curve (absorption isotherm) is obtained in which the vapor pressure rises very slowly in the initial stages of absorption but increases sharply at approximately 3–4 per cent moisture and continues to increase until the saturation point of the sample is reached. When the same sample is dried, the relative vapor pressure on the desorption isotherm is found to be lower than that on the absorption isotherm for the same percentage of moisture or, in other words, the desorption curve shows higher moisture content values than the absorption curve for the same relative vapor pressures. This phenomenon is known as the hysteresis effect and must be regarded as characteristic for cellulose.[10]

Some typical results are shown in Fig. 22. Urquhart has explained this phenomenon on the basis of the following deliberations.[11]

"When cellulose is formed inside the cotton hair, it is precipitated in the presence of water, and the hydroxyl groups will have water molecules attached. As the hair dries these groups will be freed, and it is reasonable to assume that there will be a tendency for the cellulose molecules to rearrange themselves so that the residual (secondary) valences of the hydroxyl groups will be mutually satisfied. This

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[9] See, however, Valkó, "Die kolloidchemischen Grundlagen der Textilveredelung," Springer, Berlin (1937), p. 108.

[10] Urquhart and Williams, *J. Textile Inst.*, **17**, T38 (1926); Urquhart, *ibid.*, **18**, T55 (1927); **20**, T117 (1929); Urquhart and Eckersall, *ibid.*, **21**, T499 (1930); Filby and Maass, *Can. J. Research*, **B13**, 690 (1935). The hysteresis effect on cellulose seems to have been observed first by Masson and Richards, *J. Chem. Soc.*, **78**, 412 (1906).

[11] Urquhart and Williams, *J. Textile Inst.*, **20**, T126 (1929). See also Simril and Smith, *Ind. Eng. Chem.*, **34**, 226 (1942); Nickerson, *ibid.*, **34**, 1152 (1942).

process is likely to go on when the cotton is dried until all the absorbed water has been removed. In addition to the rearrangement of the molecules in the micelles, some deformation (twisting) of the micelles themselves may occur and assist in bringing free hydroxyl groups nearer to each other.

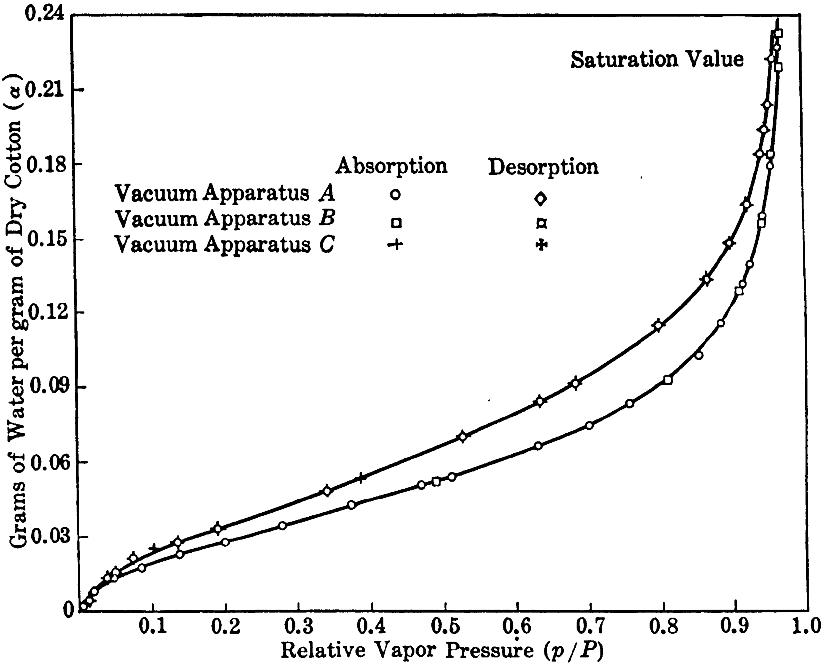

FIG. 22. Absorption and desorption of cotton. Hysteresis effect. Urquhart and Williams.

"It is not assumed that the arrangement (change of configuration) always does occur. It is probable that some molecules (or micelles) will be held more rigidly than others, and it may be that a change of configuration is possible only when a loosely bound molecule attains momentarily to a sufficiently large amplitude of vibration, so that even in the dry condition there will be a large number of free active groups on the micellar surfaces.

"If the cellulose is allowed to absorb water, the absorption will take place in the first instance at these remaining groups, but this absorbed water will by its attraction tend to restore the original orientation of the surface, so that during absorption the number of active groups will increase. This increase, however, will not be so great as the original decrease, since the amplitude of vibration of a molecule held to another by the attraction of one or more active groups will be less than that of a molecule with the active groups free, so there will be less tendency for a group to return to the surface than there was originally for it to leave it. Hence, the adsorbing surface will be in a less active condition during absorption than during desorption, and hysteresis will result."

Filby and Maass[12] have offered a somewhat different explanation of the hysteresis effect which is based upon the assumption that part of the water absorbed enters into chemical combination with a corresponding number of hydroxyl groups. According to their hypothesis the absorption of water is accompanied by an increase in cellulose surface which may be supposed to take place in the following way. The cellulose micelles are held together in the first place by the mutual surface attraction of cellulose for cellulose; the water first absorbed satisfies the free cellulose surface, and subsequently added liquid water is able to compete with the cellulose for cellulose attraction, thus increasing the effective surface. Part of the water entering between the cellulose surfaces becomes chemically bound and therefore on desorption is not subject to evaporation at the same vapor pressure as that at which it was absorbed. It is suggested, therefore, that there is a larger amount of chemically bound water present in cellulose during desorption than during absorption. Filby and Maass believe that evidence for part of the water absorbed being in chemical combination with cellulose may be derived from the volume contraction observed when cellulose comes into contact with water. Measurements were made to ascertain the specific volume of cellulose in helium gas and to apply the procedure to the system cellulose-water vapor.

The specific volume of cellulose in helium was found to be 0.640 ± 0.001 cc., a value which is in very good agreement with that given earlier by Davidson[13] (0.638–0.642 cc.). The volume of the system cellulose-water vapor was found to be much smaller than that of the components (cellulose and condensed water) alone as long as the amount of absorbed water was below 4 per cent. With more than 8 per cent of absorbed water the density of the subsequently sorbed water was found to be the same as that of the normal liquid. Thus, in the beginning of the sorption process, a definite contraction takes place which is regarded as being indicative of a chemical combination

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[12] Filby and Maass, *Can. J. Research,* **7,** 162 (1932).

[13] Davidson, *J. Textile Inst.,* **18,** T175, 275 (1927); see also Valkó, "Kolloidchemische Grundlagen der Textilveredelung," p. 93.

of cellulose with water. Subsequently absorbed water, however, first causes an increase in cellulose surface due to its swelling action which opens up the spaces between the micelles. This phase is followed by further contraction of the two components and then by a filling up of the capillary spaces in which the water maintains its liquid properties.

Sheppard[14] has calculated the chemically bound water to amount to not more than 5 per cent, which would correspond to a cellulose hydrate in which 1 molecule of water is in combination with 2 glucose residues $[(C_6H_{10}O_5)_2 \cdot H_2O]$.[15] On the other hand, Peirce[16] arrived at a calculated value of 10 per cent of chemically bound water, which would correspond to a combination of 1 molecule of water with only 1 glucose residue $(C_6H_{10}O_5 \cdot H_2O)$. In contrast to these interpretations, Bancroft and Calkin,[17] basing their conclusions upon the results of efficient centrifuging of water-soaked cellulose samples, found no indications of a chemical combination—at least none of the formation of stoichometric cellulose hydrates.

Again, results which were obtained[18] by applying a modification of Schreinemakers'[19] method for the determination of the composition of double salts ("Bodenkörper-Analyse") to cellulose have been interpreted to supply evidence of the existence of the hydrate $(C_6H_{10}O_5)_2 \cdot H_2O$. Champetier's technique consisted in adding to the cellulose-water system a third substance, for example, sodium thiosulfate or pyridine, substances which are supposed not to combine with cellulose and not to attack it and which may be estimated easily and accurately. The absorption of water was followed by determining the change in concentration of the auxiliary substance in samples taken at intervals while the system was being subjected to a certain but considerable measure of pressing.

The formulation of the cellulose hydrate as $(C_6H_{10}O_5)_2 \cdot H_2O$—a derivative which contains 1 molecule of water per 2 glucose residues—makes it probable that the reaction, if any, takes place only with the hydroxyl groups which are exposed on the surfaces of the chain bundles. This view is supported by the result of x-ray analysis. The

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[14] Sheppard, *loc. cit.*, p. 81; see also Wilson and Fuva, *Ind. Eng. Chem.*, **14**, 913 (1922).

[15] In this and like formulas throughout this book the polymeric character of the cellulose portion is implied.

[16] Peirce, *J. Textile Inst.*, **20**, T133 (1929).

[17] Bancroft and Calkin, *Textile Research*, **4**, 371 (1934).

[18] Champetier, *Compt. rend.*, **192**, 1593 (1931); **195**, 280, 499 (1932); *Ann. chim.*, **20**, 5 (1935).

[19] Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893).

x-ray pattern of the dry cellulose undergoes no alteration when exposed to water. Considering the results of Meyer's calculation, according to which up to 50 per cent of all available hydroxyl groups might be exposed on the surface, the formula could be interpreted to mean that of the three hydroxyl groups exposed per glucose unit only one carries a water molecule.

The fact that the x-ray pattern does not change is not, according to Champetier and Vaillard,[20] a safe argument against the inability of the water molecules to enter the intramicellar spaces because, if the dimensions of the particles of the reagent are small enough to pass through the spaces of the inner micellar system; the x-ray lattice may remain unaltered. This has been observed to be true of inorganic substances, for example, zeolite.[21] However, it is not very probable that this observation is applicable to cellulose.

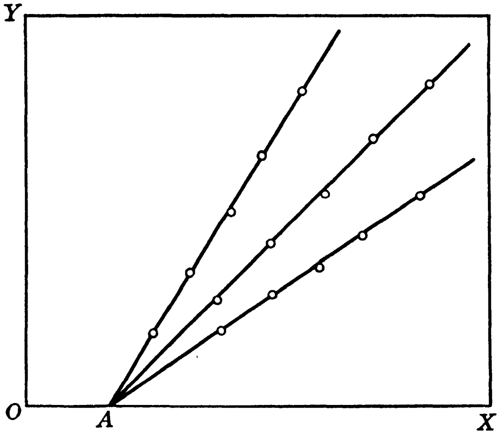

FIG. 23. Water chemically combined in a system of cellulose, water, and sodium thiosulfate or pyridine. Tankard.

Champetier's results were confirmed by Tankard,[22] who found that, for different initial concentrations of sodium thiosulfate (or pyridine), the composition of the pressed-out cellulose samples was found to follow a straight line, indicating that the concentration of the expressed solution remained constant over the range of pressure applied. Tankard has represented his results graphically by means of rectangular co-ordinates, the composition of the various pressed-out samples being given in terms of a constant quantity of cellulose. In Fig. 23 each

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[20] Champetier and Vaillard, *Compt. rend.*, **205**, 1387 (1937); *Bull. soc. chim.*, [5] **5**, 1042 (1938).

[21] Champetier, *Ann. chim.*, **20**, 5 (1933).

[22] Tankard, *J. Textile Inst.*, **28**, T263 (1937).

point represents a single pressed-out sample, the amounts of water and the auxiliary substance associated with the samples being measured along the axes *OX* and *OY*, respectively. The various lines corresponding to solutions of different initial concentrations cut the axis *OX* at very nearly the same point (*A*). This is interpreted to mean that there is a definite amount of water (represented by *OA*) which does not dissolve any of the auxiliary substance (nondissolving water[23]) and which is not reduced in quantity by the pressure applied. The distance *OA* is therefore regarded as a measure of the "water of hydration," i.e., water entering into chemical combination with the cellulose.

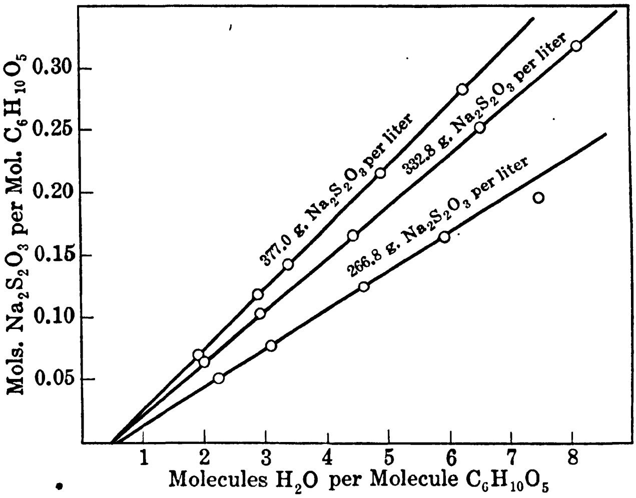

FIG. 24. Water chemically combined in a system of bleached cotton yarn, water, and sodium thiosulfate. Tankard.

The results thus obtained on bleached cotton yarn are represented in Fig. 24. They indicate that the maximum amount of water which can enter into chemical combination with the material used is 0.5 molecule H_2O per glucose residue (corresponding to 5.5 grams of H_2O per 100 grams of cellulose) or 1 molecule of water per 2 glucose anhydride units, in accordance with the formula $(C_6H_{10}O_5)_2 \cdot H_2O$. This result is in good agreement with Sheppard's calculation, as well as with the results obtained by Champetier with cotton linters. The same result was obtained with linen cellulose (bleached linen yarn).[24]

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[23] See Valkó, *loc. cit.*, p. 109.

[24] Tankard, *loc. cit.*, p. T277.

However, Tankard has interpreted his results to show the maximum amount of water which may be regarded as entering into chemical combination with cellulose rather than to demonstrate the existence of a definite cellulose hydrate as claimed by Champetier.

For cellulose acetate (a commercial acetate rayon yarn, Celanese, containing 51.5 per cent combined acetic acid or 2.17 molecules of acetic acid per glucose residue), Tankard has recorded values which correspond to 2.3 molecules of water per glucose residue (16.4 grams of water per 100 grams of dry Celanese yarn). This figure would correspond to 3 molecules of water per glucose residue for fully acetylated cellulose (triacetate) or six times that for cellulose itself.[25]

This result is extremely surprising in view of the findings reported earlier for cellulose acetates by other investigators. Similar results were obtained by Tankard with the monomethylene ether of cellulose (containing 17.2 per cent methylene oxide). This cellulose derivative, too, was found to combine with 3 molecules of water per glucose residue.

It is difficult to explain these results. As has been seen, the method is based upon the assumption that pressing removes all the mechanically held water and does not affect the "water of hydration." Possibly, this assumption is not correct; a more exact distinction between water mechanically held between the individual fibers or filaments of the yarn and that being held within the intermicellar spaces of the chain bundles of the single fiber would appear desirable. It is true that reactions such as esterification cause the cellulose fiber to swell. As a result, the intermicellar as well as the intramicellar spaces are widened, so that the capacity of the cellulose esters to accommodate water would appear to be greater than that of the original cellulose fiber.

Indeed, Tankard observed, although again as a result of the pressing method, that the "water of hydration" increased with increasing degree of acetylation, thus:

Acetate Moles of CH_3COOH per Glucose Residue	Acetate Moles of H_2O Combined
0.19	1.63
0.68	1.84
0.80	1.98
0.96	2.04
2.17	2.30

At the same time, these results seem to reflect the probability that, in the case of partial acetylation (such as that applied for making commercial acetate yarn), intramicellar swelling also increases the accessibility for water of those hydroxyl groups which remained unacetylated so that the final material, when brought into contact with water, will have an increased opportunity of taking up water also by way of chemical combination.

Thus, with acetates of increasing acetyl content, both the mechanically entrained inter- and intramicellar water and the water of hydration would increase. However, this should occur to a limited extent only since the increase must be expected to be counterbalanced by inactivation of hydroxyl groups

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[25] Tankard, *loc. cit.*, p. T282.

by substitution. Obviously, the final result depends on which of the two effects preponderates. It is probable that a clearer insight could be obtained if sorption experiments were made on individual cellulose acetate fibers rather than on yarn (see also p. 57).

The results obtained with the use of *heavy water* (deuterium oxide, D_2O) have likewise been interpreted to point in the direction of chemical combination in stoichiometric proportions. Deuterium oxide is supposed to undergo reaction with hydroxyl groups whereby the hydrogen atoms of these groups are exchanged for deuterium atoms:

$$2ROH + DOD \rightleftarrows 2ROD + HOH$$

This reaction was first studied with sugars. Bonhoeffer and Brown,[26] on dissolving sucrose in heavy water, observed that the density of the latter decreased considerably, whereas with ordinary water the change was very small. It was found that in sucrose approximately one-half of all hydroxy-hydrogen atoms, and in *d*-glucose all five are exchangeable for deuterium.[27] These results make it seem probable that in cellulose all three hydroxy-hydrogen atoms of the glucose residues would be exchangeable.

Various methods have been applied to the study of the action of heavy water on cellulose. King and Ouellet,[28] using McBain's quartz-fiber spring balance, simply measured the increase in weight which a sample of cellulose attains when in contact with heavy-water vapor for a certain length of time. The same technique had been applied previously by Filby and Maass [29] for studying the sorption (and desorption) of ordinary water on cellulose (see p. 44). The results with deuterium oxide were found in good agreement with those obtained with water as shown in Fig. 25. The curves are very similar. The ratio of the sorbed weight of deuterium oxide and of water is virtually constant and roughly equal to that of the molecular weights of the two substances. Both curves follow a normal absorption isotherm which, as the vapor pressure approaches saturation, becomes a rapidly rising curve, showing that a new process sets in. This phenomenon has been attributed both to condensation of water and to a liberation of residual valences resulting in an increased capacity for sorption.[30] Since in

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[26] Bonhoeffer and Brown, *Z. physik. Chem.*, **B23**, 172 (1933).

[27] Moelwyn-Hughes, Klar, and Bonhoeffer, *Z. physik. Chem.*, **A169**, 114 (1934).

[28] King and Ouellet, *Can. J. Research*, **B14**, 444 (1936).

[29] Filby and Maass, *Can. J. Research*, **B13**, 1 (1935); see also Pidgeon and Maass, *J. Am. Chem. Soc.*, **48**, 690 (1926); Sheppard and Newsom, *Ind. Eng. Chem.*, **26**, 285 (1934); Urquhart and Williams, *J. Textile Inst.*, **15**, T138 (1924).

[30] Filby and Maass, *loc. cit.*

their investigation King and Ouellet could find no indication for condensation, they believed that liberation of residual valences may account for the phenomenon.

Turning their attention to the desorption of the heavy water-exposed cellulose sample, King and Ouellet found that the weight of the sample did not return to its original value. The excess of weight was 0.59 per cent and, on re-exposing the desorbed sample to heavy water and subsequent desorption, 0.87 per cent of the dry weight. It would thus appear that the "dry weight" of cellulose gradually increases in the presence of heavy water. This increase in weight of the cellulose after desorption was found to be permanent and is regarded as indication of the exchange reaction between deuterium and the hydrogen atoms of cellulose. The total effect (0.87 per cent) corresponds to the substitution by deuterium of 0.8 of one of the 10 hydrogen atoms in the basic unit, $C_6H_{10}O_5$. It is possible that the reaction was not complete, because it obviously proceeds very slowly.

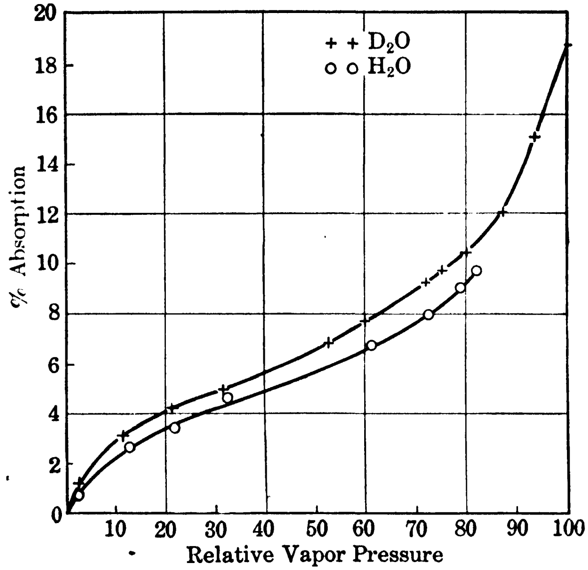

FIG. 25. Sorption isotherms of water and deuterium oxide. Purified wood cellulose. King and Ouellet.

Champetier and Vaillard[31] have studied the reaction of heavy water with various cellulosic materials, such as filter paper, cotton linters,

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[31] Champetier and Vaillard, *Compt. rend.*, **205**, 1387 (1937); *Bull. soc chim.*, [5] **5**, 1042 (1938).

and mercerized cotton linters, by determining the decrease in density which the deuterium oxide undergoes in contact with the cellulosic materials. The reaction was found to come to a standstill with filter paper after 24, with cotton linters after 36, and with the mercerized product after 18 hours at 30°. At 100° the time was shorter, 13 hours being sufficient for filter paper. It is claimed that the exchange reaction reaches completion and that it may thus be expressed by the following equation:

$$C_6H_7O_2(OH)_3 + 3D_2O \rightleftarrows C_6H_7O_2(OD)_3 + 3DOH$$

This formulation would imply that the deuterium oxide molecules penetrate the micellar system of the fiber completely, i.e., that all free hydroxyl groups become substituted. However, no x-ray photographs which would show whether such a reaction occurred were taken.

The cellulose-water relationship has an important bearing on many technical processes, for example, the conditioning and drying of textile fibers or the mechanical treatment of rag or wood pulp fibers in the beating process, as a step preparatory to the manufacture of paper.

The process of beating, by which the cellulose fibers are cut, bruised, and fibrillated in the presence of water for a shorter or longer period of time in order that a uniform coherent and strong sheet of paper may be obtained, has always been regarded as a particularly suitable means of studying the cellulose-water relationship. In view of the fact that on cutting, and still more so on bruising and fibrillation, the external surface of the fibers increases enormously, such fibers ought to be in a condition particularly suited for establishing an intimate contact with water. Indeed, as beating proceeds, it becomes more and more difficult to free the beaten stock of its water content. It is quite conceivable, therefore, to assume that the water plays an essential part in the beating process.

At the time the phenomenon, which in the papermakers' language is termed "hydration," first interested scientists, the question arose whether the water unites with the fibers merely according to physical laws or combines with it chemically in a sense of true hydration. At that time the majority of investigators seems to have favored the "chemical" hypothesis. "Hydration" in the beater was likened by some to true hydration, as observed, for instance, with inorganic salts. However, later workers in the field could find no indication of hydration in a chemical sense.[32]

According to other authorities of that time (for example, Cross and Bevan[33]), the rôle of the water was regarded as that of exerting a physical effect on the fibers, inasmuch as continuous agitation and water would combine to cause the fibers to absorb increasing amounts of water and to acquire a state of gelatinization which was thought to be a prerequisite for establishing the

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[32] Strachan, *Proc. Tech. Sect., Papermakers' Assoc. Gt. Britain & Ireland,* **6,** 149 (1926); **13,** 61 (1932); **14,** 447 (1934).

[33] Cross and Bevan, "A Textbook of Paper Making," 5th ed., London, Spon (1920).

mutual and intimate contact between fibers and fiber fragments when the water is removed from a mat of beaten pulp fibers.

For some time the opinion prevailed that, on beating, the fiber underwent changes similar to mercerization, that is, intramicellar swelling under the influence of strong alkali with subsequent increased capacity of the alkali-freed fiber to hold water.[34] Although most investigators were unable to establish a substantial and unequivocal difference between the sorption of dried beaten and unbeaten cellulosic material,[35] recently Seborg, Simmonds, and Baird[36] found that the hygroscopicity of wood pulp was definitely increased after excessive beating. In other words, the beaten stock attained distinctly higher equilibrium moisture contents than in its unbeaten state.

Still, it remains doubtful whether this difference can be explained on the assumption that the fibers have gone through a process of intramicellar swelling. No attempt seems to have been made to demonstrate whether the x-ray diagram of the beaten cellulose fiber reveals the change which is characteristic of the submicroscopic structure of mercerized cellulose and which differs from that of the original fiber.

As long as this proof is missing it appears safer to explain the increased hygroscopicity of the beaten fiber observed by Seborg and co-workers by the fact that on excessive beating the external surface[37] of the fiber becomes enormously increased. Thus, the fibrils, many of which compose the fiber, would expose a greater number of hydroxyl groups than the undivided fiber and, consequently, offer a much increased opportunity for the water molecules to become attached—chemically or physically—to the hydroxyl groups.

On the other hand, Kress and Bialkowsky[38] demonstrated that intermicellar swelling, i.e., as much swelling as water is capable of accomplishing, must be regarded as an essential prerequisite for achieving the common beating effect in papermaking. In the presence of nonswelling agents (fuel oil, butyl alcohol, furfural, amyl alcohol, etc.) the beating device exerts only a cutting effect on the fibers but causes no bruising or fibrillation, and, on evaporation of the liquids, no coherent sheet of any strength properties is obtained. On the other hand, organic liquids (such as formamide and ethylene glycol) which exert a pronounced swelling effect on the fibers cause them to become bruised and fibrillated and, as a result, a coherent sheet of normal strength properties is obtained.

Various hypotheses have been suggested to explain the bonding between fibers when a sheet is formed upon the removal of the water, as well as the increased physical strength properties shown by a sheet of beaten pulp in com-

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[34] See for example Strachan, *loc. cit.*

[35] Campbell, "The Cellulose-Water Relationship," *Can. Forest Service, Bull.*, Ottawa, No. 84, 25 (1933); *Pulp Paper Mag. Canada,* **16,** 178 (1935); Cottrall, *Proc. Tech. Sect., Papermakers' Assoc. Gt. Britain & Ireland,* **14,** 241 (1934); Seborg and Stamm, *Ind. Eng. Chem.,* **23,** 1271 (1931); *J. Phys. Chem.,* **39,** 133 (1934); Sheppard and Newsome, *Ind. Eng. Chem.,* **26,** 285 (1934).

[36] Seborg, Simmonds, and Baird, *Paper Trade J.,* **107,** No. 19, 45 (1938); *Ind. Eng. Chem.,* **28,** 1245 (1936); see also Schwalbe and Becker, *Z. angew. Chem.,* **20,** 2166 (1907); **33,** 58 (1920).

[37] Campbell, "The Cellulose-Water Relationship," pp. 12, 16, 29.

[38] Kress and Bialkowsky, *Paper Trade J.,* **93,** No. 20, 35 (1931).

parison with a sheet prepared from unbeaten fibers. Some investigators believe that fibrillation, with subsequent entanglement and matting of the fibers, suffices to account for the coherence and the strength of the sheet. Strachan, who earlier held this belief, later postulated, however, that the forces binding the fibers together during the formation of the sheet on the paper machine are those of cohesion between colloidal surfaces "according to well-known physical laws." These colloidal surfaces may be in a state of gelatinization and, as such, may be fused or glued together, when the water is removed by pressing and drying. This view (see also Cross and Bevan) has found a number of followers.[39]

However, the experimental facts which have been invoked to prove that such effects actually take place may be interpreted in a different way. In addition, the theory which tries to explain the properties of a sheet of paper solely by fibrillation and entanglement of fibrillated fibers has lost much of its ground since Doughty[40] has shown that a coherent and strong sheet of paper, as usually obtained by beating and drying the beaten stock, may also be obtained by removing the water from the unbeaten or only slightly beaten stock by compression. Likewise, Clark[41] showed that untreated, well-cleaned cellophane sheets, when wetted, pressed together, and subsequently dried, stick rather firmly together; i.e., the tensile force required to pull the joining sheets apart is quite considerable. Obviously, no fibrils are involved in this union of cellulose surfaces.

Thus, the essential condition under which the final effect is accomplished seems to be such that intimate contacts between the fiber surfaces must be established. On this assumption, the fibrillation of the fibers would be merely a means of increasing the points of contact.[42]

It would appear most plausible to attribute the establishment of such contacts to the forces which are operative between the hydroxyl groups of the cellulose. On this assumption the function of the water is not confined to intermicellar swelling, in which capacity it enables the beating device to exert the desired mechanical effect upon the fibers. In addition, the water has a second important function.

This second function of water is best understood on the basis of Urquhart's theory on the behavior of the secondary valences of the hydroxyl groups when water is admitted and subsequently removed. As mentioned above, this theory postulates that the water molecules which enter the intermicellar spaces of the dry fiber release the secondary valences (those involved in binding micelles together in the lateral direction) and attach themselves to the freed hydroxyl groups. On removal of water a state will be reached in which the hydroxyl groups of the micelles release the water molecules so that the secondary

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[39] Porvik, *Papier-Fabr.*, **27**, 372 (1929); Bell, *J. Soc. Chem. Ind.*, **52**, T109, T119 (1933).

[40] Doughty, *Tech. Assoc. Papers*, **14**, 243 (1931).

[41] Clark, *Paper Trade J.*, **96**, No. 26, 25 (1933).

[42] With reference to the part which finest fibrillation of fibers plays in the paper sheet making process, attention is directed to the results of studies with the electron microscope by Sears and Kregel, *Paper Trade J.*, **114**, No. 12, **43** (1942).

valences are in a position to satisfy each other and thus restore most of the original condition.

On the basis of such considerations and others derived from Strachan's work, Campbell has developed a hypothesis on the bonding of beaten fibers which seems to explain the phenomenon quite satisfactorily. This hypothesis may be briefly summarized as follows.

When cellulose comes into contact with water, its hydroxyl groups are capable of holding water molecules against the movements of the freely moving molecules of the surrounding water. Thus, surface layers of water are formed. Such layers would be in effect layers of hydrated cellulose and, because of the increased freedom of movement of the surface molecules in comparison with those of the interior of the fiber, could be considered as representing a state of solution or "near solution" of micelles (chain bundles) in water. The attraction between the fibers is thus reduced. As a result, additional water enters the structure through the capillaries between the micelles and causes imbibition and swelling. Under the influence of beating, the swollen and softened structure of the fibers is disrupted and fibrillated, resulting in an increase in their external surface and an increased formation of layers of hydrated cellulose. On drying, strong forces of surface tension are developed between the interfaces of hydrated cellulose layers of adjacent fibers or fibrils which draw their surfaces closer together until they approach each other so closely that the secondary valences, now almost or entirely freed of water molecules, come into play and complete the contact between the cellulose surfaces. It is thought that this last stage of the union involves a process of recrystallization. The cellulose micelles contained in the surface solution (layer of hydrated cellulose) have lost the orientation which they possessed in the original dry fiber. Possibly, some or all of the micelles are even further subdivided into single chain molecules. When sufficient water has been removed, the micelles and the individual chains undergo reorientation followed by recrystallization. Since this recrystallization takes place in the interfaces between adjacent fibers and fibrils, a bondage of "crystallized" cellulose is established.

The strength of the bonds depends upon the degree of orientation to which the micelles and chain molecules align themselves in the stage prior to recrystallization. If the degree to which the micelles of adjacent fiber surfaces are oriented is identical, a bond of maximum strength and insolubility is produced. Bonds of lower strength and greater solubility result if the adjacent micelles are less perfectly oriented. Campbell has furnished a good deal of experimental evidence to support his hypothesis.

Direct proof that hydration of cellulosic materials and the subsequent bonding between adjacent fibers in a sheet of paper are a function of their hydroxyl groups was furnished independently by Bletzinger[43] and by Brown and Harrison.[44] It was shown that hydration and bonding are seriously impeded and even entirely eliminated when a number of hydroxyl groups are blocked by

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[43] Bletzinger, doctoral dissertation, under the direction of E. Heuser, The Institute of Paper Chemistry, Appleton, Wis., 1940; *Ind. Eng. Chem.*, **35**, 474 (1943).

[44] Brown and Harrison, *Proc. Tech. Sect., Papermakers' Assoc. Gt. Britain & Ireland*, **21**, 225 (1940); *The World's Paper Trade Review*, **117**, Tech. Supp., 25 (1942); Wiltshire, *ibid.*, **117**, 62 (1942).

acetyl groups. Obviously, these observations are in agreement with the fact that the hygroscopicity of cellulose fibers decreases with increasing acetyl content (p. 43). If, however, a medium is chosen for the beating of the acetylated fibers which, in contrast to water, is compatible with the acetyl groups (without dissolving the acetate)—for example, acetone—a coherent sheet of excellent physical strength properties is obtained.[45] For an explanation, Campbell's hypothesis on the fiber-to-fiber bonding in the presence of water may be invoked and the assumption made that layers of acetone-solvated acetylcellulose are formed which, on the removal of the acetone, undergo recrystallization, resulting in an intimate union of fiber surfaces.

An interesting phenomenon was observed (Bletzinger), when fibers which were acetylated only to a limited extent were beaten. With such fibers, the physical properties of the sheets increased as the acetyl content was increased and reached a maximum at 6 per cent. For an explanation, the assumption may be made that the introduction of ester groups widens the distance between the micelles and the individual chains and that the looser structure thus produced favors the development of external surface on beating. As a result, an increased number of hydroxyl groups becomes accessible to water (hydration) with subsequent increased bonding between fiber surfaces when the water is removed. However, when the acetyl content is increased above the optimum value, the increased availability of free hydroxyl groups would have less and less effect, because the hydrophobic character of the fibers becomes more and more pronounced and eventually predominates the hydration effect.

It is interesting to note that the maximum physical strength properties of the sheet (as a result of maximum bonding and hydration) coincided with a maximum in hygroscopicity (Aiken).

The function of the hydroxyl groups as discussed above was also demonstrated with partially butyrylated and partially stearylated cellulose fibers.[46]

Methylation of some of the hydroxyl groups of cellulose was found to have an effect similar to that of acetylation[47] (see also the chapter on cellulose ethers, p. 399).

More recently, the affinity of cellulose for water has been explained by the existence of *hydrogen bonds.* Such bonds are also assumed to be operative between hydroxyl groups of neighboring chain molecules in cellulose itself and may be regarded as representing a more specific type of the secondary valences which hitherto have been invoked to explain the lateral coherence of micelles and individual chain molecules in the cellulose system.

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[45] Bletzinger, *loc. cit.;* see also Aiken, doctoral dissertation, under the direction of E. Heuser, The Institute of Paper Chemistry, Appleton, Wis., 1942; *Ind. Eng. Chem.*, **35**, 1206 (1943).

[46] J. Harrison, doctoral dissertation, under the direction of E. Heuser, The Institute of Paper Chemistry, Appleton, Wis. (1943).

[47] Jayme and Froundjian, *Cellulosechem.*, **18**, 9 (1940); Froundjian, doctoral dissertation, Darmstadt, Germany, 1940. Further references to beating: Kanamaru, *J. Soc. Chem. Ind., Japan, Supplementary Binding,* **41**, 1823 (1938); *Kolloid-Z.*, **84**, 222 (1938); Bailey and Brown, *Ind. Eng. Chem.*, **32**, 57 (1941).

The presence of hydrogen bonds or hydrogen bridges is illustrated in Fig. 26. In Fig. 26*A* the hydrogen atoms are supplied by the hydroxyl groups of the cellulose, whereas in Fig. 26*B* the water molecules form double bridges in two directions with the hydroxyl groups of the opposite chains.

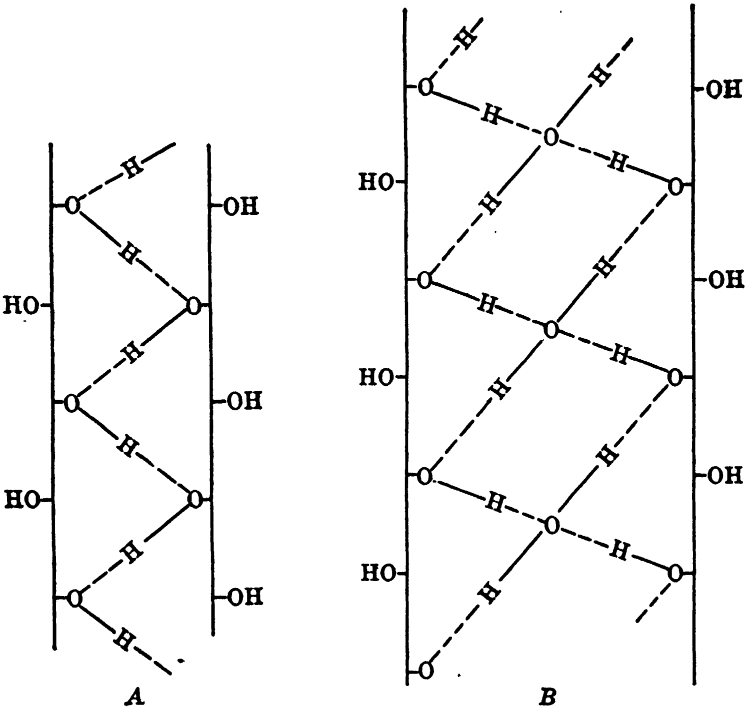

Fig. 26. *A*. Parallel cellulose chains laterally linked through hydrogen bridges in the dry fiber. *B*. Parallel cellulose chains linked by water molecules through hydrogen bridges in the wetted fiber.

The application of the hydrogen bond concept to cellulose was first suggested by Huggins.[48] Huggins believes that many properties of organic substances which have been vaguely attributed to van der Waals forces, secondary valences, polarity, steric hindrance, etc., are definitely due to the existence of hydrogen bridges.

Evidence for the occurrence of hydrogen bridges is derived mainly

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[48] Huggins, *J. Org. Chem.*, **1**, 407, 439, 440, 455 (1936); see also Rideal, *J. Textile Inst.*, **30**, T238 (1939); "Symposium on the Hydrogen Bond," *Trans. Faraday Soc.*, **36**, 871–928 (1940); Pauling, "The Nature of the Chemical Bond, etc.," Cornell Univ. Press, Ithaca, New York (1940). The rôle of the hydrogen bond in textile fibers has been reviewed by Barrer, *J. Soc. Dyers and Colourists*, **57**, 264 (1941).

from infrared absorption spectra. These reflect any change in frequency of vibration of hydrogen atoms such as would occur if a hydrogen atom attached itself to other atoms of the structure. Ellis and Bath[49] determined the infrared absorption spectrum of cellulose and concluded that all or practically all its hydroxyl groups are involved in hydrogen bridges. It would seem to be in agreement with the heterogeneous structure of the cellulose fiber that the perturbation of the hydroxyl groups corresponds to hydrogen bridges of variable distances and variable bond angles between such groups of adjacent cellulose chains.

On the other hand, Mark[50] has directed attention to the probability that hydrogen bridges are confined to a certain part of the cellulose structure, namely, to the groups along the *a*-axis within the *a*-*b* plane of the basic cell (see Fig. 14). Here, the glucose units are in rather close proximity, the distance between the centers of the two nearest oxygen atoms of two such units being about 2.5 Å. This is considerably closer than the distance between groupings held together by van der Waals forces (3.0 Å). It appears reasonable, therefore, to assume that the forces operative in the *a*-*b* plane are stronger than van der Waals forces. Expressed in calories per mole, the strength of the hydrogen bond would correspond to 15,000, whereas the energy of van der Waals forces would correspond to only 8000 calories. van der Waals forces are assumed to be operative along the *c*-axis, the shortest distance between hydroxyl groups of parallel chains being as much as 3.8 Å. The strongest forces are, of course, the primary valence forces along the *b*-axis, corresponding to an energy of 50,000 calories per mole.

This differentiation between two types of weak linkages in the structure of cellulose would suggest that water molecules could be linked to the hydroxyl groups in two different ways. It may be hoped that the rapid development in the field will yield experimental evidence suitable to approach a decision.[51]

Although absorption may be regarded as the first process which occurs when the cellulose fiber comes in contact with water or other liquids, the phenomenon of *swelling* is closely related to it; in fact, both phenomena are intimately interwoven. As already indicated, x-ray analysis has proved to be a great aid to the study of swelling phenomena. The late J. R. Katz, to whom we owe much of our knowledge in this field,[52] considered x-ray analysis the only experi-

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[49] Ellis and Bath, *J. Am. Chem. Soc.*, **62**, 2859 (1940).

[50] Mark, *Chem. Reviews*, **26**, 169, 181 (1940).

[51] For other hypotheses on the mechanism involved in the attachment of water to cellulose see Koets and Kruyt, *Kolloid-Z.*, **82**, 315 (1938).

[52] Katz, "Die Micellar-Theorie und die Quellung der Cellulose," in Hess, "Die Chemie der Cellulose," Akad. Verlags-Ges., Leipzig (1928); Katz, "The Laws of Swelling," *Trans. Faraday Soc.*, **29**, 279 (1933). See also Heuser and Rowland, *J. Chem. Education*, **16**, 153 (1939).

mental method which allows us "to penetrate into the intimate mechanism of swelling." A distinct change of the x-ray diagram of the fiber is believed to indicate that the liquid has advanced into the interior of the chain bundles (intramicellar swelling) and entered into a reaction, which results in the formation of a compound between cellulose and the swelling agent. The lack of a distinct change in the x-ray pattern generally indicates that the molecules of the liquid have attached themselves only to the outer surface of the fiber and to the interfaces between micelles or chain bundles (intermicellar swelling).

It is generally believed that pure water causes only intermicellar swelling, in contrast to aqueous sodium hydroxide, cuprammonium hydroxide, and similar solutions which penetrate into the interior of the chain bundles. In this way, water is carried also into the intramicellar spaces. In some cases, as with cuprammonium hydroxide solution, the reagent is capable of overcoming the forces of cohesion which hold the chains together in lateral direction and, thus, of eventually dissolving the fiber. One should expect, therefore, that the forces of cohesion within the fiber would become weaker merely on intermicellar swelling and hence decrease the tensile strength of the fiber. This anticipation, however, is not always in agreement with the experimental facts. Thus, the cotton hair possess greater wet than dry strength, and the strength even increases with increasing moisture content.[53] This increase in physical strength must, therefore, involve such phenomena which counteract the weakening of the cohesive forces.[54]

It seems to be in keeping with the microscopic and the submicroscopic structure of cellulose that the fiber swells considerably more in the lateral than in the longitudinal direction. Thus, the diameter of a cotton hair wetted with water may increase by 40 per cent and more of its dry diameter, whereas its length increases seldom more than 1 per cent.[55]

Attention has been directed on previous pages to the observations that cellulose in contact with water shows a certain volume contraction; i.e., the volume of the swollen fibers is smaller than the volume of the dry fibers and the water absorbed in the free state.[56]

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[53] Karger and Schmid, *Z. tech. Physik.*, **6**, 124 (1925); Obermiller, *Melliand Textilber.*, **7**, 71 (1926); Brown, Mann, and Peirce, *J. Textile Inst.*, **21**, T186 (1930); Smith, *Am. Dyestuff Reptr.*, **27**, P. 213 (1938).

[54] Valkó, "Kolloidchemische Grundlagen der Textilveredelung," p. 115; Nickerson, *Ind. Eng. Chem.*, **34**, 1152 (1942).

[55] Clayton and Peirce, *J. Textile Inst.*, **20**, 315 (1929); Collins, *ibid.*, **21**, 311 (1930).

[56] Valkó, "Kolloidchemische Grundlagen der Textilveredelung," p. 93.

Such contraction has also been encountered in the determination of the specific volume of cellulose by means of the displacement method. Using different liquids, Davidson[57] observed that the quantity of the displaced liquid per gram of fiber weight depended on the nature of the liquid. Thus, the apparent specific volume of cellulose was found to be different in water and in toluene. However, it may be assumed that helium causes no volume contraction because it does not combine with cellulose. It is also probable that, owing to its very small molecular volume, helium will enter even the finest capillaries of the fiber.[58] On these assumptions, the values obtained by Davidson for various cotton types by the use of helium (average 0.640 cc. per gram of cellulose) may be regarded as the true specific volume of these materials. As has been seen (p. 46), Davidson's values are in good agreement with those reported by Filby and Maass[59] (0.640 ± 0.001 cc. per gram of cellulose). The specific gravity of cellulose would thus be 1.562.

The somewhat higher values for the specific volume in toluene (and other organic liquids) would indicate that these liquids do not fill all the pores and capillaries of the fiber, whereas the lower value obtained with water is best explained on the assumption that volume contraction occurs. If the contraction on swelling in water is calculated from Davidson's data as the difference between the apparent specific volumes in water and in helium, it is found to be 2–3 cc. per 100 grams of cellulose. Thus, the density of the water absorbed appears to be 5–7 per cent higher than that of the free water.

Filby and Maass' figure for volume contraction is somewhat higher, namely, 3–4 cc. per 100 grams of cellulose, whereas Stamm and Seborg's[60] value of 1.7 cc. approaches that of Davidson's. It is likely that the discrepancy is due to a difference in the values used for the specific volume of the dry cellulose. Stamm and Seborg used the figure 0.645 which was derived from a specific gravity value (1.549) determined in benzene with the pycnometer method.

The volume contraction of cellulose in water has also been interpreted to mean that very small amounts of cellulose dissolve in water.[61] However, direct experimental evidence for this interpretation is questionable. For example, Strachan,[62] who determined the water-solubility of cotton cellulose after repeated treatments to be 1.4–2.1 parts per 100,000, found the dispersion of these small amounts to be accompanied by some breakdown of the cellulose, the nature of which is still to be determined. Similar observations were made by Wislicenus and Gierisch[63] who found cellulose, which had been subdivided into fine particles by grinding, to be soluble to an extent of 0.05–0.39 per cent. However, the copper number and the methylene blue absorption were markedly increased, indicating that either some breakdown of the dissolved portion had occurred or the dissolved portion represented degradation products originally present in the cellulose.

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[57] Davidson, *J. Textile Inst.*, **18**, T175, 275 (1927).

[58] See, however, Babbitt, *Can. J. Research*, **20**, A143 (1942).

[59] Filby and Maass, *Can. J. Research*, **7**, 162 (1932).

[60] Stamm and Seborg, *J. Phys. Chem.*, **39**, 133 (1935).

[61] Campbell, "The Cellulose-Water Relationship," p. 21.

[62] Strachan, *Nature*, **141**, 332 (1938); see also Turner, *Proc. Tech. Sect., Papermakers' Assoc. Gt. Britain & Ireland*, **19**, 171, 182 (1938–1939).

[63] Wislicenus and Gierisch, *Kolloid-Z.*, **34**, 169 (1924).

Likewise, the small quantities dissolved may be but traces of noncellulosic impurities which remain even after the most thorough purification.

Sorption of water and swelling are accompanied by heat development; the "heat of swelling" may be measured and may serve for calculating the energy which is liberated on swelling.[64] The fact that the heat of swelling is considerable has been taken as evidence that absorption of water and swelling are not merely phenomena of diffusion and distribution of water within the micellar system but, rather, are governed by forces of molecular attraction as pointed out above.[65]

When cellulose swells, considerable pressure is developed. Katz[66] has pointed to the ancient Egyptians who filled holes in rocks with carefully dried wood and poured water over it. The forces developed by the swelling wood material would burst the rock.

Swelling pressure may be measured by various methods. Thermodynamically it appears to be identical with osmotic pressure or, as Steinberger[67] has put it, "osmotic pressure is nothing but swelling pressure, made evident by the external device of a semipermeable membrane."[68]

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[64] Katz, *Trans. Faraday Soc., loc. cit.; J. Textile Inst.*, **15**, T328 (1924); Haller, *Kolloid-Z.*, **49**, 74 (1929); Argue and Maass, *Can. J. Research*, **10**, 564 (1935); Stamm and Loughborough, *J. Phys. Chem.*, **39**, 121 (1935).

[65] See also the latest discussion of the subject by Babbitt, *Can. J. Research*, **20**, A143 (1942).

[66] Katz, *loc. cit.;* see also Heuser, *Paper Trade J.*, **64**, No. 23, 41 (Dec. 5, 1935).

[67] Steinberger, *Textile Research*, **4**, 451, 531 (1934).

[68] See, however, Barkas, *Trans. Faraday Soc.*, **38**, 194 (1942). Compilations on absorption, swelling, and related phenomena may be found also in Mark, "Physik und Chemie der Cellulose"; Stamm, "Colloid Chemistry of Cellulosic Materials," U. S. Department of Agriculture, Misc. Publ. No. 240, Washington (1936); and Valkó, "Kolloidchemische Grundlagen der Textilveredelung."

CHAPTER IV

THE REACTION OF CELLULOSE WITH AQUEOUS ALKALIES

The cellulose fiber is capable of taking up alkali from aqueous alkali solutions; the reactions involved may consist of mere absorption of alkali hydroxide by the fiber, of chemical combination between them, or of both. Whatever the reactions are, they are accompanied by swelling of the fiber. Aqueous alkali containing only a small percentage of alkali enhances the swelling effect which water alone exerts upon the fiber. But strong alkali, ranging from about 12 to 18 per cent, has a considerable effect, depending on various factors. Moreover, with such solutions the swelling of the fiber reaches a maximum; i.e., with alkali stronger than 12 to 18 per cent the swelling tends to diminish and, with sufficiently strong solutions, becomes almost zero.

This peculiar physical behavior of the cellulose fiber in strong aqueous alkali was recognized relatively early. In 1848, John Mercer[1] observed that cotton yarn and fabrics steeped for a short time in an aqueous solution containing about 16–18 per cent sodium hydroxide by weight and subsequently freed of alkali by washing with water had undergone a number of changes which resulted in a new and characteristic behavior. These changes, which soon proved to be of great commercial value, were later collectively termed mercerization after the discoverer.

Mercer recognized chiefly the following characteristic changes: (1) The diameter of the cotton hair had increased and its length had decreased; i.e., the hair had shrunk. (2) The tensile strength of the yarn or fabric had become greater than that of the original materials. (3) The treated materials showed a greater affinity for dyestuffs. (4) The sensitivity of the materials to chemical treatment had increased.

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[1] Parnell, "The Life and Labours of John Mercer," Longmans, Green and Co., London (1866); *News Edition, Am. Chem. Soc.*, **18**, 538 (1940); Marsh, "Mercerizing," Chapman and Hall, Ltd., London (1941).

Many years later (1889) Lowe[2] discovered that the yarn or fabric, if prevented from shrinking by being kept under tension (i.e., in a stretched-out condition) while it was being treated with strong caustic soda solution, would, after washing and drying, show intensified silk-like luster. This effect added greatly to the commercial value of the treatment.

The effect of shrinkage may be demonstrated in a simple way on a piece of silk fabric through which a number of parallel cotton threads are sewed. When such a fabric is steeped in sodium hydroxide solution of "mercerizing" strength, the cotton threads shrink but the silk fabric remains unchanged. The result is a crepe effect.

Shrinkage in length and increase in diameter may be observed on the single cotton hair in strong caustic soda solution under the microscope. The spiral-shaped cotton hair (Fig. 3, p. 12) uncoils until all convolutions disappear. Simultaneously, the fiber becomes thicker and shorter and more cylindrical; the lumen contracts and sometimes almost disappears.

Numerous results of measurements of the changes in diameter and length of single cotton hairs are available.[3] The figures reported by different investigators vary, depending upon the type of cotton used and the conditions employed. Although the uncoiling causes the helical hair to lengthen, under the forces of swelling the diameter enlarges and the fiber shrinks in length. This phenomenon may be explained in the light of the modern concept of submicroscopic fiber structure which, as has been shown, provides for lateral contacts between the micelles (chain bundles) and individual chains, arranged more or less parallel. Swelling forces these units apart in the lateral direction, and the contacts prevent them from expanding in length. Consequently, as its diameter increases the fiber becomes shorter.[4]

The swelling of the cotton fiber in strong caustic soda solution is considerably increased by the addition of small amounts of lyotropic substances, such as urea, thiourea, resorcinol, etc.[5]

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[2] Lowe, British patent 4452 (1890).

[3] Willows, Barrat and Parker, *J. Textile Inst.*, **13**, T229 (1922); Willows and Alexander, *ibid.*, T237; Collins and Williams, *ibid.*, **14**, T287 (1923); Nodder and Kinkead, *ibid.*, **14**, T142 (1923); Calvert, *ibid.*, **21**, T293 (1930); Heuser and Bartunek, *Cellulosechem.*, **6**, 19 (1925); Koshal and Ahmad, *J. Textile Inst.*, **30**, T63 (1939).

[4] Neale, *J. Textile Inst.*, **20**, T373 (1929); **21**, T225 (1930); **22**, T320, 349 (1931).

[5] Katz and Seiberlich, *Rayon Textile Monthly*, **21**, 746 (1940).

METHODS FOR THE DETERMINATION OF THE AMOUNT OF ALKALI TAKEN UP BY CELLULOSE

Mercer, in his studies on the action of aqueous alkali upon cotton, observed that the concentration of sodium hydroxide solution decreased in contact with cellulose. He explained this phenomenon as the result of a chemical combination of cellulose with sodium hydroxide and gave the compound thus formed the formula $C_6H_{10}O_5 \cdot NaOH$. This formula is interpreted to mean that the compound, termed alkali cellulose or soda cellulose, contains 1 molecule of sodium hydroxide per glucose residue.

Mercer's formula was acknowledged by Cross and Bevan and others, whereas Gladstone and, later on, Vieweg arrived at the formula $(C_6H_{10}O_5)_2 \cdot NaOH$—alkali cellulose containing 1 molecule of sodium hydroxide per 2 glucose residues. Whereas Vieweg used Mercer's indirect method, Gladstone attempted to determine the amount of sodium hydroxide taken up by cellulose directly.

Gladstone[6] allowed cotton cellulose to remain in contact with 16–18 per cent sodium hydroxide solution for a certain length of time at room temperature. The product of reaction was freed of the greater portion of excess alkali by pressing, and of the remainder by washing with alcohol. The point at which the alcohol no longer showed the phenolphthalein reaction was taken as that at which all excess alkali had been removed and, consequently, the remaining part of the sodium hydroxide was thought to be in chemical combination with the cellulose. This part was analytically determined and found to correspond to 1 molecule of sodium hydroxide per 2 glucose residues. The same result was obtained when potassium hydroxide solution was used.

Alkali cellulose thus prepared is stable in the dry state, but on being left in air, sodium hydroxide is split off; this is indicated by the fact that the phenolphthalein reaction becomes positive.

The probability that the alkali taken up from the solution is in chemical combination with cellulose is further supported by the observation that the length of treatment has no effect upon the sodium hydroxide content of the product of reaction, it being the same, for example, after 1 and after 18 hours of contact. Moreover, according to Karrer,[7] it makes no difference whether the initial concentration

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[6] Gladstone, *J. Chem. Soc.*, **5**, 17 (1852); see also Hübner and Teltscher, *J. Soc. Chem. Ind.*, **28**, 641 (1909).

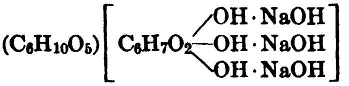
[7] Karrer, *Cellulosechem.*, **2**, 126 (1921); Karrer and Nishida, *ibid.*, **5**, 69 (1924).

of the caustic soda solution is 25 or 40 per cent. In all cases, the amount of sodium hydroxide taken up by cotton cellulose was between 12 and 13 per cent, whereas the theoretical quantity is 12.34 per cent, corresponding to a sodium hydroxide content of a compound $(C_6H_{10}O_5)_2 \cdot NaOH$ of 10.98 per cent.

Karrer's results seem to obviate the criticism which has been raised against Gladstone's method. It has been pointed out that the strong alcohol which was used for removing the excess alkali tends to precipitate alkali and in part fix it upon the fiber surface, thus increasing the quantity of alkali above that which might be bound chemically. However, under such conditions one would expect that the amount of alkali taken up by the cellulose would increase over a certain range of increasing alkali concentration. On the other hand, if more dilute alcohol were used, the possibility exists that the alkali would be dissolved by the water contained in the alcohol and that the extraction of the excess alkali from the alkali cellulose would reach no end point.

No doubt, these two possibilities exist and probably are the reason for the contradictory results which have been reported by investigators using Gladstone's method.[8]

The results of a more recent study[9] seem to confirm these conclusions. Although isopropyl alcohol was found a more efficient washing agent than ethyl or methyl alcohol, the end point was not sharp. In spite of this defect, the quantity of sodium hydroxide taken up by cotton cellulose under these conditions was regarded as the end point of a chemical reaction and the compound was given the formula $(C_6H_{10}O_5)_2 \cdot 3NaOH$—a compound containing three times more sodium hydroxide than the compound obtained by Gladstone's method. This formula has been interpreted to mean that the sodium hydroxide molecules are distributed over the hydroxyl groups of cellulose in accordance with the probability that only about 50 per cent of all the hydroxyl groups are located on the surface of the micelles, whereas the other 50 per cent are located within the micelles[10] and are therefore not accessible to sodium hydroxide. The formula thus implies that sodium hydroxide molecules are attached only to hydroxyl groups on the surface of the micelles and, therefore, has been written in the following form:



$$(C_6H_{10}O_5)\left[C_6H_7O_2\begin{cases}OH \cdot NaOH\\ OH \cdot NaOH\\ OH \cdot NaOH\end{cases}\right]$$

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[8] Rassow and Wadewitz, *J. prakt. Chem.*, **106**, 266 (1923); Heuser, *Z. angew. Chem.*, **37**, 1010 (1924); Heuser and Niethammer, *Cellulosechem.*, **6**, 14 (1925); Trogus and Hess, *Cellulosechem.*, **13**, 81 (1932); Percival, Cuthbertson, and Hibbert, *J. Am. Chem. Soc.*, **52**, 3257 (1930).

[9] Lieser, Henrich, and Fichtner, *Ann.*, **538**, 99 (1939); see also Saito, *Kolloid-Beihefte*, **49**, 365 (1939).

[10] Meyer, *Z. angew. Chem.*, **41**, 945 (1928); *Cellulosechem.*, **11**, 99 (1930).

The glucose residue in the parentheses is representative of the hydroxyl groups which are located in the interior of the micelles, whereas the portion in brackets carries the hydroxyl groups which are exposed on the surfaces of the micelles, all three being available (per glucose residue) for reaction with sodium hydroxide.

This formulation implies further that the ratio of micelle surface to micelle interior is 1 : 1 and that the alkali cellulose which results from the washing with alcohol is completely surface-saturated with sodium hydroxide.

In the light of the evidence that aqueous alkali of mercerizing strength penetrates the interior of the micelles (causing intramicellar swelling of the fiber) and thus should be capable of reacting with interior hydroxyl groups in much the same way as with those exposed on the micelle surfaces, Lieser's interpretation appears rather doubtful.

Vieweg's[11] method consists in allowing a certain quantity of cellulose to stand in sodium hydroxide solution and titrating the alkali which has not been taken up by the cellulose in aliquot parts of the solution. By using solutions of increasing sodium hydroxide content and plotting these concentrations against the grams of sodium hydroxide taken up per 100 grams of cellulose a curve is obtained which shows a distinct inflection when the concentration of the sodium hydroxide solution is about 16 per cent and which does not rise until the concentration of the sodium hydroxide solution reaches about 24 per cent. Within this range the cellulose takes up 12–13 per cent NaOH, which corresponds to 1 molecule of NaOH per 2 glucose residues (theoretically 12.34 per cent). This result seems to indicate that chemical reaction takes place when the alkali reaches a certain minimum concentration. Vieweg's results and those obtained by other investigators[12] are shown in Fig. 27.

That a minimum concentration is required is obviously due to two reasons. Since alkali cellulose decomposes easily in the presence of water, a certain quantity of water in the solution suffices to prevent its formation, but with solutions of higher concentration the decomposing influence of the water is restricted. For we are dealing with an equilibrium reaction. Thus:

$$(C_6H_{10}O_5)_2 + NaOH + H_2O \rightleftarrows (C_6H_{10}O_5)_2 \cdot NaOH + H_2O$$

Secondly, at about the concentration at which the inflection occurs, the swelling of the fiber reaches a maximum and has changed from inter- to intramicellar; further, interior hydroxyl groups have become accessible, so that the sodium hydroxide molecules may select whichever—for reasons as yet unknown—are predestined for the combina-

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[11] Vieweg, *Ber.*, **40**, 3876 (1907); **41**, 3269 (1908).

[12] Heuser and Bartunek, *Cellulosechem.*, **6**, 20 (1925).

tion. Thus, if the reaction is of a chemical nature at all, it becomes complete only at maximum swelling.

This concept of the relationship between the concentration of the sodium hydroxide solution (as well as of other alkali solutions), maximum swelling, and compound formation is largely supported by the results of x-ray analysis.[13] With increasing alkali concentration, the interference lines characteristic of the original (native) cellulose lose their intensity and new lines are observed. At the concentration at which the equivalence of 1 NaOH : 2 $C_6H_{10}O_5$ is reached, the original pattern has disappeared entirely and is replaced by a new diagram, indicating that a chemical compound has been formed. The concentration of the sodium hydroxide solution below which the x-ray pattern remains unchanged was found to be about 9 per cent.[14]

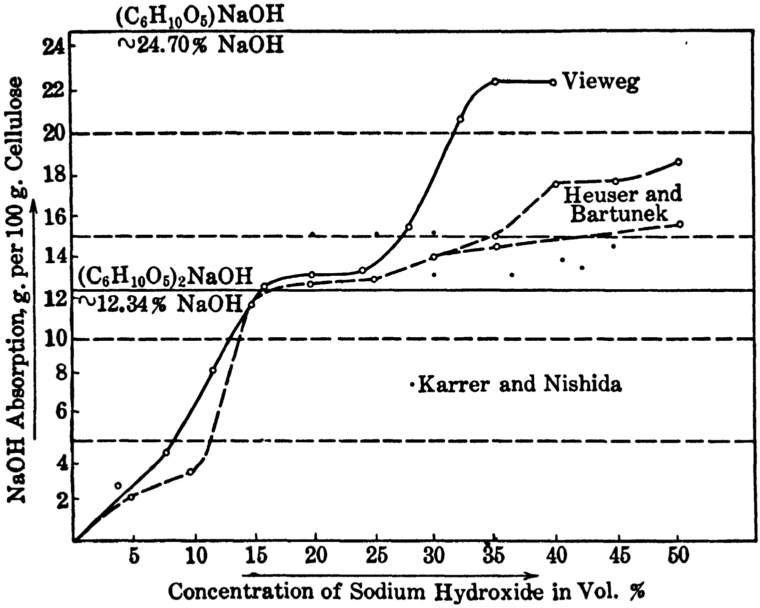

FIG. 27. Sodium hydroxide taken up by cotton from solutions of varying concentrations. Heuser and Bartunek.

To obtain reproducible results with Vieweg's method a number of

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[13] Katz and Mark, *Z. Elektrochem.*, **31**, 105 (1925); Katz and Vieweg, *ibid.*, **31**, 157 (1925); Katz, *Cellulosechem.*, **6**, 35 (1925); von Susich and Wolff, *Z. physik. Chem.*, **B8**, 221 (1930); Schramek and Schubert, *ibid.*, **B13**, 462 (1931).

[14] Hess and Trogus, *Z. physik. Chem.*, **B11**, 381 (1931); Calkin, *J. Phys. Chem.*, **40**, 27 (1936); Katz and Seiberlich, *Pulp Paper Mag. Can.*, **41**, 337 (1940).

precautions have to be observed. Under such conditions, Vieweg's results have frequently been confirmed.[15]

As is seen from Fig. 27, the amount of sodium hydroxide taken up by the cellulose increases further when the concentration of the caustic soda solution rises above 25 per cent, a second inflection being observed at a concentration of about 35 per cent, but the curve remains flat when the concentration is raised still further. The amount of sodium hydroxide taken up during this second inflection period (22.5 per cent) approaches the ratio of 1 NaOH : 1 $C_6H_{10}O_5$ (theoretically 24.7 per cent). Likewise, the formation of this second alkali compound seems to be confirmed by the results of x-ray analysis (see later).

The second inflection has not always been observed; this is probably due to the fact that cellulose adsorbs sodium carbonate which is nearly always present in solutions containing more than 35 per cent sodium hydroxide. In such cases, the second chemical reaction, which the second inflection seems to indicate, would appear to be obscured by the absorption of sodium carbonate.

On the influence of the addition of alcohol[16] and of certain electrolytes[17] to the sodium hydroxide solution see the literature referred to below.

As would be expected, other alkalies, like potassium and lithium hydroxide, react with cellulose in a similar way.

Potassium hydroxide is taken up by cotton to an extent of 16.75 per cent; this is in approximate agreement with the formula $(C_6H_{10}O_5)_2 \cdot KOH$ requiring 17.31 per cent.[18] When Vieweg's method was applied under all possible precautions,[19] the inflection was observed at a concentration of 35 per cent, and at this point the cellulose had taken up 17.31 per cent potassium hydroxide. As is seen from Fig. 28, the inflection is similar to that with sodium hydroxide solution. It is of

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[15] König and Dehnert, *Cellulosechem.*, **5**, 107 (1924); Heuser and Bartunek, *ibid.*, **6**, 19 (1925); Knecht and Platt, *J. Soc. Dyers and Colourists*, **41**, 53 (1925); Karrer and Nishida, *Cellulosechem.*, **5**, 69 (1924); D'Ans and Jäger, *ibid.*, **6**, 137 (1925); Schramek, Schubert, and Velten, *ibid.*, **12**, 126 (1931); Vieweg, *Z. angew. Chem.*, **37**, 1008 (1924).

[16] Vieweg, *Z. angew. Chem.*, **37**, 1008 (1924); *Ber.*, **59**, 1918 (1924); Hess, *Z. angew. Chem.*, **38**, 230 (1925); Heuser and Bartunek, *Cellulosechem.*, **8**, 31 (1927); Rassow and Wadewitz, *loc. cit.*; see also Katz and Vieweg, *Z. Elektrochem.*, **31**, 157 (1925) and Katz, *ibid.*, **32**, 125 (1926).

[17] Miller, *Ber.*, **40**, 4903 (1907); **41**, 4927 (1908); **43**, 3430 (1910); Joyner, *J. Chem. Soc.*, **121**, 2395 (1922); D'Ans and Jäger, *Cellulosechem.*, **6**, 142 (1925); Lieser, Henrich, and Fichtner, *loc. cit.*

[18] See Hübner and Teltscher, *loc. cit.*; Heuser and Niethammer, *loc. cit.*

[19] Heuser and Bartunek, *Cellulosechem.*, **6**, 19 (1925); König and Dehnert, *loc. cit.*, p. 110.

interest that even from a 60 per cent solution, not more than 18.4 per cent potassium hydroxide was taken up, and there was no indication of the formation of a compound of the formula $C_6H_{10}O_5 \cdot KOH$.[20]

The curve for lithium hydroxide (Fig. 28) shows that the inflection occurs at concentrations between 9 and 12 per cent of the hydroxide. With liquors of these concentrations, cellulose had taken up 7.92 per cent lithium hydroxide, whereas 7.39 per cent is required for $C_6H_{10}O_5 \cdot LiOH$.

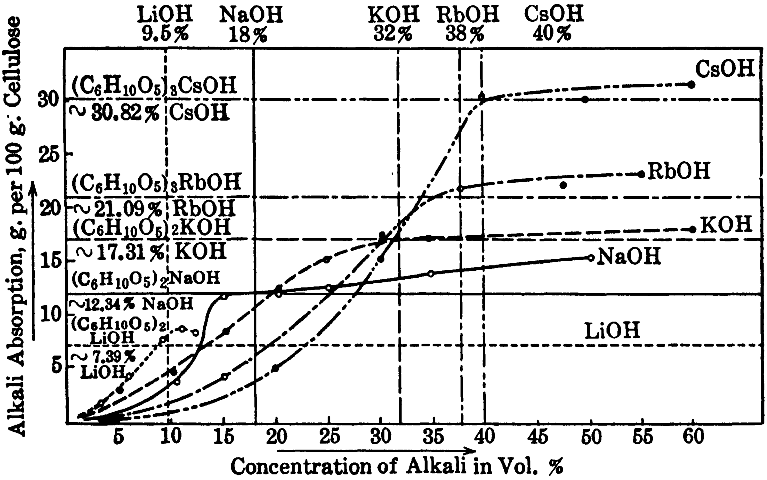

FIG. 28. Alkali hydroxide taken up by cotton from solutions of various alkalies. Heuser and Bartunek.

Heuser and Bartunek's results with lithium hydroxide have not been fully confirmed by other investigators. Thus, König and Dehnert[21] found that, from a 7.6 per cent lithium hydroxide solution, cellulose had taken up as much as 14 per cent LiOH. Similar results were reported by Lottermoser and Radestock,[22] as well as by Saito.[23] These investigators found that the ratio of 1 LiOH to 2 $C_6H_{10}O_5$ is reached before the inflection begins, at which point the ratio is 1 LiOH to 1 $C_6H_{10}O_5$.

However, the results of x-ray analysis seem to show that a compound is formed only when the concentration of the lithium hydroxide solution is above 9 per cent.[24]

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[20] See, however, Percival, Cuthburton, and Hibbert, *J. Am. Chem. Soc.*, **52**, 3257 (1930), who found the amount of potassium hydroxide taken up by cellulose to be in agreement with this formula.

[21] König and Dehnert, *Cellulosechem.*, **5**, 107 (1924); **6**, 1 (1925).

[22] Lottermoser and Radestock, *Z. angew. Chem.*, **40**, 1506 (1927).

[23] Saito, *Kolloid-Beihefte*, **49**, 438 (1939).

[24] Katz, *Cellulosechem.*, **6**, 35 (1925); von Susich and Wolff, *Z. physik. Chem.*, **B8**, 221 (1930); Hess and Trogus, *ibid.*, **B11**, 381 (1931).

Surprisingly, the ratio of 1 molecule of alkali hydroxide to 2 glucose residues changes with cesium and rubidium hydroxide. The inflection appears at a concentration of about 40 per cent in both cases (Fig. 28) and the ratio of alkali hydroxide to glucose residues is in both cases 1 : 3, the compounds having been given the formulas $(C_6H_{10}O_5)_3 \cdot RbOH$ and $(C_6H_{10}O_5)_3 \cdot CsOH$. Whereas 21.09 per cent RbOH and 30.82 per cent CsOH are required, 21–22 and 31–32 per cent, respectively, were found.

It is difficult to explain why, in sodium, potassium and lithium hydroxides, only 1 molecule reacts per 2 glucose residues, whereas in rubidium and cesium hydroxides the ratio is 1 : 3.

This result would make it appear doubtful whether cellulose reacts with the alkalies in stoichiometric proportions. Possibly, we are dealing with complex compounds in the Werner sense. The formation of such compounds seems to be in analogy with the behavior of simple and higher alcohols, of polyalcohols, and of other polyhydroxy-compounds, such as sugars. With many of these compounds, the number of hydroxyl groups participating in the reaction with alkali hydroxide varies with the type of alkali and even with the same alkali.[25]

Some disaccharides display a striking illustration. Whereas lactose adds 1 molecule of potassium hydroxide to its glucose and 2 to its galactose constituent, cellobiose, being isomeric with lactose, takes up only 1 molecule on each of its 2 glucose constituents.[26] The reasons for such preferential reactions are not yet understood.

As has been seen, the concentration at which the alkali compound is formed differs for the various alkalies. This observation seems to be explained by the different swelling effects which the various alkalies exert upon cellulose. In Table 1 the concentrations at which the swelling maxima occur (expressed in percentage increase of fiber width as against the original fiber) are compiled from the experiments previously discussed. The swelling maximum is greatest with lithium and smallest with cesium hydroxide, and the swelling maxima are reached at those concentrations at which inflection occurs, i.e., at which the alkali compounds are formed (Fig. 29).

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[25] Grün and Bockisch., *Ber.*, **41**, 3465 (1908); Grün and Husmann, *ibid.*, **43**, 1291 (1910); Grün, Husmann, and Nassowitsch, *Monatsh.*, **37**, 205 (1916); Kullgren, *Papier-Fabr.*, **24**, 153, 186 (1926); see also Karrer, *Cellulosechem.*, **2**, 124 (1921); Pfeiffer, "Organische Molecülverbindungen," Stuttgart (1927), 2nd ed.

[26] Percival and Ritchie, *J. Chem. Soc.*, 1160 (1934); 1765 (1936); Heddle and Percival, *ibid.*, 1681 (1938).

TABLE 1

ALKALI CONCENTRATIONS AND SWELLING MAXIMA WITH VARIOUS ALKALIES

Alkali	Concentration %	Swelling Maximum %
LiOH	9.5	97
NaOH	18.0	78
KOH	32.0	64
RbOH	40.0	53
CsOH	40.0	47

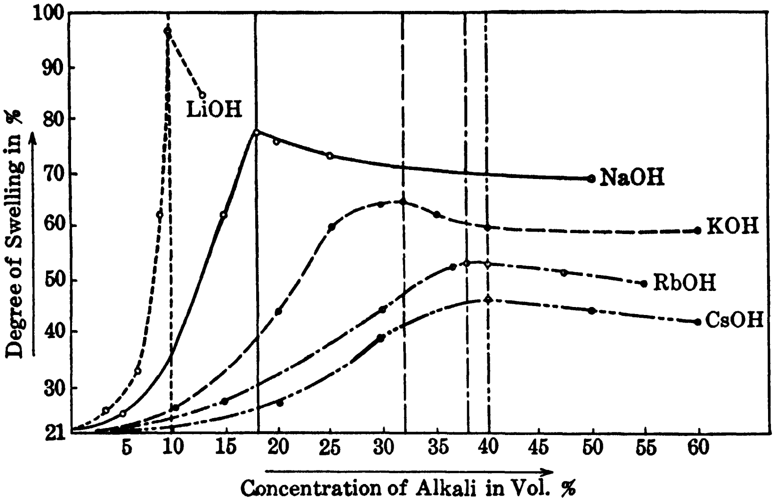

FIG. 29. Relation between swelling of cotton and concentration of various alkali solutions. Heuser and Bartunek.

Collins and Williams[27] have directed attention to the fact that sodium and potassium hydroxide solutions, showing the greatest electric conductivity, exert the greatest swelling effect upon cellulose.

The apparent relation between swelling and conductivity maximum, which has been confirmed for the other alkalies,[28] seems to be in agreement with the rules governing the hydration of the ions. Those ions possessing the smallest atomic volume carry the greatest number of water molecules and *vice versa*. According to Remy,[29] one mole of

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[27] Collins and Williams, *J. Textile Inst.*, **14**, T287 (1923); **15**, T149 (1924).

[28] Heuser and Bartunek, *loc. cit.*, p. 24. Schramek and Christoph (*Kolloid-Beihefte*, **48**, 234 (1938) failed to observe the coincidence of electrical conductivity and maximum swelling with mercerized cellulose. It will be seen later that with mercerized cellulose also other phenomena seem to take a somewhat different course.

[29] Remy, *Z. physik. Chem.*, **89**, 467, 529 (1915).

the various alkali ions combines with moles of H_2O, in infinite dilution, in the following way:

	Li	Na	K	Rb	Cs	H
Moles H_2O	120	66	16	14	13	0*

* Should be changed to 1; see Schramek and Christoph, *Kolloid-Beihefte*, **48**, 227 (1938).

The alkali ion, when combining in some form with the cellulose, carries its water shell along and forces the chain bundles and the individual chains apart, thus causing the fiber to swell. On this hypothesis one would expect that the alkali ion which is capable of carrying the greatest amount of water would produce the greatest swelling of cellulose. Thus, the lithium ion, possessing the greatest water-binding capacity, ought to exert the greatest, and the cesium ion, possessing the smallest water-binding capacity, the smallest swelling effect upon cellulose.

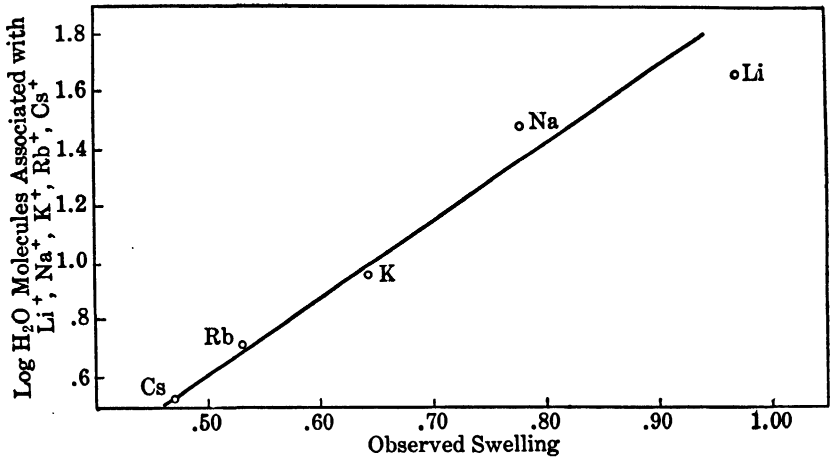

FIG. 30. Relation between water associated with alkali cations and swelling maxima.

This hypothesis[30] is also capable of explaining the fact that the swelling curves pass through a maximum. It is seen from Fig. 29 that swelling decreases most in lithium hydroxide and least in cesium hydroxide solution. On the assumption that the hydration of the ions decreases with increasing concentration of the alkali hydroxide solution, each cation would carry less water in a highly concentrated

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[30] See also Saito, *Kolloid-Beihefte*, **49**, 424 (1939); Lieser, Henrich, and Fichtner, *loc. cit.*

than in a more dilute solution. As a result, a sample of cellulose in the stronger solution would swell to a lesser extent. Since it is conceivable that ions carrying the largest amount of water dehydrate fastest with increasing concentration, swelling may be expected to decrease fastest in a lithium hydroxide and slowest in a cesium hydroxide solution, and this is what actually occurs.

According to Rowland the relationship between swelling and degree of hydration of the cations of the various alkalies may be expressed by a curve plotted from the log of the water molecules associated with the various alkalies against the swelling maxima (Fig. 30).[31] Table 2 shows the number of water molecules associated with the number of cations present in the aqueous alkalies at the critical concentration, the log values, and the swelling maxima taken from Table 1. The figures of the first column of Table 2 were calculated according to the formula

$$\frac{ciw}{a}$$

where c is the concentration of the alkali solution at which maximum swelling was observed,

i is the weight of cation in 1 mole of alkali hydroxide,

a is the atomic weight of the cation,

w is the number of moles of water associated with 1 mole of the cation (Remy's table, p. 73).

TABLE 2

WATER ASSOCIATED WITH VARIOUS CATIONS AND SWELLING MAXIMA OF COTTON

Cations	Number of Water Molecules Associated	Log Water Molecules Associated	Maximum Swelling %
Li	47.0	1.67	97
Na	31.0	1.49	78
K	9.2	.96	64
Rb	5.2	.71	53
Cs	3.3	.52	47

Swelling thus appears to be a logarithmic function of the degree of hydration of the cations of the various hydroxides.

The concentration at which cellulose fibers attain their swelling maximum in sodium hydroxide solution varies a great deal when the experimental data available are compared. Whereas the older literature gives this concentration as ranging between 16 and 18 per cent (by weight), the range of 10–12 per cent

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[31] This is the result of a discussion with Dr. B. W. Rowland of The Institute of Paper Chemistry, Appleton, Wis.

is found frequently in more recent investigations.[32] Unfortunately distinction between concentration by weight and by volume is not always made. Evidently, the range of concentration varies with the type of fiber used, the method of purification, and other still unknown factors, all of which may either favor or reduce the adsorption of alkali on the fiber and thus overshadow the chemical reaction to a greater or lesser extent.

THE REACTION BETWEEN CELLULOSE AND AQUEOUS ALKALI AT LOW TEMPERATURES

The cellulose fiber swells to a greater extent in aqueous alkali of a certain strength if the temperature is lowered. Accordingly, the shrinkage becomes more pronounced and increases quite uniformly as the temperature of the caustic soda solution is lowered.[33]

For producing the same mercerization effect, temperature and concentration of the caustic soda solution are interchangeable to a certain extent. Thus, the effect which is obtained with an 18–25 per cent sodium hydroxide solution at 15–20° may be also produced with a 12.5–16 per cent solution at 2–9°. At a temperature of $-10°$ a 6.5 per cent solution suffices to produce the same effect.[34] For an explanation of the difference, it may be assumed that the cations are capable of carrying larger water shells at lower than at higher temperatures. As a result, at the lower temperature, an alkali solution of lower concentration suffices to bring about maximum swelling of the fiber.

It is probable that the low temperature-low concentration combination results in the same alkali compound that is produced under ordinary conditions, since even a 6.5 per cent caustic soda solution would still supply the quantity of sodium hydroxide necessary to form an alkali cellulose corresponding to the formula $(C_6H_{10}O_5)_2 \cdot NaOH$.

D'Ans and Jäger,[35] who carried out comparable experiments, observed that the inflection occurred at 12 per cent sodium hydroxide concentration and a temperature of 2° instead of at 16 per cent and 23°; but the amount of alkali taken up by the cellulose at the lower temperature was distinctly greater than at the higher temperature. Their findings have been advanced as an argument against the concept of chemical combination, since chemical combination should

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[32] Faust, *Cellulosechem.*, **7**, 154, 155 (1926); D'Ans and Jäger, *loc. cit.;* Lottermoser and Radestock, *Z. angew. Chem.*, **40**, 1506 (1927); Richter and Glidden, *Ind. Eng. Chem.*, **32**, 480, 1122 (1940).

[33] Willows, Barratt, and Parker, *J. Textile Inst.*, **13**, T229 (1922); Clibbens, Geake, and Ridge, *ibid.*, **21**, T85 (1930); Saito, *Kolloid-Beihefte*, **49**, 388 (1939).

[34] Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 34.

[35] D'Ans and Jäger, *loc. cit.*, pp. 137, 141 (1925).

be independent of the temperature.[36] However, in this case also, the chemical reaction is probably obscured by the phenomenon of adsorption.

Inversely, the mercerization effect becomes the less pronounced, the higher the temperature of the mercerizing solution, and it fails to appear altogether in hot solutions, although x-ray analysis has been interpreted to indicate that, for example, with a 25 per cent sodium hydroxide solution at 75° partial mercerization has occurred.[37] With such a strong solution and at such a relatively high temperature, the cellulose may be partially degraded. If so, it would appear to make it difficult to draw unequivocal conclusions from the x-ray pattern.

Chemical Reaction Versus Adsorption

Vieweg's change-in-titer method as a means of determining the amount of alkali bound by cellulose has been criticized because this method does not consider the amount of water which cellulose is said to take up preferentially from an alkali solution, and which would result in a higher alkali concentration in the liquid surrounding the alkali cellulose. On the assumption that cellulose actually takes up such "nondissolving" water (water which dissolves none of the alkali) from the solution, two processes would counteract each other to a certain extent: the combination of sodium hydroxide with cellulose, which would result in a decrease of the alkali concentration of the solution, and the preferential absorption of water by cellulose from the solution, which would result in an increase of the alkali concentration of the surrounding liquid. In other words, the increase in alkali concentration due to loss of water would compensate for a part of the loss of alkali which is due to the combination with the cellulose. Thus, the "true" amount of alkali taken up by the cellulose would be greater than it would be if the concentration of the alkali in the liquid within the cellulose and in the liquid surrounding it were the same. The Vieweg method, being based on this latter assumption, would thus yield only the "apparent" amount of alkali taken up by cellulose.

Various ways have been suggested for determining the water preferentially absorbed by the cellulose fiber from an aqueous alkali solution of mercerizing strength, and the data thus obtained have been utilized for calculating the "true" amount of alkali bound. Measure-

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[36] Bancroft and Calkin, *Textile Research*, **4**, 163 (1934).

[37] Sisson, *J. Phys. Chem.*, **44**, 513 (1940); Sisson and Saner, *ibid.*, **45**, 717 (1941).

ments of this kind were carried out by Schwarzkopf[38] who made use of Schreinemakers' proportionality method, using sodium chloride as the auxiliary substance.

Schwarzkopf's results obtained with ramie fiber and sodium hydroxide solution at 20.5° are shown in Fig. 31. The curve representing the nondissolving water shows a maximum when the alkali concentration of the caustic soda solution is about 13 per cent, corresponding to 6 moles of water bound per glucose residue or to 68 grams of water per 100 grams of cellulose. At about the same initial alkali concentration (12.5 per cent) both curves—that representing the apparent and that representing the true amount of alkali bound—change their

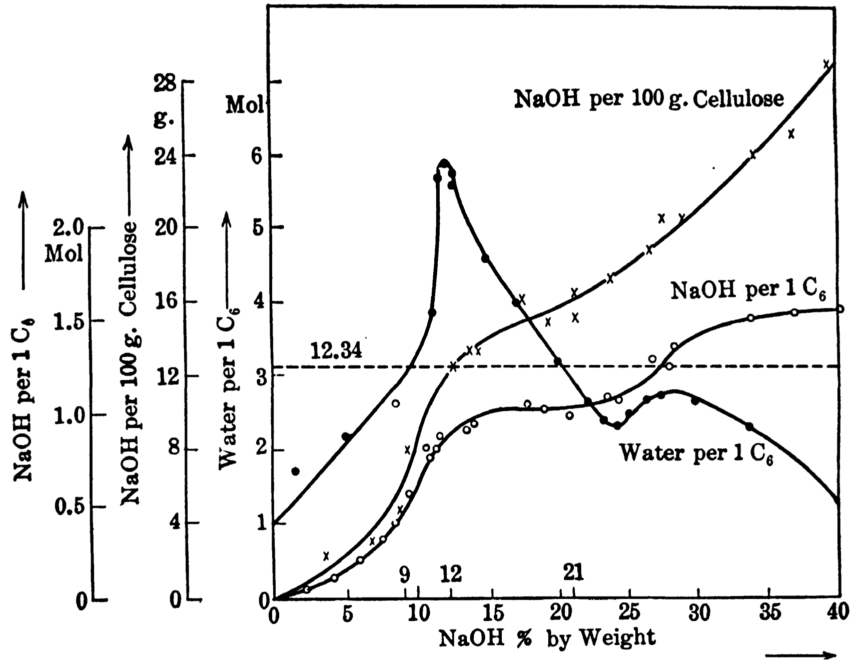

FIG. 31. "Apparent" and "true" amounts of alkali bound and nondissolving water against concentration of sodium hydroxide solution. Ramie fiber. Schwarzkopf. "NaOH per 100 g. cellulose" represents the apparent amount of alkali bound, "NaOH per 1 C_6," the true amount, and "Water per 1 C_6," the amount of the nondissolving water. The horizontal line (12.34) represents the flat portion of the Vieweg curve (apparent amount of alkali bound).

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[38] Schwarzkopf, *Z. Elektrochem.*, **38**, 353 (1932); see also Hess, Trogus, and Schwarzkopf, *Z. physik. Chem.*, **A162**, 187 (1932); van der Want, *Chem. Weekblad*, **28**, 507 (1931).

direction. The inflection, however, is much more pronounced with the curve representing the true amount of alkali bound. Obviously, the cellulose takes up the maximum of nondissolving water in the state of maximum swelling which in turn coincides with the inflection, i.e., with the formation of the alkali compound.

However, if the true amount of alkali bound by the cellulose within the inflection is calculated from the experimental data of the curve, it is found to correspond to 1 molecule of NaOH per 1 glucose residue ($C_6H_{10}O_5 \cdot NaOH$); i.e., the alkali compound holds a quantity of sodium hydroxide which is twice as high as that in the alkali compound derived from the Vieweg method.

It has been pointed out[39] that clarification of the alkali cellulose problem may be expected only if it can be shown that the reaction represents an equilibrium which is entirely reversible. This is not the case with cellulose in its natural form. The mercerization which the fiber undergoes during the treatment with the strong alkali solution changes its behavior so that the reverse process takes place on a cellulosic material which is different from the initial sample.

If, however, mercerized cellulose is subjected to the alkali treatment, in which event the reaction is regarded as representing a reversible equilibrium,[40] no inflection in the curve corresponding to the true amount of alkali taken up by the fiber is observed. Rather, the amount of alkali steadily increases as the initial alkali concentration of the solution is increased. The same observation was made when cuprammonium rayon, another representative of cellulose in its hydrate modification, was the starting material. The steady increase in the amount of alkali taken up by the fiber seems to indicate that the alkali does not react with the cellulose chemically but is merely adsorbed, unless again the assumption is made that the adsorption of alkali, which obviously can never be entirely eliminated, obscures the chemical reaction under the prevailing conditions. Particularly is it difficult to eliminate adsorption when mercerized cellulose is the starting material. As will be seen more in detail later, on mercerization the original space lattice of cellulose changes into one which is capable of accommodating larger quantities of sodium hydroxide within its inter- and intramicellar spaces. Hence, it is conceivable that cellulose, being in this condition from the start, is capable of merely adsorbing

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[39] See for example Valkó, "Kolloidchemische Grundlagen der Textilveredlung," p. 180.

[40] The investigations of Trogus [*Z. physik. Chem.*, **B32**, 39 (1933)] and of Schramek and Görg [*Kolloid-Beihefte*, **42**, 302 (1935)] seem to indicate that, even with mercerized cellulose, the reaction is not entirely reversible.

greater amounts of sodium hydroxide and thus of entirely obscuring the chemical reaction,[41] a reaction which, moreover, is confined to only relatively few of the total number of hydroxyl groups.

Another method of ascertaining the quantity of nondissolving water is based upon the assumption that it is possible by centrifuging to remove from a suspension of cellulose in strong aqueous alkali the excess solution but to retain the nondissolving water together with the reacting alkali. The amount of nondissolving water and of reacting alkali may then be determined by analyzing the residue after centrifuging.

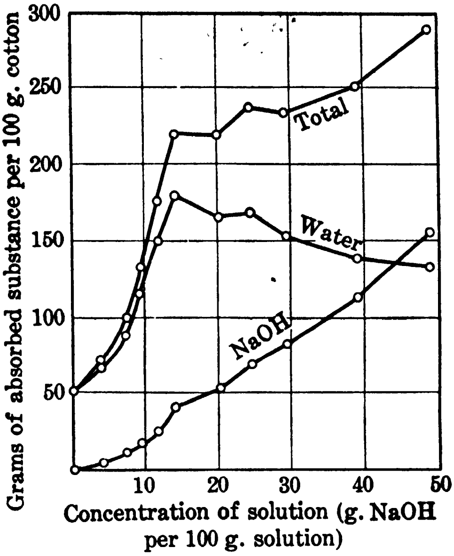

FIG. 32. Total solution, water and sodium hydroxide retained by cotton after centrifuging, at increasing sodium hydroxide concentrations. Coward and Spencer.

This method, which seems to have been used first by Leighton,[42] was improved by Coward and Spencer,[43] particularly by using a more efficient centrifuge. Their results are shown in Fig. 32. The curve representing the amount of water retained (the nondissolving water) reaches a maximum when the initial alkali concentration is about 14 per cent. This result is thus in good agreement with the findings of Schwarzkopf. It is seen also that the maximum water retained by

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[41] Schramek and Görg, *loc. cit.*, p. 304; Saito, *Kolloid-Beihefte*, **49**, 413 (1939); Schramek, *Kolloid-Z.*, **94**, 92 (1941).

[42] Leighton, *J. Phys. Chem.*, **20**, 32 (1916).

[43] Coward and Spencer, *J. Textile Inst.*, **14**, T28, 32 (1923).

the cotton coincides with the break shown by the curve representing the total solution retained. Evidently, with a solution of 14 per cent and further increase of the alkali concentration, the total solution retained increases only slowly because the amount of water retained has passed through its maximum value.

Again, the curve representing the sodium hydroxide retained shows no inflection but in general steadily ascends as the initial concentration of the alkali solution is increased. This slope of the curve has been interpreted to mean that no chemical reaction occurs and that the retention of alkali by the fiber is the result of mere adsorption.

The centrifugal method was also applied by Bancroft and Calkin.[44] Their results are shown in Fig. 33. For comparison Vieweg's curve is inserted into the figure. It is seen that, whereas the change-in-titer method at 16 per cent initial concentration shows 0.5–0.6 moles sodium hydroxide to be taken up per glucose residue, the centrifugal method yields as much as 2.0 moles or about four times more than Vieweg's method.

At about the same concentration, the water absorbed (nondissolving water) reaches a maximum. This point thus coincides with that initial concentration of the caustic soda solution at which the inflection in Vieweg's curve occurs. It will also be noticed that the curve for total alkali adsorbed shows a change of direction. This change appears to be significant since it coincides with the change of the x-ray pattern, the latter approaching that which is characteristic for alkali cellulose.

Nevertheless, Bancroft and Calkin have interpreted the curve for total alkali adsorbed to show "no signs of the occurrence in mass of any definite chemical compound in stoichiometric proportions between caustic soda and cellulose."[45]

A check on the x-ray findings under more exactly controlled conditions showed that the x-ray pattern of the residue after centrifuging changed between concentrations of 13.4 and 14.1 per cent sodium hydroxide. Moreover, this result was found to be in agreement with that obtained after the residue had been freed of alkali by washing and dried in the air. The alkali concentration of the mercerizing solution at which the x-ray pattern of the alkali-free cellulose hydrate changes was found to be 12.8 per cent, and the new pattern became complete at concentrations between 14.3 and 14.4 per cent.[46]

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[44] Bancroft and Calkin, *Textile Research,* **4,** 119, 159 (1934); *J. Phys. Chem.,* **39,** 1 (1935).

[45] Bancroft and Calkin, *loc. cit.,* p. 8.

[46] Calkin, *J. Phys. Chem..* **40,** 28 (1936).

Bancroft and Calkin's interpretation as derived from the application of the centrifugal method is thus in contrast to the interpretation of the x-ray findings. But it appears fairly safe to conclude that this contradiction is explained by the inability of the centrifugal method to reveal the occurrence of the chemical reaction with sufficient accuracy. As long as methods are used which are obviously incapable of eliminating the well-known ability of cellulose to retain alkali and other electrolytes merely mechanically, there seems to be little hope of recognizing the chemical reaction.[47] But the significance of the x-ray findings can hardly be overlooked. In fact, Calkin[48] later recognized this significance and has interpreted his results to show that the two possibilities—formation of a solid solution and adsorption—are ruled out and that the only possibility which is in agreement with the x-ray findings is the chemical combination of alkali and cellulose.

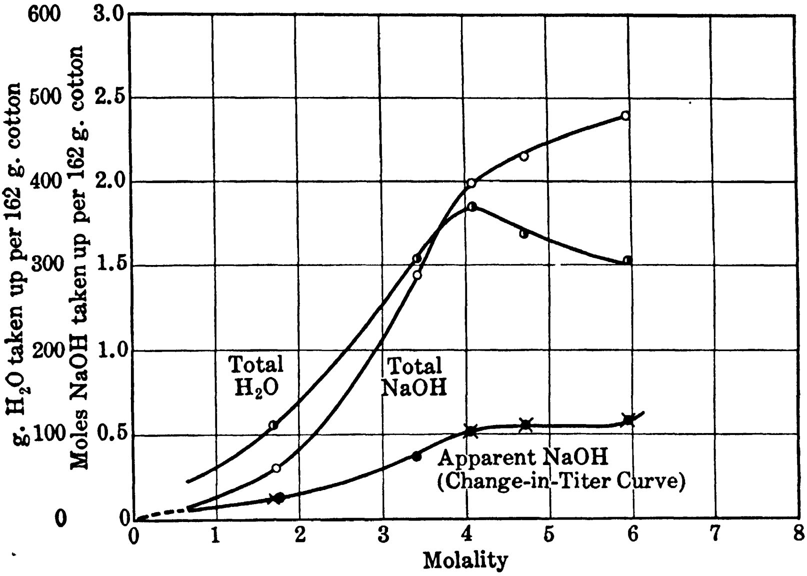

FIG. 33. Sodium hydroxide and water taken up by standard cotton cellulose. Bancroft and Calkin.

Whether, as Calkin assumes, a cellulosate is formed or whether cellulose adds alkali hydroxide to form a complex compound—a behavior analogous to that of other polyhydric alcohols, sugars, etc.—cannot be decided by x-ray analysis. Nor can it be decided by chemical an-

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[47] See also Karrer, "Polymere Kohlenhydrate," p. 152.

[48] Calkin, *loc. cit.*, p. 33.

alysis. For clarification of the issue—chemical compound formation versus adsorption—a distinction between the two types of chemical compounds seems to be irrelevant. Vieweg's method, although not yielding the true quantity of alkali taken up by the cellulose, seems, however, to be free of the error which is introduced by the centrifugal method and thus to reveal the occurrence of a chemical reaction which the other method obscures.

Attempts to elucidate the reaction between cellulose and aqueous sodium hydroxide and to ascertain the chemical composition of the product of reaction have also been made by applying Gibbs' phase rule to the cellulose-sodium hydroxide-water system.[49] D'Ans and Jäger[50] have interpreted their results to show that an alkali compound of a composition corresponding to $(C_6H_{10}O_5)_2 \cdot NaOH$ is formed within the range of an initial concentration between 16 and 24 per cent and of a second compound, $C_6H_{10}O_5 \cdot NaOH$, which appears at a concentration of 36 per cent sodium hydroxide.

Hess, Trogus, and Schwarzkopf,[51] assuming the existence of two solid phases (cellulose and cellulosate), regard the evaluation of the results of the phase rule application as justifying the existence of at least two alkali compounds, both probably showing a ratio of $NaOH:C_6H_{10}O_5$ as 1 : 1; one of these, "NaCell I," however, possesses 4–8 molecules of chemically bound water, whereas the other, "NaCell II," is water-free or has less chemically bound water.

Bancroft,[52] obviously in an attempt to reconcile his earlier concept of adsorption with the results of x-ray analysis, allows for only one solid phase, namely, sodium cellulosate adsorbed on cellulose. On the assumptions that each cellulosate modification formed adsorbs the other and that an adsorbed substance can give an x-ray diagram, any discrepancies between the results of phase rule evaluation and x-ray analysis would in fact disappear.

A technique similar in principle to that involved in the centrifugal method has been employed by Neale.[53] The difficulty of separating the entrained liquid from a mass of fibrous material was overcome by the use of cellulose in the form of cellophane. Strips of this sheet material were steeped in sodium hydroxide solutions of increasing concentration for 2 days at 25°. The swollen sheets were then removed, rapidly dried by blotting with filter paper,[54] and weighed ("swollen weights," comprising the cellulose, the nondissolving water, and the alkali retained). After the alkali taken up by the cellophane had been determined by titration with hydrochloric acid, the cellulose sheets were

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[49] Kolthoff, *Pharm. Weekblad,* **58,** 46 (1921).

[50] D'Ans and Jäger, *Cellulosechem.,* **6,** 146 (1925).

[51] Hess, Trogus, and Schwarzkopf, *Z. physik. Chem.,* **A162,** 189 (1932).

[52] Bancroft, *J. Phys. Chem.,* **40,** 43 (1936).

[53] Neale, *J. Textile Inst.,* **20,** T373 (1929); **21,** 225 (1930).

[54] A similar technique had previously been applied by Beadle and Stevens [*8th Int. Congress Appl. Chem.,* **13,** 25 (1912)] to cuprammonium rayon.

washed for several days in distilled water to remove sodium chloride, dried and weighed. The results are shown in Fig. 34.

It is seen from the figure that the maximum amount of water retained and, hence, the maximum swelling, is observed at an initial alkali concentration of 11.3 per cent, the quantity of water retained amounting to about 50 moles per glucose residue. At about the same concentration the curve for the alkali taken up shows a change in direction in much the same way as subsequently observed by Bancroft and Calkin. This general agreement could be anticipated from the similarity of the techniques employed.

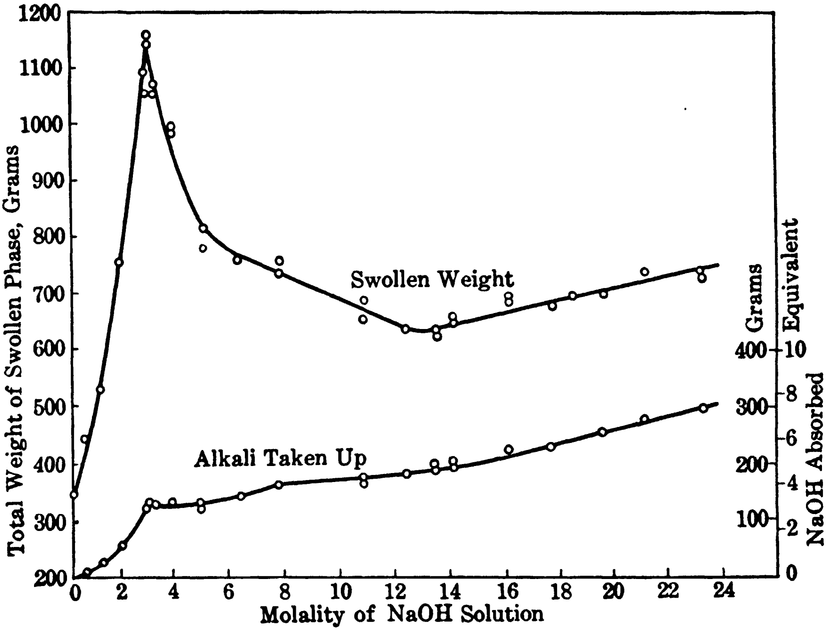

Fig. 34. Sodium hydroxide and water taken up by cellophane. Neale.

Neale has interpreted his results as supporting the following hypothesis for the mechanism of the reaction between cellulose and aqueous alkali hydroxide. Cellulose in the presence of a strong base reacts as a weak acid,[55] its hydroxyl groups yielding small amounts of hydrogen ions. These hydrogen ions react with the hydroxyl ions

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[55] See also Katz, *Z. Elektrochem.*, **32**, 269 (1926); Katz in Hess, "Die Chemie der Cellulose." This weak acid character of cellulose is not to be confused with the acidity of cellulose which is caused by the presence of carboxyl groups (see p. 429). This acidity may, of course, increase the amount of alkali taken up by the cellulosic material and thus influence the results to a varying degree.

of the alkali to form water and a salt (sodium cellulosate) which is practically entirely dissociated into its sodium and hydroxyl ions. In such a system, cellulose functions as a membrane penetrable by the water and alkali molecules. The extent of salt formation should depend on the concentration of free hydroxyl ions in the gel phase, and this, in turn, should be determined by the Donnan equation of membrane equilibrium.[56] Thus, cellulose would be in a state of osmotic equilibrium with the surrounding liquid. Swelling, then, as Neale puts it "arises from the osmotic water attraction of the gel phase, owing to the concentration of ions, resulting from salt formation, being greater than that of the external solution. This also explains why the swelling at first increases up to a maximum, and then falls as the alkali concentration is increased. In the first stage—that of increasing swelling—the amount of alkali 'fixed' by salt formation is increasing rapidly, and so the osmotic water attraction of the gel increases more rapidly than that of the solution. During the second stage of increasing concentration, the extent of cellulose salt formation is virtually complete and the increasing osmotic water attraction of the solution withdraws water from the gel phase, i.e., the cellulose is less swollen."

With this hypothesis Neale also explains why, as has been seen, swelling increases with lower temperature. At the lower temperature the hydrolysis of the cellulosate is less pronounced; hence, the amount of salt formation and, consequently, of swelling should be greater.

The hypothesis appears well supported by the good agreement found between the calculated amounts of alkali retained by the cellophane and the values actually ascertained by analysis.

Obviously, the amount of sodium hydroxide taken up by cellulose from an aqueous solution is the sum of two factors: (1) the sodium corresponding to the partial conversion of cellulose into the ionized sodium salt, and (2) the excess alkali, the amount of which is determined by the Donnan equation of membrane equilibrium. Both the amount of sodium present as sodium salt and the concentration of excess alkali present in the cellulose phase increase steadily with the alkali concentration of the solution, the actual amount of the excess alkali being dependent also on the water absorption and on the volume of the swollen cellulose.

The more or less flat portions of the curve representing total alkali taken up are, according to Neale, to be attributed to a fortuitous balance between the rising concentration of alkali and the decreasing

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[56] See also Neale, *J. Soc. Chem. Ind.*, **50**, 177T (1931).

swelling of the cellulose and not to a discontinuous compound formation.

With reference to the conclusion drawn by Vieweg and his successors from the change-in-titer method, Neale points out that they rest on the assumption that the uncombined sodium is at the same concentration relative to water in the cellulose and in the liquid phases. Only on this basis would the preferential absorption represent the combined sodium. If, however, the concentration of uncombined alkali in the cellulose is not equal to that in the surrounding liquid but is determined by the Donnan equation, it follows algebraically that the amount of salt formation is not equal to the preferential absorption, but, at high concentration, where the amount of combined sodium is small in relation to the total alkali absorption, is approximately twice the preferential absorption. For these reasons Neale holds that the composition of the compound formed is more probably $C_6H_{10}O_5 \cdot NaOH$ and not $(C_6H_{10}O_5)_2 \cdot NaOH$.[57]

HEAT OF REACTION

The action of sodium hydroxide on cellulose is accompanied by the development of considerable heat, this heat of reaction amounting to much more than when cellulose is allowed to swell in water alone. This difference is noticeable even with low concentrations of alkali. Barrat and Lewis [58] have determined the heats of reaction on kier-boiled cotton in sodium hydroxide solutions of increasing concentration at 19°. Whereas the heat of reaction of this cellulosic material in pure water was 3.6 calories per gram of cotton, it amounted to 6.7 calories when the alkali concentration was only 7.4 per cent by weight. In general it was found that the heat of reaction increased with increasing alkali concentration. This observation was confirmed and extended over a wider concentration range by Neale.[59]

According to Neale the heat of reaction evolved is composed of (1) the positive heat of neutralization of the OH^- ions of the sodium hydroxide by the H^+ ions of the cellulose, (2) the negative heat of dissociation of the salt (cellulosate) formed, and (3) the positive heat of dilution of the sodium hydroxide solution. This dilution is a re-

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[57] See the criticism by Hess, Trogus, and Schwarzkopf, *loc. cit.*, p. 202, and the comments by Valkó, "Kolloidchemische Grundlagen der Textilveredlung," p. 186.

[58] Barrat and Lewis, *J. Textile Inst.*, **13**, T113 (1922).

[59] Neale, *J. Textile Inst.*, **20**, T373 (1929); see also Chilkin, *Chem. Abstr.*, **24**, 3899 (1930).

sult of the removal of alkali from the solution by the cellulose and of the liberation of water of reaction as the cellulosate is formed.

The observation that heat of reaction continues to be developed over the whole range of alkali concentration, i.e., that it does not cease to be developed when the cellulosate formation has come to an end, may possibly be explained as follows. Whereas the heat of neutralization must come to a standstill because salt formation ceases, the heat of dilution, diminished only by the fraction which is due to dilution with the water of the reaction, continues to be developed as the concentration of the sodium hydroxide solution is increased because increasing quantities of sodium hydroxide are taken up by the cellulose (see Fig. 34).

The values for the total heat of reaction are, of course, dependent to a considerable extent upon the moisture content of the samples investigated. Moist samples may be expected to develop less heat on mercerization than dry material because the heat of wetting[60] (the heat developed on contact of cellulose with water only), depending upon the extent of the wetting, is more or less completely absent. In order to eliminate all the heat of wetting one may, in accordance with Neale's procedure, allow the samples to come to equilibrium with the water vapor of the alkali solution to be subsequently used.

Okamura[61] has subjected dried samples (mercerized and unmercerized ramie fiber) to the action of water and aqueous sodium hydroxide solution. The heat of wetting thus determined separately was subtracted from the total heat developed on mercerization. The following figures were obtained. (The concentration of the sodium hydroxide solution was 9 per cent.)

	Heat of Wetting cal./g.	Heat of Mercerization Corrected, cal./g.
Ramie	3.66	6.0
Ramie, mercerized	6.09	8.0

The difference in heat of mercerization, which is maintained as the concentration of the caustic soda solution is increased, is obviously due to the greater reactivity of cellulose in its mercerized (hydrate) form; a greater quantity of sodium hydroxide is taken up, resulting in greater dilution of the solution and, hence, in greater heat of dilution.

Morrison, Campbell, and Maass'[62] measurements seem to afford the most accurate calorimetric data on the up-take of alkali by cellulose; they include measurements of standard cotton cellulose in sodium hydroxide, as well as in lithium and potassium hydroxide solutions. The measurements in sodium hydroxide solution over the same range

[60] Argue and Maass, *Can. J. Research,* **12,** 564 (1935); Morrison, Campbell, and Maass, *ibid.,* **18B,** 168 (1940).

[61] Okamura, *Naturwissenschaften,* **21,** 393 (1933).

[62] Morrison, Campbell, and Maass, *Can. J. Research,* **16B,** 195 (1938).

of concentration (10.70–15.20 per cent sodium hydroxide by weight) and calculated to the same basis are in excellent agreement with Neale's results. This is seen from Table 3.

TABLE 3

NEALE'S HEAT OF REACTION VALUES COMPARED WITH RESULTS OBTAINED BY MORRISON, CAMPBELL, AND MAASS (SODIUM HYDROXIDE SOLUTION. COTTON.)

Sodium hydroxide, % by weight	8.08	10.70	13.90	15.20
Neale's values calculated to basis of Morrison, *et al.*—calories	12.92	16.85	25.72	27.84
Morrison, *et al.*, values—calories	14.50	16.90	24.80	27.82

Morrison, Campbell, and Maass' results for the three types of alkali are shown in Fig. 35. Although the curves for potassium and lithium hydroxide cover only a comparatively small range of con-

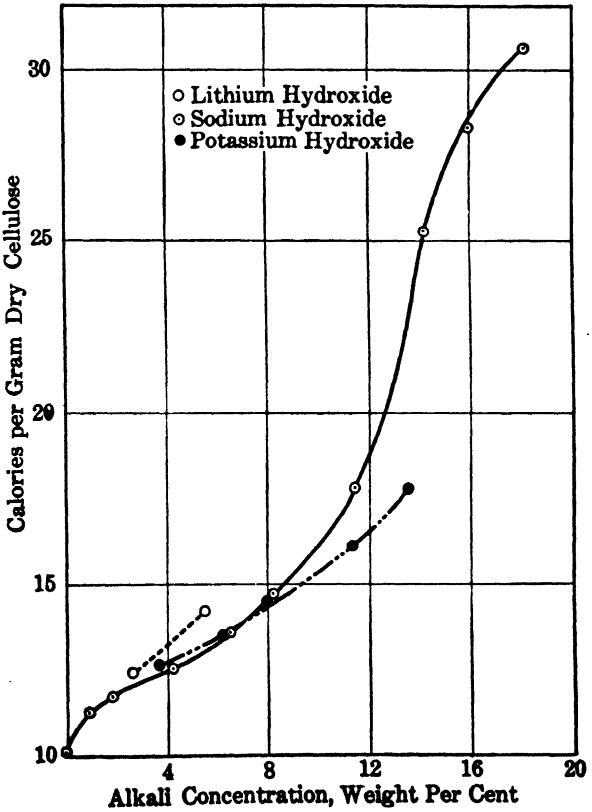

FIG. 35. Heat of reaction produced by the action of various alkalies on standard cotton. Morrison, Campbell, and Maass.

centration, the differences are obvious. Lithium hydroxide evolves the smallest and potassium hydroxide the largest amount of heat, whereas the curve for sodium hydroxide lies in between.

The difference in the evolution of heat is explained in the light of Neale's hypothesis as follows. The cations of the three alkalies are hydrated in decreasing order as follows: Li^+, Na^+, K^+; and this difference in the degree of hydration may be expected to influence the availability of their OH^- ions. The most hydrated Li^+ ion would partly prevent its OH^- ions from forming water with the hydrogen from the weakly acidic cellulose. Further, the ease with which the cation could attach itself to the cellulose, subseqeunt to the neutralization process, would be influenced in the same direction by hydration. These considerations would explain the differences in the quantity of heat evolved by the three alkalies.

The shape of the heat of reaction curve with sodium hydroxide also seems to be in agreement with Neale's speculations on the increase and decrease of the swelling of cellulose under the influence of aqueous sodium hydroxide of increasing concentration.

A striking difference exists between the heats evolved from ordinary and from mercerized cotton.[63] The results are shown in Fig. 36.[64] (See also Okamura's results above.) According to Morrison, Campbell, and Maass, the measured heat of adsorption of standard cellulose may be considered to be made up of the heat of adsorption of sodium hydroxide, that of water, and that involved in irreversible changes of the cellulose structure (crystal lattice) and the formation of any new surface (see later). On the other hand, the measured heat of adsorption of mercerized cotton may be considered to be made up merely of the heat of adsorption of sodium hydroxide and of water, any heat involved in structural and surface changes having been eliminated.

The difference between the two values has been termed "heat of mercerization" (not to be confused with the total heat of adsorption of alkali of mercerizing concentration). This difference represents the heat involved in any permanent irreversible changes that occur when cotton cellulose is mercerized. This heat is of an endothermic nature as may be seen from Table 4. Morrison, Campbell, and Maass have explained the endothermicity of the "heat of mercerization" as follows: Obviously, the change into another crystal form and the

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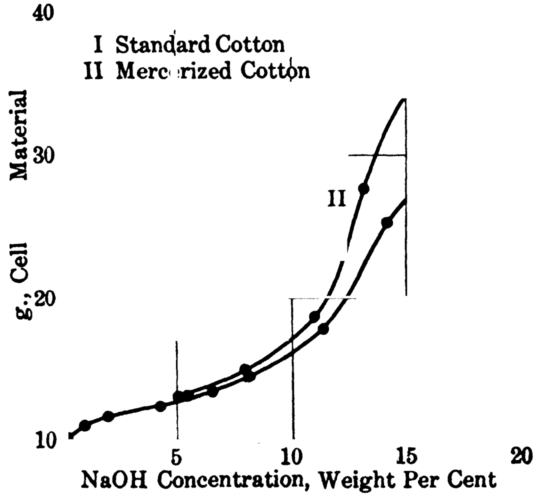
[63] Morrison, Campbell, and Maass, *Can. J. Research*, **18B**, 168 (1940).

[64] The mercerizing procedure was carried out in alkali solutions of the same concentration as that used for measuring the heat of adsorption. Thus the data in Fig. 36 pertain to a number of mercerized cotton samples prepared by treatment with alkali solutions of concentrations as shown on the abscissa.

TABLE 4

HEAT OF ADSORPTION OF SODIUM HYDROXIDE BY STANDARD COTTON AND BY MERCERIZED COTTON AND THE "HEAT OF MERCERIZATION"

Sodium Hydroxide % by weight	Heat of Adsorption of NaOH on Standard Cotton Cal./g. cotton	Heat of Adsorption of NaOH on Mercerized Cotton Cal./g. cotton	"Heat of Mercerization" Cal./g. cotton
5.04	12.96	13.19	−0.23
8.00	14.41	15.02	−0.61
11.00	17.30	18.63	−1.33
13.18	22.57	27.69	−5.12
15.69	22.80	35.22	−6.42
18.14	30.56	37.19	−6.63



I. Standard cotton.
II. Mercerized cotton.

FIG. 36. Heats of adsorption of sodium hydroxide by standard and by mercerized cotton. Morrison, Campbell, and Maass.

development of a new surface require energy, and this change of energy, if it comes from heat, would give rise to an endothermic effect. This view appears to be supported by the observation[65] that mercerized cotton has a higher heat capacity (specific heat) than unmercerized cotton; this indicates more internal or potential energy, and heat would have to be adsorbed for the cellulose to assume such a

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[65] Shipley, Maass, and Campbell, unpublished data, quoted by Morrison, Campbell, and Maass, *Can. J. Research*, **18B**, 175 (1940).

condition. The endothermic "heat of mercerization" is probably the heat so employed.

This interpretation seems to be in good agreement with the observation that, as seen in Table 4, the negative heat of mercerization, i.e., the potential energy, increases with increasing concentration of the mercerizing alkali, obviously because the degree of mercerization—the change into another crystal modification and the development of a new surface—increases until the reaction is completed.

Recent x-ray studies of the action of alkali hydroxide solutions on cellulose seem to indicate that a variety of alkali cellulose compounds is formed, depending essentially upon the alkali concentration and the temperature. The various compounds are classified as alkali cellulose I, alkali cellulose II, etc. (NaCell I, NaCell II, etc.). This classification is the result of an attempt to relate the various x-ray diffraction patterns of the alkali-containing samples to their chemical composition. As for details, the reader is referred to the literature.[66]

THE REACTION WITH CELLULOSE IN SOLUTION

The hydroxyl groups of cellulose may be expected to be more accessible to alkali if the cellulose is dissolved. Depending upon the degree of dispersion, the solution may contain cellulose in the form of micelles or of individual chain molecules. In the latter case, all three hydroxyl groups per glucose residue may be expected to react to form the corresponding alkali compound.

A solution of cellulose suitable for an investigation of this type may be prepared by dispersing coagulated cellulose, freshly precipitated from viscose by boiling with water, in sodium hydroxide solution.[67] Such regenerated cellulose was found to give a stable solution within a concentration range of 4.8 and 14.4 per cent, i.e., on dilution to concentrations below 4.8 per cent or on increasing concentrations to above 14.4 per cent, the regenerated cellulose preparations again became insoluble. Within the soluble range, however, the alkali compounds could be precipitated from the solution by adding alcohol.

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[66] Hess and Trogus, *Z. physik. Chem.*, **B11**, 381 (1931); Trogus and Hess, *Cellulosechem.*, **13**, 81, 84 (1932); **15**, 1 (1934); Trogus, *Z. physik. Chem.*, **B22**, 139 (1933); Hess and Trogus, *Z. Elektrochem.*, **42**, 696, 704 and 710 (1936); Hess and Gundermann, *Ber.*, **70**, 527 (1937); Schwarzkopf, *Cellulosechem.*, **12**, 33 (1931); *Z. Elektrochem.*, **38**, 353 (1932); Hess, Trogus, and Schwarzkopf, *Z. physik. Chem.*, **A162**, 187 (1932). See also Schramek, *Kolloid-Beihefte*, **40**, 88 (1934); Schramek and Görg, *ibid.*, **42**, 302 (1935); Schramek and Sukolowsky, *Kolloid-Z.*, **80**, 129 (1937); Sobue, Kiessing, and Hess, *Z. physik. Chem.*, **B43**, 309 (1939); Sisson and Saner, *J. Phys. Chem.*, **45**, 717 (1941).

[67] Koets and Kruyt, *Kolloid-Beihefte*, **47**, 123 (1937).

The alkali which had combined with the cellulose was ascertained by analyzing the spontaneous as well as the alcoholic precipitates obtained over a concentration range from 0 to 40 per cent (0–10 *N*). The precipitates, freed of the excess liquor (probably by centrifuging), were analyzed for total sodium hydroxide, water, and cellulose. By deducting the alkali found in the liquor retained in the precipitate (by titration) from the total alkali, the difference was regarded as the amount of alkali that had combined with the cellulose. The authors are aware of the defects of the analytical procedure and their results are to be regarded as preliminary only.

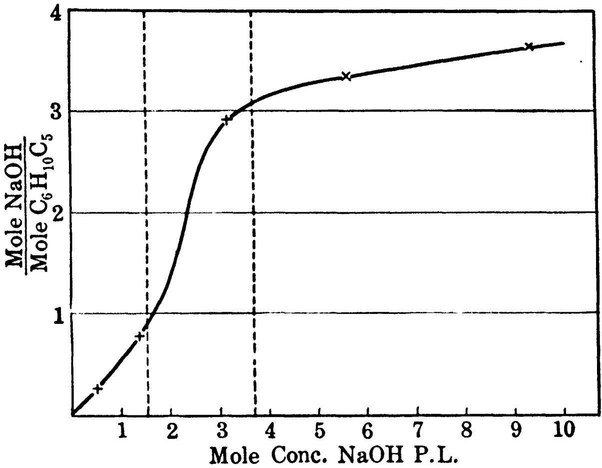

FIG. 37. Ratio of NaOH to cellulose in precipitates obtained from solutions of regenerated cellulose in aqueous sodium hydroxide. Koets and Kruyt.

The data obtained are represented in Fig. 37, in which the concentration of the sodium hydroxide solution is plotted against the ratio mole NaOH/mole $C_6H_{10}O_5$. The curve shows that the ratio of NaOH to $C_6H_{10}O_5$ in the precipitates increases with the alkali concentration. The change of direction which the curve shows is interpreted to indicate that, at a concentration somewhat above 12 per cent, the cellulose has taken up 3 molecules of sodium hydroxide per glucose residue. The slight continued increase of the ratio is probably not significant and is due to the deficiency of the analytical procedure.

CELLULOSATES

Sodium metal dissolved in liquid ammonia reacts with cellulose with the liberation of hydrogen to yield cellulosates. This reaction is analogous to the formation of alcoholates by the action of sodium metal upon alcohols:

$$2C_6H_9O_4OH + 2Na = 2C_6H_9O_4ONa + H_2$$

Earlier attempts to introduce sodium into cellulose were not successful,[68] whereas sugars,[69] starch, lichenin, and inulin[70] were found to react to form the corresponding alcoholates when sodium dissolved in liquid ammonia was allowed to act upon these compounds.

Application of the liquid ammonia method to dry cellulose in the form of standard cotton cellulose, *alpha* wood pulp and viscose rayon by Scherer and Hussey[71] resulted in the formation of mono-, di-, and trisodium cellulosates. A difference was noted in the reactivity of the three available hydroxyl groups. Whereas one hydroxyl group reacted rather quickly (requiring only a few minutes for the liberation of the corresponding quantity of hydrogen), the other two were slow to react, and many hours were required to complete the substitution reaction. Scherer and Hussey's results were confirmed by Schorigin and Makarowa-Semljanskaja[72] on cotton linters, sulfite pulp, and cuprammonium rayon.

The rate and completeness of reaction are to a considerable extent influenced by the degree of polymerization of the cellulosic materials. Thus *alpha* pulp and cellulose regenerated from viscose were found to react more readily than cotton linters and cotton, even if ground to a fine powder.[73]

The sodium cellulosates are, as would be anticipated, very sensitive to water. Indeed, moisture has to be carefully excluded or the reaction remains incomplete. The decomposition of sodium cellulosate with water is accompanied by considerable evolution of heat. The reaction may become rather violent, resulting in complete carbonization (charring) of the cellulose constituent. Great care is therefore recommended when bringing the cellulosate into contact with water; a drop of water may result in a violent explosion. However, decomposition may be accomplished without violence by allowing water vapor to act upon the cellulosate.[74]

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[68] Rassow and Wadewitz, *J. prakt. Chem.*, **106**, 266, 272 (1923).

[69] Muskat, *J. Am. Chem. Soc.*, **56**, 693 (1934).

[70] Schmid and Becker, *Ber.*, **58**, 1966 (1925).

[71] Scherer and Hussey, *J. Am. Chem. Soc.*, **53**, 234 (1931).

[72] Schorigin and Makarowa-Semljanskaja, *Ber.*, **69**, 1713 (1936).

[73] Heuser and Wiley, unpublished data.

[74] Heuser and Green, unpublished data.

Thallium cellulosate has been obtained by allowing thallium ethylate to react upon cellulose at room temperature.[75] The reaction may be represented by the equation:

$$TlOC_2H_5 + ROH = ROTl + C_2H_5OH$$

Thallium cellulosate seems to be somewhat more resistant to atmospheric influences than sodium cellulosate. However, thallium may be extracted from the compound with cold dilute acetic acid.

That the thallium was not merely adsorbed on the fiber but had reacted chemically in the way indicated above is seen from the fact that the reaction product with methyl iodide yields thallium iodide and methyl cellulose ether.

The amount of thallium which reacted with the hydroxyl groups of cellulose under the conditions used was relatively small and obviously involved only a few hydroxyl groups on the surface of the micelles. More thallium was merely occluded in unknown forms and variable amounts within the fiber. This mechanical deposition of the metal is evidently due to the ease with which the thallium ethylate decomposes.

THE NATURE OF MERCERIZED CELLULOSE

Alkali cellulose decomposes in the presence of water and cellulose is regenerated. Complete removal of the alkali requires long washing with large amounts of water. Sometimes it is necessary to neutralize the remainder of the alkali with dilute acid (preferably organic, such as acetic acid) and follow with renewed washing with (preferably distilled [76]) water.

The changes which cellulose shows after regeneration are essentially of a physical nature. Oxidation, which may occur under the influence of the oxygen of the air activated in the presence of strong caustic soda solution, can be avoided by excluding the air during mercerization, i.e., by allowing the process to take place in a vacuum or in an atmosphere of nitrogen.

Earlier investigators[77] have ascribed 1 molecule of water chemically bound to mercerized cellulose; this explains the term cellulose hydrate for mercerized cellulose. However, after thorough drying, mercerized cellulose shows the same elementary composition as the unmercerized material[78] and the x-ray pattern of the preparation gives no indication of water being chemically bound.[79]

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[75] Harris and Purves, *Paper Trade J.*, **110**, No. 6, 29 (1940).

[76] Cellulose eagerly absorbs numerous electrolytes from aqueous solutions. Hence, washing with ordinary water may increase the ash content rather than decrease it.

[77] See Schwalbe, "Chemie der Cellulose," 1st ed., p. 166.

[78] Ost and Westhoff, *Chem.-Ztg.*, **33**, 197 (1909); Miller, *Ber.*, **43**, 3430 (1910)

[79] Sobue, Kiessig, and Hess, *Z. physik. Chem.*, **B43**, 323 (1939).

Physical Changes

The fact that cellulose in its mercerized form represents merely a physically different modification is in agreement with the results of x-ray analysis[80] inasmuch as the length of the repeated pattern along the fiber axis remains unchanged, indicating that the distances between the glucose anhydride units in the length direction are not altered by mercerization. In other words, the primary valences are not attacked by the mercerization process.

On the other hand, the alterations which the x-ray diffraction diagram of mercerized cellulose reveals are relatively slight and do not seem to account sufficiently either for the very pronounced physical changes to be observed directly or for the different behavior of the mercerized fiber when in contact with various agents.

Thus, one would expect the increased diameter of the swollen fiber to be reflected by an enlarged distance between the chain bundles (micelles) and the individual chains. However, the x-ray pattern of the mercerized fiber furnishes only limited support for this assumption. The more pronounced alteration revealed by the x-ray diagram consists of a change in the position of neighboring chains relative to each other. The chains appear to have rotated around their long axis, resulting in a rhomboid, the angles of which deviate from 90° to a greater extent than do the angles in unmercerized cellulose (β here being 84°, see p. 24).[81] This alteration of the position of the chains is assumed to be equal to a "loosening up" of the lattice,[82] i.e., a disturbance of the parallel arrangement of the chains (orientation) within the crystalline portions, which results in an increase of the amorphous portions of the lattice.[83]

According to Ellis and Bath,[84] the shift in the natural arrangement of the cellulose chains is probably accompanied by a rearrangement of the hydrogen bridging between the hydroxyl groups of neighboring chains (see p. 59). The

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[80] Polanyi, *Naturwissenschaften*, **9**, 339 (1920); Herzog, *J. Phys. Chem.*, **30**, 462 (1926); Herzog and Jancke, *Z. physik. Chem.*, **A139**, 257 (1928).

[81] Sponsler and Dore, *J. Am. Chem. Soc.*, **50**, 1940 (1928); Meyer and Mark, *Ber.*, **61**, 600 (1928); Andress, *Z. physik. Chem.*, **B4**, 190 (1929); see also Sisson, *J. Phys. Chem.*, **40**, 343 (1936); **44**, 513 (1940); *Contrib. Boyce Thompson Inst.*, **9**, 381 (1938); *Chem. Reviews*, **26**, 187 (1940); Clark, "Applied X-rays," 3rd ed., p. 605.

[82] See in this connection Katz in Hess, "Die Chemie der Cellulose," pp. 687 *ff.*, who summarizes the effect as an "enlargement of the crystal lattice."

[83] Sisson and Saner, *J. Phys. Chem.*, **45**, 717 (1941); see also Sobue, Kiessig, and Hess, *Z. physik. Chem.*, **B43**, 309 (1939).

[84] Ellis and Bath, *J. Am. Chem. Soc.*, **62**, 2859 (1940).

observation that the infrared absorption band characteristic of hydrogen bridging in cellulose disappears on mercerization indicates that certain hydroxyl groups having orientations in the direction of the fiber axis are released from hydrogen bridging.

Other physical characteristics of the cellulose fiber which undergo change on mercerization to a greater or lesser extent are its density, its surface, and its refractive index.

The density of the mercerized cellulose fiber has been found to be somewhat lower than that of the native cellulose fiber. Herzog and Jancke[85] mention 1.58 g./cc. for native and 1.52 g./cc. for mercerized cellulose without disclosing the method used. Davidson,[86] using helium as a displacement agent, found the values shown in Table 5. The data show the specific volume to be slightly greater and, thus, the density to be slightly lower for the mercerized modifications and for the rayon types.

TABLE 5

SPECIFIC VOLUME AND DENSITY OF VARIOUS CELLULOSIC MATERIALS

Materials	Specific Volume	Density
American upland cotton	0.638 ± 0.002	1.567
Mercerized	0.645	1.550
Sea Island cotton	0.642	1.557
Mercerized	0.647	1.545
Viscose rayon	0.646	1.548
Cuprammonium rayon	0.653	1.531
Nitrocellulose rayon	0.648	1.543

Other available data show the difference between the naturally grown fibers and rayon. Wünnenberg, Fischer, and Biltz,[87] using a certain fraction of petroleum as the displacement agent, found for cotton 1.540–1.563 and for rayon 1.506–1.537; the results of Staudinger and Jurisch,[88] obtained by the use of Biltz's method, were as follows: cotton, 1.535; ramie, 1.549; viscose rayon, 1.433–1.454; cuprammonium rayon, 1.478.

A great number of data are available on the density of native cellulose. A compilation of the older data is found in Collins' publication.[89] Of the more recent data, the following may be mentioned. Filby and Maass' values,[90] ob-

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[85] Herzog and Jancke, *Z. physik. Chem.*, **139**, 253 (1928).

[86] Davidson, *J. Textile Inst.*, **18**, T175, 275 (1927).

[87] Wünnenberg, Fischer, and Biltz, *Z. physik. Chem.*, **151**, 65 (1930).

[88] Staudinger and Jurisch, *Melliand Textilber.*, **20**, 693, 696 (1939).

[89] Collins, *J. Textile Inst.*, **13**, T204 (1922).

[90] Filby and Maass, *Can. J. Research*, **7**, 162 (1932).

tained with helium as the displacement agent for purified rag stock, check quite well with those obtained by Davidson for cotton, the specific volume being 0.640 ± 0.001 corresponding to a density of 1.562 (see also p. 61). The helium method was also used by Stamm and Hansen,[91] who found the density of cotton linters to be 1.585 ± 0.0012.

As mentioned in Chapter III, the values ascertained by using helium are evidently more reliable than those obtained by the use of water or organic liquids as displacement agents.[92] With water, Stamm and Hansen found for cotton linters a density of 1.6028 ± 0.0003 and with benzene 1.571 ± 0.0005 (previously[93] 1.549 for cotton).

Lyons[94] has directed attention to the fact that, of all the values reported for the density of cellulose, Stamm and Hansen's value of 1.585 for cotton linters checks best with the value which may be calculated from the dimensions of the unit cell of cellulose. Using Meyer and Misch's model of the unit cell (see p. 27), Lyons calculated the "true" or "crystal" density of cellulose and obtained a value of 1.582 g./cc.

According to Lyons, the most persistent systematic experimental error to be expected in true density measurements on cellulose is that arising from void spaces. The low values previously reported (with some exceptions) differ from the theoretical value in the direction which would be expected if inadequate correction is made for porosity.

Lyons regards Stamm and Hansen's figure of 1.585 g./cc. as an experimental verification of the Meyer and Misch model of the unit cell of cellulose.

Data for sulfite pulp, obtained by using various displacement agents, are shown in Table 6.[95] The figures for the beaten pulp seem to indicate that pulp in this state is subject to denser packing, as would be anticipated.

TABLE 6

DENSITY OF UNBEATEN AND BEATEN SULFITE PULP

	Displacement Agent		
	Helium	Water	Benzene
Sulfite pulp, unbeaten	1.570 ± 0.0024	1.590 ± 0.0005	1.555
Sulfite pulp, beaten	1.593 ± 0.0022	1.616 ± 0.0008	

The statement that *the mercerized fiber possesses an increased surface compared with the native fiber* has been made quite frequently, but quantitative data are rather scarce. Schuster[96] has measured the

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[91] Stamm and Hansen, *J. Phys. Chem.*, **41**, 1007 (1937).

[92] See also Stamm, "Colloid Chemistry of Cellulosic Materials," p. 63, on the influence of the volume contraction of water adsorbed by cellulose ("adsorption compression").

[93] Stamm and Seborg, *J. Phys. Chem.*, **39**, 133 (1935).

[94] Lyons, *J. Chem. Phys.*, **9**, 377 (1941).

[95] Stamm and Hansen, *loc. cit.*

[96] Schuster, quoted by Mark and Meyer, *Z. physik. Chem.*, **B2**, 130 (1929); see also Mark, "Physik und Chemie der Cellulose," p. 182; Kälberer and Schuster, *Z. Elektrochem.*, **35**, 600 (1929).

adsorption by dry cotton fiber of dry gases, such as nitrogen, ethane, and other inert gases and from the heat of adsorption has calculated the adsorbing surface to amount to 7×10^7 cm.^{2}/g. This value was found to be about twice as high with the mercerized fiber.

Harris and Purves[97] have estimated the internal surface from the amount of thallous ethylate reacting with cellulose in ether or benzene solution to form thallium cellulosate. They found a value of 3.7×10^4 cm.^{2} per gram of ramie fiber. Highly mercerized ramie and a cellulose hydrate regenerated from cuprammonium solution gave 4×10^5 cm.^{2}/g.

The value for the adsorbing surface as determined by Schuster by the above method was found to be distinctly smaller than the geometrical value derived from x-ray data, which was $3–7 \times 10^7$ cc.^{2}/g. This deviation is explained on the assumption that the total surface is not available for the gases because the micelles adhere to each other and thus eliminate a certain portion of the micellar surface. It is only by intermicellar swelling that this portion is made available.

If, in accordance with H. K. Meyer,[98] the number of accessible hydroxyl groups is taken as a measure of the reactive micelle surfaces, it may be calculated that with native cellulose about one-quarter[99] and with mercerized cellulose about one-half of the free hydroxyl groups are exposed on the micelle surfaces.

Differences in the adsorbing surface between the dry fiber and the swollen fiber have been reported by Stamm and Millett.[100] These investigators have calculated a number of values from data taken from the literature, such as adsorption data for gases and vapors, data on selective adsorption from solution, data on heat of swelling, and on adhesion tension, and also from new data on selective adsorption. The values so obtained were divided into two groups. Systems in which the cell wall was not swollen gave surfaces of about 2×10^3 cm.^{2}/g., whereas systems in which the cell walls were swollen gave surfaces of about 2×10^6 cm.^{2}/g. All data refer to swelling (or heat of swelling) in *water,* i.e., to intermicellar swelling. It is conceivable that surfaces of intramicellar swollen fibers, i.e., in strong swelling agents, such as aqueous sodium hydroxide of mercerizing strength, would be still greater.

Considerable confusion seems to exist in applying the correct term for the type of surface involved in the various measurements. It would appear logical to distinguish between the external and the internal surfaces and the total surface of a cellulose fiber, the total surface being the sum of the external and the internal surface. The external surface may be defined as the entire circumferential surface area. In the light of the modern concept of fiber structure, the internal surface of a fiber would include not only the inner surface of the microscopically visible lumen but also that of the entire submicroscopic tubular or

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[97] Harris and Purves, *Paper Trade J.*, **110,** No. 6, 29 (1940).

[98] H. K. Meyer, "Hochpolymere Chemie," Vol. II, "Die Hochpolymeren Verbindungen," Akad. Verlags-Ges., Leipzig (1940), p. 249.

[99] Previous estimations were 30–50 per cent (see p. 42).

[100] Stamm and Millett, *J. Phys. Chem.*, **45,** 43 (1941).

capillary system of the fiber, i.e., the inter- and intramicellar spaces of the system. Part of the internal surface, namely, that of the lumen, may be measured microscopically, but that of the submicroscopic capillary system can be measured only if this system is made accessible to the agent to be adsorbed. With water (which enters only the intermicellar spaces) only a part of the internal surface is measured, but with swelling agents which cause intramicellar swelling, the total internal surface is measured. Both the total internal and external surfaces are measured only if the agent enters both the inter- and the intramicellar spaces.

It would appear desirable that such distinctions in the definition of the types of surface be made, for it would greatly facilitate the interpretation of the data and the understanding of their meaning.

The double refraction is lower for mercerized and still lower for regenerated than for native cellulose and seems to be quantitatively related to the degree of orientation of the micelles in the fibers, the more highly oriented fiber showing the more pronounced double refraction.[101] The differences are large enough to make possible a distinction between native and mercerized cellulose. For example, Frey-Wyssling[102] found that the double refraction of cotton decreased on mercerization from 0.068 to 0.049.

Reference has been made above to the similarity which exists between mercerized cellulose and viscose rayon and certain other forms of regenerated cellulose. This similarity is found with all types of regenerated cellulose, such as that regenerated from solutions in cuprammonium hydroxide, in quaternary ammonium bases, in saturated salt solutions, and in strong acids. Likewise, cellulose regenerated from certain derivatives, such as cellulose acetate and cellulose nitrate (either as coagulum or in fibrous form), shows the characteristics of mercerized cellulose.[103] Although mercerized cellulose and the various forms of regenerated cellulose have been collectively termed cellulose hydrate, it appears desirable to differentiate between the terms mercerized cellulose and cellulose hydrate (for regenerated cellulose).

The transformation of cellulose into a physically different modification without alteration of its molecular structure designates cellulose as a polymorphous substance. This designation seems to be the more justified because, as will be seen later, mercerized cellulose may revert to its original form after certain treatments.

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[101] Preston, *Trans. Faraday Soc.*, **29**, 65 (1933); van Iterson, *Chem. Weekblad*, **30**, 2 (1933); Bredée, *ibid.*, **30**, 51 (1933).

[102] Frey-Wyssling, *Helv. Chim. Acta*, **19**, 900 (1936); see also Valkó, "Kolloidchemische Grundlagen der Textilveredlung," p. 213.

[103] Katz and Hess, *Z. physik. Chem.*, **122**, 126 (1926); Katz and Mark, *ibid.*, **115**, 385 (1925); *Z. Elektrochem.*, **31**, 105 (1925); Sisson, *J. Phys. Chem.*, **44**, 513 (1940).

The physical changes which cellulose undergoes on mercerization and on regeneration manifest themselves chiefly in the ability of the mercerized and regenerated cellulose to take up larger quantities of liquids, bases, and other salts as well as dyestuffs and to display increased swelling ability under such conditions. In addition, the physically modified cellulose exhibits greater reactivity compared with the original cellulose.

Sorption and Swelling of Mercerized Cellulose

That mercerized cellulose possesses greater hygroscopicity than the original cellulose was known to Mercer and has been confirmed by many subsequent investigators. As an example, we may quote the results of Ost and Westhoff,[104] who observed that the hygroscopicity (grams of water taken up by 100 grams of mercerized cellulose) of cotton increased on mercerization from about 6 to 9–10, i.e., by about 63 per cent. Schwalbe [105] recognized that the hygroscopicity of cellulose increases with the concentration of the mercerizing liquor and that the greatest increase in water-binding capacity occurs at concentrations between 8 and 16 per cent, i.e., while the cotton passes through its swelling maximum. Frequent measurements under exact control of the humidity of the surrounding atmosphere have confirmed this observation.[106] Urquhart and Williams,[107] as a result of numerous determinations, found that mercerized cotton took up on an average 1.5 times as much water as the unmercerized material. Table 7 shows the relationship between the concentration of the mercerizing liquor and the water-binding capacity of the mercerized product.

TABLE 7

RATIO OF WATER-BINDING CAPACITY OF MERCERIZED AND UNMERCERIZED COTTON DEPENDENT UPON CONCENTRATION OF MERCERIZING LIQUOR

Mercerizing solution NaOH, %	4.8	9.3	13.4	15.0	17.5	20.0	24.9	36.6
Ratio mercerized to unmercerized cotton *	1.01	1.07	1.53	1.57	1.56	1.54	1.65	1.44

* Times more water taken up by mercerized cellulose.

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[104] Ost and Westhoff, *loc. cit.*; see also Miller, *loc. cit.*, p. 728.

[105] Schwalbe, *Z. angew. Chem.*, **22**, 197 (1909).

[106] Higgins, *J. Soc. Chem. Ind.*, **28**, 188 (1909); Coward and Spencer, *J. Textile Inst.*, **14**, T41 (1923); Sheppard and Newsome, *J. Phys. Chem.*, **33**, 1817 (1929).

[107] Urquhart and Williams, *J. Textile Inst.*, **16**, T155 (1925); **18**, T55 (1927).

Like native cellulose, mercerized cellulose shows the hysteresis effect. The regain was found to be about 1.57 times as great when the material was absorbing moisture, and 1.46 times as great when losing moisture, as the regains of the unmercerized cotton, and these changes were found to be independent of the prevailing humidity.[108]

Results similar to those reported by Urquhart and Williams were obtained by Birtwell and co-workers.[109] They are graphically shown in Fig. 38. The hygroscopicity, here again expressed as the ratio of the hygroscopicity of the mercerized to that of the unmercerized cotton fiber, is shown also for cotton which had been mercerized at −10° as compared with +18°; it is seen that the hygroscopicity ratio is slightly but distinctly higher at the lower temperature. It is also seen that, in order to bring about the increased hygroscopicity of the mercerized fiber at the lower temperature, the concentration of the mercerizing liquor may be lower than at the higher temperature.

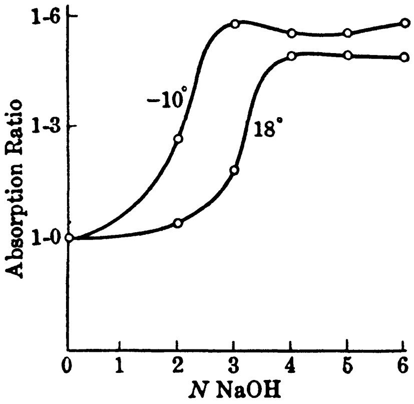

FIG. 38. Hygroscopicity ratio of cotton and mercerized cotton and concentration of mercerizing liquor. Birtwell, Clibbens, Geake, and Ridge.

On the assumption that the mercerized cellulose fiber represents a system in which not only the intermicellar but also all or part of the intramicellar hydroxyl groups are accessible to liquids, one would expect water molecules to attach themselves to such interior hydroxyl groups. If such an attachment were of a chemical nature, it should be detectable by x-ray analysis. In fact, if cellulose at the end of the mercerization process is washed with cold water and is examined in the *wet* state under x-irradiation, a diagram is obtained which differs distinctly from that of dry mercerized cellulose and thus seems to indicate that the water has chemically combined with intramicellar hydroxyl groups of the mercerized fiber. The water-containing mercerized product has been termed water cellulose,[110] which is evidently

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[108] Urquhart and Williams, *loc. cit.*, p. T158; Urquhart, Bostock, and Eckersall, *J. Textile Inst.*, **23**, T135 (1932).

[109] Birtwell, Clibbens, Geake, and Ridge, *J. Textile Inst.*, **21**, T85 (1930).

[110] Sakurada and Hutino, *Kolloid-Z.*, **77**, 340 (1936); Sakurada and Kawada, *J. Soc. Chem. Ind. Japan*, **42**, 227 (1939); *Cellulosechem.*, **18**, Abstracts, 42 (1940).

a "cellulose hydrate" in the chemical sense. This water of hydration is, however, lost on thorough drying (p. 93).

The swelling which cellulose undergoes if, at the end of the mercerization procedure the alkali is quickly replaced by cold water, is considerable. It is still more pronounced with regenerated cellulose, as has been shown by Neale[111] with cellophane. Since this excessive swelling is of a temporary nature, it has been termed "transient swelling."

Transient swelling is recognized as a quite undesirable phenomenon when mixed cotton-rayon fabrics are subjected to mercerization. Rayon, apart from being much more sensitive to alkali than cotton, may suffer a great deal in strength and even become partly soluble when the mercerized mixed fabric is washed with water to remove the alkali. Transient swelling, however, may be reduced by washing with a concentrated sodium chloride solution.[112] (See also the section on the solubility of cellulose in aqueous alkalies, p. 125).

The ability of mercerized cellulose to accommodate water within the micelles seems to be lost, however, if the alkali is washed out with *boiling* water. This is probably due to the tendency of mercerized cellulose to revert to its natural modification under such treatment. In fact, under the influence of boiling water, the x-ray pattern of mercerized cellulose changes to a considerable extent into that of unmercerized cellulose.[113] This observation is in agreement with the fact that the mercerized cellulose loses much of its increased water-binding capacity if it is boiled in water for several hours; losses up to 23 per cent have been observed.[114] Likewise, drying decreases the hygroscopicity of the mercerized fiber.[115] This may be explained on the assumption that, on drying, linkages between hydroxyl groups of the cellulose which previously were combined with water are reformed, resulting in a denser system than before (see Urquhart and Williams, p. 44).

Mercerization carried out on cellulose material while under tension produces considerably less hygroscopicity than is shown by the loosely mercerized material.[116] Obviously, the stress exerted upon the fiber prevents, to a certain extent, the chain molecules from becoming dis-

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[111] Neale, *J. Textile Inst.*, **20,** T373 (1929); see also Lottermoser and Schwarz, *Kolloid-Beihefte*, **42,** 411, 419 (1935).

[112] Marsh and Wood, "Introduction to Cellulose Chemistry," p. 63; see also Vieweg, *Papier-Fabr.*, **36,** 181 (1938); Saito, *Kolloid-Beihefte*, **49,** 402 (1939).

[113] Hess and Gundermann, *Ber.*, **70,** 525 (1937).

[114] Coward and Spencer, *J. Textile Inst.*, **14,** T32 (1923).

[115] Coward and Spencer, *loc. cit.;* Bancroft and Calkin, *Textile Research*, **4,** 119 (1934).

[116] Urquhart and Williams, *loc. cit.*

oriented. In other words, a great deal of the degree of orientation which is present in the original fiber is preserved.[117]

Regenerated cellulose, for example, in the form of rayon, i.e., coagulated from viscose or cuprammonium solution, possesses still greater hygroscopicity than the mercerized fiber.[118] For an explanation of this behavior we must bear in mind that, on preparing a cellulose solution which is suitable for "spinning," that is, for being forced through very fine openings into a coagulating bath, cellulose loses its fibrous structure entirely. On coagulation a new structure is built up, and this structure is even less condensed than that of the fibrous mercerized cellulose. The hydroxyl groups in such a system are thus still more accessible than in the mercerized fiber. This explanation would seem to be in agreement with the observation (which is supported by the results of x-ray analysis) that in the rayon fiber the cellulose chain molecules are less oriented than in the natural fiber in both the mercerized and the unmercerized states. On the other hand, on stretching in the plastic state, the filaments acquire a state of higher orientation.[119] As a result, their crystalline portions are increased and the system becomes denser. Indeed, such a system is less hygroscopic than a system to which less stretching has been applied. Staudinger and Jurisch have illustrated the difference in degree of orientation in natural and artificial fibers in the following schematic pictures[120] (Figs. 39, 40).

In contrast to cotton and other natural cellulose fibers, rayon fibers lose strength when wetted. This different behavior is evidently a result of the less condensed structure of the rayon fiber. Consequently, the forces of cohesion which are active between the chain molecules are weaker and, therefore, are more easily overcome by the forces of expansion which are operative when the fiber swells in water.

Schwertassek[121] has directed attention to the fact that the rayon fiber possesses no outer layer to protect it from excessive swelling, in contrast to the cotton fiber which, even after removal of the cuticle, is quite resistant to excessive swelling, a property attributed to the outer layer of the primary wall.

Much interesting information on the relation between the degree of deformation of artificial fibers and films and their physical properties may be obtained from the studies of Kratky, Hermans, and others.[122]

Hygroscopicity and swelling ability of regenerated cellulose decrease on dry-

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[117] See Katz, in Hess, "Die Chemie der Cellulose," p. 761.

[118] Obermiller, *Melland Textilber.*, **6**, 765 (1925); *Z. angew. Chem.*, **39**, 46 (1926); Weltzien, "Chemische und physikalische Technologie der Kunstseiden," p. 133; Urquhart and Eckersall, *J. Textile Inst.*, **21**, T499 (1930); **23**, T163 (1932).

[119] Schorger, *J. Soc. Chem. Ind.*, **49**, 157T (1930); Baule, Kratky, and Treer, *Z. physik. Chem.*, **B50**, 255 (1941).

[120] Staudinger and Jurisch, *Melliand Textilber.*, **20**, 695 (1939).

[121] Schwertassek, *Melliand Textilber.*, **22**, 1 (1941).

[122] Kratky, *Kolloid-Z.*, **64**, 213 (1933); **68**, 347 (1934); **70**, 14 (1935); Breuer, Kratky, and Saito, *ibid.*, **80**, 139 (1937); Kratky, *ibid.*, **84**, 149 (1938); Kratky and Platzek, *ibid.*, **84**, 268 (1938); **88**, 78 (1939); Hermans, *ibid.*, **83**, 71 (1938); **84**, 168 (1938); **86**, 107 (1939); **88**, 68, 73 (1939); **83**, 344 (1939); Hermans and Platzek, *ibid.*, **89**, 349 (1939).

ing in much the same way as observed with mercerized cellulose. Again, these changes are essentially a result of increased orientation.[123] Boiling the regenerated cellulose fiber in water seems to have the same effect, obviously because the cellulose hydrate is partially converted into native cellulose.

Complete transformation into native cellulose has been accomplished by heating viscose rayon for 30 minutes at 250° in glycerine[124] or in other polar liquids.[125] This effect is explained on the assumption that the molecular attraction between the polar groups of the liquid and the polar (hydroxyl) groups of the cellulose places the chain molecules in a state of greater mobility in which they are more easily subject to rearrangement. Under these conditions, the polar liquid would penetrate the whole micellar system and thus insure thorough reaction.

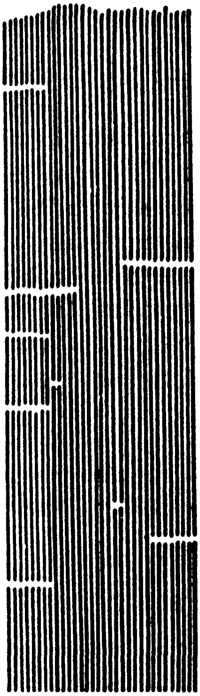

FIG. 39. Arrangement of macromolecules in natural cellulose fibers. Staudinger and Jurisch.

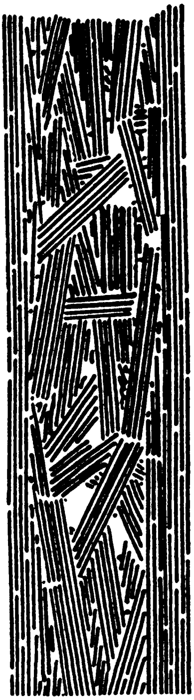

FIG. 40. Arrangement of macromolecules in artificial cellulose fibers. Staudinger and Jurisch.

The transformation of the cellulose hydrate modification into the original form is still more facilitated, if the hydrate modification is first converted

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[123] Kanamaru, *Helv. Chim. Acta,* **17,** 1427 (1937).

[124] Meyer and Bodenhuizen, *Nature,* **140,** 281 (1937).

[125] Kubo and Kanamaru, *Z. physik. Chem.,* **A182,** 341 (1938); Kubo, *Kolloid-Z.,* **96,** 41 (1941); Sisson and Saner, *J. Phys. Chem.,* **45,** 717 (1941).

into an addition or molecular compound. Thus, the alkali compounds[126] or the hydrazin and the ethylenediamine compounds[127] of viscose rayon may be converted into native cellulose within 2 to 3 minutes if subjected to the glycerine treatment at 250°.

The transformation of coagulated cellulose into its original form ought to be of considerable commercial interest, for such a transformation would result in improved water-resistance of certain types of rayon, such as viscose and cuprammonium.

Absorptivity of Mercerized Cellulose for Bases and Salts

The increased ability of the mercerized fiber to take up alkali from solutions, as compared with the unmercerized fiber, is quite pronounced. We also observe this ability to increase with the degree of mercerization, i.e., with increasing concentration of the mercerizing liquor and, hence, with increasing swelling. The relation between increasing concentration of the mercerizing liquor and the amount of sodium hydroxide retained by mercerized cotton from a 2 per cent solution is shown in Table 8, which is taken from Vieweg's work.[128]

TABLE 8

ALKALI TAKEN UP FROM 2 PER CENT SODIUM HYDROXIDE SOLUTION BY COTTON MERCERIZED WITH LIQUORS OF INCREASING CONCENTRATION

Concentration of mercerizing caustic NaOH, %	0	4	8	12	16	20	24	28	32	50
NaOH taken up from solution, %	1.0	1.0	1.4	1.8	2.8	2.8	2.8	2.9	2.9	2.9

Similar results, obtained with 2 per cent sodium hydroxide solution, are shown in Fig. 41.[129] The absorption ratio figures indicate how much more sodium hydroxide is taken up from a 2 per cent solution by mercerized than by unmercerized cotton. It is seen that, when the mercerizing liquor has reached a concentration of 15 per cent, the absorption of alkali becomes constant or increases more slowly. At this point, the mercerized cellulose has taken up 2.4 times more sodium hydroxide than cellulose which has not been mercerized. With 0.25 *N* barium hydroxide solution, more accurate results were obtained, be-

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[126] Kubo, *Kolloid-Z.*, **88**, 62 (1939); *Z. physik. Chem.*, **A187**, 297 (1940).

[127] Kubo, *Cellulose Ind.* (Tokyo), **15**, Abstracts, 13 (1939).

[128] Vieweg, *Ber.*, **40**, 3879 (1907); see also Schwalbe, "Chemie der Cellulose," p. **635**; Dehnert and König, *Cellulosechem.*, **6**, 6 (1925).

[129] Neale, *J. Textile Inst.*, **22**, T320 (1931).

cause the amounts taken up are greater than from sodium hydroxide solution.[130]

The relationship between the concentration of the liquor used for mercerization and the amount of sodium hydroxide taken up from dilute solutions may be used as a means of determining the degree of mercerization.

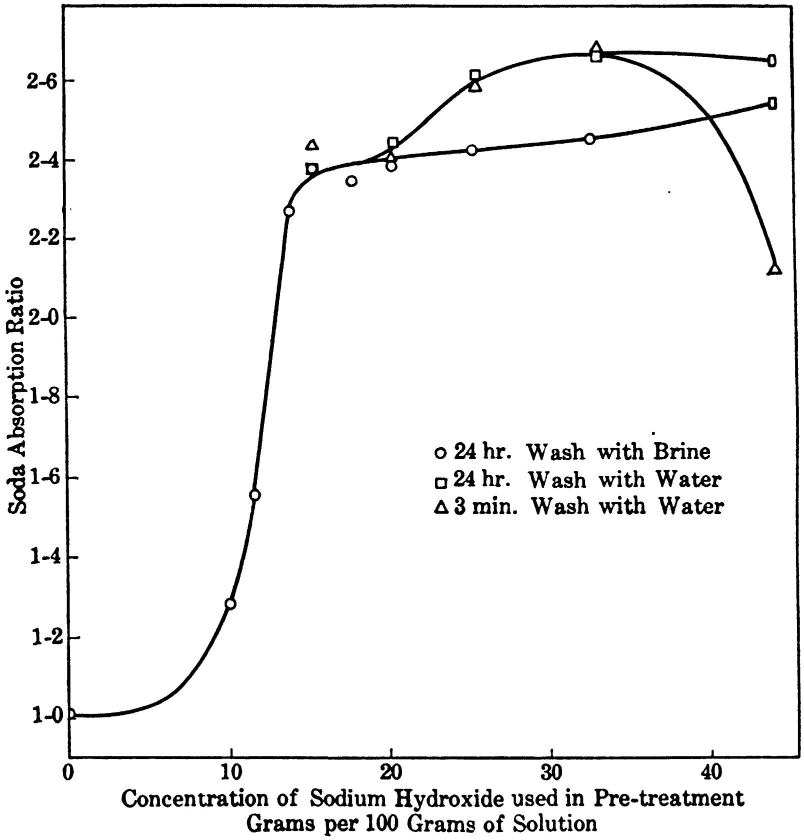

FIG. 41. Sodium hydroxide absorption ratio of mercerized cotton. Neale.

Regenerated cellulose in the form of the various rayon types shows similar behavior with dilute alkali solutions as does mercerized cellulose. However, the phenomena are more complex because regenerated cellulose is rather sensitive to even dilute alkali solutions, parts of it going into solution. Some data on the increased absorption of alkali

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[130] Neale, *J. Textile Inst.*, **22**, T319 (1931); *J. Soc. Chem. Ind.*, **50**, 177 (1931)

by cuprammonium rayon from dilute sodium and barium hydroxide solutions are available from Neale's studies.[131]

What is known about the *absorptive ability of mercerized cellulose for salts or other substances* may be summarized as follows.

Mercerized cellulose absorbs more copper from a dilute cuprammonium hydroxide solution than does the original cellulose; the same holds true for a zinc chloride solution [132] and a copper sulfate solution.[133] On washing with water, the salt is retained. Since this also occurs when cellulose is in contact with Fehling solution, as when the copper number is determined, Schwalbe, in his original publication, suggested that the copper number should be corrected by deducting from the latter the amount of copper due to copper sulfate absorption. The latter amount is termed "cellulose number." In other words, the true copper number of cellulose represents the copper number minus the cellulose number.[134] Mercerized cellulose also takes up more iodine from a solution of iodine in potassium iodide.[135] Both copper absorption and iodine absorption depend upon the concentration used for mercerizing the cellulose and, hence, may likewise be used for determining the degree of mercerization. There is also a direct relation between the amount of iodine absorbed and the hygroscopicity of the mercerized cellulose.[136]

The behavior of mercerized cellulose with iodine, zinc chloride, etc., is also used as a qualitative test for its identification and for distinguishing it from native cellulose. Thus, the violet coloration which a zinc chloride-iodine solution produces with native cellulose may be easily washed out with water, whereas the coloration remains much longer when mercerized cellulose is used.[137]

As regards the general behavior of cellulose with salt solutions, the older literature records numerous investigations, but the results are often contradictory because these investigations were made on very different cellulosic materials and little attention was paid to the degree of purity. A compilation of

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[131] Neale, *J. Soc. Chem. Ind.*, **50**, 177 (1931).

[132] Brownsett, Farrow, and Neale, *J. Textile Inst.*, **22**, T357 (1931).

[133] Schwalbe, "Chemie der Cellulose," 1st ed., p. 634; see also A. Herzog, *Z. Farbenindustrie*, **7**, 186 and 281 (1908); Leuchs, doctoral dissertation, Leipzig, 1910.

[134] See Dorée, "The Methods of Cellulose Chemistry," p. 34.

[135] Hübner, *J. Soc. Chem. Ind.*, **27**, 105 (1908); see also Hall, "Cotton Cellulose," p. 80; Schwertassek, Heidler, and Kasche, *Melliand Textilber.*, **20**, 433 (1939).

[136] Higgins, *J. Soc. Chem. Ind.*, **28**, 188 (1909).

[137] Hübner, *loc. cit.*, p. 110; see also Hall, *loc. cit.*, p. 88; Harrison, *J. Soc Dyers Colourists*, **31**, 198 (1915).

these investigations may be found in Schwalbe's book.[138] The same author, in numerous studies, has pointed to the rôle which inorganic and organic impurities of the cellulosic material play whenever it comes in contact with salt solutions.[139]

The concentration of a salt solution decreases when it is passed through cellulosic material; however, the decrease, in most cases, comes very soon to a standstill. Of the neutral salts, the heavy metal salts (such as copper, iron, zinc, etc., salts) are retained more readily. The absorption of copper sulfate, already mentioned, is also used to distinguish between cotton, flax, and ramie cellulose because the latter two types take up almost twice as much as cotton cellulose.[140] Lead and iron salts, unlike the light metal salts, can be washed out only with difficulty or not at all; on the contrary, they seem to become the more firmly fixed upon the fiber, the longer the washing with water is continued. Indeed, cellulose may serve as a means of purifying water.[141]

Viewing cellulose as a colloid, we may expect it to retain the salts by adsorption. Although the ability of cellulose to adsorb salts and other substances has been denied by some investigators,[142] others have found that adsorption, governed by physical laws, takes place.[143]

On the other hand, the ash constituents of the fiber often play an important part in the behavior of cellulosic materials with salt solutions inasmuch as these constituents give rise to certain ion-exchange reactions. Such reactions have been frequently observed and discussed.[144] (See also later.)

The cations in cellulosic materials are present in the form of inorganic and organic salts. Whereas the inorganic salts can, in most cases, be removed from the fiber by thorough leaching with water, the organically bound cations are retained unless the fiber is subjected to a treatment with acid. Under these conditions, the cations (which in cotton were found to consist chiefly of Ca, Mg, Fe, and Al [145]) neutralize or bind an equivalent quantity of acid.[146]

The organic substances to which the cations are bound in cotton are, for the

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[138] Schwalbe, "Chemie der Cellulose," 1st ed., p. 78.

[139] See the review of these and previous studies in Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 163.

[140] See Heuser, *loc. cit.*, p. 164.

[141] Schwalbe, "Chemie der Cellulose," *loc. cit.*, p. 79; McLean and Wooten, *Ind. Eng. Chem.*, **31**, 1138 (1939).

[142] Kolthoff, *Pharm. Weekblad*, **57**, 1510, 1571 (1920); **58**, 46, 94, 152, 233 (1922); Rona and Michaelis, *Biochem. Z.*, **103**, 19 (1920).

[143] Percival, Cuthbertson, and Hibbert, *J. Am. Chem. Soc.*, **52**, 3448 (1930); Lottermoser and Hönsch, *Kolloid-Z.*, **57**, 206 (1931); Gavoret, *Ann. chim.*, **15**, 97 (1941).

[144] Kolthoff, *loc. cit.*; Kullgren, *Svensk Kem. Tid.*, **42**, 179 (1930); **43**, 161 (1931); **44**, 15 (1932); *Zellstoff u. Papier*, **13**, 558 (1933); **14**, 19 (1934); Lüdtke, *Papier-Fabr.*, **32**, 509, 528 (1934); *Biochem. Z.*, **268**, 372 (1934); Gavoret, *Compt. rend.*, **204**, 1643 (1937); Wurtz, *Papier-Fabr.*, **35**, 84 (1937); Du Rietz, "Über das Ionenbindungsvermögen fester Stoffe," doctoral dissertation, Stockholm, 1938, pp. 13, 107, 122; Rath and Dolmetsch, *Klepzig's Textil-Z.*, **41**, 475 (1938).

[145] Walker and Quell, *J. Textile Inst.*, **24**, T123, 131 (1933); see also Heymann and Rabinow, *J. Phys. Chem.*, **45**, 1154 (1941).

[146] McLean and Wooten, *loc. cit.*

greater part, pectic acid and, to a smaller extent, cellulose itself by virtue of the presence of carboxylic groups in the cellulose chains. Such groups may, as has been seen, be present even in carefully isolated cotton cellulose and to a greater extent in cellulose which has been subjected to oxidation. Part of the carboxyl groups may also be attached to noncellulosic carbohydrates as, for example, polyglycuronic acids. As a matter of fact, the acid-binding capacity of wood pulp has been found to be greater than that of cotton.[147]

A detailed study of the acid-binding capacity of cotton fibers over a wide range of *p*H values has shown that this is determined by the cationic ash of the fiber at any hydrogen-ion concentration. Moreover, by evaluating the titration curves and the hydrogen-ion equivalence of the ash, it has been possible to ascertain the maximum acid bound by different samples of cotton which, in turn, permitted the quantitative allocation of the acid bound to the principal constituents of the fiber itself (see also Chapter XV).[148]

The manner in which cotton and other cellulosic materials bind acid may thus be considered as an ion-exchange reaction, i.e., an exchange between the hydrogen ions of the acid and the cations associated with the acidic groups of the fiber.

Free carboxyl groups seem to play an essential part in the reactions which occur when cellulose is brought into contact with aqueous salt solutions. Thus, the observation of Harrison,[149] which was confirmed by Masters,[150] i.e., that an aqueous dilute sodium chloride solution becomes acid when filtered through cotton cellulose, seems to be explained by the presence of free carboxyl groups in cellulose. Obviously, these groups combine with the sodium ions, thus liberating hydrochloric acid.

Masters observed acidity in the filtrate also with the aqueous dilute solutions of ammonium chloride, sodium sulfate, calcium and barium chloride, as well as of cadmium iodide and sodium formate.

An earlier observation by Vignon[151] seems to point to the same explanation. When an aqueous dilute solution of mercuric chloride was filtered through medical cotton, almost the entire chlorine constituent was found as hydrochloric acid in the filtrate. However, part of the mercury was retained as mercuric hydroxide by the fiber. This result indicates that this part of the mercuric chloride was hydrolyzed by the water to give mercuric hydroxide and hydrochloric acid. However, it is obvious that the entire cellulose substance plays an essential part in this reaction. Not only does it seem to accelerate the hydrolytic dissociation of the mercuric chloride, but it also seems to act as a flocculating agent and as a filtering membrane for the hydroxide.

The retention by cellulose of metal hydroxides from aqueous salt solutions is shown to a greater extent with salts which are subject to far-reaching hydrolytic dissociation in aqueous solution, as, for example, aluminum sulfate. If

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[147] McLean and Wooten, *loc. cit.*

[148] Sookne and Harris, *Textile Research,* **10,** 405 (1940); see also Sookne, Fugitt, and Steinhardt, *ibid.,* **10,** 380 (1940).

[149] Harrison, *J. Soc. Dyers and Colourists,* **28,** 359 (1912).

[150] Masters, *J. Chem. Soc.,* **121,** 2026 (1922).

[151] Vignon, *Compt. rend.,* **116,** 517, 584, 645 (1893).

cellulose is allowed to remain in aqueous aluminum sulfate solution for some time and, thereafter, is separated from the solution by filtration, practically the entire sulfuric acid constituent is found in the filtrate, whereas all the aluminum constituent is retained by the fiber essentially in the form of aluminum hydroxide.[152, 153]

Another part of the metal hydroxide may be retained by the fiber because of an exchange reaction between the salt solution and the fiber ash.[154] For example, the calcium and magnesium carbonate constituents of the ash in wood pulp may react with aqueous aluminum sulfate to form carbon dioxide, calcium (magnesium) sulfate, and aluminum hydroxide:

$$3CaCO_3 + Al_2(SO_4)_3 + 3H_2O \rightarrow 3CO_2 + 3CaSO_4 + Al_2(OH)_6$$

The calcium sulfate is washed out and appears as combined sulfuric acid in the filtrate, whereas the aluminum hydroxide is retained by the fiber.

That the retention of metal hydroxides from the solution of salts which are subject to far-reaching hydrolytic dissociation is essentially a colloidal phenomenon is seen from the fact that the available surface area and the surface conditions of the fiber exert a pronounced influence upon the extent to which aluminum hydroxide is adsorbed. Thus it was found that cellulose mucilage, which may be obtained by excessive beating of cellulose fibers, retained considerably greater quantities of aluminum hydroxide than fibrous cellulose,[155] whereas cotton, the surface of which had undergone physical changes on long storage or on drying, failed to adsorb any aluminum from an aluminum sulfate solution.[156]

The behavior of cellulose with salts plays an important part in a number of commercial processes—for example, in the dyeing of cotton in which mordant salts are used for the fixation of basic dyes or in which the cellulose fiber is loaded with metal hydroxides which combine with certain dyes to form dye lakes. In the sizing of paper, aluminum sulfate is used for decomposing the sizing agent (an emulsion of free rosin in aqueous sodium resinate) and for depositing the rosin (partly as such and partly in the form of aluminum resinate) upon the fiber. Likewise, that part of the aluminum which is deposited upon the fiber as aluminum hydroxide seems to play an essential part in the sizing mechanism.[157]

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[152] Schwalbe and Robsahm, *Wochbl. Papierfabr.*, **43**, 1454 (1912); Haller, *Chem.-Ztg.*, **42**, 597 (1918); Tingle, *J. Ind. Eng. Chem.*, **14**, 198 (1922); see also Percival, Cuthbertson, and Hibbert, *J. Am. Chem. Soc.*, **52**, 3448 (1930).

[153] Heuser, *Cellulosechem.*, **1**, 2 (1920).

[154] Schwalbe and Robsahm, *loc. cit.*; Lew, *Papier-Fabr.*, **12**, Nos. 34, 35, and 36 (1914); *ibid.*, **16**, 741 (1918); Heuser, *ibid.*, **12**, 1196, 1205 (1914); Sieber, *Zellstoff u. Papier*, **2**, 134 (1922).

[155] Schwalbe and Becker, *Z. angew. Chem.*, **32**, 265, 355 (1919); Schwalbe, *ibid.*, **37**, 125 (1924).

[156] Schwalbe and Teschner, *Papier-Fabr.*, **23**, 144 (1925); see also Schwalbe, *ibid.*, **21**, 73 (1923).

[157] Rowland, *J. Phys. Chem.*, **41**, 907 (1937).

Alkali Compound Formation with Mercerized and Regenerated Cellulose

It might be expected that mercerized and regenerated cellulose are capable of forming alkali compounds, and x-ray analysis of alkali-containing mercerized cellulose shows this to be true.[158] In addition, mercerized cellulose is capable of taking up a quantity sufficient to form an alkali compound from alkali solutions of lower concentration than that required for native cellulose. The critical change of the x-ray pattern has been observed to occur at concentrations between 10.8–11.85 per cent sodium hydroxide when mercerized cellulose was the starting material, compared with 13.4–14.1 per cent for native cellulose.[159] Likewise, the inflection of the Vieweg curve has been shown to occur at a concentration of 10 per cent when cuprammonium rayon was the starting material against 15 per cent with native cotton.[160]

At the same concentration at which the equivalence of 2 $C_6H_{10}O_5$: 1 NaOH appears, swelling reaches its maximum. This coincidence is shown in Fig. 42. The swelling curve was obtained by allowing cuprammonium rayon to remain in contact with sodium hydroxide solutions of increasing concentration and removing the excess liquid by pressing.[161] The points of the upper curve represent the weights of sodium hydroxide solution in grams taken up by 100 grams of cuprammonium rayon. The lower curve represents results obtained with cotton by using the Vieweg method. The part of the upper curve drawn as a dotted line indicates that a considerable part of the regenerated cellulose has become soluble in the alkali, a fact which interferes with the exact determination of the point of maximum swelling. With viscose rayon, which is much more soluble in alkali, this interference is still more pronounced, but here, also, swelling maximum is reached with a mercerizing liquor of about 10 per cent concentration.[162] Weltzien and zum Tobel's results have been confirmed by Saito.[163]

Potassium hydroxide solution possesses less pronounced swelling power for cellulose than the sodium base.[164] This difference in the two alkalies, which

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[158] von Susich and Wolff, *Z. physik. Chem.*, **B8**, 221 (1930).

[159] Calkin, *J. Phys. Chem.*, **40**, 27 (1936).

[160] Weltzien and zum Tobel, *Seide*, **31**, 131 (1926); Weltzien, "Chemische und physikalische Technologie der Kunstseiden," p. 98.

[161] Weltzien and zum Tobel, *loc. cit.*

[162] Saito, *Kolloid-Beihefte*, **49**, 394 (1939); see also Katz in Hess, "Die Chemie der Cellulose," p. 742 (native cellulose).

[163] Saito, *loc. cit.*, p. 413.

[164] Hall, "Cotton Cellulose," p. 61; *J. Soc. Dyers Colourists*, **45**, 98, 171 (1929).

has been noticed frequently,[165] is commercially utilized in the mercerization of mixed fabrics which contain cotton and rayon. By using aqueous potassium hydroxide instead of sodium hydroxide as the mercerizing liquor, the danger of rayon becoming unduly attacked is reduced.

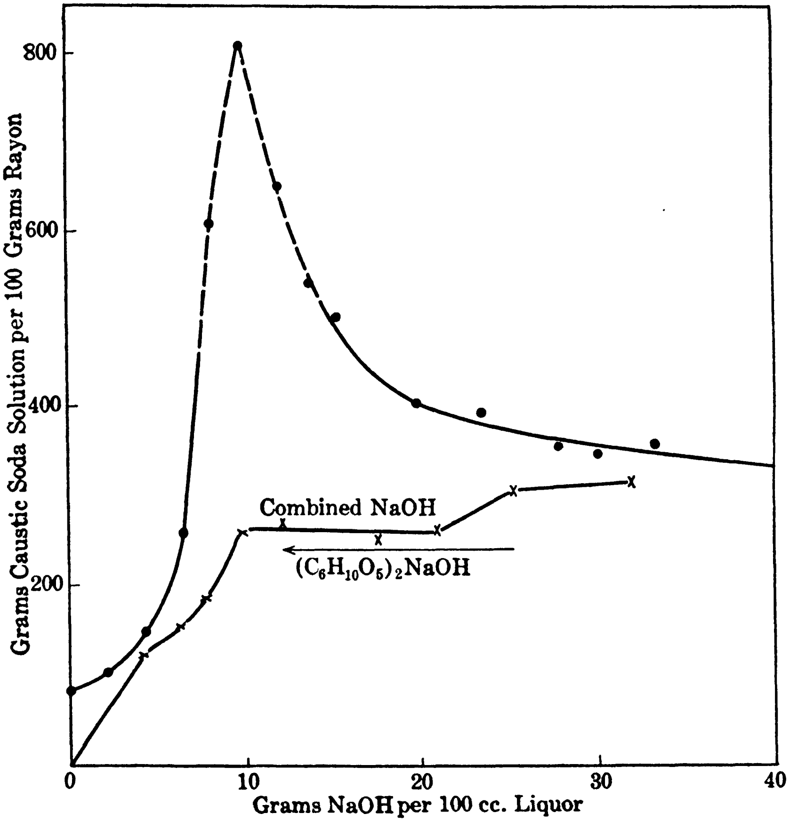

FIG. 42. Swelling of cuprammonium rayon in sodium hydroxide solution of increasing concentration. Weltzien and zum Tobel.

Owing to the complexity of the physical structure of cellulose fibers and the multitude of physical phenomena resulting therefrom, difficulties are encountered in reproducing comparable results on different cellulosic materials. As has been seen in the foregoing sections, the degree of swelling of the cellulosic material influences the chemical reaction greatly. Saito[166] regards swelling as a phenomenon which "in-

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[165] See, for example, Davidson, *J. Textile Inst.*, **25**, T174 (1934); **27**, T112 (1936).

[166] Saito, *loc. cit.*, p. 418.

terferes" with the mechanism of the chemical reaction, inasmuch as the completeness of this reaction depends upon the extent to which the cellulosic material is capable of swelling. Bearing this in mind, due consideration must be given to the fact that different cellulosic materials swell under the same conditions of treatment to a different extent. As Saito has put it, the materials display different "resistance to swelling." Thus, in comparing ramie with cotton (both having the same degree of polymerization), Saito found the former to show the swelling maximum and the inflection point of the Vieweg curve at a lower alkali concentration than required by cotton, the ramie fiber being thus less resistant to swelling than the cotton fiber. Still less resistant to swelling are the artificial cellulosic fibers; here, maximum swelling and inflection occur at a still lower alkali concentration. Saito has confirmed this observation on cuprammonium rayon.

Thus, the amount of alkali taken up by different cellulose fibers may be regarded as a function of their resistance to swelling. The greater this resistance, the higher must be the concentration of the mercerizing liquor or the lower the temperature to force the alkali (and the water) into the intramicellar system.

Differences in resistance to swelling are chiefly a result of the differences in the submicroscopic structure prevailing in different cellulose fibers. For example, the angle at which the micelles are oriented in respect to the fiber axis and the ratio of the crystalline to the noncrystalline portion of the micellar system, varying in different types of fibers, influence the resistance to swelling. In addition, the degree of polymerization of the cellulosic material is of pronounced influence. No doubt, this influence is operative in rayon fibers (which have a degree of polymerization much lower than naturally grown fibers) and contributes to their lower resistance to swelling.[167]

Dyestuff Absorption of Mercerized and Regenerated Cellulose

Mercer seems to have paid particular attention to this feature of the process which bears his name. Most of the numerous investigations which followed were undertaken for practical reasons rather than from a scientific viewpoint. Of the various types of dyestuffs, direct and vat dyes are most suitable to show the increased absorptive capacity of mercerized cellulose, which is twice or more that of native cellulose. Similar increased absorption is observed with sulfur dyes.

As would be expected, the dyeing capacity of the cellulose fiber in-

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[167] See also Sisson and Saner, *loc. cit.*

creases with increasing concentration of the mercerizing liquor, that is, the dyeing capacity reaches a maximum when the concentration of the mercerizing liquor produces maximum swelling, and rather sharply decreases with further increasing alkali concentration.[168]

Cellulose mercerized with potassium hydroxide possesses less absorption capacity for dyes than cellulose mercerized with sodium hydroxide. This result is evidently due to the lower swelling power exerted by the potassium base.

Because drying of the mercerized fiber reduces its ability to absorb water and to take up alkali, it also lowers its dyeing capacity. An example is shown in Table 9 (Knecht).

TABLE 9

INFLUENCE OF DRYING ON THE DYEING CAPACITY OF UNMERCERIZED AND MERCERIZED COTTON YARN

Cotton Yarn	Benzopurpurin, % Absorbed	Chrysophenin, % Absorbed
Unmercerized	1.77	0.58
Mercerized, dyed without drying	3.24	0.96
Mercerized, air-dried before dyeing	3.03	0 92
Mercerized, dried at 110° before dyeing	2.51	0.84

Regenerated cellulose, for example, rayon, possesses a similar or even a greater capacity for dyestuffs than the mercerized fiber.[169] With rayon, this capacity depends to a large extent upon the conditions of the spinning process, particularly upon the degree of stretching and the composition and the temperature of the setting bath. The effect of these and other factors on the dyeing capacity of the various rayon types and upon the uniformity of the dye absorption has been thoroughly investigated by Weltzien and collaborators.

The behavior of native cellulose to dyestuff solutions has been and is still being the subject of numerous investigations. Likewise, numerous theories of dyeing have been suggested. Most of the older theories[170] have now been abandoned. The more recent development is presented in various compilations.[171] The elucidation of the fine structure of the textile fibers has influ-

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[168] Hübner and Pope, *J. Soc. Chem. Ind.*, **23**, 404 (1904); see also Knecht, *J. Soc. Dyers Colourists*, **24**, 67, 107 (1908); Boulton and Morton, *ibid.*, **56**, 151, 155, 1156 (1940).

[169] Hanson, Neale, and Stringfellow, *Trans. Faraday Soc.*, **31**, 1718 (1935). Regarding studies of the dyeing of cellophane sheets, see the same authors, *ibid.*, **29**, 1167 (1933); **30**, 271, 386, 395, 905 (1934).

[170] See the brief review in Heuser, "Lehrbuch der Cellulosechemie" (1927), 3rd ed., p. 29.

[171] Boulton and Morton, *J. Soc. Dyers Colourists*, **56**, 145 (1940); Valkó, "Kolloidchemische Grundlagen der Textilveredelung," p. 389.

enced and furthered this development to a great extent. Today, it is generally believed that the cotton dyes, i.e., substantive (direct) and leuco vat dyes, are absorbed from their aqueous solution and that the dye forms a molecular compound with the cellulose. The forces which are operative in binding the dye to the fiber are probably the same that are instrumental in holding the individual chain molecules together. These forces may be operative as secondary valences or as co-ordinative hydrogen bonds between the hydroxyl groups of the cellulose and certain polar (amino, hydroxyl, etc.) groups of the dye molecule.[172]

The capillary system of the fiber on the one side and the particle size of the dye molecules on the other are of great importance, because the dye molecules must penetrate the capillaries to reach the interior of the fiber, and only dyes of sufficiently small particle size can enter the finer and finest capillaries. Even in the swollen state, which is a prerequisite for dye absorption, the chains within the crystalline regions of the micellar system are probably packed too closely to be reached by the common dye molecules; for this reason penetration is generally limited to the amorphous regions.

The dye is evidently absorbed not only on the surface but is distributed through the whole fiber. The rate of absorption, depending upon such factors as the ratio of dye bath to fiber, the temperature and the salt concentration of the dye bath, decreases until an equilibrium is reached. In this state, the amount of dye absorbed by the fiber is in equilibrium with the concentration of the dye dissolved in the bath.[173]

A study of the kinetics of dyeing, a diffusion process, has shown that dye absorption follows to a first approximation the course expected of a process obeying the simplest diffusion law. However, the diffusion of dyes into naturally grown cellulose fibers seems to be more complex than it is with regenerated cellulose fibers.

The Reactivity of Mercerized and Regenerated Cellulose

The reactivity of mercerized and the various types of regenerated cellulose is greater than that of the untreated, original material. However, this holds true only if the cellulosic materials are not dried at an elevated temperature.

The greater reactivity of mercerized cellulose may be demonstrated in various ways. For example, mercerized cellulose is hydrolyzed by acids at a faster rate than the original material. A method of demonstrating this difference[174] consists in determining the copper numbers of the original cellulosic material and of the product after hydrolysis with sulfuric acid for a definite length of time.

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[172] Meyer, *Melliand Textilber.*, **9**, 572 (1928); Eistert and Valkó, in Valkó's book, p. 408. See also Broda and Mark, *Papier-Fabr.*, **35**, 471 (1937).

[173] Boulton and Morton, *loc. cit.*, pp. 150, 152.

[174] Schwalbe, *Z. angew. Chem.*, **21**, 1323 (1908); **22**, 200 (1909); **23**, 924 (1910); see also Bernardy, *Z. angew. Chem.*, **39**, 259 (1926); Dorée, "Methods of Cellulose Chemistry."

Table 10 gives some results.[175] It is seen that, for the same period of time, mercerized cellulose and the rayon types are degraded to a greater extent than the original cellulose. The "difference due to hydrolysis" may be used as a measure of the reactivity of cellulosic materials. The reactivity increases with the degree of mercerization and is no doubt dependent upon the degree of orientation which prevails in the physically modified form of cellulose.

TABLE 10

REACTIVITY OF CELLULOSE, MERCERIZED AND REGENERATED CELLULOSE. COPPER NUMBER BEFORE AND AFTER HYDROLYSIS (15 MINUTES' BOILING WITH DILUTE SULFURIC ACID)

Cellulosic Material	Copper Number	Copper Number after Hydrolysis	Difference due to Hydrolysis *
Medical cotton	1.1	3.3	2.2
Mercerized cotton	1.3	5.0	3.7
Cuprammonium rayon	1.5	12.8	11.3
Viscose rayon	1.9	14.0	11.5

* *Hydrolysier-Differenz* according to Schwalbe.

Nickerson[176] has shown that the rate of carbon dioxide evolution from cellulose under the action of boiling dilute hydrochloric acid in the presence of a catalyst (see p. 503) is considerably higher with mercerized than with unmercerized cellulose. This difference was used for calculating the amorphous portion present in the two cellulose types. Whereas this portion was 5 per cent for cotton it amounted to 11 per cent for the mercerized product.

Another way to demonstrate the higher reactivity of mercerized, as compared with unmercerized, cellulose is to subject both materials to a certain degree of oxidation. This[177] may be conveniently accomplished by means of a standardized treatment with sodium hypobromite. Again, the copper number is determined on both the original materials and the samples which have been oxidized. The difference between the copper number before and after oxidation indicates the rate of oxidation. The reactivity increases with the concentration of the mercerizing liquor and passes through a maximum. In Fig. 43 the concentration of the mercerizing liquor is plotted against the ratio of the two rates of reaction, i.e., the reactivity ratio. It is seen that the greatest increase of the reactivity ratio occurs at a concentration of

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[175] Schwalbe, "Chemie der Cellulose," 1st ed., p. 172.

[176] Nickerson, *Ind. Eng. Chem.*, **34**, 85, 1149 (1942).

[177] Birtwell, Clibbens, Geake, and Ridge, *J. Textile Inst.*, **21**, T85 (1930).

the mercerizing liquor of between 8 and 16 per cent; then (at 18°) the curve becomes flatter with the tendency to decrease when the concentration of the mercerizing liquor further increases. The range of maximum reactivity coincides with the swelling maximum. A comparison with Fig. 38 shows that it also coincides with the maximum hygroscopicity of the cotton, the material having been the same in both sets of experiments. We also note the favorable influence of low temperature, the maximum reactivity being reached at a lower concentration, i.e., at 12 instead of 18 per cent sodium hydroxide.

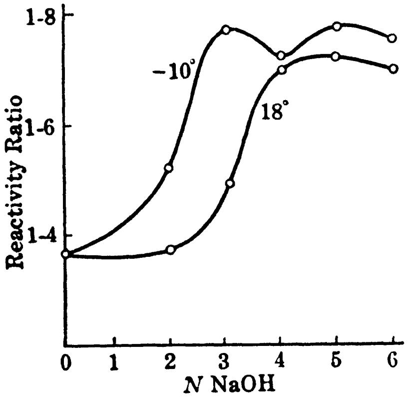

FIG. 43. Concentration of mercerizing liquor and reactivity ratio of cotton. Birtwell, Clibbens, Geake, and Ridge.

Besides hydrolysis and oxidation, other types of reaction may be selected to demonstrate the greater reactivity of mercerized and regenerated cellulose. Thus, acetylation will be found to proceed at a faster rate with mercerized cellulose, provided it has not been subjected to drying.

Mercerized and regenerated cellulose are also more susceptible to the action of certain enzymes than native cellulose. The enzyme which was found to perform this action most suitably is present in the liver secretion of the Roman snail, *Helix pomatia*.[178]

SOLUBILITY OF CELLULOSE IN AQUEOUS ALKALIES

In earlier sections reference has been made to the partial solubility of cellulose in aqueous alkali solutions as a source of interference with the exact estimation of the amount of alkali taken up by a cellulosic material, as well as with the accurate location of the maximum swelling point (p. 110).

In this connection a brief review of what is known about the solubility of cellulose in aqueous alkali, in addition to information discussed earlier in this chapter, might be of interest.

As far as can be ascertained from available experimental data, the solubility of cellulose in dilute and in strong alkali hydroxide solu-

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[178] Karrer, *Z. angew. Chem.*, **37**, 1003 (1924); Karrer and Illing, *Kolloid-Z.*, 36 (Supplement Volume), 91 (1925); *Helv. Chim. Acta*, **8**, 245 (1925); Karrer, Schubert, and Wehrli, *ibid.*, **8**, 797 (1925); Karrer, "Polymere Kohlenhydrate," Akad. Verlags-Ges., Leipzig (1925), p. 212. See also Pringsheim and Thilo, *Cellulosechem.*, **11**, 100 (1930).

tions depends, in general, upon the degree of polymerization of the cellulosic material and upon the concentration and the temperature of the alkali solution. Of secondary influence is the type of alkali chosen. In addition, the visible and invisible morphological structure of the cellulosic material is a controlling factor.

Whenever cellulose is brought into contact with strong aqueous alkali, it is subject to oxidation unless the air, which is held within the fibers and which is present in the aqueous alkali, is carefully excluded. If the conditions are such that the cellulosic material exposes a large surface, the effect may reach considerable proportions.

For an exact comparison of the action of aqueous alkali upon cellulosic materials the influence of oxidation should therefore be eliminated. Weltzien[179] has recommended carrying out alkaline treatments in an atmosphere of nitrogen, and Staudinger and Jurisch[180] have suggested that, in addition, the aqueous alkali be freed of dissolved oxygen by distillation in the nitrogen atmosphere. These precautions, which, as will be seen later, are not sufficient in certain cases, were seldom taken in earlier studies, and therefore the results obtained by different or even the same investigators are not always strictly comparable.

Data on the solubility of cotton and other naturally grown textile fibers are scarce. It is generally believed that these cellulosic materials, provided they have been isolated from their respective sources with reasonable care, are practically insoluble in dilute alkali but soluble to a varying extent in stronger aqueous alkali.[181] Thus, cotton cellulose in the form of bleached cotton fiber, which may be practically insoluble in aqueous alkali up to a concentration of 5 per cent, may lose 1–2 per cent when treated with aqueous alkali of higher concentration. The solubility of all cellulosic materials shows a maximum at that concentration at which maximum swelling is produced.

The change in the solubility of bleached cotton fiber and of sulfite wood pulp is seen from the data below, which are taken from the work of D'Ans and Jäger.[182] It is seen that, in both cases, the solu-

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[179] Weltzien, *Papier-Fabr.*, **32**, 433 (1934).

[180] Staudinger and Jurisch, *Kunstseide und Zellwolle*, **21**, 7 (1939).

[181] Schwalbe, "Chemie der Cellulose," 1st ed., pp. 37, 40. See also Birtwell, Clibbens, and Geake, *J. Textile Inst.*, **19**, T349 (1928); Davidson, *ibid.*, **25**, T174 (1934). Schieber, *Melliand Textilber.*, **20**, 622 (1939), reports a solubility of 1.5–2.0 per cent in 10 per cent sodium hydroxide solution at 20° for cotton (not specified).

[182] D'Ans and Jäger, *Cellulosechem.*, **6**, 146 (1926); see also Lewis, *Paper Trade J.*, **95**, No. 24, 29 (1932); Neumann, Obogi, and Rogovin, *Cellulosechem.*, **17**, 87 (1936).

bility reaches its maximum at 12 per cent sodium hydroxide. A comparison of the two sets of data also shows the influence of polymerization of the cellulosic material: The solubility of wood pulp is considerably greater than that of cotton. Part of this greater solubility is, of course, due to the presence of noncellulosic carbohydrates (pentosans and hexosans) but this portion would amount to hardly more than 4–6 per cent, so that there is a noticeable difference after this correction has been made.

TABLE 11

Solubility of Cotton and Wood Pulp in Aqueous Alkali of Increasing Concentration

Cotton

Concentration NaOH, %	8.0	12.0	16.5	19.7	24.0	28.0	31.0	35.2	38.6
Dissolved, %	1.7	6.7	4.4	3.3	2.9	2.8	2.2	1.3	0.1

Wood Pulp

Concentration, %	8.3	12.3	15.7	19.9	24.1	27.8	31.6	35.2	37.8	42.6
Dissolved, %	14.5	21.4	15.6	14.2	12.1	10.2	8.5	5.0	3.0	1.4

That the solubility of wood pulp varies considerably with its type may be seen from results obtained by Weltzien[183] on a number of wood pulps used for conversion purposes and for paper manufacture. Although, again, all pulps investigated showed a solubility maximum at 10–12 per cent alkali concentration, the quantities dissolved (at 12 per cent concenfration) varied for various rayon pulps, for instance, from 14.1 to 12.5 to 15.8 per cent; this no doubt is due chiefly to the difference in degree of polymerization.

The degree of polymerization of wood pulps changes with the conditions of pulping and bleaching. The influence of such conditions is clearly seen from the results published by Lottermoser and Radestock.[184] In addition, the type of the pulping process was found to be of substantial influence, for pulps resulting from alkaline (sulfate) cooking showed a higher maximum solubility than those which originated from sulfite cooking. Although it would appear that this difference is chiefly a result of a characteristic and pronounced difference in the chain length distribution of the two pulps,[185] the physical

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[183] Weltzien, *Papier-Fabr.* (1928), Special number, 115; *Seide*, **33**, 261 (1928); "Chemische und physikalische Technologie der Kunstseiden," p. 91.

[184] Lottermoser and Radestock, *Z. angew. Chem.*, **40**, 1506 (1927).

[185] Atchison, doctoral dissertation, Institute of Paper Chemistry, Appleton, Wis. (1942), carried out under the direction of E. Heuser. *Paper Trade J.*, **116**, No. 22, 23 (1943).

structure of the fiber might also be affected differently by the two processes. The effect of a change in the physical state of the fiber is also revealed by the fact that pulps which have been beaten are soluble in aqueous alkali to a greater extent than those which are used in the unbeaten state.

On the basis of the relationship which exists between degree of polymerization and alkali solubility,[186] it should be possible to separate shorter from longer chain material by extraction with alkali. In fact, such a separation is accomplished when the *alpha*-cellulose fraction is isolated from a cellulosic material and the *beta*- and *gamma*-cellulose fractions are left in solution. Moreover, by employing alkali solutions of varying concentration or of constant concentration, but of decreasing temperatures, it is possible to subdivide the long-chain *alpha*-cellulose still further. Attempts of this kind have been made with various cellulosic materials[187] and with modified cellulose, such as oxycellulose and hydrocellulose (see later).

The time of treatment has relatively little influence upon the solubility of cellulosic materials. With wood pulps, a slight increase with time was observed, although the relatively long time of 30 hours was required before the end point was reached, which then did not change even over several days (Lottermoser and Radestock). On the other hand, Cross and Bevan[188] have observed that when cellulose is allowed to stand in strong alkali solution for several months it is almost entirely dissolved.

Temperature has a greater effect; it causes the solubility to increase (Lottermoser and Radestock). However, under these conditions, swelling cannot be responsible for this increase because, as we have seen, it decreases with temperature. The effect, therefore, is due to the degrading influence which the alkali exerts at the higher temperature and in the presence of air. The reactions which take place under these conditions are discussed later (see Chapter X).

On the other hand, lower temperature favors solubility because it favors swelling, even at a considerably lower alkali concentration. Reference is made to Lilienfeld's patents[189] according to which cotton linters and other cellulosic materials are said to be entirely soluble in 4–10 per cent sodium hydroxide solutions at temperatures from 0 to

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[186] Mark, "Physik und Chemie der Cellulose," p. 200.

[187] Neumann, Obogi, and Rogovin, *Cellulosechem.*, **17**, 87 (1936); see also Schieber, *Melliand Textilber.*, **20**, 622 (1939); Marschall, *Kunstseide und Zellwolle*, **23**, 160 (1941); Eisenhuth, *Cellulosechem.*, **19**, 45 (1941).

[188] Cross and Bevan, *Chem.-Ztg.*, **33**, 368 (1909).

[189] Lilienfeld, British patent 212,864.

−10°. It is likely, however, that complete solution is achieved only if the materials are of a relatively low degree of polymerization.[190] The relationship between alkali concentration and temperature is also seen from data published by Fukushima and Takamatsu.[191]

By repeated freezing and thawing of a mixture of cellulose and aqueous alkali, larger quantities of cellulose may be dissolved.[192] Obviously, freezing results in the formation of numerous fine cracks in the fiber which increase its internal accessibility to the aqueous alkali.

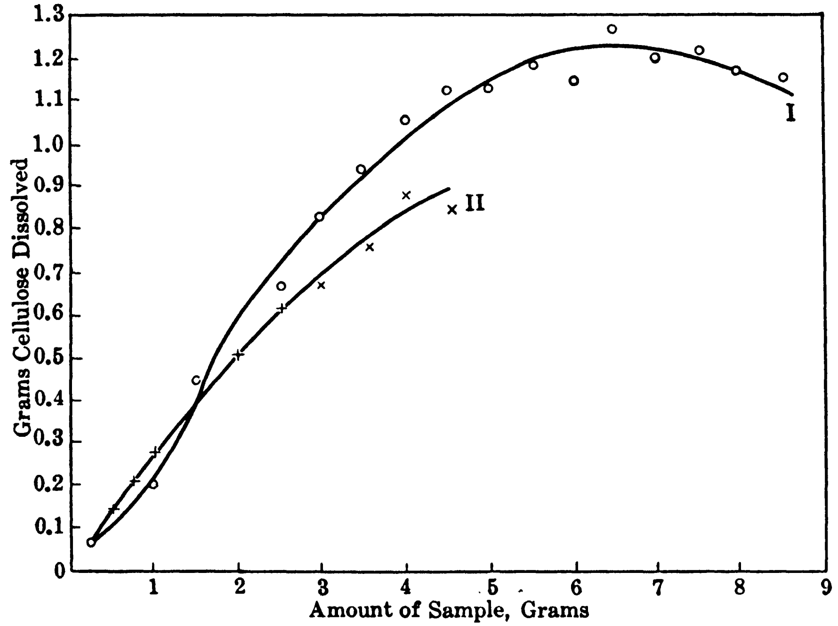

FIG. 44. Influence of amount of cellulose used upon alkali solubility. von Neuenstein.

Considering the fact that cellulose is capable of taking up alkali from the solution it will be understood that, with increasing amounts of insoluble material present ("Bodenkörper"), the concentration of the surrounding alkali solution and, thus, its dissolving power decreases. von Neuenstein[193] has studied the influence of the quantity of cellulosic material upon its solubility in a 9.4 per cent sodium

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[190] Hall, *J. Soc. Dyers Colourists,* **45**, 98 (1929).

[191] Fukushima and Takamatsu, *Cellulose Ind.* (Tokyo), **27** (1929).

[192] Staudinger and Sorkin, *Ber.,* **70**, 1565 [1575] (1937).

[193] von Neuenstein, *Kolloid-Z.,* **43**, 241 (1927); see also Davidson, *loc. cit.,* p. T174; reference 181.

hydroxide solution at 20°, using a sulfite wood pulp. By plotting the grams of cellulose used against the quantities dissolved in 100 cc. of the solution, the influence of the decrease in alkali concentration is recognized when the quantity of cellulose brought into contact with the alkali solution has reached a certain value (Fig. 44). Curve I refers to a time of contact between the sample and the sodium hydroxide solution of 44 hours and curve II to a time of 5 days. The solubility decreases as the amount of cellulose becomes larger. This result suggests that, in order to determine the "true" alkali-solubility of cellulosic materials, the concentration of the alkali solution must be adapted to the amount of cellulose used. In other words, the concentration of the alkali solution should be so high that the concentration-lowering effect is sufficiently counterbalanced.

Solubility of Regenerated Cellulose

Weltzien[194] has made a comprehensive study of the solubility of various rayon types. The concentration at which the maximum solubility occurred was about 10 per cent at 20°. The amount dissolved at this concentration varied widely with the type of rayon. It was found to be 40–50 per cent for viscose rayon, 31 per cent for cuprammonium rayon, and 98–99 per cent for nitro and acetate rayons.

The quality of rayon has since been much improved, and lower alkali solubility figures are reported, even as low as 5–10 per cent for viscose rayon staple fiber (at 9 per cent alkali concentration, at which maximum solubility was observed), although a great variety of alkali solubility still exists.[195] More recent tests[196] show the alkali solubility of viscose staple fiber (*Zellwolle*) to vary from 3.5 to 25 per cent, whereas cuprammonium rayon staple fiber was found to be soluble to the extent of 12 per cent in 10 per cent sodium hydroxide solution, i.e., at optimum alkali concentration.

Table 12, which contains some of the numerous data published by Schramek and Christoph,[197] shows the solubility in 10 per cent sodium hydroxide solution at 20° and the degree of polymerization of various

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[194] Weltzien, *Seide*, **32**, 367 (1927); see also *Melliand Textilber.*, **6**, 355 (1925); Weltzien and zum Tobel, *Seide*, **31**, 132 (1926); Weltzien, *Papier-Fabr.*, **32**, 433 (1934); Weltzien, "Chemische und physikalische Technologie der Kunstseiden," p. 140. See also Davidson, *J. Textile Inst.*, **25**, T174 (1934); Saito, *J. Chem. Soc. Japan* (Supplementary Binding), **37**, 639 (1934).

[195] Schramek and Christoph, *Kolloid-Beihefte*, **48**, 260 (1938).

[196] Schieber, *Melliand Textilber.*, **20**, 621 (1939).

[197] Schramek and Christoph, *loc. cit.*, pp. 319, 328, 330.

samples of viscose rayon staple fiber. The degree of polymerization was calculated from the cuprammonium viscosities (expressed in centipoises; cellulose concentration 1 per cent; falling ball method) according to Staudinger's equation. The wood pulp from which the rayon was manufactured had a degree of polymerization of 580. The data show that the alkali solubility is much greater with the samples having a lower degree of polymerization, but no straight relationship can be deduced from these data, possibly because the samples were not manufactured under comparable conditions.

TABLE 12

MAXIMUM ALKALI SOLUBILITY AND DEGREE OF POLYMERIZATION OF VISCOSE RAYON STAPLE FIBER

Maximum solubility, %	5.4	9.8	41.9	36.6	41.8	40.1
Degree of polymerization	430	380	285	270	265	255

Another set of data is represented in Fig. 45, from which it will be seen that a direct relationship seems to exist between alkali solubility and degree of polymerization. Obviously, in this case, the samples (viscose rayon staple fiber) were directly comparable.[198]

If the degrees of polymerization as shown in Table 12 and in Fig. 45 are compared with that of sulfite wood pulp, which usually serves as the starting cellulosic material for viscose rayon, and which may range between 500 and 800, it is seen that the cellulose has been considerably degraded during the various steps of rayon manufacture.[199]

In judging the alkali solubility of natural cellulose, rayon, and other synthetic fibers, it is not the degree of polymerization alone which is responsible for the result. The degree of crystallite orientation, which, as we have seen, varies widely with the type of fiber, may play an equally important part. In fact, with the degree of polymerization kept constant, the alkali solubility decreases with the degree of orientation,[200] the more highly oriented fiber being less subject to swelling than a fiber which still contains a considerable portion of amorphous material.

Recent studies by Staudinger and co-workers have furnished us

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[198] Schieber, *loc. cit.*, p. 621.

[199] Staudinger and Feuerstein, *Ann.*, **526**, 72 (1936); Staudinger, *Papier-Fabr.*, **35**, 233 (1937); Staudinger, Sorkin, and Franz, *Melliand Textilber.*, **18**, 681 (1937); Staudinger and Jurisch, *Kunstseide und Zellwolle*, **21**, 6 (1939).

[200] Schramek and Christoph, *loc. cit.*, pp. 275, 304; see also Atsuki and Shimoyama, *loc. cit.*; Micheels, Schmitz, and Weber, *Melliand Textilber.*, **17**, 725, 804 (1936); see also Wannow, *Kolloid-Z.*, **93**, 180 (1942).

with some interesting data on the different behavior of original and regenerated cellulose when these are subjected to the action of alkali solutions of optimum dissolving concentration. A number of fibrous cellulose samples of decreasing degree of polymerization were prepared from cotton and from ramie by degrading treatments with various acids. It was found[201] that preparations from cotton having a degree of polymerization below 400 were completely soluble in 11 per cent caustic soda solution, whereas the ramie preparations were soluble therein up to a degree of polymerization of 1000. Moreover, it was found that lithium hydroxide, which, as we have seen, exerts a greater swelling effect than sodium hydroxide,[202] also possesses a greater solvent power. A solution containing 7.5 per cent lithium hydroxide dissolved cotton cellulose of degrees of polymerization up to 500 and ramie cellulose of up to 1200.

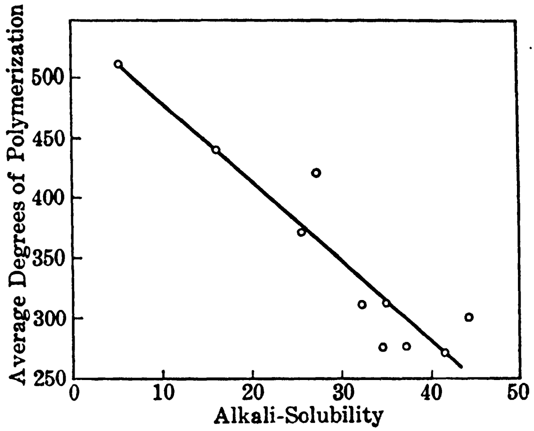

FIG. 45. Maximum alkali solubility and degree of polymerization of viscose rayon staple fiber. Schieber.

When cellulose preparations, regenerated from their solution in cuprammonium, in the wet state, were brought into contact with aqueous alkali, their solubility had considerably increased relative to the original preparations. That any degrading influence during regeneration was eliminated is seen from the fact that the degree of polymerization had not changed during this procedure. Such regeneration without degradation may be accomplished by careful elimina-

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[201] Staudinger and Sorkin, *Ber.*, **70**, 1565 (1937); Staudinger and Jurisch, *Kunstseide und Zellwolle*, **21**, 6 (1939).

[202] See also Lottermoser and Radestock, *Kolloid-Z.*, **40**, 1509 (1927).

tion of air on solution and precipitation (by means of Rochelle salt solution).[203]

The solubility of the regenerated (moist) cellulose preparations could be increased considerably by lowering the temperature of the alkali solutions. At a temperature of −10 to −15° regenerated cellulose with a degree of polymerization of up to 1500 dissolved in the sodium hydroxide solution and that with a degree of polymerization of 1500 up to 2500 dissolved in the lithium hydroxide solution. Such solutions were found to have a very high viscosity; the sodium hydroxide solution gave a transparent gel.

In view of the fact that the *fibrous* celluloses used in these experiments, that is, of such high degrees of polymerization corresponding to molecular weights of 243,000 and 405,000, are practically insoluble in aqueous alkali, the results obtained with the regenerated preparations are quite interesting, for they show that native cellulose may be converted into a completely alkali-soluble modification without degradation.

The solubility of moist regenerated cellulose (even of very high degree of polymerization) at low temperature is very probably a result of the enormous swelling ability which regenerated cellulose displays under such conditions. Moist regenerated (precipitated) cellulose may be assumed to have its crystallites oriented only to a small extent. The prevalence of disordered, that is, amorphous, regions favors the ability of the system to swell and consequently to become hydrated in water or aqueous alkali to such an extent that the secondary valency forces are no longer capable of holding the crystallites in shape. Eventually the cellulose dissolves. Lowering the temperature enhances this behavior considerably, but drying seems to impede it, causing the system to contract and the crystallites to orient themselves in such a manner that the secondary valency forces again come into play. The system is now in a state in which it approaches that of the original fibrous cellulose.

In the light of this interpretation, it is of considerable interest that Staudinger and Jurisch found the regenerated cellulose preparations to dissolve in aqueous alkali of optimum concentration even after drying, provided the time of contact was long enough. This result is in contrast to the usual experience, namely, that the process of drying is reversible only to a limited extent.[204] Probably much depends upon the

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[203] Staudinger and Ritzenthaler, *Ber.*, **68**, 1225 (1935); Staudinger and Feuerstein, *Ann.*, **526**, 72 (1936).

[204] Hess, "Chemie der Cellulose," p. 321.

method and the intensity of drying, and it is conceivable that regenerated cellulose, if carefully dried, might regain its ability to swell and to dissolve entirely because careful drying may mean that the regenerated cellulose has not acquired a sufficient amount of orientation.[205]

Solutions of regenerated cellulose (of degrees of polymerization up to 1000) in 10 per cent sodium hydroxide solution at −5° are said to be unsusceptible to oxygen and may therefore be used for viscosity determinations to replace the sensitive cuprammonium hydroxide solution.[206]

The dissolving power of alkali solutions may be increased by the addition of zinc oxide. Howlett and Urquhart[207] have suggested such a solution for the estimation of rayon in cotton-rayon mixed fabrics; rayon dissolves in this solution, whereas cotton does not. As may be anticipated from this effect, addition of zinc hydroxide increases the swelling power of alkaline solutions. This was known to Mercer,[208] who found that even an 8.5 per cent sodium hydroxide solution had a mercerizing action at room temperature if a certain amount of zinc hydroxide had been added. Likewise, Lewis[209] used such mixtures as a means of enhancing the swelling of cotton. An explanation of the effect of the zinc oxide is still missing.

Other electrolytes (for example, sodium chloride) reduce the solubility of cellulose. Commercial practice makes use of this fact when the alkali solution employed for mercerization is to be removed by washing. As the solubility of cellulose decreases after it has passed through its maximum, it will inversely increase again when the strong solution, left in the mercerized material after centrifuging, is diluted with water, because the concentration will pass through the maximum solubility point and, further, through such points on the ascending portion of the solubility-concentration curve at which the dissolving power of the solution is greater. This phenomenon will become particularly pronounced with rayon, and it is here that the dissolving effect on washing may be reduced by adding a certain amount of salt to the wash water.[210] Obviously, the presence of the salt counteracts the hydrating effect of the aqueous alkali (see also p. 101).

The different solubilities of fibrous cellulosic materials in sodium hydroxide solution are utilized in the cellulose industries for assaying the value of cellulosic materials. The degree of resistance of a cellulosic material to strong aqueous alkali serves as a criterion of the nature of the treatment to which the material was subjected on isolation. The alkali resistance drops with the severity of the isolating procedures and *vice versa*. According to general experience, a cellulosic material is the more suitable for the manufacture of durable, i.e., age-resistant, paper, rayon, and other cellulose conversion products, the more

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[205] See also Staudinger and Daumiller, *Ann.*, **529**, 226 (1937); *Ber.*, **70**, 2058 (1937).

[206] Schramek, *Kunstseide und Zellwolle*, **24**, 144 (1942).

[207] Howlett and Urquhart, *J. Textile Inst.*, **29**, T43 (1938).

[208] Marsh and Wood, "Introduction to Cellulose Chemistry," p 47.

[209] Lewis, *J. Textile Inst.*, **24**, T122 (1933).

[210] Schramek and Christoph, *Kolloid-Beihefte*, **48**, 287 (1938).

alpha-cellulose it contains. The contents of *beta*- and *gamma*-cellulose are sometimes used as additional characteristics in the evaluation of wood pulp. Staudinger and Jurisch[211] have found for *beta*-cellulose a D.P. from 10 to 150, and for *gamma*-cellulose, below 10 in wood pulp. *Beta*-cellulose thus consists partly, and *gamma*-cellulose entirely, of oligosaccharides. *Gamma*-cellulose has lost its cellulosic nature altogether.

Purified cotton cellulose consists of 98–100 per cent *alpha*-cellulose, whereas commercial wood pulp may vary from 86 to 90 per cent. In order to obtain a rough idea of how much of the noncellulosic carbohydrate material takes part in the alkali-solubility of wood pulp, it has been suggested that the material, before being subjected to the *alpha*-cellulose determination treatment, be extracted with 5 per cent sodium hydroxide solution in which most of the pentosans and hexosans are said to dissolve, whereas the cellulose portion is only slightly soluble.[212]

Data on the composition of "hemicelluloses" (see p. 8) from unbleached spruce sulfite pulp and from soda pine pulp have been reported by Hägglund and Klingstedt;[213] data on the composition of those from bleached sulfite (spruce) pulp, by Heuser and Brötz.[214]

The possibility of removing cellulose portions of a lower degree of polymerization together with noncellulosic carbohydrates from wood pulp is utilized commercially in the manufacture of so-called *alpha* pulp.[215]

THE AGING OF ALKALI CELLULOSE

If alkali cellulose, freed of excess sodium hydroxide solution by pressing or by centrifuging, is allowed to stand, it undergoes certain changes which are designated by the term "aging." The essential result of aging upon the cellulose constituent is seen in an increase of its alkali-solubility and in a decrease of its solution-viscosity. Both effects are due to oxidation with simultaneous cleavage of glycosidic linkings produced by the air oxygen which is present in the system or enters from the outside. In order that the air may exert this effect within a reasonable time it must have access to many parts of the fibrous structure. This condition may be assumed to exist in the pressed-out or centrifuged material, particularly if such a material is subjected to mechanical disintegration, which increases its external surface. If enough liquid has been removed by pressing or centrifuging, we may assume the capillary system of the fiber to hold a cer-

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[211] Staudinger and Jurisch, *Kunstseide und Zellwolle*, **21**, 6 (1939).

[212] Hess, "Die Chemie der Cellulose," p. 254.

[213] Hägglund and Klingstedt, *Cellulosechem.*, **5**, 57 (1924); *ibid.*, **9**, 77 (1928).

[214] Heuser and Brötz, *Papier-Fabr.*, **25**, 238 (1927).

[215] See Jayme, *Paper Trade J.*, **106**, No. 21, 37 (1938); *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **18**, 389 (1938); Rys and Bonisch, *Paper Trade J.*, **108**, No. 19, 31 (1939); Olsen, *Ind. Eng. Chem.*, **30**, 524 (1938).

tain quantity of air. Thus, the air would act on a large internal surface.

This favorable condition does not seem to exist to the same extent if the disintegrated alkali cellulose is allowed to stand in the sodium hydroxide solution, because, in this case, the capillaries of the fibers are partly filled with liquid and the internal surface on which the air oxygen may act is much reduced; under these conditions, alkali cellulose shows the effect of aging to a lesser extent.[216] On the other hand, aging has been observed to occur with alkali cellulose covered with ether.[217] Although an explanation of this behavior which would be compatible with the interpretation of the difference just described is still to be found,[218] this observation shows that for accomplishing the aging effect it is not necessary that air be given access to the material from the outside. On the other hand, alkali cellulose absorbs air from the outside very readily and, unless precautions are taken to prevent this absorption, the aging effect becomes more pronounced.

In commercial practice, the aging of alkali cellulose is an important step in the manufacture of viscose (cellulose xanthate). Its purpose is to decrease the viscosity of the cellulose and, consequently, of the viscose prepared therefrom to such an extent that a solution is obtained which may be filtered and thereafter forced through the spinning nozzles without difficulties.

The increase in alkali-~~solubility~~ during aging is seen in the decrease of the *alpha*-cellulose content of the treated material. For example, the *alpha*-cellulose content [219] of cotton linters which had been steeped in 17.8 per cent sodium hydroxide solution, centrifuged and kept in stoppered glass bottles, had dropped from 98.48 to 97.17 per cent after 24 hours and to 95.79 per cent after 73 hours.[220] If outside air is admitted, the effect becomes more pronounced, particularly if the time of aging is extended. Thus, Waentig [221] found that the *alpha*-cellulose content of wood pulp decreased from 85 per cent to 57 per cent after 30 days of aging, and Heuser and Schuster [222] observed that cotton

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[216] Waentig, *Textile Forschung,* **1,** 154 (1921); *Kolloid-Z.,* **41,** 152 (1927); Rassow and Wadewitz, *J. prakt. Chem.,* **106,** 274, 314 (1923); see also Zimmermann, *Melliand Textilber.,* **23,** 73 (1942); Schramek, *Kunstseide und Zellwolle,* **24,** 144 (1942).

[217] Rassow and Wadewitz, *loc. cit.,* p. 294.

[218] See also Weltzien, "Die chemische und physikalische Technologie der Kunstseiden," p. 211.

[219] *Alpha*-cellulose was determined by washing the alkali cellulose with water until free of alkali.

[220] Heuser and Schuster, *Cellulosechem.,* **7,** 42 (1926).

[221] Waentig, *Kolloid-Z.,* **41,** 155, 156 (1927).

[222] See above; also Weltzien and zum Tobel, *Ber.,* **60,** 2024 (1927).

cellulose had become entirely soluble in 8 per cent sodium hydroxide solution after several months of aging. With the alkali cellulose covered with sodium hydroxide solution, the *alpha*-cellulose content decreased only from 82.5 to 78.6 per cent after 30 days of aging (Waentig).

The decrease in viscosity with the time of aging is shown in Fig. 46. Samples taken at intervals during aging were washed with dilute acetic acid, whereby both *alpha*- and *beta*-cellulose were obtained as a residue. The dried samples were dissolved in cuprammonium hydroxide solution (2 per cent cellulose concentration) and the viscosities were determined with an Ostwald outflow viscometer. The drop in viscosity indicates that the average chain length of the cellulose decreases as aging proceeds.

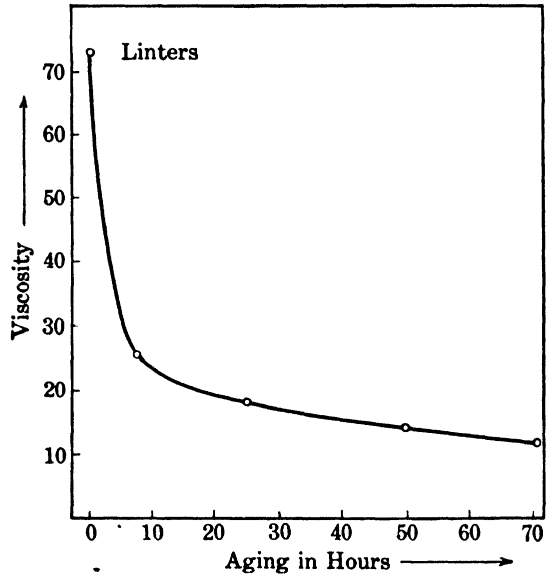

FIG. 46. Decrease of cuprammonium viscosity on aging of cotton linters alkali cellulose. Heuser and Schuster.

Results such as these have been confirmed by later investigators, for example, by Staudinger and Reinecke[223] who applied the same technique to commercial alkali cellulose prepared from wood pulp and calculated from the specific viscosities in cuprammonium solution the degree of polymerization. As an example, the latter was found to

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[223] Staudinger and Reinecke, *Papier-Fabr.*, **36**, 558 (1938). See also Böhringer and Seyffert, *Melliand Textilber.*, **20**, 354 (1939).

have dropped from about 1000 (molecular weight 160,000) for the original wood pulp to 900 (145,800) after 4 hours, and to 300 (48,600) after 113 hours of aging.

Some data from Compton's work[224] enable us to compare the effect of aging on cotton fiber (carefully purified), commercial bleached cotton linters, and commercial rayon pulp. The viscosities of the samples taken at intervals and representing, as in the previous investigation, the total *alpha-* and *beta*-cellulose were determined in cuprammonium solution (0.5 per cent cellulose concentration; modified Clibbens and Geake viscometer[225]) at 25° and expressed in centipoises (η^{25}_{cp}). The results are given in Table 13. The figures show, in accordance with the data represented in Fig. 46, that the greatest degradation during aging occurs in the early stages. A comparison of the three cellulosic materials reveals that, the higher the initial viscosity, the greater the percentage drop. In agreement with Compton's statement, the aging process may therefore be viewed as being essentially a homogenizing process capable of reducing the viscosity of different cellulosic materials to a common viscosity value.

TABLE 13

Effect of Aging upon Cuprammonium Viscosity of Various Cellulosic Materials

Time of Aging (Hours)		η^{25}_{cp}	
	Cotton Fiber	Cotton Linters	Wood Pulp
0	33.0	8.77	5.44
4	27.2	. .	5.14
4.5		8.00	. .
7	. .	7.13	.
22	.	4.76	3.64
48	4.86	3.25	2.85
72	3.75	2.87	2.64
120	.	2.43	2.33

Goldfinger and Mark[226] showed that with wood pulp a small portion of the cellulose went into solution during the early stages of aging before degradation began to become noticeable. The loss in weight was determined on samples, taken at intervals and freed of alkali by washing with dilute alkali, acetic acid and water. Obviously, the material that went into solution was of a low degree of polymerization, for the viscosity of the samples taken at these early stages had

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[224] Compton, *Ind. Eng. Chem.*, **31**, 1251 (1939).

[225] Clibbens and Geake, *J. Textile Inst.*, **19**, T77 (1928).

[226] Goldfinger and Mark, *Paper Trade J.*, **115**, No. 16, 27 (1942).

slightly increased before it dropped when aging was continued. It is noteworthy that after some time the weight of the samples practically ceased to decrease, whereas the viscosity continued to drop.

That the loss in weight came to a standstill seems to indicate that at this point low-molecular-weight material which would dissolve in the alkali of the alkali cellulose was no longer present and that the degrading effect had not yet become so pronounced that it would produce further quantities of alkali-soluble material.

Goldfinger and Mark observed a remarkable resistance to degradation of cotton linters compared with wood pulp and have explained this difference on the assumption that the chain molecules in wood pulp, having undergone a much more drastic treatment during its preparation than cotton linters, have a considerable number of weakened points which render them more susceptible to chemical attack than the chains in cotton linters in which such points of weakness are limited or absent (see also Chapter X).

Goldfinger and Mark have made an attempt to calculate reaction rate constants for the two reactions—the solubilization and the degradation of the cellulose during aging—to which the reader is referred.

The method of ascertaining the change in degree of polymerization of the cellulosic constituent during aging of alkali cellulose described above has been modified by some investigators by converting the samples of *alpha*-cellulose or *alpha*- and *beta*-cellulose, taken at intervals, into cellulose nitrates with subsequent determination of the viscosity of the nitrates dissolved in a suitable organic liquid. On the assumption that the cellulose is not attacked during nitration, the solution-viscosity of the nitrates reflects the degree of polymerization of the cellulose in alkali cellulose. This technique has been applied by Rassow and Wadewitz [227] and by Inoue [228] who, in addition, studied the physical strength of films prepared from the various nitrocellulose samples. It was found that the folding endurance of the films dropped with the time of aging, again indicating a decrease in the average chain length of the cellulosic constituent of the alkali cellulose.

There would appear to be no necessity of employing the nitration method, for estimating the degree of polymerization of cellulose, unless one wishes to go one step further and ascertain its homogeneity, i.e., the chain length distribution and a probable change on aging. The separation of the nitrate into various fractions is easier and more complete than a direct fractionation of the cellulose. As will be seen

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[227] Rassow and Wadewitz, *J. prakt. Chem.*, **106**, 295 (1923).

[228] Inoue, *Cellulose Ind.* (Tokyo), **15**, 94 (1939).

later, various methods for the fractionation of cellulose nitrate are available.

Results on the distribution of chain length in alkali cellulose[229] show that the percentage of short-chain material was higher in a rayon staple fiber prepared from alkali cellulose which was aged for a longer period than in a fiber prepared from alkali cellulose with a shorter aging period.

Acetylation has also been used as a means of converting alkali cellulose into a material which may be more easily and more completely fractionated than alkali cellulose itself. However, if the usual methods of acetylation are employed, the cellulose is considerably degraded, and the viscosities of the acetates (in an organic solvent) of samples taken at intervals can hardly be used for drawing reliable conclusions on the behavior of cellulose during the aging process. Indeed, the statement by Lachs and co-workers,[230] that the relative degree of heterogeneity of cellulose does not change on aging, would appear to be rather improbable.

The process of aging is influenced by a number of factors. The conditions under which the alkali cellulose is prepared—such as the time of contact between cellulose and sodium hydroxide solution (steeping time), the concentration of the latter and the ratio of alkali to cellulose (degree of pressing)—influence the results of aging to varying extents. In addition, the temperature and the action of sunlight during aging are controlling factors. (See also Chapter VIII.)

The rate of aging is distinctly influenced by the presence of certain metals,[231] such as iron, nickel, cobalt, cerium, vanadium, chromium, and manganese; nickel was found the least, and chromium and manganese the most, effective. The effect of iron lies between these two. As little as 0.1 per cent in wood pulp was found to reduce the aging time of the alkali cellulose prepared therefrom to one-fourth of the normal time. Even much smaller quantities of iron—as little as 0.0018–0.015 per cent in wood pulp—were found to have an appreciable effect, the degree of polymerization being reduced by 63 per cent after 25 hours of aging. But with an iron content above 0.015 per cent, no further decrease was observed. It appears that the presence of copper has no influence.[232]

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[229] Böhringer and Seyffert, *loc. cit.*, p. 354; Schieber, *Melliand Textilber.*, **20**, 622 (1939); *Angew. Chem.*, **52**, 561 (1939); Eisenhuth, *Melliand Textilber.*, **20**, 628 (1939); *Angew. Chem.*, **52**, 568 (1939); Mark, *Paper Trade J.*, **113**, No. 3, 34 (1941).

[230] Lachs, Kronman, and Wajs, *Kolloid-Z.*, **84**, 199 (1938).

[231] Wilson, *J. Soc. Chem. Ind.*, **39**, 177T (1920); Davidson, *J. Textile Inst.*, **23**, T113, T121, T122 (1932).

[232] Lottermoser and Wultsch, *Kolloid-Z.*, **83**, 182 (1938); regarding the action of manganese, see also Bartell and Cowling, *Ind. Eng. Chem.*, **34**, 607 (1942).

If the aging process is essentially a process during which the cellulose is degraded by oxidation, the effect should become more pronounced when the amount of oxygen is increased over that which is present in the form of air in the system. The additional oxygen may be supplied in different ways, for example, by adding a certain amount of peroxide or a hypochlorite to the mercerizing liquor. The time of aging may thus be shortened in proportion to the activity of the oxidizing agent employed.[233] (See also Chapter X.)

Inversely, reduction or elimination of the amount of oxygen present in the system ought to diminish or altogether quash the aging effect. Obviously, it does not suffice to allow aging merely to take place in the nitrogen atmosphere, for, depending upon the conditions under which this technique is applied, aging is only more or less diminished but not entirely suppressed.[234] The same situation was encountered when aging was allowed to take place under reduced atmospheric pressure (Waentig). These results suggested that possibly sufficient air had remained in, or subsequently entered into, the system to exert an appreciable effect.

Indeed, even if rigid precautions are taken to remove all air from the surrounding atmosphere (evacuation, nitrogen) and to prevent any air from entering the system, the air which is occluded in the alkali cellulose (originating from steeping, pressing, etc.) and which withstood evacuation suffices to cause a drop in viscosity of the alkali cellulose during aging. However, under such conditions, the viscosity ceases to drop after some time, indicating quite convincingly that this occurs when all air oxygen has been used up. The same effect may be demonstrated by introducing into the alkali cellulose a certain quantity of hydrogen peroxide: the viscosity drops only until the peroxide is consumed, but a further drop occurs after a fresh quantity of peroxide has been added.

The experimental evidence thus indicates that no aging ought to take place at all, if it were possible to prevent any air from being carried into the system from the start and if precautions were taken to prevent it from entering afterwards. In fact, if the steeping, pressing, and shredding operations are carried out under such precautions, and if the aging process proper is allowed to take place in nitrogen-filled sealed flasks, the viscosity and the *alpha*-cellulose content remain practically constant over the whole aging period.

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[233] Wilson, *loc. cit.;* Heggen, doctoral dissertation, Dresden, 1936.

[234] Weltzien and zum Tobel, *loc. cit.;* Compton, *Ind. Eng. Chem.,* **31,** 1251, 1252 (1939).

The nature of the process of oxidation and the various hypotheses which have been offered to explain its mechanism are discussed in Chapter X.

MERCERIZATION OF CELLULOSE WITH ACIDS

A short treatment with concentrated mineral acids at room temperature, or preferably below, exerts an effect upon cellulose which, in its physical aspect, is very similar to that of strong aqueous alkali. The fiber swells in the lateral and shrinks in the longitudinal direction, and displays the behavior of mercerized cellulose, i.e., it possesses higher hygroscopicity, greater capacity for dyestuffs, salts, etc., and greater reactivity.

As will be easily understood and as will be seen more in detail in Chapter XI, the mercerization effect with strong mineral acids is obtainable only if the time of treatment is relatively short, i.e., not longer than a few minutes, because a longer time results in the dissolution of the cellulosic material accompanied by hydrolysis.

The physical changes which the fiber undergoes under the influence of strong acids originate from the same source which is involved when cellulose is treated with strong aqueous alkali, namely, the swelling. This phenomenon may be observed under the microscope. Hübner and Pope [235] have shown that the convolutions of the cotton fiber (see Fig. 3) submerged in strong sulfuric acid become untwisted, the lumen of the fiber is narrowed, the diameter increases, and the fiber shrinks in the longitudinal direction. The shrinkage was found to amount to 9.5 per cent of the original length. Similar effects were observed in strong phosphoric, nitric, and hydrochloric acids.

As with aqueous alkali, the swelling of the fiber increases with increasing acid concentration. This has been demonstrated with concentrated phosphoric acid by Champetier [236] and, over a wider range of concentration, by af Ekenstam [237] who ascertained the extent of swelling of cotton fibers by measuring the increase of their width by the method suggested by Heuser and Bartunek [238] for measuring the swelling in strong aqueous alkali. af Ekenstam's results are presented in Fig. 47.

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[235] Hübner and Pope, *J. Soc. Chem. Ind.*, **23**, 409 (1904).

[236] Champetier, *Ann. Chim.*, [10] **20**, 5 (1933).

[237] af Ekenstam, "Über Celluloselösungen in Mineralsäuren," Blom, Lund, p. 56 (1936).

[238] Heuser and Bartunek, *Cellulosechem.*, **6**, 19 (1925).

It is seen that the swelling tends to reach a maximum. When the maximum has been reached and the concentration is not further increased, the swelling becomes "unlimited"—i.e., the cellulose goes into solution. If, however, the fibers, having attained their maximum swelling, are brought into acid of concentrations above the maximum, the swelling is more and more reduced.

Considering the probability that cellulose forms addition compounds with strong mineral acids (see Chapter XI), the mechanism of the swelling of cellulose in such acids may be visualized as similar to what is involved when cellulose is treated with strong aqueous alkali. However, whereas in aqueous alkalies it is the cation which acts as a vehicle for the water, in strong aqueous acids this function is taken over by the negative ions. It would appear that the strong attraction which cellulose, probably through its hydroxyl groups, displays for the acids directs the water molecules into the intramicellar spaces of the fiber so that they may attach themselves to a considerable number of the interior hydroxyl groups. However, when the acid has reached a certain concentration, it does not hold and does not transport a sufficient amount of water to the interior of the micellar system, and less swelling results.

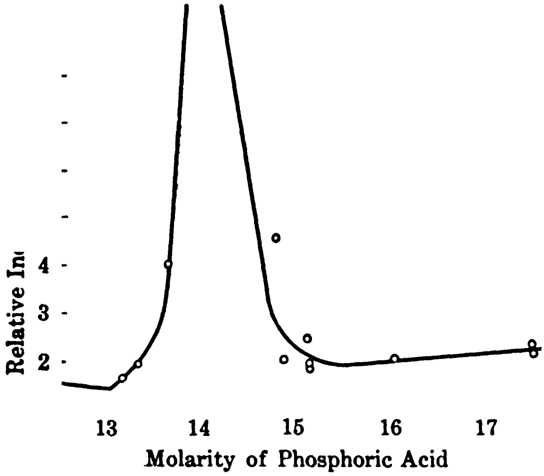

FIG. 47. Swelling of cotton in concentrated phosphoric acid of increasing concentration. af Ekenstam.

The view that the swelling of cellulose in acids is a function of their anions seems to be supported by the observation that the effect of the hydrogen-ion concentration upon the swelling appears to be negligible.[239] On the other hand, it is conceivable that the extent of the swelling is dependent upon the nature of the anion. Although exact measurements seem to be lacking, the greater dissolving power of sulfuric compared with phosphoric acid for cellulose seems to support this view.

The greater reactivity of cellulose which has been mercerized with strong mineral acids and subsequently washed free of acid, relative to the unmercerized material, has been demonstrated for cotton in strong sulfuric acid by Clibbens, Geake, and Ridge.[240] The ratio of the reactivity of the mercerized to that of the unmercerized fiber (the "reactivity ratio," see p. 115) was found to be as high as 1.6 and 2.07. The reactivity was determined by subjecting the materials to oxidation with hypobromite solution.

Similar to the behavior of cellulose mercerized with strong alkali, the reactivity ratio increases with the acid concentration (degree of mercerization), and so does the hygroscopicity ratio.

Sulfuric and nitric acids have been used for the commercial mercerization of textile materials.[241] The mercerization effect which sulfuric acid produces on cellulose has been utilized also in the manufacture of parchment paper (an imitation of the sheepskin parchment of the Middle Ages). Parchment paper is made by steeping a sheet of unsized paper containing a minimum of impurities (small amounts of lignin cause a pronounced brown discoloration) in cooled strong sulfuric acid (68–70 per cent) for a short time, and subsequently diluting the acid (which is held by the sheet) with cold water, and then thoroughly washing and drying.

It would appear that the action of the acid extends beyond the mercerization stage; i.e., the surfaces of the sheet or, if it is thin enough, the entire sheet become peptized, and the peptized material is coagulated (or precipitated) by the water of dilution, the coagulated material filling the pores and voids of the sheet structure. Indeed, parchment paper is water- and oil-repellent and its tensile strength is greatly improved; in addition, the sheet has acquired a considerable degree of transparency. For a number of uses parchment paper has been replaced by Glassine or Greaseproof paper, which is obtained by long beating of suitable wood pulp types, resulting in a very dense sheet structure.

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[239] Stamm, *J. Am. Chem. Soc.*, **56**, 1195 (1934); see also Kanamaru, *Kolloid-Z.*, **66**, 164 (1934); Stamm, "Colloid Chemistry of Cellulosic Materials," p. 55.

[240] Clibbens, Geake, and Ridge, *J. Textile Inst.*, **21**, T85 (1930).

[241] Hall, "Cotton Cellulose," p. 90; Berl, *Z. angew. Chem.*, **37**, 406, 689 (1924); Budnikoff, *Faserstoffe u. Spinnpflanzen*, **6**, 66 (1925); see also Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 26.

CHAPTER V

REACTIONS OF CELLULOSE WITH ORGANIC BASES, AMMONIA, AND CONCENTRATED SALT SOLUTIONS

ACTION OF ORGANIC BASES

A number of organic bases have been found to exert upon the cellulose fiber a mercerizing effect similar to that of strong alkalies. Possibly Knecht and Harrison[1] were the first to make this observation when they allowed aqueous tetramethylammonium hydroxide to act on cotton. Later, Dehnert and König[2] investigated the action of this and other quaternary ammonium bases on cellulose. In fact, these bases exert a pronounced swelling effect upon the fiber, particularly at lower temperatures and, within certain ranges of concentration, they seem to result in chemical compound formation. Thus, trimethylsulfonium hydroxide, $[(CH_3)_3S]OH$, and guanidinium hydroxide, $[(NH_3)_2C]OH$, investigated by means of the change-in-titer method, seem to combine in the ratio of 1 molecule of the base to 2 glucose residues. With other bases, the ratio is less exact. Calculations based upon the size of the entering organic base molecule and the increase in volume of the unit cell by Sisson and Saner[3] produced data which favor a ratio of 1 molecule of the organic base to 1 glucose residue.

The same authors have studied the action of a number of quaternary ammonium bases, such as tri- and tetramethylammonium hydroxides and dimethyl-, dibenzyl-, and trimethylbenzylammonium hydroxides on cotton cellulose and found that, as in the system cellulose-aqueous alkali hydroxide, the range of the x-ray pattern is associated with a minimum concentration for each reagent, below which the x-ray diagram of the original cellulose is not affected. If the concentrations of the various bases are expressed in terms of normality of the solution, the normalities necessary to change the pattern decrease linearly when plotted against increasing molecular weights of the bases.

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[1] Knecht and Harrison, *J. Soc. Dyers Colourists*, **28**, 224 (1912).

[2] Dehnert and König, *Cellulosechem.*, **6**, 1 (1925).

[3] Sisson and Saner, *J. Phys. Chem.*, **43**, 695 (1939).

The change of the x-ray pattern corresponds to a distention of the crystal lattice, whereas the fiber period of 10.3 Å remains unchanged. After the base has been removed, the x-ray pattern of the treated cellulose is that of the mercerized (hydrate) modification.

Some of the organic bases are able to dissolve cellulose, for example, tetramethyl-, tetraethyl-, and phenyltrimethylammonium hydroxides.[4] These bases may be used in aqueous solution. Usually, a solution having a concentration of 35–40 per cent of the base is a good cellulose solvent.[5] Again, a straight-line relationship seems to exist between the normality of the base necessary to dissolve cellulose and the molecular weight of the base.[6]

The best solvents are the benzylammonium hydroxides; they are also more stable to elevated temperature than the aliphatic derivatives.[7] Further, quaternary phosphonium, arsonium, and selonium bases are able to dissolve cellulose.[6]

Cellulose which has previously been dissolved in a quaternary ammonium base becomes more easily soluble in aqueous sodium hydroxide. Thus, cellulose regenerated from its solution in tetramethylammonium hydroxide by dialysis against aqueous sodium hydroxide was found to become soluble when the latter showed a concentration of 0.7 N sodium hydroxide.[8] Alkali of such a low concentration exerts hardly any dissolving power on fibrous cellulose. It will be recalled that cellulose regenerated from viscose showed a similar behavior.[9]

Other derivatives of ammonia, such as hydrazine, (NH_2NH_2), ethylenediamine, ($NH_2CH_2CH_2NH_2$), and tetramethylenediamine, [$NH_2(CH_2)_4NH_2$], do not seem to exert a permanent mercerizing effect upon cellulose, because after removal of the base the cellulose preparation shows the x-ray diagram of unmercerized cellulose. In contrast, aqueous solutions of these weak bases, having a concentration of about 40 per cent, cause the x-ray pattern to change. As in the cases discussed before, this change is directly proportional to the molecular weight of the diamines. Analysis of the reaction products by the pressing method seems to indicate the formation of one or more chemical compounds.[10]

Dimethyldibenzylammonium hydroxide has been recommended as a solvent for cellulosic materials in connection with viscosity determinations.[11]

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[4] Lilienfeld, U. S. patent 1,771,462 (1930).

[5] Bock, *Ind. Eng. Chem.*, **29**, 985 (1937).

[6] Lieser and Leckzyck, *Ann.*, **522**, 56 (1936); Lieser and Ebert, *Ann.*, **532**, 96 (1937); Staudinger and Daumiller, *Ber.*, **70**, 2509 (1937).

[7] Bock, *loc. cit.*, p. 986.

[8] Lieser and Leckzyck, *loc. cit.*

[9] Koets and Kruyt, *Kolloid-Beihefte*, **47**, 123 (1937).

[10] Trogus, *Z. physik. Chem.*, **B14**, 387 (1931); *Ber.*, **62**, 140 (1933); Trogus and Hess, *Z. Elektrochem.*, **42**, 704, 710 (1936); Hess and Gundermann, *Ber.*, **70**, 1788 (1937).

[11] Russell and Woodbury, *Ind. Eng. Chem., Anal. Ed.*, **12**, 151 (1940); Mease and Gleystein, *J. Research, National Bur. Standards*, **27**, 543 (1941).

ACTION OF AMMONIA

Aqueous ammonia, even in concentrated form (23–28 per cent), seems to be without effect on cellulose.[12] Ammonia in gaseous form is retained in large amounts by the fiber. Thus, cotton may occlude 115 times its volume of gaseous ammonia.[13] After the ammonia has evaporated, the cellulose appears unchanged.

Quite different results are obtained by the action of *liquid* ammonia on cellulose. No doubt, the low temperature is the important factor, the temperature of liquefaction of ammonia being −33 to −35°. Liquid ammonia, as first shown by Bernardy,[14] is capable of swelling and mercerizing the cellulose fiber in a way similar to the action of strong aqueous alkali. This observation was confirmed by Barry, Peterson, and King.[15] Confusion, however, seems to exist concerning the degree of swelling and the changes of the x-ray pattern from the original, both in the presence of ammonia and after the ammonia has been removed from the fibrous material.

Clark and Parker[16] found that the fiber is in a state of swelling as long as it is in contact with liquid ammonia, the diameter of the fiber being increased threefold. On evaporation of the ammonia the fiber returned to its original size.

Observation of the x-ray pattern of the fiber in contact with ammonia indicates that swelling increases continuously without passing through a maximum; it also indicates that a chemical compound is formed, although of a very labile character, because the ammonia evaporates easily on slight heating.

The change of the x-ray pattern of the regenerated cellulose is either entirely or partly reversible, depending upon the means used for separating the compound into its constituents. For example, concentrated aqueous ammonia completely reverts the pattern of the ammonia cellulose to that of native cellulose, whereas water and dilute acetic acid accomplish only a partial reversal. The best means of retaining the changed x-ray pattern in the regenerated cellulose seems to consist of allowing the ammonia to evaporate slowly. However, the regenerated cellulose appears to be less stable than alkali-mercerized cellulose since

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[12] Schwalbe, "Chemie der Cellulose," 1st ed., p. 52.

[13] Bowman, "The Structure of the Cotton Fiber," p. 201.

[14] Bernardy, *Z. angew. Chem.*, **38**, 838, 1195 (1925).

[15] Barry, Peterson, and King, *J. Phys. Chem.*, **41**, 777 (1937).

[16] Clark and Parker, *J. Am. Chem. Soc.*, **58**, 333 (1936); see also Hess and Trogus, *Ber.*, **68**, 1986 (1935).

it, at least partly, reverts into native cellulose under treatment with concentrated aqueous ammonia or on boiling with water for 12–15 hours.

Liquid ammonia has been found to have no degrading influence upon cellulose.[17]

Ammonia cellulose should not be confused with amino cellulose, a compound which has been described as resulting from the action of ammonia on the *p*-toluenesulfonic acid ester of cellulose and more recently from the action of sodium amide upon cellulose nitrate (see later).

ACTION OF STRONG SALT SOLUTIONS

Cellulose shows the phenomenon of intramicellar swelling in concentrated aqueous solutions of a number of neutral salts. Swelling was first observed by Mercer. Later, Hübner and Pope[18] found that a saturated aqueous solution of barium mercuric iodide swelled the cotton fiber to almost the same extent as a sodium hydroxide solution of mercerizing strength. Moreover, shrinkage and increase in tensile strength were found to be very similar in the two cases.[19] Likewise, zinc chloride, the effect of which on cellulose has often been investigated, is found to have a mercerizing effect on cellulose similar to that of aqueous alkali solutions.[20] A lower temperature favors the mercerizing effect of these salts.

The swelling and peptizing effect of aqueous zinc chloride on cellulose is used commercially in the manufacture of "vulcanized fiber" boards.[21] Cellulose in sheet form is impregnated with zinc chloride solution and layers of the impregnated and subsequently washed sheets are united by drying and pressing.

Letters[22] investigated the colloidal changes which take place when cellulose is treated with zinc chloride solution by determining the viscosity of the solution over a certain period of time and at a certain temperature. The viscosity curve constructed from these data re-

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[17] Heuser and Green, unpublished data.

[18] Hübner and Pope, *J. Soc. Chem. Ind.*, **22**, 70 (1903); **23**, 410 (1904).

[19] However, the luster was not improved; this is obviously due to the fact that, in contrast to sodium hydroxide solution, the cotton fiber does not untwist in this reagent. Hübner and Pope found untwisting and improvement of luster to be directly related.

[20] Grandmoujin, *Bull. Mulhouse*, **68**, 348 (1898); Katz, *Physik. Z.*, **25**, 321 (1924).

[21] Piest, "Die Zellulose," F. Enke, Stuttgart (1910), p. 24; Meyers, *Ind. Eng Chem.*, **8**, 1108 (1916); Allison, *Chem. Met. Eng.*, **22**, 1126 (1920).

[22] Letters, *Kolloid-Z.*, **58**, 229 (1932).

flects the various physical phenomena that take place: solvation and swelling, decrease in size of the solvated cellulose particles, and, finally, decrease of the chain length due to hydrolysis produced by the acidic character of the zinc chloride solution. Hydrolysis occurs to a lesser degree at lower temperatures.

It is probable that, rather than liberation of hydrochloric acid, it is the tendency of the zinc chloride to form complex compounds with water, such as $[ZnCl_2OH]H$ or $[ZnCl_2(OH)_2]H_2$, that is responsible for the hydrolysis of the cellulose, because these compounds possess a much more pronounced acidic character than hydrochloric acid.[23]

Other chlorides of the heavy metals, such as $SbCl_3$, $HgCl_2$, $BiCl_3$, $SnCl_4$, and $TiCl_4$ likewise appear to exert a swelling effect upon cellulose.[24] Again, a low temperature ought to favor the effect and lessen the degradation of the cellulosic material.

von Weimarn, who investigated the effect of concentrated aqueous solutions of a great number of neutral salts (including various thiocyanates), was the first to direct attention to the fact that the swelling power of the various salts depends upon the degree of hydration of their cations.[25] This behavior is analogous to that of cellulose with aqueous solutions of the various alkalies. Further studies in this direction by Herzog and Beck[26] have confirmed this conclusion. The swelling effect proceeds parallel with the position of the ion in the Hoffmeister series (or Freundlich's[27] lyotropic series), thus:

$$\mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Ca}$$
$$\mathrm{Mg} > \mathrm{Ca} > \mathrm{Sr} > \mathrm{Ba}$$
$$\mathrm{CNS} > \mathrm{I} > \mathrm{Br} > \mathrm{Cl} > \mathrm{F}$$

Salts which exert a particularly high swelling effect upon cellulose are LiI, KCNS, $KHgI_3$, and LiCSN. In this connection it is interesting to note that the swelling effect of the thiocyanates upon the cell membrane, starch, and other colloids has been known for a long time.[28]

Possibly these and other salts combine with cellulose to form complex addition compounds,[29] although attempts to substantiate this

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[23] Meerwein, *Z. angew. Chem.*, **39**, 1191 (1926); *Ann.*, **453**, 16 (1927); **455**, 250 (1927).

[24] Deming, *J. Am. Chem. Soc.*, **33**, 1515 (1911).

[25] von Weimarn, *Kolloid-Z.*, **11**, 41 (1912); **36**, 103 (1923); see also the compilation by Steingroever, *Cellulosechem.*, **8**, 37 (1927).

[26] Herzog and Beck, *Z. physiol. Chem.*, **111**, 287 (1920); *Kolloid-Z.*, **39**, 98 (1926).

[27] Freundlich, "Kapillarchemie," Akad. Verlags-Ges., Leipzig (1929).

[28] Meusel, "Die Quellkraft der Rhodanate," A. Reisewitz, Gera (1886).

[29] Mark, "Physik und Chemie der Cellulose," p. 252.

assumption by x-ray evidence[30] have succeeded only in the case of lithium thiocyanate. Katz and Derksen[31] observed that, under the influence of increasing concentration of the lithium salt at room temperature, the x-ray diagram of ramie fiber changed distinctly. If cellulose in its hydrate modification was used, the x-ray pattern changed at a lower salt concentration than when native cellulose was used. This is analogous to the behavior of cellulose hydrate with aqueous alkali solutions.

The addition compounds are, as would be expected, easily decomposed with water. Unexpected, however, is the finding that cellulose regenerated from its combination with the salt shows the x-ray pattern of the original cellulose. No doubt, these findings need reinvestigation.

Some of the salts mentioned above and some others are capable of peptizing and eventually dispersing cellulose if they are applied in the form of aqueous solutions of sufficient strength.

Zinc chloride has been known for a long time as a dispersing agent for cellulosic materials.[32] An aqueous solution possesses optimum dispersing power at a concentration of about 65 per cent, but the amount of cellulose which may be dispersed is limited,[33] probably depending upon the degree of polymerization of the cellulosic material.

More recently, studies have been made on the action of the chlorides and perchlorates of beryllium ("glucinium"). Bodforss,[34] using a parchment paper membrane for dialyzing a beryllium chloride solution, observed that the membrane was considerably hydrolyzed. According to Dobry,[35] neither the neutral perchlorate [$Be(ClO_4)_2$] nor the basic salt [$2Be(ClO_4)_2 3BeO$] exert a dissolving effect upon cellulose, whereas a mixture of 57 per cent of the neutral salt and 43 per cent of the basic salt dissolves cellulose at 0° to a clear solution; however, at this temperature a time as long as 15 days is required, and it is not surprising that under these conditions the cellulose becomes degraded. This degradation increases considerably at higher temperature. On dilution of the solution with water, the cellulose is regenerated as a precipitate; it may also be regenerated in the form of a transparent film.

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[30] Katz, *Z. physik. Chem.*, **124**, 352 (1926).

[31] Katz and Derksen, *Rec. trav. chim.*, **50**, 149, 736, 746 (1931).

[32] Cross and Bevan, "Cellulose," Longmans, Green and Co., London (1918) p. 8; Schwalbe, "Chemie der Cellulose," 1st ed., p. 153.

[33] Letters, *Kolloid-Z.*, **58**, 229 (1932).

[34] Bodforss, *Z. physik. Chem.*, **124**, 67 (1936).

[35] Dobry, *Bull. soc. chim.*, [5] **3**, 312 (1936).

Whereas it is probable that in zinc and beryllium chloride it is the hydrolyzing effect of acidic complex compounds, which aids in the process of dispersing the cellulosic material, this additive effect is absent if neutral alkali chlorides are used—for example, the chlorides of lithium, barium, and calcium. These and a number of thiocyanates[36] were used by von Weimarn[37] in his extensive studies on the dispersion of cellulose and other fibrous materials in concentrated salt solutions. von Weimarn arrived at the conclusion that aqueous solutions of any neutral salt ought to peptize and eventually disperse cellulose, if only certain conditions of concentration, pressure, temperature and time of contact were maintained, conditions which, in turn, depend upon the nature of the salt. Still, it has been found difficult to accomplish dispersion even if such conditions are employed.[38] Moreover, the elevated temperature and pressure which in most cases are necessary tend to degrade the cellulose considerably.

Herzog and Beck found that the dispersing power of the salts is governed by the same rule which controls the effect of swelling; in other words, the dispersing effect is essentially a function of the hydration of the ions and, moreover, of the additive hydration of both ion constituents of the salt.

But this is not the only factor. The type of cellulose and, more particularly, the degree of polymerization of the cellulosic material determines, in part, and probably more than other factors, whether or not a complete and fiber-free dispersion may be obtained.[39] Whereas filter paper (usually of a medium to low degree of polymerization) disperses relatively easily in a concentrated calcium thiocyanate solution, native cellulose (in the form of cotton or cotton linters) only swells in this solution without being dispersed.[40]

Erbring and Geinitz found the following salts to be particularly active: $Al(CNS)_3$; $AlCl_3$; $ZnCl_2$; NaCNS; $K_2(HgI_4)$ and a mixture of $HgCl_2$ and NaCl. Calcium chloride, however, had no effect.

Iodine chloride is reported[41] to dissolve cellulose rapidly at a temperature of 90°. The product regenerated from this solution is said to be soluble in

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[36] See also Dubosc, *Z. angew. Chem.*, **19**, 689 (1906); Deming, *J. Am. Chem. Soc.*, **33**, 1523 (1911).

[37] von Weimarn, *loc. cit.; Kolloid-Z.*, **36**, 103, 338 (1925); **42**, 43 (1927); see also Williams, *J. Soc. Chem. Ind.*, **40**, 221 (1921).

[38] Heuser, *Kunststoffe*, **5**, 126 (1915); Haller, *Klepzig's Textil-Z.*, **44**, 645 (1941).

[39] Staudinger, "Die hochmolekularen organischen Verbindungen," p. 492; Staudinger and Daumiller, *Ber.*, **70**, 2508 (1937).

[40] Erbring and Geinitz, *Kolloid-Z.*, **84**, 25 (1938).

[41] Beubel and Kutzelnigg, *Monatsh.*, **66**, 249 (1935).

alcohol and, on evaporation of the alcohol, to remain as a resinous mass. These changes indicate that the cellulose has been degraded considerably.

If dispersions of cellulose in aluminum, zinc, and other salt solutions are allowed to stand, they tend to become less fluid and eventually coagulate to a solid gel. Frequently, depending upon the cellulose concentration, the hot solution coagulates on cooling, resulting in a gel similar in appearance to those which may be prepared from gelatin, agar-agar, and other colloids.[40]

The cellulose may be regenerated also by diluting the solution with water or alcohol or by means of acids, etc. The regenerated product shows all the properties of cellulose hydrate. This change is reflected in the x-ray pattern.[42]

It has been suggested that dispersions of cellulose in salt solutions might be utilized for the manufacture of films and threads (von Weimarn). Although the films were found to be clear and transparent, and both films and threads to possess good physical strength properties, the process is not being used commercially, probably because of the complications involved in handling and recovering such highly concentrated salt sloutions.

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[42] Herzog, *Z. physik. Chem.*, **127**, 108 (1927).

CHAPTER VI

THE ACTION OF CUPRAMMONIUM HYDROXIDE ON CELLULOSE

The base whose action on cellulose has been studied most extensively is copper tetrammino hydroxide, $[Cu(NH_3)_4](OH)_2$, usually called cuprammonium hydroxide or just cuprammonium.[1] It forms on dissolving cupric oxide in ammonia and contains the same complex cation, $[Cu(NH_3)_4]$, as the crystalline copper tetramine salts; for example, copper tetrammino sulfate, $Cu(NH_3)_4SO_4$. The base exists only in the presence of an excess of ammonia, and on evaporation of the latter, copper hydroxide precipitates: $[Cu(NH_3)_4]OH_2 \rightleftarrows Cu(OH)_2 + 4NH_3$. Since the solution also contains a certain amount of water, a corresponding amount of the ammonia is present as ammonium hydroxide.

Like ammonia, some of its derivatives, such as the 1,2-diamines—for example, ethylenediamine $(NH_2CH_2CH_2NH_2)$—are capable of dissolving cupric oxide. The reaction occurs, in contrast to that of ammonia, in a stoichiometric proportion, the ratio of copper to diamine always being 1 : 2 which seems to indicate the existence in the solution of a base of the following composition:

$$[(CuNH_2CH_2CH_2NH_2)_2](OH)_2,$$

copper ethylenediamine hydroxide.[2] This compound could be regarded as a copper tetrammino hydroxide in which the four ammonia molecules are replaced by two ethylenediamine molecules. The base possesses about the strength of barium hydroxide.

Both the copper tetrammino hydroxide and the copper ethylenediamine hydroxide solution swell, peptize, and eventually disperse cellulose.

The observation that cellulose disperses in cuprammonium solution seems to originate from Mercer[3] but the first published record bears the name of

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[1] Dawson and McCrae, *J. Chem. Soc.*, **77**, 1239 (1900); Hantzsch and Robertson, *Ber.*, **41**, 4328 (1908).

[2] Traube, *Ber.*, **44**, 3319 (1911).

[3] Schwalbe, "Chemie der Cellulose," 1st ed., p. 145; Farr, *Contrib. Boyce Thompson Inst.*, **10**, 71 (1938).

Eduard Schweizer;[4] for this reason the cuprammonium solution is also called Schweizer's reagent. It also was Schweizer, followed by Cramer,[5] who observed the bead-like swelling phenomenon described in Chapter I. Traube was the first to observe that copper ethylenediamine hydroxide and other copper diamine hydroxides, such as the hydroxide of propylenediamine, $NH_2CH(CH_3)$-CH_2NH_2, dissolve cellulose even to a greater extent than the ammonia compound.

Cuprammonium hydroxide solution[6] may be prepared in two ways. Either copper hydroxide, prepared from copper sulfate and ammonia or sodium hydroxide, is dissolved in an excess of ammonia[7] or copper metal is subjected to the simultaneous action of air oxygen and ammonia.[8] In the latter process, the copper is readily oxidized, and the oxide, as it is being formed, dissolves in the ammonia. The solution prepared at room temperature contains from 2 to 2.5 per cent copper; prepared at a lower temperature, i.e., below 5°, the copper content may reach 4 per cent; at still lower temperature, even higher values. It may be further increased by adding small amounts of copper sulfate or sodium hydroxide.[9]

The second method gives rise to the formation of a certain amount of ammonium nitrite (NH_4NO_2), as a result of oxidation of part of the ammonia by the cupric oxide, which takes place more easily at temperatures above 5°. The nitrite seems to decrease the dissolving power of the solution rather than to increase it and it should therefore be kept at a low level. Clibbens and Geake's way of preparing the solution limits the nitrite content to 0.05 per cent.[10] For the analysis of cuprammonium solutions, the reader is referred to Dorée's book.[11]

Cellulose may be dissolved in cuprammonium either directly or it may be mixed with copper hydroxide and the mixture dissolved in ammonia.[12] The latter way has the advantage that a greater quantity of cellulose may be dissolved, because the solubility of the copper hy-

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[4] Schweizer, *J. prakt. Chem.*, **72**, 109, 344 (1857).

[5] Cramer, *J. prakt. Chem.*, **73**, 1 (1858).

[6] Schwalbe, "Chemie der Cellulose," 1st ed., p. 145; Dorée, "The Methods of Cellulose Chemistry," p. 52; standard method, suggested by the American Chemical Society, *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929); Hess, "Chemie der Cellulose," pp. 314, 317; Mark, "Chemie und Physik der Cellulose," p. 246.

[7] Dawson, *J. Chem. Soc.*, **95**, T370 (1909).

[8] Joyner, *J. Chem. Soc.*, **121**, T154 (1922).

[9] Hess and Trogus, *Z. physik. Chem.*, **A145**, 401 (1929); Brownsett, Farrow and Neale, *J. Textile Inst.*, **22**, T357 (1931).

[10] Clibbens and Geake, *J. Textile Inst.*, **19**, T79 (1928).

[11] Dorée, *loc. cit.*, p. 55; see also Jolley, *J. Textile Inst.*, **30**, T16 (1939).

[12] Ost, *Z. angew. Chem.*, **31**, 141 (1918).

droxide in ammonia increases in the presence of cellulose.[13] Sometimes a mixture of cellulose and fine copper powder is subjected to the simultaneous action of air and ammonia.[14] This method, however, gives rise to oxidation of the cellulose which, for scientific studies, should be avoided.

The solvent power of the cuprammonium hydroxide solution depends essentially upon its copper content. The higher the copper content, the more cellulose may be dissolved. The following is an example (2g of cellulose).[15]

Copper content, %	0.61	0.70	0.75	0.82	0.92
Cotton linters dissolved, %	7	19.1	22.3	28.6	42.5

Other factors which govern the solubility of cellulose in cuprammonium hydroxide are the physical structure of the fiber and the degree of polymerization of the cellulose. Thus, cotton and cotton linters are more difficult to dissolve than wood pulp.[16] Any pretreatment which leads to a loosening up of the structure, like swelling (mercerization) without subsequent drying, facilitates solution. As pointed out before, drying decreases the ease with which cellulose dissolves and may entirely offset the beneficial effect of swelling and mercerization. If possible, the cellulosic material should be opened up in water by violent stirring, and the bulk of the water removed on a Büchner funnel. Cellulosic material thus prepared may be partially dried in a stream of conditioned air and dissolved in its partly moist state (about 35 per cent moisture). The water thus introduced into the cuprammonium solution does not decrease its dissolving power to any noticeable extent if the cellulose concentration remains within 1–2 per cent. With higher concentrations of cellulose, one should use a cuprammonium solution of high copper content[17] and possibly strengthen the solution, after mixing, with gaseous ammonia. Experience has shown that cellulose, particularly wood pulp, may thus be dissolved within one hour, whereas dried cellulose may need twelve and more hours.

Recently, Rich[18] has shown that the time of dissolving may be shortened to 2 minutes or even less by allowing the cellulose sample to swell in ammonia before adding the cuprammonium hydroxide solution. Mark[19] has recommended that the cellulosic material be extracted with hot alcohol or benzene in order to free it of fats and waxes. The presence of such substances—for example, in raw cotton linters—impedes the speed of reaction considerably. On the other hand, such treatments are liable to reduce the penetrability of the fiber by the cuprammonium solution.

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[13] Traube, *Ber.*, **54**, 3230 (1921); **55**, 1899 (1922).

[14] Süvern, "Die Künstliche Seide," Springer, Berlin (1910), p. 269.

[15] Neumann, Obogi, and Rogovin, *Cellulosechem.*, **17**, 87 (1936). The amounts of cellulose dissolved were determined after 1 hour of contact at 15°. See also Kumichel, *Papier-Fabr.*, **36**, 497 (1938).

[16] Hess and Sakurada, *Ber.*, **63**, 2027 (1930).

[17] Folley, *J. Textile Inst.*, **30**, T10 (1939).

[18] Rich, *Paper Trade J.*, **112**, No. 6, 35 (1941); see also Mease, *J. Research Natl. Bur. Standards*, **27**, 551 (1941).

[19] Mark, "Physik und Chemie der Cellulose," pp. 245, 246.

The more the cellulose is degraded, the more easily it dissolves; thus, the cellulose modifications dissolve considerably more easily than untreated cellulose.

If all the cellulose is not dissolved, the undissolved part absorbs copper from the solvent and this decreases its solvent power.[20] It follows that more complete dispersion and higher cellulose concentration are achieved if the cellulose is dissolved in portions. It has been claimed[21] also that addition of cuprous chloride (3 per cent of the weight of cellulose) is particularly efficient in increasing the dissolving power of the cuprammonium hydroxide. It is said that a solution of as much as 10 per cent cellulose content may be obtained within 2.5 hours.[22]

Cellulose dissolved in cuprammonium solution is very sensitive to air.[23] Very small amounts of oxygen suffice to attack it, and therefore the solution should be prepared under careful exclusion of air if it is to be used for scientific studies.

The change due to oxidation, which becomes measurable after only a few minutes, is indicated particularly by a decrease in viscosity and an increase in the solubility of the regenerated cellulose in an 8 per cent sodium hydroxide solution.

Earlier investigators, particularly Berl and Innes[24] and Ost[25] recognized the influence of air upon the viscosity when they attempted to determine this characteristic of the cellulose solution in various types of viscometers. But it was Gibson and co-workers[26] who eliminated this influence by displacing the air in the system with hydrogen; they also suggested the falling sphere method[27] and adapted the capillary viscometer to cuprammonium cellulose solutions.[28]

The considerable influence of oxygen upon the viscosity is illustrated in Table 14. The figures, taken from Scheller's work, also demonstrate the existence of a variety of sources from which oxygen may enter the system.

The influence of atmospheric oxygen upon the alkali-solubility of the cellulose regenerated from its cuprammonium solution was demonstrated by Heuser and Bartunek,[29] who found the solubility of the regenerated cellulose was 5–6

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[20] Sakurada, *Kolloid-Z.*, **54**, 43 (1931).

[21] Gonscharov and Burvasser, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, **9**, 124 (1938); *Chem. Abstr.*, **32**, 9480 (1938).

[22] Scheller, *Melliand Textilber.*, **16**, 787 (1935); Staudinger and Jurisch, *Papier-Fabr.*, **49**, 469 (1937).

[23] Prud'homme, *J. Soc. Dyers Colourists*, **7**, 148 (1891), quoted from Schwalbe, "Chemie der Cellulose," 1st ed., p. 144.

[24] Berl and Innes, *Z. angew. Chem.*, **23**, 987 (1910).

[25] Ost, *Z. angew. Chem.*, **24**, 1892 (1911).

[26] Gibson, *J. Chem. Soc.*, **117**, 479 (1920); Gibson, Spencer, and McCall, *ibid.*, **117**, 484 (1920).

[27] Gibson and Jacobs, *J. Chem. Soc.*, **117**, 473 (1920).

[28] Gibson, Spencer, and McCall, *loc. cit.*

[29] Heuser and Bartunek, in Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 176.

TABLE 14

VISCOSITY OF A 1 PER CENT SOLUTION OF COTTON IN CUPRAMMONIUM HYDROXIDE

Manner of Preparation of the Solution	Viscosity in Centipoises (Water = 1)
Solution prepared in air	4
Prepared in N_2 containing 2.4% O_2	50
Prepared in N_2 containing 0.7% O_2	173
Prepared in O_2-free N_2	248
Cotton boiled with water	281
Cotton boiled with water *in vacuo*	317
O_2-free N_2; 0.1 g. CuCl, no boiling	800
O_2-free N_2; 0.3 g. CuCl, no boiling	893
O_2-free N_2; 0.5 g. CuCl, boiling *in vacuo*	928

per cent after 2 hours of contact with the cuprammonium hydroxide, 10 per cent after 2 days, and 32 per cent after 8 days.

Another source of attack is the copper tetrammino hydroxide itself. The solution of this base tends to decompose on standing, forming copper hydroxide. In the presence of cellulose the bivalent copper is transformed into the monovalent copper, the oxygen liberated being consumed in the oxidation of cellulose. The formation of oxycellulose is indicated indirectly by a discoloration of the deep blue solution which acquires a greenish tinge and, on still longer standing, a deposit of red cuprous oxide is observed on the bottom of the flask.[30] The formation of this compound is due to the ability of oxycellulose to reduce cupric copper.

The rayon industry, which uses a solution of cellulose in cuprammonium hydroxide for the manufacture of cuprammonium rayon, prevents any undesirable oxidation of cellulose by adding to the solution substances which are more readily oxidized than cellulose itself, such as sucrose or glucose, and which thus protect the cellulose. The addition of such substances, however, is said to decrease the solvent power of cuprammonium hydroxide somewhat.[31]

The reaction which lowers the viscosity of cellulose is furthered by the presence of light, even in a hydrogen atmosphere.[32] For this reason, both the cuprammonium and the cellulose solution should be kept in brown glass bottles or in bottles coated with red lacquer.[33] Obviously, a photochemical reaction takes place. Indeed, it has been observed that light exerts a greater effect than air [34] and that ultraviolet light waves—particularly those which pass through glass (300 to

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[30] Heuser, *loc. cit.*, p. 175.

[31] Jolley, *J. Textile Inst.*, **30**, T13 (1939).

[32] Gibson, Spencer, and McCall, *J. Chem. Soc.*, **117**, 486 (1920).

[33] Staudinger, "Die hochmolekularen organischen Verbindungen," p. 494.

[34] Staudinger, *loc. cit.*, p. 495, footnote 1.

400 mμ)—are the active source.[35] If light and air are carefully eliminated, the drop in viscosity remains within reasonable limits, even for a long period of time.[36]

A cellulose cuprammonium solution shows pronounced levorotation, a phenomenon which was first observed by Lavallois.[37] Although his observation could not be confirmed by others,[38] it was finally established with certainty by Hess and Messmer.[39] At first glance, this seems surprising because solutions of cellulose in other solvents show no optical rotation, unless the cellulose is in a highly degraded state.[40] Hess and Messmer found that the levorotation of the cellulose cuprammonium solution is exerted by a cellulose copper complex compound (see below), the degree of rotation depending solely on the copper content of this complex compound. Moreover, the degree of rotation is, over wide ranges, independent of the degree of polymerization of the cellulosic material, so that celluloses of most varying past history at the same concentration produce almost identical rotation values.[41]

THE MECHANISM OF THE REACTION

Some of the physical phenomena which may be observed when the cellulose fiber is brought into contact with a cuprammonium solution were discussed in Chapter II. Here, it may be added that a cuprammonium solution with a copper concentration of below 0.25 per cent exerts hardly any swelling effect upon the fiber. Above this concentration, swelling gradually increases, and the cellulose becomes peptized, until, on still further increase of the copper concentration, it dissolves.

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[35] Bancroft, paper presented before the Am. Chem. Soc. meeting, Cellulose Division, Pittsburgh, Sept., 1936 (not published except in the "Abstracts" of the papers presented).

[36] Staudinger, *loc. cit.*, p. 495.

[37] Lavallois, *Compt. rend.*, **98**, 44, 732 (1884); **99**, 1122 (1884); **100**, 456 (1885). A 1 per cent solution of cellulose in cuprammonium hydroxide was found to rotate the plane of the polarized light in the 20-cm. tube by about 20° to the left.

[38] For example, Willstätter, *Z. angew. Chem.*, **32**, 332 (1919).

[39] Hess and Messmer, *Ber.*, **54**, 834 (1921).

[40] Murray, Staud, and Gray, *J. Am. Chem. Soc.*, **52**, 1508 (1930).

[41] Hess, Messmer, and Ljubitsch, *Ann.*, **444**, 299, 325 (1925); Messmer, *Z. physik. Chem.*, **126**, 402 (1927). See also Freudenberg and Kuhn, *Ber.*, **63**, 191 (1930); Mark, "Chemie und Physik der Cellulose," pp. 235, 248; Compton, *Contrib. Boyce Thompson Inst.*, **10**, 60 (1938); Hägglund, "Holzchemie," Akad. Verlags-Ges. (1928), p. 56.

This influence of the copper concentration on the solubility of cellulose[42] has been utilized for separating it into fractions of varying degrees of polymerization, employing the principle of fractional solution.[43] By steadily increasing the amount of copper in the solution, Kumichel found that, with a cuprammonium solution of up to 0.26 per cent copper, chiefly the noncellulosic carbohydrates, together with the short-chain cellulosic material of wood pulp, are dissolved, whereas the high molecular cellulose portion is still insoluble. With more copper in the solution, this cellulose portion becomes soluble, whereas the noncellulosic carbohydrates and part of the degraded cellulose precipitate. The threshold values indicated by the occurrence of a certain turbidity are different for different pulps and depend upon their degree of bleaching, purification, etc.

A more effective fractionation of cellulose may be accomplished by the successive addition of sulfuric acid to a solution of cellulose in cupriethylenediamine, according to Straus and Levy.[44] Cellulose of high molecular weight is precipitated first; each new addition of sulfuric acid precipitates a fraction of lower molecular weight than that shown by the previous fraction.

The step which follows the disruption and the disintegration of the fiber structure under the influence of the cuprammonium solution may be visualized as a dispersion of the visible structural elements into microscopically invisible particles. Herzog and Krüger attempted to determine the particle size by means of diffusion measurements[45] and arrived at a diameter of 53 Å (5.3 mμ), a value which is within the range derived from x-ray data for the thickness of the micelles.[46] However, it is probable that the particles are smaller than the dispersion measurements seem to indicate.[47] On the basis of viscosity measurements, Staudinger[48] holds the view that, if the solution contains a very large excess of cuprammonium hydroxide over cellulose, dispersion proceeds beyond the micelle stage to individual chain molecules ("macro" or "thread" molecules).[49]

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[42] See also Farrow and Neale, *J. Textile Inst.*, **19**, T79 (1928).

[43] Neumann, Obogi and Rogovin, *Cellulosechem.*, **17**, 87 (1936); Kumichel, *Papier-Fabr.*, **36**, 497 (1938).

[44] Straus and Levy, *Paper Trade J.*, **114**, No. 18, 33 (1942).

[45] Herzog and Krüger, *Kolloid-Z.*, **39**, 250 (1926); see also *Ber.*, **58**, 1264 (1925); *Z. physik. Chem.*, **30**, 457 (1926); **33**, 79 (1929); Herzog and Kudar, *ibid.*, **A167**, 343 (1933).

[46] Hengstenberg, *Z. Kryst.*, **69**, 271 (1928).

[47] Krüger and Grunski, *Z. physik. Chem.*, **150**, 115 (1930); Stamm, "Colloid Chemistry of Cellulosic Materials," p. 28.

[48] Staudinger, "Die hochmolekularen organischen Verbindungen," p. 475; *Ber.*, **70**, 2516 (1937).

[49] See, however, McBain, *J. Phys. Chem.*, **30**, 245 (1925). See also the discussion on micelles *versus* individual chain molecules by Kratky, *Angew. Chem.*, **53**, 153, 155 (1940), and Lieser's view that the reaction between cellulose and cuprammonium hydroxide is confined to the surface of the micelles, *Ann.*, **533**,

> An entirely different concept of the behavior of the cellulose fiber with cuprammonium solution is held by Farr and co-workers.[50] As will be recalled, Farr has claimed that the cotton fiber is built up from cellulose particles and cementing substance. It is said that, on treatment of the fiber with cuprammonium solution, it is merely the cementing substance which goes into solution and which thus causes the viscosity of the solution to increase, whereas the cellulose particles remain undissolved and take no part in the viscosity increase. However, apart from the problematical nature of the cementing substance, it was found that the presence or absence in the raw cotton fiber of pectin material (which could possibly be regarded as a cementing substance) has no influence upon the viscosity of the cellulose solution.[51]
>
> It is probable that, in the dispersions which Farr and co-workers investigated, the cotton fiber material was not completely dispersed. Indeed, when precautions were taken to insure complete dispersion by preparing a cellulose solution of very low concentration (e.g., that used for determining the molecular weight of cellulose), practically all the raw cotton material went into solution. Moreover, the molecular weights of the cellulose samples (raw cotton fiber and pectin-free cotton fiber) were found to be of a magnitude usually ascribed to such cellulosic materials. This result is incompatible with the assumption that only a few per cent of the cellulosic material dissolve and that the bulk remains undissolved. Hence, the solution viscosity of cellulose in cuprammonium hydroxide must be regarded as a property of the entire fiber.[52]

The dispersion of cellulose in cuprammonium hydroxide is accompanied by chemical reactions. The investigations of Traube and of Hess have thrown much light upon the mechanism involved. However, due credit should be given to Lehner,[53] because he obviously recognized the essential steps of the mechanism.

A better understanding of the reactions will be assured if the tendency of certain polyhydroxy compounds—of a less complex nature than cellulose—to form complex compounds with bases and copper hydroxide is briefly reviewed.

As Bullnheimer and Seitz [54] have shown, the action of copper hy-

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110 (1939) and previous publications, as Lieser and Ebert, *Ann.*, **532**, 95 (1937); **528**, 276 (1937); also Lieser *et al.*, *ibid.*, **548**, 212 (1941); Lieser, *Kolloid-Z.*, **98**, 142 (1942).

[50] Farr, *Contrib. Boyce Thompson Inst.*, **10**, 71 (1938); Compton, *ibid.*, **10**, 57 (1938); Sisson, *ibid.*, **10**, 113 (1938).

[51] Whistler, Martin, and Harris, *Textile Research*, **10**, 269 (1940); Hock and Harris, *ibid.*, **10**, 323 (1940); Nickerson and Leape, *Ind. Eng. Chem.*, **33**, 83 (1941); Howells, *Paper Trade J.*, **113**, No. 13, 88 (1941); Leger and Larson, *Can. J. Research*, **B19**, 61 (1941).

[52] Heuser and Green, *Ind. Eng. Chem.*, **33**, 838 (1941).

[53] Lehner, *Z. angew. Chem.*, **19**, 1584 (1906); see also Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 176.

[54] Bullnheimer, *Ber.*, **31**, 1453 (1921); Bullnheimer and Seitz, *Ber.*, **32**, 2347 (1899).

droxide upon a mixture of glycerol and sodium hydroxide leads to the formation of a sodium copper glycerate ($[C_3H_5O_3Cu]Na$). The first phase of this reaction may be assumed to consist in the formation of sodium glycerate. In a second phase, the glycerate dissolves copper hydroxide and combines with copper to form a complex anion, $[C_3H_5O_3Cu]^-$.

If the sodium hydroxide is replaced by tetramethylammonium hydroxide $[N(CH_3)_4OH]$, an analogous compound is formed.[55] Again, in the first phase of this reaction, a certain amount of alcoholate (tetramethylammonium glycerate) is formed. The alcoholate then combines with the copper hydroxide to form the complex salt, thus:

$$CH_2(OH)CH(OH)CH_2ON(CH_3)_4 + Cu(OH)_2 \rightleftarrows [C_3H_5O_3Cu]N(CH_3)_4 + 2H_2O$$

Instead of allowing the ammonia base and the copper hydroxide to act as such on glycerol we may choose their combination in the copper ethylenediamine hydroxide $[Cu(NH_2CH_2CH_2NH_2)_2(OH)_2]$. Again, the primary reaction consists of the formation of an alcoholate, the copper ethylenediamine glycerate,[56] thus:

$$2CH_2(OH)CH(OH)CH_2OH + Cu(ene)_2(OH)_2 \rightleftarrows (CH_2(OH)CH(OH)CH_2O)_2[Cu(ene)_2] + 2H_2O$$ [57]

This glycerate is capable of combining with another atom of copper, which is taken from the excess of copper ethylenediamine, thus:

$$(CH_2(OH)CH(OH)CH_2O)_2[Cu(ene)_2] + [Cu(ene)_2](OH)_2 \rightleftarrows [(OCH_2CH(OH)CH_2O)_2Cu][Cu(ene)_2] + 2(ene) + 2H_2O$$

It will be observed that in this reaction 2 molecules of ethylenediamine are liberated and that the final complex compound contains 2 copper atoms which are differently combined. One is part of the anion, comprising the glycerol residue, and the other is part of the cation, the copper ethylenediamine residue.

Traube has shown that an analogous reaction takes place if, instead of glycerol, cellulose (being likewise of a "cupriphyllic" nature[58]) is dissolved in copper ethylenediamine hydroxide, the first phase of the reaction being the formation of an "alcoholate," copper ethylene-

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[55] Traube, *Ber.*, **54**, 3220 (1921); **55**, 1899 (1922); **56**, 268, 1653 (1923).

[56] Traube and Funk, *Ber.*, **69**, 1476 (1936).

[57] "ene" stands for the ethylenediamine residue.

[58] Traube, *Ber.*, **49**, 3319 (1911); Traube and Funk, *Ber.*, **69**, 1476 (1936).

diamine cellulosate, $(C_6H_9O_5)_2[Cu(ene)_2]$, and the second phase consisting of the entry into the cellulosate of a second copper atom, this being obtained from a second molecule of copper ethylenediamine. The final complex compound is expressed by the formula

$$[C_6H_8O_5)_2Cu][Cu(ene)_2],$$

and the equations for the two reactions may be formulated thus:

$$\text{I. } 2C_6H_{10}O_5 + Cu(ene)_2(OH)_2 \rightleftarrows (C_6H_9O_5)_2[Cu(ene)_2] + 2H_2O$$

$$\text{II. } (C_6H_9O_5)_2[Cu(ene)_2] + Cu(ene)_2(OH)_2 \rightleftarrows [(C_6H_8O_5)_2Cu][Cu(ene)_2] + 2(ene) + 2H_2O$$

As a matter of fact, on dissolving cellulose in copper ethylenediamine, liberation of ethylenediamine is observed. Moreover, Traube and collaborators[59] succeeded in isolating the complex compound from a solution of cellulose in copper ethylenediamine hydroxide and found that, in the complex anion, the ratio of cellulose to copper is 2 : 1; i.e., 2 glucose anhydride units combine with 1 atom of copper in the complex anion.

Although it has not been possible to isolate the complex compound from a solution of cellulose in cuprammonium hydroxide, it is very probable that the reactions involved are analogous. Thus the base active in cuprammonium hydroxide, $Cu(NH_3)_4(OH)_2$, would form copper tetrammino cellulosate, $(C_6H_9O_5)_2[Cu(NH_3)_4]$, in the first phase of the reaction, and the cellulosate would subsequently take up a second atom of copper from another molecule of copper tetrammino hydroxide to form the complex anion $(C_6H_8O_5)_2Cu^-$, thereby liberating a corresponding quantity of ammonia.[60] The final complex compound may be written $[(C_6H_8O_5)_2Cu][Cu(NH_3)_4]$ and may be termed "copper tetrammino copper cellulose" (reading the formula from right to left).

The liberation of ammonia results in an increase of the ammonia concentration of the solution. This empowers the solution to take up additional amounts of copper hydroxide which, in turn, enables it to dissolve more cellulose. In this way, the concentration of cellulose may be increased as the amount of copper is augmented, a procedure which is common practice in the preparation of cellulose cuprammonium solutions in rayon plants.

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[59] Traube, Glaubitt, and Schenck, *Ber.*, **63**, 2088 (1930); see also *Ber.*, **56**, 274 (1923). Jolley's criticism, *J. Textile Inst.*, **30**, T122 (1939), has been shown to be unfounded by Straus and Levy, *Paper Trade J.*, **114**, No. 3, 31 (1942); see also *Tech. Assoc. Papers*, **25**, 734 (1942).

[60] Traube and Funk, *Ber.*, **69**, 1476 (1936).

It is doubtful whether the stoichiometrical ratio of 2 $C_6H_{10}O_5$: 1 Cu, as found in the complex anion of the solid copper ethylenediamine copper cellulose (and which is probably the same for the copper tetrammino compound), may also be assumed to exist *in solution*. The results of Hess and Messmer[61] indicate that the ratio in the complex anion existing in solution is 1 $C_6H_{10}O_5$: 1 Cu. This ratio is derived from an investigation of the optical rotation of the solution which, as stated before, is ascribed to the existence of a complex copper cellulose compound. The rotation values are dependent upon both the cellulose and the copper concentration in the solution and are thus indicative of an equilibrium between cellulose, copper, and the active cellulose copper complex anion. When the cellulose concentration is kept constant, the rotation increases with the copper concentration; it also increases with the cellulose concentration if the copper concentration is kept constant. The influence of the copper and the cellulose concentration upon the rotation values reaches a pronounced maximum when 1 copper atom is present for each $C_6H_{10}O_5$ residue in the complex anion (Fig. 48). On the basis of this equivalence, which is in agreement with the law of mass action, Hess and Messmer have expressed the formation of the optically active copper cellulose complex compound by the following equation:

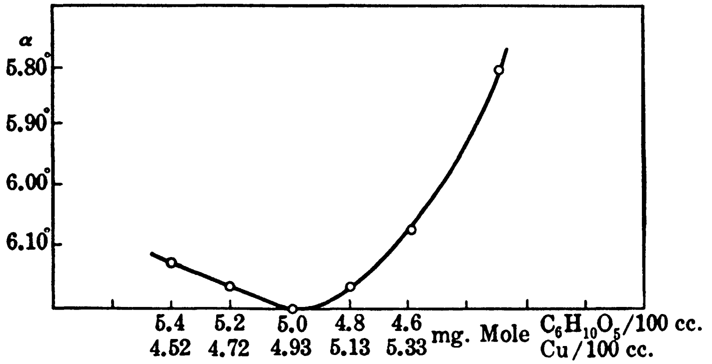

FIG. 48. Influence of cellulose and copper concentrations upon optical rotation. Hess and Messmer.

$$[C_6H_9O_5]_2[Cu(NH_3)_4] + 2[Cu(NH_3)_4](OH)_2 \rightleftarrows [C_6H_7O_5Cu]_2[Cu(NH_3)_4] + 8NH_3 + 4H_2O$$

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[61] Hess and Messmer, *Ber.*, **54**, 834 (1921); **55**, 2441 (1922); **56**, 587 (1923). *Z. physik. Chem.*, **145**, 430 (1929); Hess, "Chemie der Cellulose," p. 289.

One of the suppositions underlying the evaluation of the data in accordance with the law of mass action is that the reacting copper is exclusively consumed in the formation of the optically active complex anion. This prerequisite is actually not fulfilled, because the cation of the complex compound also contains copper. However, on addition of a small amount of aqueous sodium hydroxide to the cellulose cuprammonium solution, the rotation increases distinctly and reaches a maximum at a concentration of 0.25 mole of sodium hydroxide per liter of the cuprammonium solution. Since cellulose dissolved in aqueous sodium hydroxide shows practically no levorotation, Hess explains the marked increase and the occurrence of the maximum on the assumption that the equilibrium is shifted in direction which increases the concentration of the cellulose copper complex. This change is brought about if the sodium hydroxide decomposes the cation of the complex compound, thereby replacing it by sodium and favoring the formation of a cellulose copper-sodium complex compound; in other words, the copper of the cation of the original complex compound has been shifted entirely into the anion. Thus:

$$[C_6H_7O_5Cu]_2[Cu(NH_3)_4] + C_6H_{10}O_5 + 3NaOH \rightleftarrows 3[C_6H_7O_5Cu]Na + 4NH_3 + 3H_2O$$

This reaction may also be written as follows:

$$3C_6H_{10}O_5 + 3Cu(NH_3)_4(OH)_2 + 3NaOH \rightleftarrows 3[C_6H_7O_5Cu]Na + 12NH_3 + 6H_2O$$

The occurrence of this reaction would explain the observation, mentioned earlier in this section, that the addition of alkali increases the solvent power of the cuprammonium solution, an observation which is also utilized commercially.

On increasing the amount of sodium hydroxide beyond the maximum rotation value, a precipitate is obtained which is known as Normann's compound, after its discoverer.[62] Its composition is $[(C_6H_8O_5)_2Cu]Na_2$. It contains less copper than the previously discussed compound, the ratio of cellulose to copper being 2 : 1. Thus it appears that in the attempt to isolate a cellulose copper-sodium complex compound, the cellulose-copper ratio changes from 1 $C_6H_{10}O_5$: 1 Cu to 2 $C_6H_{10}O_5$: 1 Cu. The formation of the solid compound

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[62] Normann, *Chem.-Ztg.*, **30**, 584 (1906); Hess and Messmer, *Ber.*, **55**, 2432 (1922); Traube, *Ber.*, **55**, 1899 (1922); Heuser and Brötz, *Papier-Fabr.*, **25**, 238 (1927); Hess and Trogus, *Z. physik. Chem.*, **145**, 401 (1929); Lieser and Swiatowski, *Ann.*, **538**, 110 (1939).

from its solution may therefore be imagined to take place by way of hydrolysis. Thus:

$$2[C_6H_7O_5Cu]Na + 2H_2O = [(C_6H_8O_5)_2Cu]Na_2 + Cu(OH)_2$$

The Normann compound is soluble in dilute ammonium hydroxide but the mechanism of the reaction has not yet been sufficiently elucidated. When exposed to the atmosphere, it decomposes gradually, thereby forming copper hydroxide, which oxidizes the cellulose to oxycellulose which, in turn, reduces more copper hydroxide. These reactions are indicated by a change of the color of the compound from blue to green and an increase in the solubility of the regenerated cellulose in 8 per cent sodium hydroxide.[63]

Further evidence that it is the copper tetrammino hydroxide base in a cuprammonium solution which is responsible for the dissolution of cellulose is derived from the following observation.[64]

Whereas a solution of a neutral copper salt in an excess of ammonia, copper sulfate, for example, exerts no solvent power on cellulose, it becomes a solvent at once when a quantity of alkali equivalent to the sulfuric acid radical of the salt is added, for the following reaction then occurs:

$$Cu(NH_3)_4SO_4 + 2NaOH \rightleftarrows Cu(NH_3)_4(OH)_2 + Na_2SO_4$$

That is, copper tetrammino hydroxide is formed and it dissolves the cellulose.

Earlier, it has been mentioned that the copper tetrammino base tends to decompose into copper hydroxide and ammonia, if a sufficient quantity of concentrated ammonia is lacking. Thus, the solvent power of the ammoniacal copper sulfate solution very soon decreases unless the ammonia concentration is very high. However, the decomposition of the copper tetrammino base may be prevented, even at rather low ammonia concentration (5–6 per cent or less), if cellulose is added to the solution immediately after the solution has been prepared, i.e., before the copper tetrammino base has had time to decompose. In this way it is possible to dissolve considerable quantities of cellulose within a relatively short time.

The Normann compound may be reconverted to the cellulose copper complex compound by allowing it to react with copper tetrammino sulfate.[65] Thus:

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[63] Heuser and Brötz, *loc. cit.*

[64] Traube and Funk, *Ber.*, **69**, 1476 [1480] (1936).

[65] Traube and Funk, *loc. cit.*, p. 1482.

$$[(C_6H_8O_5)_2Cu]Na_2 + Cu(NH_3)_4SO_4 \rightleftarrows [C_6H_8O_5)_2Cu][Cu(NH_3)_4] + Na_2SO_4\,^{66}$$

The system cellulose-cuprammonium-sodium hydroxide has been further investigated in various ways. Hess, Trogus, and Uhl[67] found that in this system the solvent power of the solution depends upon the alkali content. When the copper concentration is kept constant, the solubility of cellulose (ramie fiber) first increases and then decreases with the alkali concentration, until, owing to lack of copper, cellulose becomes insoluble.

In addition, the authors also investigated the cellulose-cuprammonium-alkali system under conditions in which the cellulose is not completely dissolved but remains as a solid, swollen phase (*Bodenkörper*) in the solution. The results seem to indicate that cellulose, while it is still in the solid phase, undergoes complex formation with copper and alkali in varying proportions. We may infer, therefore, that in the alkali-free cuprammonium solution also, the primary phenomenon is the formation of the cellulose copper complex and that this complex subsequently dissolves in the excess cuprammonium hydroxide.

Similar investigations of the solid phase in alkali-free cuprammonium solution and in copper ethylenediamine solution were undertaken by Sakurada[68] and by Trogus and Sakurada.[69]

The evidence for the formation, in the presence of alkali, of various complex compounds, which is derived from chemical investigation, has been substantiated by x-ray findings. Two crystalline phases, copper alkali cellulose I and II, have been described; I seems to be identical with the Normann compound, whereas II contains a greater quantity of copper.[70] X-ray data on the alkali-free cellulose cuprammonium system are not available, however.

Although the mechanism of the reactions which take place when cellulose is dissolved in cuprammonium hydroxide and which have been discussed above appears to be generally accepted, other hypotheses have been suggested. Thus, Neale[71] has expressed the opinion that the solvent power of the copper tetrammino hydroxide is not due to a specific effect of the copper but is merely a result of its extremely high basicity, so that, in solution, a simple salt would exist, consisting of cellulose, which acts as a weak acid, and the strong copper

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[66] Following Hess's formulation of the copper cellulose compound, the equation should be written thus:

$$[(C_6H_8O_5)_2Cu]Na_2 + 2Cu(NH_3)_4SO_4 \rightleftarrows [C_6H_7O_5Cu]_2[Cu(NH_3)_4] + Na_2SO_4 + (NH_4)_2SO_4 + 2NH_3$$

[67] Hess, Trogus, and Uhl, *Z. physik. Chem.*, **145**, 401 (1929).

[68] Sakurada, *Ber.*, **63**, 2027 (1930).

[69] Trogus and Sakurada, *Ber.*, **63**, 2174 (1930). See also Mark's attempt to evaluate the data supplied by Hess and Trogus and by Trogus and Sakurada from the phase rule viewpoint, "Physik und Chemie der Cellulose," pp. 233, 239.

[70] Trogus and Hess, *Z. physik. Chem.* **B6**, 1 (1929); Hess and Trogus, *ibid.*, **145**, 422 (1929).

[71] Neale, *J. Textile Inst.*, **16**, T363 (1925); see also Traube and Funk, *Ber.*, **69**, 1476 (1936).

base. However, Hess and Trogus[72] argue that, if this were correct, the copper base ought to be much stronger than aqueous sodium hydroxide which, as we have seen, is generally without effect on undegraded cellulose. Hess and Trogus proved that the copper base, in spite of having a much more pronounced solvent power, is weaker than sodium hydroxide, the ratio of the basicities being 65 : 100.

Considering the relatively low activity of the organic constituent in the system and the fact that only little heat is evolved from the reaction, Mark[73] is inclined to believe that the action of cuprammonium hydroxide on cellulose possibly does not involve such far-reaching alterations as would result from a chemical interchange reaction, but could be explained by the activity of dipole forces.

The copper base seems to be the only compound which dissolves cellulose directly. Attempts to obtain the same effect with nickel or cobalt tetrammino hydroxide have failed. If, however, cobalt metal powder is added to a copper ethylenediamine solution of cellulose, the copper precipitates but the cellulose remains in solution. Obviously, no complex compound is formed, because all the cobalt is found to have combined with the ethylenediamine. The solution is still more sensitive to oxygen than a cuprammonium solution, the cellulose being oxidized to a considerable extent.[74]

COAGULATION AND REGENERATION OF CELLULOSE

As indicated earlier, coagulation of the cuprammonium solution occurs under the influence of a number of substances, of which sodium hydroxide, barium chloride, and other metal salts have been mentioned previously. The coagulates thus obtained consist of complex compounds in which the complex copper cation is replaced by the metal of the salt used.

A number of other salts, as ammonium chloride and ammonium sulfate, bring about coagulation with simultaneous regeneration of the cellulose. If aqueous ammonium sulfate is added to the solution of cellulose in cuprammonium hydroxide, the following reaction occurs:

$$Cu(NH_3)_4(OH)_2 + (NH_4)_2SO_4 = Cu(NH_3)_4SO_4 + 2NH_4OH$$

That is, the ammonium sulfate reacts with the free base to yield copper tetrammino sulfate in which, as has been seen, cellulose is insoluble. Kumichel[75] has utilized this reaction in an attempt further to elucidate the coagulation process. If the ammonium sulfate solution is added in small portions from a burette, the increasing amount of sulfate ion gradually diminishes the solvatizing power of the base

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[72] Hess and Trogus, *Z. physik. Chem.*, **145**, 434 (1929).

[73] Mark, "Die Physik und Chemie der Cellulose," p. 247.

[74] Traube and Schenck-Thiekötter, *Cellulosechem.*, **12**, 301 (1931).

[75] Kumichel, *Papier-Fabr.*, **36**, 173 (1938).

until the latter is no longer capable of keeping the copper cellulose complex compound in solution. When this point is reached, the compound decomposes. As a result, cellulose precipitates in a finely divided form and the solution becomes quickly and uniformly turbid. Hence, the "turbidity point" corresponds to the number of cubic centimeters of ammonium sulfate solution which are required to reach, or just overstep, the threshold of coagulation.

Since—according to the equation—1 mole of ammonium sulfate corresponds to 1 mole of copper, the number of cubic centimeters of ammonium sulfate solution is equivalent to the amount of "free" copper in the cellulose solution. If this is deducted from the total copper in the solution, the "combined" copper is obtained, i.e., that which is in combination with the cellulose constituent in the complex anion.

Kumichel found that the ratio of cellulose to copper, provided the copper concentration is high enough so that all the cellulose is dissolved, was 1 : 1, which is in agreement with the ratio of cellulose to copper in the complex anion of Hess's formula, $[C_6H_7O_5Cu][Cu(NH_3)_4]$. The same conclusion is derived from extrapolation of data which resulted from the investigation of the effect of the copper concentration on the percentage of cellulose solubility (p. 146, footnote 15).

Coagulation may also be accomplished by ethyl or methyl alcohol; in this event one would expect the copper tetrammino copper cellulose compound to be precipitated as such. This, however, is not so; the precipitate decomposes simultaneously and cellulose is regenerated. Water has the same effect.

As would be expected, mineral and organic acids decompose a cellulose cuprammonium solution instantaneously.

Finally it may be mentioned that the cellulosic constituent, as well as the copper, may be regenerated from the solution by means of an electric current. Copper wanders to the cathode and cellulose precipitates at the anode (electrocatophoresis).[76]

Cellulose regenerated from its cuprammonium or copper ethylenediamine solution is chemically unchanged, provided that air and light are carefully eliminated on dissolution and that precipitation is effected not too long after dissolution.[77] The regenerated material shows all the characteristics of the cellulose hydrate modification—the physical changes which are observed with mercerized cellulose

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[76] Taylor and Chandler, U. S. patent 1,590,592; Hess and Messmer, *Ber.*, **55**, 2441 (1922); Sisson, *Contrib. Boyce Thompson Inst.*, **10**, 113 (1938).

[77] Scheller, *Melliand Textilber.*, **16**, 787 (1935); Staudinger and Ritzenthaler, *Ber.*, **68**, 1225 (1935); Staudinger and Feuerstein, *Ann.*, **526**, 72 (1936).

and cellulose regenerated from other solutions.[78] The solubility of cellulose hydrate regenerated from its cuprammonium solution has been discussed earlier (Chapter IV).

For the manufacture of cuprammonium rayon[79] a solution of 8–10 per cent cellulose is forced through fine capillaries into a bath which, by virtue of its coagulating power, sets the solution to a solid thread (filament). If the setting bath consists of an acid (for example, sulfuric), alkali and copper are removed, and the thread represents regenerated cellulose. If the bath is made up of aqueous alkali, the thread consists of Normann's copper-alkali cellulose. In this form, the filaments are very pliable and may be stretched into much finer ones. The thread thus obtained approaches the fineness of natural silk (stretch spinning process). In order to remove alkali and copper, the stretched thread is passed through a second bath containing essentially aqueous sulfuric acid.

The raw material for cuprammonium rayon is cotton linters. Wood pulp, although suitable in most respects, is said to give a slight yellowish tinge to the finished rayon, whereas that prepared from cotton linters possesses a bluish white color.[80]

VISCOSITY OF CELLULOSE CUPRAMMONIUM SOLUTIONS

Cuprammonium hydroxide, because of its high solvent power and because, of all solvents, it practically does not degrade cellulose, if proper precautions are observed, is the most suitable solvent for determining the viscosity of cellulose, its modifications, and some derivatives. Various methods of viscosity determination are in use. They differ not only as to the preparation of the cuprammonium hydroxide, the method of dissolving the cellulose material, the cellulose concentration, etc., but also as to the type of viscometer. For details, the reader is referred to the pertinent literature.[81]

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[78] Mark, "Physik und Chemie der Cellulose," p. 245; Hess, *Ann.*, **435**, 112, 142 (1923); Herzog, *Naturwissenschaften*, **12**, 958 (1924).

[79] Avram, "The Rayon Industry," Van Nostrand Co., New York (1929); Wheeler, "The Manufacture of Artificial Silk," Van Nostrand Co., New York (1931); Mauersberger and Schwarz, "Rayon Handbook," Rayon Handbook Co., New York (1939), 3rd ed., and later editions.

[80] Weltzien, "Chemische und physikalische Technologie der Kunstseiden," p. 179; Vieweg, *Kunstseide und Zellwolle*, **21**, 84 (1939).

[81] Method suggested by the American Chemical Society, Cellulose Division, *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929); Grant and Billings, *ibid.*, **5**, 270 (1933); standard method suggested by the Technical Association of the Pulp and Paper Industry, TAPPI Standard T206m-37; British standard method, *Fabrics Research Committee, Dept. Sci. and Ind. Research*, H. M. Stationery Office, London (1932). German standard method, suggested by German Assoc. of Pulp and Paper Chemists and Engineers, "Merkblatt" No. 12, O. Elsner, Verlags-Ges., Berlin; see also Dorée, "The Methods of Cellulose Chemistry," p. 52.

Copper ethylenediamine solution may be used instead of a cuprammonium hydroxide solution. Methods using this agent were worked out by Brownsett and Clibbens[82] and by Straus and Levy.[83]

Solutions of cellulose in cuprammonium hydroxide frequently show the phenomenon of "structural viscosity," i.e., the viscosity decreases with increasing pressure, provided the concentration is high enough. The phenomenon has been observed with a cuprammonium solution having 1 per cent cellulose concentration, by Sakurada[84] and by Rogovin and Schlachover.[85] The results obtained by the latter investigators with cotton linters and using the Ubbelhode viscometer[86] are shown in Table 15.

TABLE 15

INFLUENCE OF PRESSURE UPON VISCOSITY OF COTTON LINTERS DISSOLVED IN CUPRAMMONIUM HYDROXIDE

Materials	Pressure, cm. of water	Time of outflow, sec.	Viscosity, poises
Linters A	30	764	0.1437
	10	2540	0.4481
	60	347	0.1319
	10	153	1.571
Linters B	30	34.2	1.052
	60	14.0	0.867
	10	177	1.816
Linters C	30	39.8	1.225
	60	16	0.985

It is likely that the occurrence of the phenomenon of structural viscosity depends, to a considerable extent, upon the chain length of the cellulosic material, for cellulose regenerated from nitrocellulose (Rogovin and Schlachover) and in the form of cuprammonium and viscose rayon (Sakurada) were found to show at the same concentration either very little or no structural viscosity.

In an attempt to prepare cellulose solutions which contain, in addition to copper hydroxide and ethylenediamine, a certain amount of sodium hydroxide,

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[82] Brownsett and Clibbens, *J. Textile Inst.*, **32**, T57 (1941).

[83] Straus and Levy, *Paper Trade J.*, **114**, No. 3, 31 (1942); see also the discussion between Levy and Clibbens, *Tech. Assoc. Papers*, **25**, 734 (1942).

[84] Sakurada, *Ber.*, **63**, 2027 (1930); see also the polemics between Sakurada and Hess, *Ber.*, **64**, 1174, 1183 (1931) and Staudinger, *ibid.*, **64**, 1688 (1931); also Staudinger and Husemann, *Ann.*, **530**, 1 (1937), and Staudinger and Sorkin, *Ber.*, **70**, 2011 (1937).

[85] Rogovin and Schlachover, *Angew. Chem.*, **48**, 647 (1935).

[86] Rogovin and Ivanowa, *Kolloid-Z.*, **72**, 86 (1935).

Hoffmann and Bruch[87] observed that such cellulose solutions, on standing, show the phenomenon of thixotropy.[88] With increasing addition of 0.1 *N* sodium hydroxide solution, the time for gelatinization first decreases and then increases. Gelatinization is followed by syneresis. The same phenomena were observed on the addition of water. However, the phenomenon of thixotropy failed to occur if the water was added to the copper ethylenediamine solvent before dissolving the cellulose.

The relation between the solution viscosity[89] of cellulose and its degree of polymerization, to which reference has been made frequently in the previous pages, has been known for a long time. It is likely that Berl and Klaye[90] and Ost[91] were the first to demonstrate this relationship on different cellulosic materials and to recognize a connection between viscosity and molecular weight. At about the same time Biltz[92] showed this connection to exist in the case of other colloids, such as starch (dextrins) and gelatin.

Berl's and Ost's studies were extended by Gibson and co-workers,[93] who, making use of an improved technique (see p. 147), were able to establish more firmly the influence of several treatments upon the solution viscosity of various cellulosic materials. Whereas unpurified cotton, the first member of a series of preparations, showed the highest viscosity, treatments of this material with sodium hydroxide solutions of varying concentration and at different temperatures decreased it. Similar observations were made and the technique of testing was further improved by Punter[94] and by Joyner.[95]

From the results of these investigations the general conclusion may be drawn that the viscosity in solution falls with the degree of degra-

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[87] Hoffmann and Bruch, *Cellulosechem.*, **14**, 53 (1933).

[88] Freundlich, "Kapillarchemie," Vol. II, p. 615.

[89] Regarding definition of viscosity of liquids and solutions in general, see Hatschek, "Viscosity of Liquids," Bell and Sons, London (1928); Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York (1922); Mark, "Chemie und Physik der Cellulose," p. 68.

[90] Berl and Klaye, *Z. ges. Schiess- und Sprengstoffw.*, **2**, 381 (1907); **4**, 81 (1909); Berl and Büttner, *ibid.*, **5**, 82 (1910); Berl and Innes, *Z. angew. Chem.*, **23**, 987 (1910); see also Ostwald, "Grundriss der Kolloidchemie," Steinkopf, Dresden (1909), 1st ed.

[91] Ost, *Z. angew. Chem.*, **24**, 1892 (1911).

[92] Biltz, *Z. physik. Chem.*, **73**, 481 (1910); **83**, 703 (1913); **91**, 719 (1916); *Ber.*, **46**, 1532 (1913).

[93] Gibson, *J. Chem. Soc.*, **117**, 479 (1920); Gibson, Spencer, and McCall, *ibid.*, **117**, 484 (1920).

[94] Punter, *J. Soc. Chem. Ind.*, **39**, 333 (1920).

[95] Joyner, *J. Chem. Soc.*, **121**, 1511, 2395 (1922).

dation. Thus a relatively high viscosity indicates that little damage has been done to the cellulosic material and *vice versa.*

Staudinger's[96] "viscosity law" postulates a quantitative relation between the solution viscosity of cellulose and its chain length or molecular weight. His deliberations are based upon his earlier discovery that, for a number of synthetic polymers of increasing chain length (such as the polystyrols, polyvinyl acetates, and other linear polymers), the specific viscosity, i.e., the increase of viscosity over that of the solvent, is, indeed, to the first approximation, directly proportional to the length of the molecule.

In the case of cellulose, it has not yet been possible to synthesize a homologous series of polymers of increasing chain length by building up large molecules from the smaller units such as the oligosaccharides. However, such a homologous series may be obtained by choosing the opposite procedure, namely, by a step-wise degradation of carefully isolated cellulose (Gibson, Staudinger).

How the relationship between viscosity and molecular weight was established with such polymer-homologous series of cellulose and cellulose-derivative preparations is discussed in Chapter XV.

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[96] Staudinger, "Die hochmolekularen organischen Verbindungen," pp. 82, 475.

CHAPTER VII

CELLULOSE ESTERS

Just as an alcohol undergoes esterification with an acid in the presence of a dehydrating agent or by the action of an acid chloride, so cellulose may be converted into esters. It is not always possible to convert all three hydroxyls into ester groups, and esterification may arrest itself at two hydroxyls and sometimes even at one. The course of the reaction is due to the peculiarities of the microscopic and submicroscopic structure of the fiber which causes the hydroxyl groups of the chain bundles to be unequally accessible. Conceivably, those hydroxyl groups may be expected to react first which are exposed on the surface of the chain bundles (intermicellar reaction), and the reaction will come to a temporary standstill when all surface hydroxyl groups have become esterified, unless some measures are taken to open up the path to the interior of the micellar system and enable an intramicellar reaction to take place. As we have seen before, swelling is an effective means for reaching this objective. Frequently, the dehydrating means present in the esterification mixture is simultaneously a swelling agent, because it usually consists of a strong mineral acid (such as sulfuric) or of certain salts (for example, zinc chloride). In other cases, the cellulose is given the opportunity of swelling before the esterifying agent is added, for example, by pretreatment with strong alkali.

The degree of swelling of cellulose during esterification is governed by the rate of diffusion by which the swelling medium and, with it, the esterifying agent are capable of penetrating to the intramicellar hydroxyl groups. Depending upon the nature of these substances and on concentration and temperature, the reaction may proceed either topochemically (i.e., advancing slowly from layer to layer of the micellar system) or in a permutoidal fashion (i.e., almost simultaneously throughout all layers of the system).[1] Although, in general, acetylation is representative of the first type of reaction, whereas nitration is a characteristic example of the latter, a permutoidal may

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[1] Meyer and Mark, *Z. physik. Chem.*, **B2**, 695 (1929); Mark, *J. Soc. Dyers Colourists*, **49**, 54 (1932).

be converted into a topochemical reaction and *vice versa*. In all cases, the reaction exhibits a more or less heterogeneous character.

The fact that the three hydroxyl groups available for esterification in each glucose residue of the chain molecule are not equivalent (one being in the primary and the other two in the secondary position) will also influence the course of the reaction. In the case in which not all of the three hydroxyl groups are substituted, six combinations are possible, namely, substitution of the hydroxyl groups in either positions 6, 3, or 2; in 3 and in 6, in 2 and in 6, or in 2 and in 3.

By analogy, one may expect the primary hydroxyl groups to react first and the secondary groups to follow. Such step-wise reactions have been observed to occur with polyvalent alcohols.[2] Whereas it is difficult to prove that this is true also with cellulose, it appears that in certain cases the manipulation with radicals which are specific for one type of hydroxyl groups furnishes some information. Likewise, by analogy, it is possible that the ability of one hydroxyl group to react is influenced by a neighboring group already esterified.[3]

Taking into consideration the difference in the functional value of the hydroxyl groups of the glucose unit, the frequent repetition of such groups in the chain, and the peculiar arrangement of the individual chains in bundles, it will be easily understood that the results of esterification, if by some reason it fails to continue after a certain time or if it is intentionally interrupted before it has come to an end, must be an aggregate of partly and completely substituted chains. On the basis of the six possibilities of substitution mentioned above, Spurlin[4] has calculated that a chain of only 100 glucose units with an average degree of substitution of 1.5 groups per glucose unit could be arranged in some 10^{85} different ways. The fact that cellulose lends itself to so many varieties of one reaction makes it impossible to produce mono- or di-substituted cellulose esters that can be regarded as homogeneous compounds. Nor has it been possible to obtain such products by fractionation. On cursory inspection, the chances of arriving at di- or mono-substituted esters would appear to be better by gradually saponifying[5] the completely substituted and hence homogeneous ester to the desired lower steps. However, saponification also

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[2] See, for example, Wegscheider, *Monatsh.*, **29**, 83, 233 (1908); Skrabal, *ibid.*, **37**, 137 (1916); **38**, 29 (1917); *Z. physik. Chem.*, **128**, 459 (1927); Smith and Olsson, *ibid.*, **102**, 26 (1922).

[3] Mark, "Physik und Chemie der Cellulose," p. 212.

[4] Spurlin, *Trans. Electrochem. Soc.*, **73**, 96 (1938).

[5] In the German literature, the term "saponification" (of an ester) is used as an equal to "hydrolysis."

seems to take a heterogeneous course. No doubt, esterification would proceed more homogeneously if it could be carried out on cellulose in solution. Unfortunately, the solvents for cellulose are either alkaline or acid and thus produce conditions under which ester groups are easily cleaved off.

The ease with which esterification takes place also depends on the size of the groups to be introduced, the difficulties becoming greater as their size increases, since, obviously, more space is required for accommodating larger groups within the micellar system than for smaller ones.

Finally, the degree of polymerization of the cellulosic material governs the rate and the homogeneity of the reaction to a considerable extent. To reach a certain degree of substitution with chains of small or medium size, a shorter time is required than when chains of considerable length are subjected to the reaction. The usual method of esterification, i.e., the use of acids or their anhydrides in the presence of a dehydrating agent, results in considerable degradation of the cellulosic constituent, although in some cases the product of reaction becomes more resistant to degradation as the degree of substitution increases. Obviously, the rate of reaction is of essential influence, for, if esterification, as for example, nitration, can be accomplished within a relatively short time, degradation remains within narrow limits. On the contrary, in acetylation, which proceeds rather slowly, the chances that the cellulose will become degraded are considerable. In certain cases, the dehydrating agent may be omitted and esterification proceeds without degradation. However, under such conditions the time for introducing an appreciable number of ester groups may amount to weeks and even months.

It has been claimed that the dehydrating agents (generally termed "catalysts"), such as mineral acids, form addition compounds with cellulose in a primary phase of the reaction, and that this facilitates the subsequent esterification with the organic acid. Moreover, since the mineral acids are also capable of esterifying cellulose, they compete with the organic acid, a phenomenon which may lead to the establishment of certain equilibria. On boiling with water, the inorganic esters decompose more easily and the organic acid ester may be obtained practically free of mineral acid esters.

On saponification the constituents of the ester, i.e., cellulose and the respective acid, are regenerated. Saponification may be accomplished by means of acids or alkalies. Whereas the action of acids results in a degradation of the cellulosic constituent, saponification with alkali may be achieved without degradation if precautions are taken to exclude atmospheric oxygen. Hence, the latter method is also a means of regenerating the cellulose in a form in which the extent of degradation which has occurred during esterification may be established.

The cellulose esters are soluble in organic solvents, each ester having one (or more) most suitable solvent or mixture of solvents. The solubility seems to be controlled by the balance of polar and nonpolar groups present in the ester and in the solvent or solvent mixture. The extent to which the esters dissolve may often be used as an indication of both the degree of substitution and the degree of polymerization. The viscosity of the solution is dependent primarily upon the extent of the degradation which the cellulose has undergone on esterification, low viscosity indicating a far-reaching degradation, and *vice versa.* In addition the degree of substitution may be a governing factor.

SULFURIC ACID ESTERS OF CELLULOSE

Cellulose may be expected to react with sulfuric acid according to the following equation:

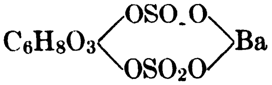
$$C_6H_9O_4OH + HOSO_2OH = C_6H_9O_4OSO_2OH + H_2O$$

When more than one hydroxyl group per glucose residue is substituted, di- and trisulfates would result: $C_6H_8O_3(OSO_2OH)_2$ and $C_6H_7O_2(OSO_2OH)_3$.

The reaction products which were obtained by early investigators from the action of sulfuric acid upon cellulosic materials of various kinds were found to be capable of forming salts with sodium, potassium, barium, etc., from which the conclusion was drawn that only one of the two hydroxyls of the sulfuric acid is involved in the exchange reaction, whereas the second hydroxyl remains free to form the salt as indicated in the formulas given above.

In the earlier investigations, sulfuric acid esters of cellulose were obtained by dissolving the cellulosic material in concentrated sulfuric acid (70–80 per cent H_2SO_4 content), allowing the solution to stand for a certain length of time, and then diluting with water to inhibit too far-reaching hydrolysis of the cellulosic material. After the excess of sulfuric acid had been neutralized with barium carbonate and the barium sulfate had been filtered off, alcohol was added to the filtrate. Thus, a precipitate was obtained which was regarded as the barium salt of a cellulose sulfate.

The composition of the barium salt is not known with certainty. Two possibilities suggest themselves. On the assumption that 2 hydroxyl groups per glucose residue are replaced by 2 sulfuric acid radicals, a barium salt could be formed by the substitution of the 2 free hydroxyl groups belonging to the 2 ester groups. Such a barium salt could be formulated thus:



$$C_6H_8O_3\begin{cases}OSO_2O\\OSO_2O\end{cases}Ba$$

Stern[6] believed that it was essentially a salt of this composition that he obtained on following the method suggested by previous investigators.[7] Stern's attempts to introduce into cellulose more than 2 sulfuric acid radicals per glucose residue were not successful, and Hönig and Schubert[8] were able to introduce only 1.5 groups.

It is conceivable also that a barium salt is formed in which the barium atom would unite 2 cellulose chains. This possibility exists if only 1 hydroxyl group of the glucose residue in each chain is substituted. Such a barium salt may be formulated thus:

$$C_6H_9O_4OSO_2OBaOSO_2OC_6H_9O_4$$

If it were possible to prepare the two products in pure form, the ratio of combined sulfuric acid to cellulose, being different in the two cases, would permit a decision between the two possibilities.

In the light of what has been said in the introduction, it is very unlikely, however, that the action of sulfuric acid leads to homogeneous mono- or disulfates, and it appears fairly safe to conclude that the barium salt obtained on adding alcohol to the neutralized solution of cellulose in sulfuric acid represents a mixture of various stages of substitution and possibly of various combinations between the barium atom and the hydroxyl groups of the ester radicals.

The degradation which cellulose suffers while the ester is being formed may, depending upon time and temperature, reach considerable proportions and proceed as far as to the formation of cellodextrins, an aggregate of chain molecules probably comprising not more than 30 glucose residues. Therefore, most of the sulfuric acid esters described by the above-mentioned investigators should, more correctly, be regarded as esters of cellodextrin rather than of cellulose. This

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[6] Stern, *J. Soc. Chem. Ind.*, **67**, 74 (1895).

[7] Blondeau de Carolles, *Ann.*, **52**, 412 (1844); see also Braconnot, *Ann. Chem. Phys.*, **12**, 185 (1819).

[8] Hönig and Schubert, *Monatsh.*, **7**, 455 (1886).

conclusion is in agreement with the observation that these esters were found to be easily water soluble and to have a high copper number.

In the light of the results obtained by Ost and Mühlmeister[9] it might appear doubtful whether the action of strong sulfuric acid on cellulose leads at all to ester formation. Mühlmeister found that the product of reaction which resulted from the action of 70 per cent sulfuric acid on cotton at 15°, even after 11 hours, contained only 12.1 per cent combined sulfuric acid. This amount would correspond to only a third to a fourth of what is required by the monosulfate (40.05 per cent). After 1 hour of contact, the reaction product showed even only 6.6 per cent combined sulfuric acid. At this point it was still insoluble in water, whereas increasing time of reaction resulted in so much degradation that the products obtained became easily water soluble. Indeed, on analyzing Mühlmeister's results and considering the results of his own investigation, af Ekenstam[10] arrived at the conclusion that no sulfuric acid esters are formed at all: After cotton had been allowed to stand in a solution containing 65.4 per cent sulfuric acid for 5–10 minutes at 0°, it precipitated quantitatively on the addition of water, but the combined sulfuric acid content of the precipitate was found to be very small.[11] Possibly, this result was due to the relatively short time of contact.

On the other hand, it is difficult to reconcile Mühlmeister's and af Ekenstam's results with those reported by earlier investigators, particularly by Hönig and Schubert, who found for products which were still insoluble in water considerably higher combined sulfuric acid contents, and by Stern, who reported values corresponding approximately to those of a disulfate (theoretically, 60.87 per cent). Unless it is assumed that the products of these investigators were simply mixtures of more or less degraded cellulose with barium sulfate in incidental proportions, it would appear impossible to explain the differences without repeating their experiments.

By allowing fumes of sulfur trioxide to act upon thoroughly dried cellulose (filter paper), Traube, Blaser, and Grunert,[12] obtained a reaction product which, from the analytical data, must be regarded as the trisulfate of cellulose. When the cellulose was actually dry, no carbonization occurred, and the filter paper appeared to have scarcely lost its fibrous structure.

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[9] Mühlmeister, doctoral dissertation, Hanover, 1913, p. 14.

[10] af Ekenstam, "Über Celluloselösungen in Mineralsäuren," p. 24.

[11] af Ekenstam, *Svensk Kem. Tid.*, **46**, 157 (1934).

[12] Traube, Blaser, and Grunert, *Ber.*, **61**, 754 (1928).

The mechanism of the reaction is not clear. If the product of reaction is a sulfuric acid ester of cellulose, i.e., having the formula $C_6H_7O_2(OSO_2OH)_3$, it is necessary to assume the addition of SO_3 molecules to the oxygen atoms of the hydroxyl groups of cellulose and a rearrangement of the hydrogen atoms to form the hydroxyl groups of the acid radicals.

It is of interest to note that on the reaction no intermediates (those containing 1 or 2 sulfuric acid radicals per glucose residue) were formed, although, owing to difficulties of penetration, not all of the cellulosic material reacted. The ester was soluble in hot water and formed a potassium salt and, because the salt is also soluble in hot water, both the free ester and its potassium salt may be extracted from the unreacted cellulose. Apparently, no organic solvent has yet been found for the ester.

In spite of the careful exclusion of water from the reaction, the cellulose appeared to be considerably degraded. Although the copper number (2.5 to 4.0) of the potassium salt was not so high as would be expected from the result of far-reaching degradation, the viscosity of a 1 per cent solution of the potassium salt was very low—practically the same as that of water.

Obviously, the ester groups are rather resistant to water and dilute alkali. Boiling with water or with potassium hydroxide solution at 150° split off very little sulfuric acid; only on boiling with dilute hydrochloric acid was it possible to recover the sulfuric acid quantitatively. Since on such a treatment cellulose is largely degraded, no conclusion can be drawn from the result of this treatment as to the extent of degradation that occurred on the process of "esterification." However, boiling with a methylalcoholic solution of hydrochloric acid, according to a method previously applied by Hönig and Schubert, is said to permit the regeneration of the cellulose without further degradation.[13] It is doubtful whether this conclusion can actually be drawn, for the degree of depolymerization was not determined.

Another way of preparing cellulose trisulfate is to shake cellulose with a solution of sulfuric acid anhydride in carbon disulfide for 20 to 30 minutes.[14] Obviously, this method of preparation insures more thorough penetration of the cellulosic material by the esterifying agent. A modification of this method consists in dissolving the anhydride in carbon disulfide, adding pyridine to the solution, evaporating the carbon disulfide, submerging the cellulose in the remaining solution, and heating the solution. However, in this way only 2.6 acid

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[13] Traube, Blaser, and Lindemann, *Ber.*, **65**, 603 [606] (1932).

[14] Traube, Blaser, and Lindemann, *loc. cit.*, p. 605.

radicals could be introduced per glucose residue, indicating that no homogeneous product was obtained.

Gebauer-Füllnegg and co-workers[15] have shown that, instead of sulfuric, chlorosulfonic acid ($ClSO_2OH$) may be used for preparing cellulose sulfates. The degrading action of this acid on cellulose, even at elevated temperature, seems to be largely reduced by the presence of pyridine. Apparently, chlorosulfonic acid forms a salt compound with pyridine[16] which is a less violent esterifying agent. The by-product formed in this reaction is hydrochloric acid, which, however, combines with pyridine and is thus neutralized. The reaction may be expressed by the following equation:

$$ROH\ (\text{cellulose}) + ClSO_2OH = HCl + ROSO_2OH$$

By submerging the cellulosic material (cotton or filter paper) in the acid-pyridine mixture under cooling and subsequent heating of the solution to 100°, a gelatinous, homogeneous paste was obtained which, on dilution with water, gave a clear, colorless, colloidal solution. The absence of reducing power and the high viscosity of the solution seem indeed to indicate that the cellulosic material did not suffer much degradation, at least not so much as when using sulfuric acid or its anhydride. On precipitation with alcohol, the product of reaction was obtained in the form of its pyridinium salt. A sodium salt, free of pyridine, was obtained by neutralizing the reaction mixture with sodium hydroxide solution. Also, a barium salt was prepared; this was insoluble in water. The barium could be eliminated by means of hydrochloric acid.

The sulfate, containing 2.7 to 2.8 combined sulfuric acid groups per glucose unit, was, as has been observed in previous cases, very resistant to attempts to remove the acid radicals without exposing the cellulose constituent to further degradation. Again, boiling with methyl alcoholic hydrochloric acid is claimed to remove the combined sulfuric acid without substantial degradation of the cellulose,[17] a claim which however is not very well supported.

The degrading action of chlorosulfonic acid on cellulose seems to be diminished if, according to Traube and co-workers,[18] a greater excess of pyridine is used and if the temperature of the reaction is decreased

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[15] Gebauer-Füllnegg, Stevens, and Dingler, *Ber.*, **61**, 2000 (1928); Stevens, chem. engineer dissertation, Princeton (1927).

[16] Baumgarten, *Ber.*, **59**, 1166, 1976 (1926).

[17] Gebauer-Füllnegg and Dingler, *J. Am. Chem. Soc.*, **52**, 2849 (1930).

[18] Traube, Blaser, and Lindemann, *loc. cit.*, p. 603.

to 80°. It was found that under these conditions, the cellulosic material retained its fibrous structure to a large extent. The degree of substitution amounted to 2.5 sulfuric acid radicals per glucose residue. The sodium salt gave an aqueous colloidal solution of a relatively high viscosity.

Traube's modification of the chlorosulfonic acid method seems to indicate the way in which possibly still less degraded products may be obtained. In analogy with Hess and Ljubitsch's method of preparing undegraded cellulose acetates (see later), one would expect that the degradation under the action of chlorosulfonic acid could be largely reduced by allowing the reaction mixture to stand in the presence of a great excess of pyridine at room temperature. This procedure would, of course, take considerable time, possibly weeks, as in actylation.

The chlorosulfonic acid-pyridine method applied to wood permits the extraction of a large part of its carbohydrate fraction (cellulose and noncellulosic carbohydrates) in the form of sulfuric acid esters, as was shown by Freudenberg and Keller.[19]

The question whether cellulose undergoes ester formation with *phosphoric acid* has obviously not yet been decided definitely. In the patent literature, the products of reaction with phosphoric acid as such or in the presence of sulfuric acid or with phosphorus oxychloride are frequently described as esters, without, however, giving proof for this concept.[20] Again, af Ekenstam denied that the products of reaction are esters and regarded them as addition compounds.[21]

CELLULOSE NITRATES

Nitric acid esters of cellulose may be obtained by the same method by which such esters are prepared from simpler aliphatic compounds (for example, glycerol), namely, by subjecting the alcohol to the action of the acid in the presence of a dehydrating agent. The main function of the latter is to take up the water of reaction. For each esterified hydroxyl group, 1 molecule of water is liberated.

Depending upon the conditions of esterification, various degrees of substitution may be obtained, the completely esterified product being the trinitrate, which requires a nitrogen content of 14.14 per cent.

The reaction may be expressed by the following equation:

$$C_6H_7O_2(OH)_3 + 3HNO_3 = C_6H_7O_2(ONO_2)_3 + 3H_2O$$

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[19] Freudenberg and Keller, *Ber.*, **72**, 331 (1939).

[20] Marsh and Wood, "Introduction to Cellulose Chemistry," p. 194.

[21] af Ekenstam, "Über die Celluloselösungen in Mineralsäuren," p. 66; see also Champetier, *Ann. chim.*, [10] **20**, 5 (1933), and *Compt. rend.*, **196**, 930 (1933).

Cellulose nitrate is more frequently called "nitrocellulose," and the process of esterification is often referred to as "nitration." Both these terms are incorrect, since we are dealing not with a nitro compound nor the introduction of nitro groups but with an ester and the introduction of ester groups. This fact should always be kept in mind, when these incorrect, but widely accepted, terms are used in this book.

As dehydrating agents, strong mineral acids are used, the most common being sulfuric acid. It may be mentioned here that the choice of sulfuric acid as a catalyst, first made by C. F. Schönbein in 1846 in Germany, was the basis of the commercial manufacture of guncotton. The discovery of nitrocellulose was made by Braconnot in France in 1832.

Cellulose nitrates may be prepared by submerging the cellulosic material in a mixture containing nitric and sulfuric acid and water in certain proportions for about an hour at a temperature not higher than 40°. The use of higher temperature, although having a favorable influence upon the velocity of the reaction, would be detrimental, because the acid mixture not only esterifies but also exerts hydrolyzing and oxidizing effects upon cellulose. The result of such undesirable side reactions are degradation products which have to be removed, because they favor the decomposition of the nitrate when stored or exposed to atmospheric influences or heat. Even on nitration at lower temperature (commercially usually at 30±5°), certain amounts of such impurities are formed. In addition, acid residues have to be removed. Part of the sulfuric acid is present in the nitrocellulose in the form of cellulose sulfates or sulfonitrates.

To remove cellulose degradation products and acid residues, the nitrate is washed with water. This is followed by washing with slightly acidified water which splits the sulfates and reduces the combined sulfuric acid content of the nitrate. This step is followed by boiling in water, washing with slightly alkaline water (Na_2CO_3), and finally again with water alone.

The purification process, which plays an important part in the commercial manufacture of cellulose nitrates, is known as "stabilization" and commercially comprises even a greater number of procedures and longer-lasting steps than are usually applied in the laboratory.

Since, on boiling the nitrate with water for a long period of time, the nitrogen content decreases somewhat, Hess and Trogus[22] have

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[22] Hess and Trogus, *Angew. Chem.*, **44**, 825 (1931); Tomonari, Trogus, and Hess, *ibid.*, **45**, 99 (1932); see also Hess, "Chemie der Cellulose," p. 381; Schiemann and Kühne, *Cellulosechem.*, **15**, 82 (1934).

recommended refluxing the water-washed nitrocellulose with 50–60 per cent acetic acid which is said to produce a stable nitrate after 1 to 2 hours.

The process of stabilization has been frequently investigated both from practical and scientific viewpoints. However, the mechanism has not yet been fully explained. Besides the above-mentioned investigations by Hess and co-workers, the reader is referred to other literature on the subject.[23]

The stabilized product may be dried at 40–45° for several hours.[24] However, it should be kept in mind that such a procedure is dangerous, because the nitrates are easily inflammable and explosive. As a matter of fact, drying of nitrocellulose is never practised commercially on account of the extreme hazards involved. Instead, it is handled wet (with water) or, if desired, the water may be replaced by alcohol or some other suitable nonsolvent for nitrocellulose.

Under conditions as briefly described above, the product of reaction is obtained in fibrous form and its appearance is hardly distinguishable from that of the original fiber.

The Mechanism of the Nitration Process

Of all factors governing the process of nitration, the water present in the nitration acid is of essential influence. This influence is chiefly reflected in the degree of substitution of the resulting nitrate. The relation between the water content of the nitration acid and the nitrogen content of the nitrate is clearly seen from the investigations of Lunge and Bebie. To a mixture of equal weights of nitric acid (94.09 per cent) and sulfuric acid (92.10 per cent) increasing amounts of water were added. While the temperature (16–18°) was kept constant, samples of cellulose, in the form of medical cotton, were subjected to the action of these acid mixtures of increasing water content. If the amounts of water added to the acid mixture are plotted against the degree of substitution of the resulting cellulose nitrates (expressed as cubic centimeters of NO liberated per gram of nitrate), a curve is obtained (Fig. 49) which shows that with increasing water content, i.e., with decreasing concentration of the acid mixture, the

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[23] Will, *Z. angew. Chem.*, **14**, 743, 774 (1901); Berl and Delphy, *Z. ges. Schiess- u. Sprengstoffw.*, **8**, 129 (1913); Duclaux, *Rev. gén. colloïdes*, **3**, 257 (1926); Demougin, *Mém. Poudres*, **23**, 262 (1930); Wiggam, *J. Phys. Chem.*, **35**, 536 (1931); Berl and Rueff, *Cellulosechem.*, **14**, 109 (1933); Krüger, *ibid.*, **15**, 89 (1934); Kullgren, *Svensk Kem. Tid.*, **53**, 233 (1941).

[24] American Society for Testing Materials, "Standard Methods," Vol. II, p. 791, Philadelphia (1939).

degree of substitution decreases rather slowly up to a water content in the acid mixture of between 16 and 17 per cent and more rapidly thereafter.

The curve thus permits the choice of that water content which is required for preparing nitrocellulose of a desired degree of substitution. The cubic centimeters of nitrogen oxide shown in Fig. 49 correspond to a nitrogen content between 8.5 and 13.7 per cent.

Similar experiments, but covering a wider range of conditions, were made more recently by Schiemann and Kühne[25] with cotton linters, the results of which in general confirm those obtained by Lunge and Bebie. In addition, it was found that an acid mixture (22.6 per cent nitric acid and 76.6 sulfuric acid) containing only about 0.82 per cent water resulted in a relatively low degree of substitution (12.38 and 12.87 per cent nitrogen), and a water content of 3.7 per cent was necessary to reach a nitrogen content of about 13.5 per cent. Whereas Lunge and Bebie's curve shows a steady decrease of the degree of substitution with increasing water content of the acid mixture, Schiemann and Kühne[25] found that the nitrogen content was rather constant for water contents from about 3.5 to about 13.5 per cent. Above 13.5 per cent water, the nitrogen content decreased steadily, and at about the same rate as shown in Lunge and Bebie's curve.

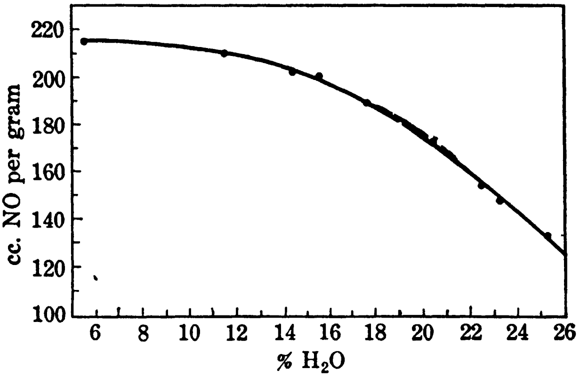

FIG. 49. Influence of water content of acid mixture upon degree of substitution of cellulose nitrate. Lunge and Bebie.

The low degree of esterification obtained with acid mixtures of very low water content seems to indicate that there is also a *lower* limit for the water content. Indeed, Schiemann and Kühne found that the corresponding nitrates were incompletely soluble in acetone,

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[25] Schiemann and Kühne, *Cellulosechem.*, **15**, 80 (1934).

fine fibers, obviously not nitrated at all or only to a very limited extent, remaining undissolved.

Schiemann and Kühne's explanation, namely, that extensive swelling of the fiber surfaces under the influence of the concentrated acid mixture prevented penetration of the acid into the deeper layers of the fiber, does not seem very convincing. Rather, it would appear that a certain water content is necessary for bringing about that degree of swelling which is required to enable the acid mixture to penetrate into the interior of the micellar system.

Apart from its influence upon the degree of substitution (which drops to about 8.5 per cent at a water content of about 24.5 per cent and to about 3.0 per cent at a water content of about 30 per cent), the lower limit of the water content of the acid mixture is determined by the hydrolyzing effect of the acid upon the cellulose as it reaches these degrees of dilution. This effect is manifest in the increasing harshness and brittleness of the nitrates prepared with an acid mixture whose water content has reached about 24 per cent, and at a water content of 27 per cent the cellulose dissolves in the acid to a great extent.

Function of the Sulfuric Acid in the Acid Mixture. From a physical point of view, sulfuric acid exerts a swelling effect upon cellulose which, however, is limited by the water content; that is, too much water decreases it. This effect is comparable with the influence of the concentration of aqueous alkali hydroxide upon the swelling ability of cellulose. The degree of swelling which cellulose undergoes in acid mixtures of various compositions has not yet been investigated systematically. Indications are that sulfuric acid exerts a greater swelling effect upon cellulose than nitric acid. Mark[26] states that the presence of small amounts of sulfuric acid favors the initial entry of nitrate groups and the rate of nitration.

A more important function of the sulfuric acid is its pronounced ability to attract water and to form hydrates. Sulfuric acid possesses this ability to a greater extent than nitric acid and, for this reason, the presence in the nitration acid of a certain amount of sulfuric acid tends to increase the concentration of the nitric acid.

The influence of the sulfuric acid on the degree of substitution was investigated as early as 1883. Vieille[27] found that the addition of sulfuric acid to dilute nitric acid increases the nitrogen content of the resulting cellulose nitrate. Moreover, Lunge and Bebie's results[28]

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[26] Mark, "Physik und Chemie der Cellulose," p. 267.

[27] Vieille, *Compt. rend.*, **95**, 132 (1882).

[28] Lunge and Bebie, *Z. angew. Chem.*, **14**, 508 (1901).

show that the addition of more than 3 parts of sulfuric acid to 1 part of nitric acid does not increase the nitrogen content of the resulting nitrate further, and a larger excess of sulfuric acid decreases the degree of substitution.

The part which sulfuric acid plays in the nitric-sulfuric acid-water system has been greatly elucidated by the investigations of Saposchnikow,[29] who followed the change in vapor pressure of dilute nitric acid to which increasing amounts of sulfuric acid were added. These changes consist of a steady increase in vapor pressure and concentration of nitric acid until a maximum has been reached; that is, further addition of sulfuric acid decreases the vapor pressure and the nitric acid concentration. The slope of the curve resulting from plotting vapor pressure against amounts of sulfuric acid added to nitric acid of specific gravity 1.48 (Fig. 50) is explained as follows.

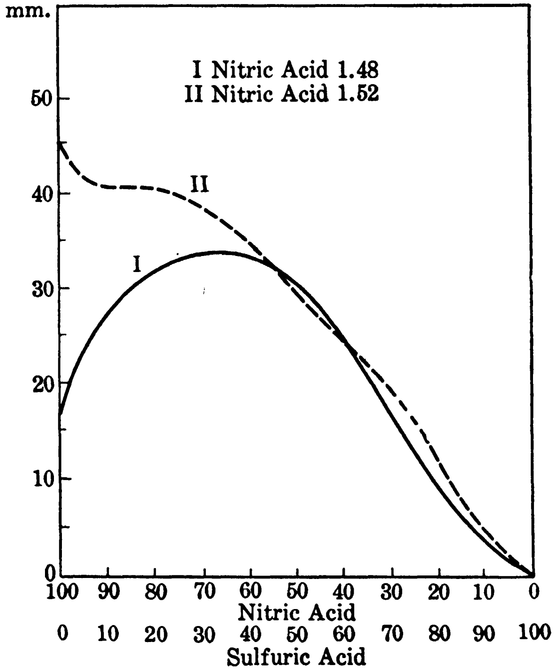

FIG. 50. Influence of sulfuric acid upon vapor pressure of nitric acid of different specific gravities. Saposchnikow.

At the beginning, the sulfuric acid deprives the nitric acid, being present in the form of its hydrate, of its water content and forms

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[29] Saposchnikow, *Z. physik. Chem.*, **49**, 697 (1904); **51**, 609 (1905); **53**, 425 (1905).

hydrates of varying composition; the concentration of free nitric acid molecules increases, and, consequently, the vapor pressure increases. The maximum occurs when all nitric acid is present as HNO_3. With still more sulfuric acid added, the nitric acid becomes gradually dehydrated to the anhydride (N_2O_5) and, because the vapor pressure of the latter is very small, the curve descends and reaches the abscissa when all nitric acid is converted.

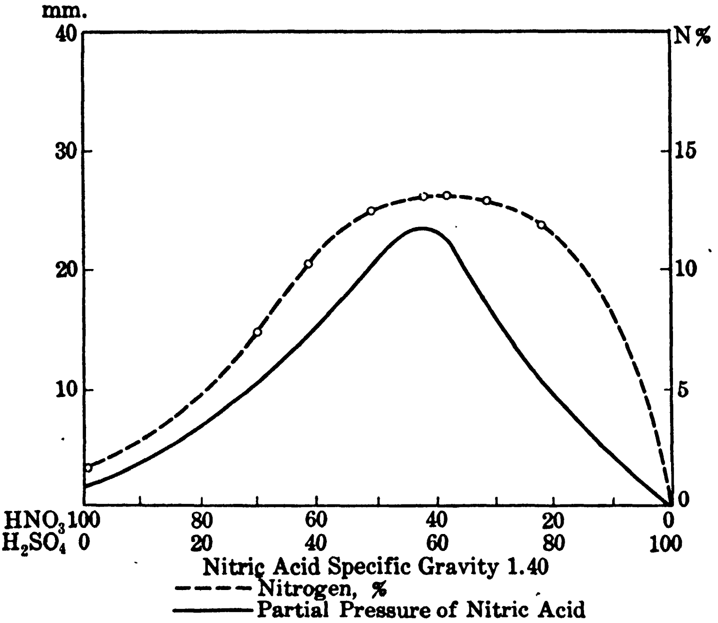

FIG. 51. Relation between nitrogen content of cellulose nitrates and vapor pressure with increasing amounts of sulfuric acid. Saposchnikow.

The two processes—the transition of nitric acid hydrate into free HNO_3 molecules and the dehydration of the latter to N_2O_5—are reversed on the addition of water. This reduces the efficiency of the sulfuric acid so that the nitric acid anhydride is reconverted into HNO_3, and the latter into its hydrate.

Saposchnikow's results show that, in the acid mixture for nitration, the amounts of sulfuric acid and water must be in a definite proportion in order that the nitric acid may reach its greatest efficiency. This is the case when all nitric acid is present as 100 per cent HNO_3.

When cellulose was subjected to the action of nitration acid of increasing sulfuric acid content under conditions similar to those chosen in the experiments without cellulose, it was found that the degree of substitution in the nitrates produced followed the vapor pressure. This is seen from Fig. 51. The highest nitrogen content coincides with the maximum vapor pressure, i.e., when the nitric acid has reached its highest concentration and when only so much sulfuric acid is present that anhydride formation has not yet begun.

The second source of water is that which is formed on esterification. This water, if not removed, would dilute the nitric acid and thus decrease its power of nitration. In other words, sufficient sulfuric acid must be present so that the water of reaction may be taken up.

Considering that each molecule of nitric acid entering the cellulose chain produces 1 molecule of water, the total amount of water formed on nitration to give a nitrogen content of between 13 and 14 per cent is considerable. Although the concentration of the nitric acid in the mixture decreases as the substitution proceeds, it is conceivable that the influence of the water of reaction will be less when the ratio of the acid mixture to cellulose is large than when it is small.

An idea of the dilution of the acid mixture may be obtained from an analysis of the composition of the acid at the end of the nitration process. Numerous data on the composition of the spent acid mixture are available.[30] Some figures taken from the work by Schiemann and Kühne[31] may serve as an illustration (see Table 16).

From his experiments Saposchnikow[32] draws the conclusion that the most suitable mixture for producing the highly nitrated stages should have the following composition:

$$24.29 \text{ per cent } HNO_3 + 65.80 \text{ per cent } H_2SO_4 + 9.91 \text{ per cent } H_2O$$

This composition approaches that which Lunge and Bebie used for obtaining a high degree of substitution (13.92 per cent N) namely,

$$25.31 \text{ per cent } HNO_3 + 63.35 \text{ per cent } H_2SO_4 + 11.34 \text{ per cent } H_2O$$

Saposchnikow's results have been confirmed by Kullgren[33] and by Berl and co-workers,[34] who studied the mechanism of nitration on a wider scale and used a more exact method for the determination of the vapor pressures. Moreover, measurements of the heat of reaction evolved from the nitric-sulfuric-acid-water system revealed

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[30] von Boltenstern, doctoral dissertation, Darmstadt (1921); Demougin, *Mém Poudres*, **23**, 262 (1928); Berl and Berkenfeld, *Z. angew. Chem.*, **41**, 130 (1928); Demougin and Bonnet, *Mém. Poudres*, **24**, 157 (1931/32).

[31] Schiemann and Kühne, *loc. cit.*, pp. 79, 80.

[32] Saposchnikow, *loc. cit.*, **51**, 623 (1905).

[33] Kullgren, *Z. ges. Schiess- u. Sprengstoffw.*, **3**, 146 (1908).

[34] Berl, Andress, and Escales, *Kunststoffe*, **27**, 23 (1937).

TABLE 16

Composition of Spent Nitration Acids

Ratio of Cellulose to Acid, 1 : 50
(N content of nitrocellulose between 13.02 and 13.49 per cent)

Nitration Acid			Acid after Nitration		
HNO_3 %	H_2SO_4 %	H_2O %	HNO_3 %	H_2SO_4 %	H_2O %
24.78	90.82	5.40	20.69	71.29	8.02
20.89	70.01	9.10	16.60	71.52	11.88
23.05	68.07	8.88	18.20	69.56	12.24
21.29	68.52	10.19	16.91	69.10	13.99
22.29	66.49	11.22	18.79	68.02	13.19

Ratio of Cellulose to Acid, 1 : 80
(N content of nitrocellulose between 12.87 and 13.46 per cent)

Nitration Acid			Acid after Nitration		
HNO_3 %	H_2SO_4 %	H_2O %	HNO_3 %	H_2SO_4 %	H_2O %
22.61	76.58	0.81	22.03	76.79	1.18
22.65	76.50	0.85	21.80	76.71	1.49
21.73	73.15	5.12	20.29	74.37	5.34
21.31	71.70	6.99	19.76	72.06	8.18
20.77	69.45	9.78	19.58	70.12	10.30

that the sulfuric acid in the mixture is present in the form of its monohydrate ($H_2SO_4 \cdot H_2O$) when the vapor pressure reaches its maximum value, i.e., when all the nitric acid is present as 100 per cent HNO_3.

In addition, it may be mentioned that according to Berl and Saenger,[35] nitric anhydride forms an addition compound with nitric acid, $N_2O_5(HNO_3)_6$. According to Berl, Andress, and Escales,[34] this addition compound, rather than the anhydride itself, is responsible for the decrease in vapor pressure and, hence, in the concentration of the free nitric acid, when the amount of sulfuric acid is increased beyond the maximum point.

In an attempt to prove the validity of the concept which resulted from Saposchnikow's and from their own investigations, Berl and co-workers have subjected the nitration data of a great number of

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[35] Berl and Saenger, *Monatsh.*, **53** and **54**, 1036 (1929) (Wegscheider-Festschrift).

previous investigators to a critical analysis.[36] The result of this analysis may be regarded as an excellent confirmation of the hypothesis. The composition of the acid which produces the highest nitrogen content should be as follows:

21.8 per cent HNO_3 (= 20 mole per cent)
66.0 per cent H_2SO_4 (= 40 mole per cent)
12.2 per cent H_2O (= 20 mole per cent)

This composition corresponds exactly to a ratio of 1 $HNO_3 : 2 (H_2SO_4 \cdot H_2O)$. On this basis, the lower degrees of substitution may be obtained by increasing the water content.

However, even with the most suitable acid composition, the nitrogen content of the resulting nitrate remains somewhat below the theoretical value. The highest nitrogen content (13.96 per cent) seems to have been obtained by Hake and Bell.[37] (Hess [38] has tabulated the nitrogen contents obtained by various investigators together with the composition of the acids and the other conditions used).

Two reasons are suggested for the failure to reach the theoretical value of the trinitrate. First, as has been pointed out earlier, the process of esterification is reversible; i.e., as with other esterification processes, we are dealing with an equilibrium reaction.[39] This has been quite convincingly demonstrated by Berl and Klaye and later by Berl and Hefter.[40] When three nitrates of different nitrogen content (10.9, 12.7, and 13.5 per cent) were left in acid mixtures of two different compositions for a sufficiently long period, the nitrates of each series emerged from the treatment with the same nitrogen content. The existence of such equilibria has been confirmed by other investigators.[41] The second reason is that the sulfuric acid participates in the process of esterification. Cross, Bevan, and Fenks,[42] as well as Berl and Klaye,[40] have expressed the belief that the formation of sulfuric acid esters is the primary reaction and that, subsequently,

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[36] Berl, Andress, and Escales, *loc. cit.*, p. 126.

[37] Hake and Bell, *J. Soc. Chem. Ind.*, **28**, 461 (1909); see also Guttmann, *ibid.*, **28**, 1461 (1909).

[38] Hess, "Chemie der Cellulose," p. 364.

[39] Vieille, *Compt. rend.*, **95**, 132 (1882).

[40] Berl and Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 403 (1907); Berl and Hefter, *Cellulosechem.*, **14**, 65 (1933); see also Brunswig, *Cellulosechem.*, **7**, 120 (1926).

[41] Miles and Melbourn, *J. Phys. Chem.*, **34**, 2598 (1930); Miles and Craik, *ibid.*, **34**, 2607 (1930); Fabel and Fritzsche, *Nitrocellulose*, **10**, 3, 24 (1939).

[42] Cross, Bevan, and Fenks, *Ber.*, **34**, 2496 (1901); Robertson, *J. Soc. Chem. Ind.*, **25**, 624 (1906).

the sulfuric acid radicals of the cellulose sulfates or sulfonitrates are replaced by nitrate groups.

Whereas the direct participation of sulfuric acid in the process of esterification might (by way of "activation") further the introduction of nitrate groups and, therefore, increase the rate of reaction,[43] the replacement of the sulfate by nitrate groups does not seem to reach completion. Berl and von Boltenstern[44] have shown that part of the sulfuric acid in the final product is combined with the inorganic constituents (ash) of the nitrate. However, the total sulfuric acid found by analysis is almost always higher than would correspond to that combined in the form of calcium sulfate. Thus, a certain quantity of the sulfuric acid seems to be still present in ester form. As a matter of fact, the sulfuric acid content of the nitrates is rather high during the first few minutes of the nitration reaction but decreases rapidly as the reaction continues and soon becomes constant. On stabilization—by boiling with slightly acidified water—the greater part of the combined sulfuric acid is removed. Table 17 shows the amount of combined sulfuric acid in the stabilized nitrates. It also shows the sulfuric acid content of the ash and the ratio of the total sulfuric acid content of the nitrates to that of the ash.[45]

TABLE 17

SULFURIC ACID LEFT IN NITRATES AFTER STABILIZATION

Nitrates % N	H_2SO_4 %		Ratio of Total H_2SO_4 to H_2SO_4 in the Ash
	Total	In the ash	
11.20	0.24	0.12	2.0 : 1
11.88	0.16	0.12	1.3 : 1
12.45	0.16	0.10	1.7 : 1
13.00	0.27	0.12	2.3 : 1
13.19	0.25	0.10	2.4 : 1
13.25	0.27	0.13	2.1 : 1

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[43] Lunge and Bebie, *loc. cit.*

[44] See especially von Boltenstern, doctoral dissertation, Darmstadt (1921); also Lunge-Berl, "Chem. Techn. Untersuchungsmethoden" (1933), Vol. 5, chapter entitled "Kunstseide."

[45] Berl and Hefter, *Cellulosechem.*, **14**, 76 (1933).

The Acid-Cellulose Ratio. A low acid-cellulose ratio favors the undesirable effect of the water of reaction upon the degree of substitution. A low ratio should be avoided also because it results in incomplete penetration of the cellulose and in nonuniform nitration. These effects are noticeable when the ratio is 1 : 25 or thereabouts. The difficulties are diminished when the ratio is increased to 1 : 40, and they disappear when it is increased to 1 : 50 to 1 : 80. Even a ratio of 1 : 40 represents a considerable excess of nitric acid over that theoretically required. This excess, with an acid mixture of 22 per cent nitric acid, 60 per cent sulfuric acid, and 18 per cent water (resulting in nitrates of 11.0–11.5 per cent nitrogen content), amounts to 10 to 12 times more than is theoretically necessary.

Since the greater part of the excess of nitric acid serves merely to maintain a suitable acid-cellulose ratio, attempts have been made to decrease the amount of nitric acid by replacing part of it by an inert diluent (which must neither become nitrated nor sulfonated nor act as a solvent for the resulting cellulose nitrate). Examples of such inert diluents are carbon tetrachloride and pentane. A small amount of naphthene sulfonic acid is used to emulsify the acid and diluent. Under such conditions it was possible to produce a nitrate of 11.0 to 11.5 per cent nitrogen content with 1.5 to 2.5 times less nitric acid than without a diluent. Also, the amount of sulfuric acid in the mixture could be reduced 15 to 20 times. It is claimed that the nitrate thus produced is less degraded than that produced without the presence of a diluent.[46]

The choice of the correct ratio is also dependent upon the physical form in which the cellulosic material is subjected to nitration. It is conceivable that, by the use of the same acid-cellulose ratio, materials like absorbent paper are more easily penetrated than, for example, loose cotton which tends to lump together and thus to impede uniform diffusion of the acid.[47] Cellulose may also be used in its regenerated form. Indeed Staudinger and Mohr [48] found that cotton-linters cellulose, regenerated from its solution in cuprammonium and freed of its water content by subsequent treatments with alcohol, ether, and cyclohexane, was easily penetrated by the nitration acid.

The Rate of Reaction. On the assumption that it is not the rate of the chemical reaction itself but rather that of the diffusion of the reacting agent into the fibrous structure which is instrumental in the

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[46] Rogowin and Pazadnia, *Cellulosechem.*, **15**, 32 (1934).

[47] Guttmann, *J. Soc. Chem. Ind.*, **28**, 461 (1909).

[48] Staudinger and Mohr, *Ber.*, **70**, 2299 (1937).

course of heterogeneous cellulose reactions,[49] Sakurada[50] has derived an equation for the kinetics of the nitration reaction. This equation, which is based upon Watanabe's[51] equation for diffusion with simultaneous chemical reaction, seems to be applicable to a number of cellulose reactions, such as acetylation, xanthation, and nitration, the experimental data being in good agreement with those calculated from the equation.

Table 18, condensed from Sakurada's work, may convey an idea of the rate of the substitution reaction. An acid mixture of 1 volume of nitric acid (d., 1.52) and 2 volumes of sulfuric acid (d., 1.84) (i.e., a mixture which contains practically no water), at a temperature of 0° was applied to unbleached ramie fiber and to the same material bleached and previously treated with 1 per cent sodium hydroxide with the exclusion of air at 95°. The figures of this table show that the entry of nitrate groups into the cellulose molecule is a rather rapid reaction. Although the temperature was kept at 0°, 45 seconds sufficed in the case of bleached ramie to produce a nitrate with 3.18 per cent nitrogen content. After 10 minutes the nitrogen content had risen to 7.67, and after half an hour to 11.07 per cent. A somewhat

TABLE 18

RATE OF NITRATION OF BLEACHED AND UNBLEACHED RAMIE FIBER

Bleached Ramie			Unbleached Ramie		
Time in seconds	Nitrogen %	Nitrate groups per $C_6H_{10}O_5$ unit	Time in seconds	Nitrogen %	Nitrate groups per $C_6H_{10}O_5$ unit
.....	.....	....	15	1.53	0.20
45	3.18	0.42	45	2.11	0.27
90	3.91	0.52	90	2.71	0.35
300	5.63	0.78	300	4.55	0.61
600	7.67	1.18	599	5.86	0.82
1,800	11.07	2.00	1,800	9.08	1.49
3,600	12.65	2.48	3,600	11.82	2.20
18,000	13.85	2.89	18,000	13.80	2.87

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[49] Hess and Trogus, *Z. physik. Chem.*, **B15**, 157 (1932); Sakurada and Shojino, *J. Soc. Chem. Ind., Japan*, **30**, Supplementary Binding, **306** (1934).

[50] Sakurada, *Cellulosechem.*, **15**, 18 (1934).

[51] Watanabe, *Kolloid-Z.*, **52**, 320 (1931).

longer time was required to reach the highest nitrogen content (13.85 per cent) which could be obtained under these conditions.

That the time to reach a high degree of substitution may be still further considerably decreased is seen from the work of Schiemann and Kühne.[52] Table 19 gives the data obtained with cotton linters and with wood pulp (manufactured for the preparation of nitrocellulose). The composition of the acids was as follows:

	HNO_3, %	H_2SO_4, %	H_2O, %
For cotton linters	42.58	53.72	3.72
For wood pulp	43.38	53.41	3.21

Ten grams of the cellulosic material were brought into contact with the acid at once, instead of adding it in portions (ratio 1 : 80). The time was counted from the beginning of contact until washing of the nitrate with water. The temperature of nitration was 17° for the cotton linters and 15° for the wood pulp.

TABLE 19

RATE OF NITRATION OF COTTON LINTERS AND WOOD PULP

Materials	Time of Nitration: Minutes	1.0	5.5	10.5	15.0	15.5	30.0	32.0
Cotton linters	% N	12.21	13.24	13.49	.....	13.58	.....	13.62
Wood pulp	% N	....	12.47	13.39	13.39	13.62	13.59	....

Materials	Time of Nitration: Hours	1	2	3	4	5	6	
Cotton linters	% N	13.61	13.58	13.62	13.59	13.61	.....	
Wood pulp	% N	13.61	13.62	.....	13.61	.....	13.62	

It is seen that a high degree of substitution—12.21 per cent nitrogen in the case of cotton linters—is obtained after as short a time as 1 minute and that after 5–6 minutes (about 10 minutes in the case of wood pulp) almost the maximum substitution obtainable under these conditions has been reached. Although Schiemann and Kühne's

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[52] Schiemann and Kühne, *Cellulosechem.*, **15**, 79 (1934).

conditions are not exactly comparable with those used by Sakurada, it is probable that the more rapid rate of substitution in the formers' experiments was due principally to the higher temperatures used (17° and 15° against 0°). According to Lunge and Weintraub,[53] this influence is considerable.

Considering the fact that cellulose is rather sensitive to mineral acids, it is remarkable that the degradation which it suffers during nitration is rather limited. In fact, sulfuric and nitric acid at concentrations as they exist in the acid mixture would cause considerable oxidation or hydrolysis or both if they were allowed to act separately on cellulose. Obviously, the cellulose is stabilized by the introduction of nitrate groups.[54] This stabilizing effect is less noticeable with cellulose of relatively low degree of polymerization.[55] Obviously, the shorter-chain molecules are more easily attacked by the nitration acid.

The high rate of the substitution reaction (Berl and Hefter[56] have reported that with nitration acid containing little water ramie fiber may be thoroughly nitrated even within 10 seconds) would permit the conclusion that this reaction is not limited to the surface of the fiber for any long period of time; rather it seems to proceed quickly throughout the whole micellar system in a permutoidal fashion.[57] If the reaction were limited to the surface of the micelles, which may be assumed to comprise only 30–50 per cent of the total available number of hydroxyl groups, one would expect the nitrogen content of the nitrate to remain constant at 4–7 per cent for some time. There is no indication that the reaction takes such a course. The curve which may be drawn from data on time and nitrogen content breaks when a nitrogen content of about 12 per cent has been reached. After that, the reaction slows down considerably.

This break may be interpreted to mean that about two-thirds of the hydroxyl groups available for reaction have become substituted. It is probable that all three hydroxyl groups present in every glucose residue participate in the nitration reaction and that, although not every chain has become fully nitrated at this point, the nitrate groups are rather uniformly distributed throughout the system. In fact, attempts to separate an incompletely substituted nitrate into mono-,

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[53] Lunge and Weintraub, *Z. angew. Chem.*, **12**, 471 (1899); see also Lunge and Bebie, *ibid.*, **14**, 515 (1901).

[54] See also Berl and Rueff, *Cellulosechem.*, **14**, 115 (1933).

[55] Staudinger and Mohr, *Ber.*, **70**, 2300, 2305 (1937).

[56] Berl and Hefter, *Cellulosechem.*, **14**, 65 (1933).

[57] Meyer and Mark, "Aufbau der hochpolymeren Naturstoffe," p. 127; Mark, "Physik und Chemie der Cellulose," p. 177.

di-, and trinitrates by fractionation have failed. Although certain physical properties, such as viscosity and solubility, are found to vary considerably with different fractions, the nitrogen content of these fractions varies very little. This result would also indicate that partially substituted nitrates contain scarcely any unnitrated cellulose, as has been observed in cases in which esterification proceeds at a much slower rate and in a more heterogeneous fashion.

Since the change of the x-ray diagram of cellulose is taken as evidence of the formation of a new compound, one would expect x-ray analysis to be a means of elucidating the course of the substitution reaction. However, this is true only to a limited extent.

That the x-ray pattern of cellulose does not change until a nitrogen content of about 7.5 per cent (a "mononitrate" requires 6.81 per cent nitrogen) has been introduced would appear conceivable, but it seems strange that the crystalline pattern disappears and gives way to an amorphous pattern which remains until the nitrogen content amounts to about 10.3 per cent (a "dinitrate" requires 11.10 per cent nitrogen). Only when a nitrogen content of about 12.5 per cent has been reached does the pattern become crystalline again and approach that of the trinitrate.[58]

These observations may be interpreted to show that only the unnitrated cellulose and the trinitrate possess a crystalline lattice structure. Mark[59] has expressed the opinion that a nonuniform distribution of ester groups prevents the development of a crystalline lattice structure. Hess and Trogus,[60] however, are inclined to believe that the appearance of the amorphous diagram is the result of the conversion of cellulose into its hydrate modification which takes place under the swelling influence of the strong acid. According to these authors, the amorphous diagram represents a mixture of unsubstituted cellulose with the trinitrates of both cellulose and cellulose hydrate.

However, if the observations were interpreted to show that the lower stages of nitration are mixtures of unchanged cellulose and trinitrate,[61]

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[58] Sisson, *Ind. Eng. Chem.*, **30**, 530 (1938).

[59] Mark, "Physik und Chemie der Cellulose," p. 172; see also Miles and Milbourn, *J. Phys. Chem.*, **34**, 2598 (1930); Miles and Craik, *ibid.*, **34**, 2607 (1930); Trillat, *J. phys. Rad.*, [7] **1**, 340 (1930); **2**, 67 (1931).

[60] Hess and Trogus, *Z. physik. Chem.*, **B15**, 208 (1931); Hess, Trogus, *et al.*, *Ann.*, **506**, 260 (1933); Trogus and Hess, *Angew. Chem.*, **47**, 30 (1934); Trogus and Hess, *Z. Elektrochem.*, **40**, 193 (1934); Tomonari, *ibid.*, **40**, 207 (1934); Trogus, *Cellulosechem.*, **15**, 104 (1934).

[61] See also the earlier investigations by Herzog and von Náray-Szabo, *Z. physik. Chem.*, **130**, 616 (1927); von Náray-Szabo and von Susich, *ibid.*, **134**, 264 (1928).

it is difficult to understand why it should not be possible to separate the substituted chains from the unsubstituted portion by extraction with solvents. It is more reasonable, therefore, to interpret the x-ray findings as indicating that the lower stages of nitration are mixtures of various degrees of substitution.[62] This would be compatible not only with the heterogeneous nature of the cellulose fiber but also with the fact that nitration, as has been seen, proceeds very fast, so that even after a short period of reaction (provided the conditions of nitration are not abnormal) hardly any portion of the cellulose would remain unsubstituted.

The process of nitration may be followed also by observing the change of the double refraction of the nitrated fibers. The double refraction of the native cellulose fiber [63] gradually disappears with increasing degree of nitration and then changes in direction.[64] The change in double refraction may also be used as an indication of the uniformity of substitution in the final product. Completely nitrated cellulose appears uniformly blue, whereas less nitrated or unnitrated portions appear bright yellow.[65]

Other Catalysts. Instead of sulfuric, *phosphoric acid* is frequently used as a dehydrating agent in the laboratory,[66] because it exerts a less degrading influence upon the cellulose and has less tendency to esterify cellulose and to hydrolyze the nitrate than sulfuric acid.[67] These characteristics should make it possible to prepare a more highly substituted nitrate of high molecular weight. Indeed, Berl and Rueff [68] found that nitrates with 13.6–13.7 per cent nitrogen may be obtained more easily when phosphoric acid is the dehydrating agent, and, with an acid mixture consisting of equal parts of nitric acid

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[62] Matthieu, *Compt. rend.*, **200**, 143 (1933); *Trans. Faraday Soc.*, **29**, 122 (1933); "Reactions topochimiques, nitration de la cellulose," Herrmann et Cie., Paris (1936).

[63] Mark, "Chemie und Physik der Cellulose," p. 113.

[64] Ambronn, *Kolloid-Z.*, **13**, 203 (1913); Demarroux and Matthieu, *Compt. rend.*, **192**, 234 (1931).

[65] Lunge and Weintraub, *Z. angew. Chem.*, **12**, 472 (1899).

[66] Warren, *Chem. News*, **74**, 239 (1896); Lunge and Weintraub, *Z. angew. Chem.*, **12**, 445 (1899); Hoitsema, *ibid.*, **11**, 173 (1898); Kranz and Blechta, *Chem.-Ztg.*, **II**, 992 (1927); Rassow and Bonge, *Z. angew. Chem.*, **21**, 732 (1908); Lunge and Bebie, *ibid.*, **14**, 514 (1901); Karrer, "Polymere Kohlenhydrate," Akad. Verlags-Ges., Leipzig (1925), p. 160.

[67] Berl and Rueff, *Cellulosechem.*, **12**, 53 (1931); Lenze and Rubens, *Z. ges. Schiess- u. Sprengstoffw.*, **27**, 114 (1932); Tomonari, *Cellulosechem.*, **17**, 29 (1936); Berl, Andress, and Escales, *Kunststoffe*, **27**, 29 (1937); Davidson, *J. Textile Inst.*, **29**, T199 (1938); Mouren and Dodé, *Mém. Poudres*, **28**, 252 (1939).

[68] Berl and Rueff, *loc. cit.;* also *Ber.*, **63**, 3210 (1930).

(99.85 per cent HNO_3) and phosphoric acid and containing 3.15 per cent phosphorus pentoxide, the maximum nitrogen content of 14.01 per cent was obtained, when the temperature was kept at 19° (±1), when the time was 4 hours, and when the cellulose-acid ratio was 1 : 60 (using absolutely dry ramie fiber). With a 1 : 100 ratio, a nitrate with 14.04 per cent nitrogen content resulted.

That the esterifying action of phosphoric acid during the nitration reaction is rather limited is seen from the greater ease with which the resulting nitrate, in contrast to that prepared with sulfuric acid, may be stabilized. Berl and Rueff found only a trace of phosphoric acid when the nitrate was subjected to the molybdate test.[69]

The less degrading influence of the phosphoric acid is reflected in the viscosity of the nitrate thus prepared, it being 8 times higher than that of a product carefully prepared with sulfuric acid.[70] These results were confirmed by af Ekenstam,[71] who found that the degrading influence of phosphoric acid upon cellulose was about 20 times less than that of sulfuric acid, as well as by Staudinger and co-workers.[72]

Acetic anhydride has been used as a dehydrating agent by several investigators with more or less success; first, apparently, by Berl and Smith[73] and later by Miles and Milbourn[74] and by Lenze and Rubens.[75] Miles and Milbourn attempted the preparation of lower substituted nitrates (those containing up to 10.5 per cent nitrogen), but the products thus prepared were weak and brittle. However, very little degradation was observed by Trogus,[76] who allowed nitric acid to act upon cellulose in the presence of acetic anhydride for 20 hours at 0–5° and obtained a nitrate having a nitrogen content of 13.85 per cent.

Nitration without the Presence of Dehydrating Agents. The first studies on nitration were made without the use of a dehydrating agent.[77] Later, it was found that very little esterification took place with an acid of 74.8 per cent (d., 1.442), but that the use of a 77.2 per cent acid (d., 1.450) resulted in a nitrate in which almost half of

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[69] Berl and Rueff, *loc. cit.*, p. 61. See, however, Davidson, *J. Textile Inst.*, **29,** T200 (1938), who found phosphorus acid contents of 0.26 to 0.41 in nitrates having a nitrogen content of about 13.75 per cent.

[70] Berl, Umstätter, and Karrer, *Z. physik. Chem.*, **152,** 284 (1931); Berl and Rueff, *Cellulosechem.*, **14,** 109 (1933); *ibid.*, **14,** 115 (1933).

[71] af Ekenstam, *Ber.*, **69,** 549 (1936).

[72] Staudinger and Sorkin, *Ber.*, **70,** 1996 (1937); Staudinger and Mohr, *ibid.*, **70,** 2296 (1937); Staudinger and Sohn, *ibid.*, **72,** 1709 (1939).

[73] Berl and Smith, *Ber.*, **41,** 1840 (1908).

[74] Miles and Milbourn, *J. Phys. Chem.*, **34,** 2604 (1930).

[75] Lenze and Rubens, *Chem.-Ztg.*, **I,** 2993 (1931).

[76] Trogus, *Ber.*, **64,** 405 (1932).

[77] Braconnot, *Ann. chim. phys.* **52,** 290 (1833); Pelouze, *Ann.*, **29,** 38 (1839).

all the hydroxyl groups were substituted; and with a 95.0 per cent acid, the degree of substitution reached about 2.75 nitrate groups per $C_6H_{10}O_5$ unit. Simultaneously, the rate of reaction increased rapidly as the concentration of the acid was increased.[78]

In addition, Vieille observed that the nitrates, with about 50–60 per cent of the available hydroxyl groups substituted, dissolved in the nitric acid. (They could be isolated from the solution by precipitation with water.) The lower and higher nitrated stages remained fibrous, however. It would appear that the solubility of cellulose in nitric acid is essentially a result of degradation, but that it is modified by the degree and the rate of substitution. Obviously, there exists a certain degree of substitution which so stabilizes the reaction product that it becomes resistant to degradation. If this degree of substitution has not been reached within a reasonable time, the partially nitrated cellulose is attacked and goes into solution. Since with very strong acid the rate of substitution increases rapidly, a sufficient number of hydroxyl groups will become substituted within a short time so that even the strong acid will no longer attack the cellulose constituent.

It is probable that a consideration of these various factors will help to explain why various investigators have found cellulose to dissolve in nitric acid of widely varying concentration.[79] Moreover, a study of the kinetics of the two reactions (degradation and substitution) by the application of modern tools would likely supply more exact information.

Vieille's results and those previously discussed lead us to expect that, in any nitration acid mixture, there should exist a concentration below which no nitration occurs. The closest average figure is probably 65 per cent. Whereas at this concentration the amount of water present seems to inhibit esterification, such acid forms an *addition compound* with cellulose. The first observation pointing to this assumption was made by Knecht,[80] who found that cotton yarn, placed in nitric acid of 65 per cent (d., 1.14), freed from the mechanically held acid and subsequently dried, liberated, when placed in water, as much nitric acid as would correspond to a nitrogen content of 7.7 per cent or approximately to 1 nitrate group per glucose residue. Knecht regarded

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[78] Vieille, *Compt. rend.*, **95**, 132 (1882); Häussermann, *Z. angew. Chem.*, **23**, 1762 (1910).

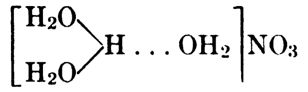
[79] See, for example, Häussermann, *Z. ges. Schiess- u. Sprengstoffw.*, **1**, 39 (1906); also Schwalbe, "Chemie der Cellulose," p. 271; Katz and Hess, *Z. physik. Chem.*, **122**, 135 (1926); Miles and Milbourn, *J. Phys. Chem.*, **34**, 2603 (1930).

[80] Knecht, *J. Soc. Dyers Colourists*, **12**, 89 (1896); *Ber.*, **37**, 549 (1904); *J. Soc. Dyers Colourists*, **24**, 68 (1908); *Färber-Ztg.*, **19**, 276 (1908).

the product of reaction as a very labile ester. However, Häussermann [81] considered this to be an addition compound, which would more adequately explain its lability. A nitrogen determination of the water-washed reaction product showed that some esterification had taken place (2.2 per cent nitrogen, which, however, dropped to 0.5 per cent when the time of contact between cellulose and acid was shortened from 1 hour to 2 minutes). Under the above conditions the acid did not degrade the cotton yarn; on the contrary, it exerted a mercerization effect. Indeed, the yarn thus treated showed increased hygroscopicity and affinity for dyestuffs and greater tensile strength.

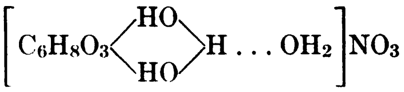
The addition compound (which according to a suggestion made by Hess and Katz [82] has been termed "Knecht compound") has a composition in agreement with the formula $C_6H_{10}O_5 \cdot HNO_3$ [82,83] rather than $(C_6H_{10}O_5)_2 \cdot HNO_3$.[84] X-ray investigation shows that the cellulose pattern disappears when the concentration of the nitric acid reaches 67 per cent and gives way to that which seems to be specific for the Knecht compound and which may be recognized while the acid concentration is increased to about 86 per cent. Indications are that in the Knecht compound the cellulose combines with the monohydrate of nitric acid: $C_6H_{10}O_5 \cdot HNO_3 \cdot H_2O$.

Hess [85] compared this compound with the trihydrate of nitric acid and suggested that the addition compound with cellulose may be regarded as an oxonium salt of nitric acid:



$$\left[\begin{array}{l} H_2O\diagdown \\ \qquad > H \ldots OH_2 \\ H_2O\diagup \end{array}\right] NO_3$$

Trihydrate of Nitric Acid



$$\left[\begin{array}{l} \qquad\qquad \diagup HO\diagdown \\ C_6H_8O_3 < \qquad > H \ldots OH_2 \\ \qquad\qquad \diagdown HO\diagup \end{array}\right] NO_3$$

Knecht Compound

The Knecht compound seems also to be formed—if only temporarily—on the nitration of cellulose with a nitric acid-sulfuric acid mixture.[86]

Numerous attempts have been made to reach a high degree of substitution with nitric acid without the presence of a dehydrating agent. From a commercial point of view, these attempts aim at the elimination of certain disadvantages involved in the present nitration process,

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[81] Häussermann, *Z. angew. Chem.*, **23**, 1762 (1910); see also Lunge and Bebie, *ibid.*, **14**, 483 (1901).

[82] Hess and Katz, *Z. physik. Chem.*, **122**, 126 (1926); Katz in Hess, "Chemie der Cellulose," pp. 689–690.

[83] Trogus, *Cellulosechem.*, **15**, 104 (1934).

[84] Andress, *Z. physik. Chem.*, **136**, 279 (1928).

[85] See Trogus, *loc. cit.*, p. 100.

[86] Trogus and Hess, *Z. Elektrochem.*, **40**, 200 (1934).

such as the dilution of the nitration acid, the necessity of employing relatively large volumes of liquid, the recovery of the nitration acid, etc. However, none of these attempts seems to have yet been capable of replacing the use of sulfuric acid.

Rogowin and Tichonow [87] exposed cotton to the vapors of a 96 per cent nitric acid (d. above 1.5), but the time to reach a certain nitrogen content was considerably longer than in the liquid medium. Whereas 96 per cent nitric acid in its liquid form gave a nitrogen content of 12.65 per cent after 2.5 hours at 20°, the vapor process required 48 hours for reaching the same degree of substitution. This result is obviously due to the fact that the vapors penetrate the cellulose at a much slower rate than does the liquid. The slow rate of reaction and the corresponding long time of contact result in considerable degradation and nonuniformity of the nitrates, and difficulties in dissolving them in organic solvents are encountered. Rogowin and Tichonow's results were confirmed by Bouchonnet, Trombe, and Petitpas.[88] Hofmann,[89] however, could not reach the high degree of substitution obtained by Rogowin and Tichonow.

Strong nitric acid diluted with an organic acid has also been used, obviously with the idea of facilitating the penetration of the cellulosic material and of avoiding the harshness and brittleness of the nitrated fiber as they are produced on nitration with undiluted nitric acid. Thus, Trogus [90] employed a mixture of nitric (d., 1.52) and acetic acid, obtaining a nitrogen content of 12 per cent after ½ hour and of 13.9 per cent after 4 hours. Bouchonnet, Trombe, and Petitpas [91] used mixtures of 100 per cent nitric acid [92] with acetic, propionic, and butyric acid and obtained a nitrogen content of 14 per cent. The latter investigators were able to increase the nitrogen content to the theoretical requirement of 14.14 per cent when, in addition to the nitric acid-acetic acid mixture, a certain amount of acetic anhydride was used.

Dalmon, Chédin, and Brissaud,[93] on the premise that in the nitration acid part of the nitric acid is present in the form of its anhydride

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[87] Rogowin and Tichonow, *Cellulosechem.*, **15**, 104 (1934).

[88] Bouchonnet, Trombe, and Petitpas, *Mém. Poudres*, **28**, 308 (1938/39).

[89] Hofmann, *Sitzber. Preuss. Akad. Wiss.*, **26–29**, 801 (1933).

[90] Trogus, *Ber.*, **64**, 405 (1931).

[91] Bouchonnet, Trombe, and Petitpas, *loc. cit.*, p. 295.

[92] A 100 per cent HNO_3 may be prepared, according to Simon and Höppner (footnote 94, p. 193), by distillation of a nitrogen oxide-free fuming nitric acid in the presence of sulfuric acid in the high vacuum at 30°.

[93] Dalmon, Chédin, and Brissaud, *Compt. rend.*, **201**, 664 (1935); see also Hoitsema, *Z. angew. Chem.*, **11**, 173 (1898).

(N_2O_5),[94] allowed vapors of nitric acid anhydride dissolved in carbon tetrachloride to act on cotton at a temperature of 13°. In order to reduce the decomposition of the anhydride, the experiments were carried out in the absence of light. After 6 hours, a nitrogen content above 14 per cent was obtained. Dalmon[95] also allowed the anhydride vapors to act directly on cotton and obtained a nitrate with 14.12 per cent nitrogen content; the yield amounted to 99.3 per cent of the theoretical. The reaction is regarded as proceeding according to the following equation:

$$C_6H_7O_2(OH)_3 + 3N_2O_5 = C_6H_7O_2(ONO_2)_3 + 3HNO_3$$

The results reported above seem to be in disagreement with the postulation made by Saposchnikow and by Berl and co-workers, namely, that the degree of substitution decreases as the nitric acid (because of the increased addition of sulfuric acid to the acid mixture) approaches the composition of the anhydride (p. 178). This postulation implies that the anhydride itself exerts no nitration effect on cellulose. Considering the results actually obtained with the anhydride, the decrease of the degree of substitution with increasing sulfuric acid above a certain amount would thus require another interpretation.

In summing up the results which have been obtained with nitric acid without the presence of dehydrating agents, it is seen that in a few cases the theoretical value of the trinitrate (14.14 per cent nitrogen) has been very closely approached and that it has been actually obtained in the case of the 100 per cent nitric-acetic acid-acetic anhydride combination. Possibly, the elimination of the formation of sulfuric acid esters is partly responsible for this result. No doubt, acetates which might be formed intermediately are more easily hydrolyzed (saponified). It may also be assumed that the absence of sulfuric acid decreases the hydrolyzing (saponifying) action of the nitration mixture upon the nitrate. However, these advantages, as has been seen, are also obtained when sulfuric is replaced by phosphoric acid. Since the values under discussion are still somewhat higher than those obtainable with phosphoric acid, an additional factor seems to exert a favorable influence unless the assumption is made that the higher nitrogen values are a result of the degradation of the cellulose, i.e., to an extent which results in an increase of the number of free hydroxyl groups.

The Fractionation of Cellulose Nitrates. Homogeneity in the trinitrate is confined to the distribution of nitrate groups; i.e., in each chain molecule, all hydroxyl groups available per glucose residue are

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[94] See also Simon and Höppner, *Kolloid-Z.*, **85**, 8 (1938).

[95] Dalmon, *Compt. rend.*, **201**, 1123 (1935).

substituted by nitrate groups. But the chain molecules are of different length. The trinitrate is thus heterogeneous in respect to its chain length distribution. On the other hand, we would expect to encounter both types of heterogeneity in the incompletely substituted nitrates because these represent mixtures of chain molecules of different lengths and of different degrees of substitution.

Although a nitrate may be separated into fractions of very different degrees of polymerization, the nitrogen content of the fractions, as has been pointed out earlier, varies relatively little.

Fractionation may be accomplished by (1) fractional solution, (2) fractional precipitation, (3) diffusion, and (4) ultrafiltration.

Of these, the method of *fractional solution*, that is, extraction with certain solvents or solvent mixtures, seems to be best suited for revealing what actual differences in degree of substitution might exist in the nitrate under investigation. In general, the lower substituted nitrates are soluble in a mixture of ether and alcohol, whereas the higher substituted products are insoluble in this solvent mixture.

By extracting a nitrate of 12.17 per cent nitrogen content with a 50 : 50 ether-alcohol mixture, Meissner[96] obtained a soluble fraction, having 10.28 per cent nitrogen (about 4 per cent of the weight of the raw nitrocellulose) and an insoluble residue having 12.32 per cent nitrogen.

Berl and Hefter[97] obtained similar results on a great number of nitrates prepared in various ways. The nitrates were first extracted with alcohol, which in general dissolved not more than 1–3 per cent, and subsequently with a mixture containing 60 volume parts of ether and 40 volume parts of alcohol. The nitrogen content of the alcohol-soluble fraction was 3–4 per cent lower than that of the original nitrate. However, the greatest difference between the nitrogen content of the ether-alcohol soluble fraction and that of the insoluble residue was not more than about 1 per cent. The figures in Table 20, which are taken from Berl and Hefter's work, may serve as an illustration.

When acetone was the extracting medium, similar results were obtained.

A lower nitrogen content in the alcoholic fraction was found by Lenze and Rubens too; these authors also found the viscosity of this fraction to be considerably lower than that of the original material.[98]

Craik and Miles[99] applied successive extractions with aqueous ace-

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[96] Meissner, *Z. ges. Schiess- u. Sprengstoffw.*, **13**, 252 (1913).

[97] Berl and Hefter, *Cellulosechem.*, **14**, 72 (1933).

[98] Lenze and Rubens, *Kunststoffe*, **21**, 3, 4 (1931).

[99] Craik and Miles, *Trans. Faraday Soc.*, **27**, 756 (1931).

tone of increasing acetone concentration to a number of commercial nitrocellulose samples. In this way a number of fractions were obtained, and it was found that the most soluble fractions had the lowest nitrogen content and that the residues after extraction showed a nitrogen content slightly higher than the original preparation. Although occasionally differences up to 2 per cent were obtained, there was rarely a greater difference in nitrogen content than 0.3–0.4 per cent.

TABLE 20

FRACTIONATION OF NITROCELLULOSE INTO ALCOHOL AND ETHER-ALCOHOL SOLUBLE PORTIONS

N of Original Nitrates, %	Solubility in		Nitrogen Content of Fractions, %		
	Alcohol, %	Ether-alcohol, %	Alcohol	Ether-alcohol	Residue
12.65	2.44	92.40	9.3	12.60	12.25
13.13	2.68	8.60	9.7	12.15	13.35
13.17	2.40	11.43	...	12.00	13.15
12.72	2.80	74.0	...	12.96	13.00

Berl and Hefter, as well as Craik and Miles, determined also the solution viscosity of the various fractions and found that the difference in viscosity was considerably greater than the difference in nitrogen content. Although Berl and Hefter's results do not permit the establishment of a relationship between viscosity and solubility, the general trend of Craik and Miles' results seems to indicate that, as the residue becomes less with successive extraction, its average viscosity continuously rises. Thus, by the technique employed it seems to be possible to extract more and more of the short-chain material.

Acetone-water mixtures were also used by Rogowin and Glasman.[100] By varying the water content of the solvent, six residual fractions were obtained. As seen from Table 21, these fractions showed increasing viscosities, again indicating that increasing amounts of short-chain material were removed. The viscosity of the original nitrate (in acetone, 2 per cent concentration) was 270–290 seconds.

The method of fractional solution has also been employed as an indirect method for the determination of the chain length distribution in various cellu-

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[100] Rogowin and Glasman, *Kolloid-Z.*, **76**, 210 (1936).

losic materials. Schieber, Dolmetsch, and Reinecke[101] converted the various materials into nitrates, fractionated them, and determined the degree of polymerization of the fractions. Since the method of nitration—treatment with a mixture of fuming nitric and phosphoric acid in the presence of phosphorus pentoxide at 18° for 1 hour—may be assumed to cause practically no degradation of the cellulose, the results are regarded as showing the chain length distribution as it exists in the original (unnitrated) cellulosic materials. (See also page 130 and the section on nitrocellulose in Chapter XV.)

TABLE 21

FRACTIONATION OF CELLULOSE-NITRATE BY ACETONE-WATER MIXTURES

Fractions from Celloxylin * with 11.53% N	Viscosity of Residues 2% Acetone Solutions, Seconds	
	I	II
I	17	16
II	34	33
III	54	62
IV	62	115
V	420	. . .
VI	1000	690

* Term commercially used for the lower nitrates.

The technique of Schieber and co-workers was to extract the nitrate with a solvent mixture consisting of alcohol and ethyl acetate and to increase the proportion of the ethyl acetate with each successive operation. In this way, the solvent power of the mixture increases, and separation into fractions is accomplished.

Fractional precipitation as a means of separating nitrocellulose into various fractions is based upon the ability of liquids which are nonsolvents for nitrocellulose to precipitate the latter from its solution. A technique frequently employed consists in dissolving the nitrate in acetone and adding to the solution water, aqueous acetone, or other liquids in increasing amounts with stirring. Each change in the proportion of acetone to water in the acetone solution of the nitrate causes precipitation of another fraction.

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[101] Schieber, *Papier-Fabr.*, **37**, 245 (1939); *Angew. Chem.*, **52**, 561 (1939); Eisenhuth, *ibid.*, **52**, 568 (1939); Dolmetsch and Reinecke, *Zellwolle*, **5**, 219 (1939); Rath and Dolmetsch, *Klepzig's Textil-Z.*, **41**, 475 (1938); see also Mark, *Paper Trade J.*, **113**, No. 3, 34 (1941).

Possibly Goebel and Stepanow [102] were among the first investigators to apply fractional precipitation. They found that the nitrogen content of the fractions thus obtained varied more than usual, but Duclaux and Wollman,[103] who used the same method, observed no such difference. The viscosities of the fractions, however, varied considerably. Similar results were obtained by other investigators.[104] Particularly interesting are those of Brunswig [105] because they show that the nitrogen contents of the fractions were practically the same as that of the original nitrocellulose (10.2 per cent)—10.15, 10.13, 10.24, and 10.19 per cent. Only the fifth fraction had 9.85 per cent, owing likely to an accumulation of inorganic and organic impurities. Quite similar in this respect are the results reported by Gluckmann.[106]

By using fractional precipitation, Kumichel [107] separated a commercial cellulose nitrate having 11–12 per cent nitrogen into two fractions, i.e., a precipitate and a filtrate. Whereas the precipitate consisted of material which was only a little degraded, the fraction isolated from the filtrate was considerably attacked and its ash content was much higher than that of the precipitate. On further fractionation of the precipitate, more portions of varying viscosity were obtained, but the nitrogen content of these portions remained practically constant.

Medwedew,[108] who separated a commercial nitrate (11.08 per cent nitrogen content) into four essential fractions and determined their viscosities in acetone (using various concentrations) and their molecular weights by the osmotic pressure method,[109] obtained the results shown in Table 22. The last two fractions were the result of further fractionation of fraction I. Although these four fractions are not quite comparable with each other, they nevertheless reveal the heterogeneity of the nitrocellulose preparation investigated, as seen from the differences in viscosities and molecular weights between fractions I and II and particularly between III and IV. It may be added that the nitrogen content of the fractions showed hardly any deviation from the original value.

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[102] Goebel and Stepanow, *Z. ges. Schiess- u. Sprengstoffw.*, **3**, 43 (1908).

[103] Duclaux and Wollman, *Bull. soc. chim.*, [4] **27**, 44 (1920); Duclaux and Nodzu, *Rev. gén. colloïdes*, **7**, 241 (1929).

[104] McBain, Harvey, Smith and Dale, *J. Phys. Chem.*, **30**, 345 (1926); Beck, Clément and Rivière, *Chimie & industrie*, **24**, 1608 (1930).

[105] Brunswig, *Cellulosechem.*, **7**, 118 (1926).

[106] Gluckmann, *Kunststoffe*, **25**, 28, 120 (1935).

[107] Kumichel, *Kolloid-Beihefte*, **26**, 161 (1928).

[108] Medwedew, *Kunststoffe*, **23**, 249, 273 (1933).

[109] See also Schulz, *Z. physik. Chem.*, **B32**, 41 (1936).

TABLE 22

SEPARATION OF NITROCELLULOSE BY FRACTIONAL PRECIPITATION INTO FRACTIONS OF VARYING MOLECULAR WEIGHTS

Viscosities of Fractions	Concentration in Acetone				Molecular Weight
	2%	1%	0.5%	0.25%	
I	21.56	3.9	1.04	0.39	25,000
II	26.37	4.67	1.30	0.43	60,000
III	24.52	4.47	1.17	0.42	40,000
IV	57.50	7.30	1.80	0.58	75,000

Separation of nitrocellulose into various fractions by *diffusion* has been attempted by Krüger[110] by allowing a solution of nitrocellulose in acetone, methyl alcohol, or amyl acetate to diffuse into the pure solvent. (A layer of the solvent is carefully placed on top of the solution.) The rate of diffusion depends upon the particle size of the diffusing substance. In the case of a mixture of substances of different particle sizes the substances having the smaller particle sizes will diffuse in advance of those having the larger particle sizes. In this way, various fractions may be obtained. Thus, Krüger was able to separate a preparation of 12.8 per cent nitrogen, after 42 days of diffusion, into two layers, the lower one showing 13.1 and the upper one 12.1 per cent nitrogen. It would appear that not only the lower nitrates but also degradation products of cellulose accumulate in the upper layer. This seems to be in agreement with the fact that the diffusion coefficient of the nitrates increased with increasing water content of the acid mixture used for nitration. Obviously the increasing water content caused hydrolysis and oxidation, i.e., a shortening of the chains ("particle size"). At the same time, the nitrogen content decreased, probably because the concentration of the nitric acid had been lowered.

Fractionation by *ultrafiltration* may be accomplished by using filters of varying pore size. Duclaux and Wollman[111] separated a commercial ether-alcohol-soluble nitrate (11.0–12.5 per cent nitrogen content) into various fractions whose viscosities varied from 3.7 to 0.08 and whose molecular weights, determined by the osmotic pressure method,

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[110] Krüger, *Z. angew. Chem.*, **41**, 408 (1928); see also Herzog, Krüger, and Yamaga, *J. Phys. Chem.*, **30**, 466 (1926).

[111] Duclaux and Wollman, *Bull. soc. ch'm.*, [4] **27**, 44 (1920).

ranged from 70,000 to 21,000, whereas the nitrogen contents of the fractions showed little difference. Although this range of molecular weights appears rather low, the figures clearly demonstrate the heterogeneity as regards chain length. Duclaux and Wollman's findings were confirmed by Kumichel.[112]

Summing up the results obtained by the various techniques of fractionation, it is seen that they reveal considerable heterogeneity with respect to molecular size but relatively little with respect to degree of substitution. This fact would lead us to believe that the nitrate groups are rather uniformly distributed over the chain molecules. It should be noted, also, that the results, in general, do not indicate the presence of chains in which less than 2 hydroxyl groups per glucose unit are substituted (the mononitrate requires 6.77 per cent nitrogen). The nitrogen content remains between that of a di- and a trinitrate (i.e., between 11.13 and 14.17 per cent). This result makes it seem improbable that any unnitrated cellulose is present in the nitrates. On the other hand, the nitrogen content of the fractions indicates the presence of a certain amount of trinitrate. This result appears to be in agreement with x-ray findings which, as has been seen, are interpreted as giving proof of the presence of trinitrate in nitrates which have a nitrogen content of about 12 per cent or more.

The heterogeneity of nitrocellulose with respect to chain length has a marked bearing on the properties of the materials into which nitrocellulose is converted. Medwedew[113] has shown that strength and elongation properties of films prepared from the various nitrocellulose fractions vary to a considerable extent. It is conceivable that these properties are best with the fractions of highest molecular weight and *vice versa*. On the other hand, the properties of films may be improved by mixing fractions of higher and lower molecular weight in certain proportions.

The effect of the heterogeneity of nitrocellulose upon its properties has been further demonstrated by Spurlin.[114] The fractions showing the higher viscosities produced the stronger films and *vice versa*. Spurlin also showed that the more uniform fractions exhibited properties superior to those of the original material. However, the benefit which Medwedew observed on admixing fractions of different viscosities could not be confirmed, except for the property of adhesion, which was improved by blending high and low viscosity fractions.[115]

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[112] Kumichel, *Kolloid-Beihefte*, **26**, 161 (1928).

[113] Medwedew, *Kunststoffe*, **23**, 273 (1933).

[114] Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938).

[115] See also Schulz, *Z. physik. Chem.*, **B47**, 137, 155 (1940).

Which of the two different types of hydroxyl groups of cellulose are esterified under conditions of limited substitution was recently investigated by Murray and Purves.[116] By analogy with results obtained in the methyl glucoside series, only nitrate groups in the 6-position are considered to be replaced by iodine when nitrocellulose is subjected to the action of anhydrous sodium iodide. When this reaction was allowed to take place with low-substituted nitrates (2.5–6.1 per cent nitrogen content), it was found that at least 44 per cent of the nitration had occurred in the 6-position. This result might be interpreted to mean that the primary alcohol groups of cellulose react at a faster rate than the secondary groups.

The Solubility of Cellulose Nitrates. The solubility of cellulose nitrates in organic solvents chiefly depends upon the average degree of polymerization and the nitrogen content. The latter determines the affinity of the nitrates for solvents, that is, their ability to become solvated, there being a difference in the affinity of substituted and free hydroxyl groups. The extent to which the nitrate becomes solvated also depends upon the nature of the solvent.

No data on systematic studies of the influence of the degree of polymerization upon the solubility of cellulose nitrates in organic solvents seem to be available. It would appear that conclusions which have been drawn from the influence of the degree of substitution have seldom given sufficient consideration to the influence of degradation. Indeed, an unequivocal answer can be expected only from studies on a polymer-homologous series of nitrates, i.e., preparations of decreasing degree of polymerization, but having the same nitrogen content. Although Staudinger and co-workers have prepared such series and have studied the changes in viscosity, they did not discuss the question of solubility.[117] However, from observations cited in previous sections of this chapter, the general conclusion may be drawn that, the lower the degree of polymerization, the more easily soluble is the nitrate, and *vice versa*.[118]

It has been known for a long time that the nitrates of medium nitrogen content (about 10.5 to 12.2 per cent) are soluble in a mixture of ether and alcohol, whereas those of a higher nitrogen content (about

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[116] Murray and Purves, *J. Am. Chem. Soc.*, **62**, 3194 (1940).

[117] Staudinger and Haas in Staudinger, "Die hochmolekularen organischen Verbindungen," pp. 498 and 503; Staudinger and Sorkin, *Ber.*, **70**, 1993 (1937); Staudinger and Mohr, *ibid.*, **70**, 2296 (1937); Staudinger and Sohn, *ibid.*, 1709 (1939).

[118] See also Scheiber and Baier, *Kolloid-Beihefte*, **43**, 363 (1936); Schiemann and Kühne, *Cellulosechem.*, **15**, 84 (1934).

12.2 to 14.17 per cent) and those below about 10 per cent are insoluble in this solvent mixture. On the assumption that, in preparing nitrates of these varying nitrogen contents, the degree of polymerization does not change appreciably, it appears that the degree of substitution governs the solubility of the nitrate in ether-alcohol.

Brunswig[119] has made a survey of the relationship between nitrogen content and solubility in ether-alcohol (2 volume parts of ether and 1 volume part of alcohol) of numerous nitrates and has expressed this relationship in a diagram which is shown in Fig. 52. This diagram permits the determination of the range of solubility for nitrates of all possible nitrogen contents. Moreover, Brunswig has shown that the relationship between ether-alcohol solubility and nitrogen content is maintained when the nitrogen content of a nitrate is increased or lowered by re-treating it with acid mixtures of different concentrations. Thus, by submerging a nitrate with 13.2 per cent nitrogen and only 5 per cent ether-alcohol solubility in a suitable acid mixture it may be converted into a product with 12.6 per cent nitrogen and 100 per cent ether-alcohol solubility. By treating this nitrate with a stronger acid mixture it may be changed to the original product, i.e., of higher nitrogen content and limited ether-alcohol solubility.

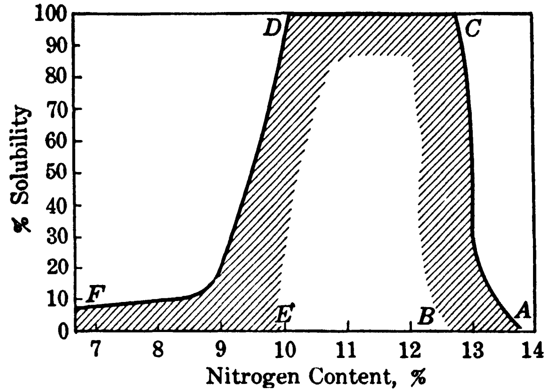

FIG. 52. Relationship between nitrogen content and ether-alcohol solubility of cellulose nitrates. Brunswig.

This experiment very clearly demonstrates the extent to which the solubility of the nitrate depends upon its nitrogen content. On the other hand, it is difficult to understand that such relatively small differences in the nitrogen content alone should bring about such a radical change in solubility, and it appears fairly safe to assume that the

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[119] Brunswig, *Cellulosechem.*, 7, 118 (1926).

greater ether-alcohol solubility of the lower substituted nitrates is also caused by more pronounced degradation during the (original) nitration procedure. As has been pointed out earlier, the degree of substitution is governed by the water content of the nitration acid. When the water content is increased above a certain level, the concentration of the nitric acid becomes insufficient to produce a higher degree of substitution in the nitrate. When this condition is approached, the solubility of the nitrate increases but, at the same time, the diluted acid gives rise to more pronounced degradation of the cellulose. This conclusion appears supported by the results obtained by Schiemann and Kühne.[120] In Table 23, the solubility of a number of nitrates in ether-alcohol (4 : 3) is shown in its relation to the water content of the nitration acid applied, the nitrogen content, and the molecular weight of the nitrates.

TABLE 23

RELATIONSHIP BETWEEN WATER CONTENT OF NITRATION ACID AND PROPERTIES OF NITROCELLULOSE

Water in Nitration Acid, %	Solubility in Ether-Alcohol, %	Nitrogen, %	Molecular Weight
3.73	1.81	13.34	220,000
5.12	3.76	13.38	150,000
6.87	1.53	13.73	240,000
6.99	3.51	13.43	170,000
9.87	3.49	13.46	185,000
9.80	2.61	13.58	215,000
12.60	2.91	13.53	225,000
12.92	3.12	13.33	190,000
13.77	3.67	13.40	185,000
15.61	89.00	12.62	150,000
15.87	100.00	12.72	130,000
18.60	100.00	11.81	90,000
18.76	100.00	11.94	95,000
21.50	36.21	10.03	40,000
22.33	28.25	9.64	25,000
24.60	0.82	8.55	.....
27.70	1.18	5.05	.....
30.92	0.57	2.91	.....
33.65	1.07	1.99	.....

It is seen that, up to a water content of 13.77 per cent, the nitrogen content is fairly constant and the solubility is between 2 and 4 per cent. When the water content is increased to 15.61 per cent, the nitrogen content drops, and the solubility increases rapidly to 89–100 per

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[120] Schiemann and Kühne, *Cellulosechem.*, **15**, 83 (1934).

cent. With still more water in the nitration acid (21.50 per cent), the nitrogen content drops further and the solubility also drops rapidly. These changes become very pronounced when the water content ranges between 24.60 and 33.65 per cent.

The influence of degradation in its relation to the water content of the nitration acid is seen from the change of the molecular weight of the nitrates. These data were derived from viscosity measurements of the nitrates in acetone (concentration 0.14 per cent) and by the use of Staudinger's equation for the conversion of viscosities into molecular weights.

It is seen that, in general, the molecular weight drops with increasing water content of the nitration acid, indicating that under the influence of the most dilute acid the cellulose suffers greatest degradation. In fact, under such conditions, the rate of the substitution reaction decreases, and the stabilization of the nitrate against degradation is retarded. Thus, the molecular weight of the nitrates decreases with decreasing nitrogen content and it is in this range of substitution that maximum solubility occurs. However, when the water content of the nitration acid becomes very high, the solubility decreases again. At this point, another factor exerts a predominating influence. The nitrogen content of the nitrates is now very low; i.e., the reaction products are similar to unsubstituted cellulose and, consequently, lose their affinity to the solvent mixture. Therefore, in spite of a still lower molecular weight, the nitrates become more and more insoluble.

Before giving further consideration to the term affinity, two additional investigations may be mentioned which show that the solvent power of a solvent mixture may be improved by changing the proportion of its components or by adding a nonsolvent to an individual solvent. These investigations also provide a method for determining the optimum solvent power for a given nitrocellulose preparation.

Gibson and McCall [121] found that the viscosity of nitrocellulose dissolved in a mixture of ether and alcohol dropped to a minimum and then increased again when the alcohol portion in the solvent mixture was steadily increased.[122] The minimum viscosity was reached when the ratio of ether to alcohol was 55 : 45 by volume or 1.1 : 1 by weight. On either side of the optimum ratio, the viscosity increased rapidly (Fig. 53) and approached the gel state. Thus the optimum ratio of

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[121] Gibson and McCall, *J. Soc. Chem. Ind.*, **39**, 172T (1920).

[122] It is not stated whether the alcohol was absolute or aqueous. It is likely that it was aqueous (perhaps 94–95 per cent) because the commercial ether-alcohol mixture does not contain absolute alcohol.

the solvent constituents coincided with the lowest viscosity, and the latter, therefore, may be used as an indication of the optimum solvent power of an ether-alcohol mixture for a given cellulose nitrate.

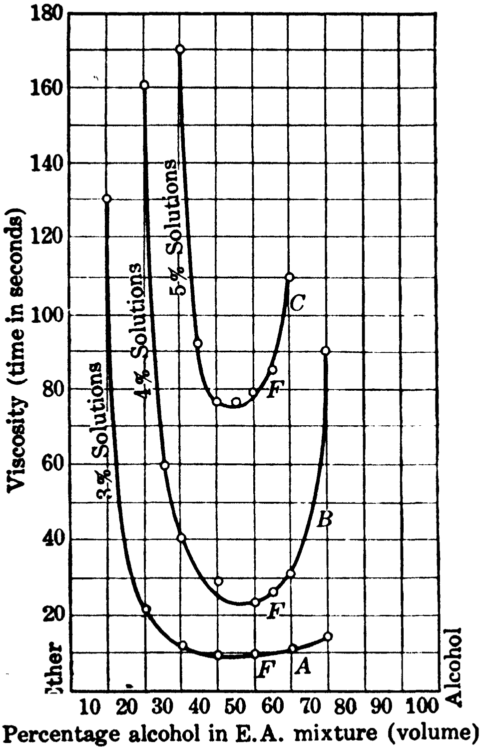

FIG. 53. Viscosity of nitrocellulose in ether-alcohol with increasing alcohol content. Gibson and McCall.

Gibson and McCall have also shown that the optimum ratio of ether to alcohol depends upon the nitrogen content of the nitrate. For three nitrates of different nitrogen content the ratios were as follows:

Nitrogen Content	Optimum Ether-Alcohol Ratio
11.80	50 : 50
12.20	53 : 47
12.55	70 : 30

The figures indicate that the nitrate with the highest nitrogen content requires the largest amount of ether for maximum solubility. Conversely, one may conclude that the solubility of Schiemann and Kühne's nitrates prepared from acids with a high water content might have been improved if the ether-alcohol ratio had been increased on the alcohol side.

A similar state of affairs exists when, according to Masson and McCall,[123] varying amounts of water are added to a nitrocellulose solution in acetone. Again, there is an optimum solvent composition at which the viscosity is at a minimum (Fig. 54). Relatively small amounts of water increase the solvent power of the mixture but, with about 12 per cent water, the liquid no longer disperses the nitrate. Apparently, acetone if containing a certain amount of water possesses a greater affinity for the particular nitrate than acetone alone.

In searching for a definition of the term affinity, two observations appear to be essential. Assuming for the moment that the influence of degradation may be eliminated, the fact that the nitrogen content of the nitrate influences its solubility suggests that it is the proportion of substituted to unsubstituted hydroxyl groups which is responsible for the solubility effect. Further, because neither of the constituents of the solvent mixture (alcohol or ether) is a good solvent for the nitrate, it would appear that the presence of two liquids in the right proportion is necessary to obtain optimum solubility.

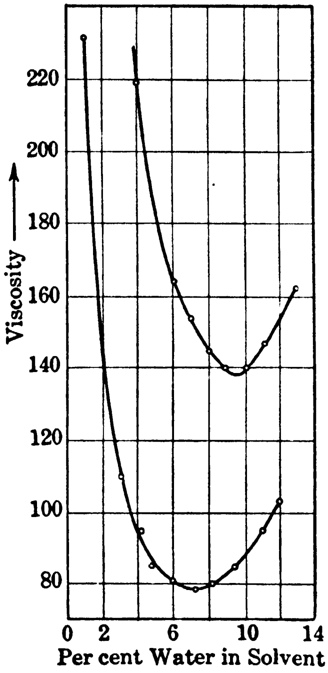

FIG. 54. Viscosity of nitrocellulose in acetone with increasing water content. Masson and McCall.

The most satisfactory interpretation of these observations has been offered by Highfield,[124] who considers the polarity of the solute and that of the solvent to be the essential factors. According to the Langmuir-Hildebrand theory,[125] the specific

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[123] Masson and McCall, *J. Chem. Soc.*, **117**, 819 (1920). With regard to solubility measurements of cellulose nitrates in mixtures of acetone and benzene at various temperatures, see Inoue, Nakazawa, and Kimura, *Cellulose Ind.* (Tokyo), **16**, 5 (1940).

[124] Highfield, *Trans. Faraday Soc.*, **22**, 57 (1926); *Z. physik. Chem.*, **124**, 245 (1926).

[125] Hildebrand, "Solubility of Nonelectrolytes," American Chemical Society Monographs, Chapter IX, Chemical Catalogue Co., New York (1936).

attractions between polar groups in solvent and solute seem to explain why polar solutes are easily soluble in polar liquids and nonpolar solutes in nonpolar liquids. Moreover, a solute containing both types of groups should require a solvent containing both types of groups. The validity of this postulate has been proved in numerous cases.

Nitrocellulose contains hydroxyl, nitrate, and hydrocarbon (—CH—) groups. These groups possess different polarity, but, likely, the hydroxyl and the hydrocarbon groups are most essential because the former represent the most strongly polar and the latter the least polar groups, the polarity of the ONO_2 group ranging between that of the two others. Highfield has pointed out that, in accordance with the hypothesis, the best solvents for nitrocellulose, indeed, contain both polar and nonpolar groups.

The following is a typical list of solvents for nitrocellulose:

Acetone
Methylalcohol
Nitrobenzene
Substituted ureas
Urethans
Furfural
Alkyl esters
Acetanilide
Glacial acetic acid
Triacetin
Camphor
Triphenyl phosphate
Phthalic esters
Benzyl cyanide
Nitrotoluidine

On the hypotheses advanced above, the polar groups in these solvents should dissolve nitrocellulose by virtue of their similarity to the OH and ONO_2 groups, whereas the nonpolar groups in the solvents are similar to the hydrocarbon groups in nitrocellulose. The balance of these two types of groups in the solvents would thus insure solution.

Since it can hardly be expected that the balance in the various solvents is precisely that required for optimum solubility, the addition of polar or weakly polar liquids should improve the solvent power of the individual solvent, which alone might either be too strongly or too weakly polar.

Highfield, using Gibson, Masson, and McCall's method for determining the optimum solvent power of solvents and solvent mixtures for nitrocellulose, has tested the validity of the hypothesis in numerous cases. As an example, an acetone-water mixture containing 9 per cent water was found to be a better solvent for a cellulose nitrate of 12.2 per cent nitrogen content than acetone alone. Acetone lacks hydroxyl groups which are, however, still present in the nitrate. Thus, the addition of hydroxyl groups to the acetone in the form of water increases the solvent power. On the other hand, excess water results in a too strongly polar solvent mixture, approaching that of water alone which is not a solvent for nitrocellulose. The same is true for ether-alcohol and a mixture of ether, alcohol, and water. It is only when the mixture contains polar and nonpolar groups balanced in the right proportion relative to the balance of such groups in nitrocellulose that optimum solubility is obtained.

With the trinitrate—with no free hydroxyl groups present—one would expect the same hypothesis to hold. In this case, the balance between the nitrate groups and the hydrocarbon groups and possibly the —COC— bridges (between the individual glucose residues of the chain molecule) may serve as a guide for the selection of the best solvent or solvent mixture. Solvents for the trinitrate, in addition to acetone, include ethyl acetate and its higher homologues, methyl and ethyl glycol acetate, cyclohexanone, amyl acetate, cyclohexanol acetate,[126] and many others.

Pyridine has also been used as a solvent;[127] however, it attacks nitrocellulose. In fact, the viscosity of the solution was found to decrease rather rapidly on standing, and the nitrocellulose, precipitated from the pyridine solution with water after 18 hours and dissolved in butyl acetate, showed a considerable decrease in the degree of polymerization.[128]

The coincidence between the optimum solubility of nitrocellulose and its lowest viscosity in solvent mixtures[129] has been further confirmed by Mardles[130] and by Dobry and Duclaux.[131]

Ostwald and Ortloff[132] conceived the idea of using the dielectric constant as a measure of the solvent power. Since the dielectric constant is in turn a measure of polarity, their method may be regarded as a further step in the direction of Highfield's work. The same may be said of the work reported by Moll.[133] The results of these studies show that the best solvents are those which possess the same dielectric constant and the same dipole moment as the solute.

For the sake of completion, the reader is referred to a number of further investigations on the determination of the solvent power of solvents and solvent mixtures.[134]

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[126] Hess, "Chemie der Cellulose," p. 366.

[127] Sakurada and Shojino, *Kolloid-Z.*, **68**, 300 (1934).

[128] Staudinger and Sorkin, *Ber.*, **70**, 2010 (1937).

[129] See also McBain, *J. Phys. Chem.*, **30**, 245 (1926).

[130] Mardles, *J. Soc. Chem. Ind.*, **42**, 207T (1923); *J. Chem. Soc.*, **125**, 2244 (1929); *Kolloid-Z.*, **76**, 200 (1936).

[131] Dobry and Duclaux, *J. chim. phys.*, **31**, 568 (1934).

[132] Ostwald and Ortloff, *Kolloid-Z.*, **59**, 25 (1932).

[133] Moll, *Kolloid-Z.*, **76**, 85, 200 (1936); *Kolloid-Beihefte*, **49**, 1 (1939).

[134] Brown and Bogin, *Ind. Eng. Chem.*, **19**, 968 (1927); Davidson and Reid, *ibid.*, **19**, 977 (1927); Wolff, Zeidler, and Toeldte, *Farben-Ztg.*, **33**, 2228, 2301, 2669 (1928); Sakurada and Shojino, *Kolloid-Z.*, **68**, 300 (1934); Scheiber and Baier, *Kolloid-Beihefte*, **43**, 363 (1936).

The Viscosity of Nitrocellulose Solutions. Next to solubility, solution viscosity is the most important characteristic of cellulose nitrates. Not only does it reveal the degree of polymerization of the cellulose constituent, but it also determines the suitability of the nitrates for their various commercial uses.

The viscosity of nitrocellulose is influenced by various factors, in much the same way as observed with lyophilic colloids. Thus, pressure,[135] temperature,[136] and concentration,[137] bring about anomalies which indicate that such solutions do not follow the Hagen-Poiseuille law. Since the results are frequently contradictory, considerable experimental work has still to be done before the viscosity phenomenon can be satisfactorily understood.

Although references are scarce,[138] nitrocellulose solutions seem to be subject to the development of structural viscosity. It has been observed that when the solution stands at room temperature, the viscosity first decreases, then gradually increases to such an extent that, after a time, it no longer can be measured, indicating that the gel state has been attained. This phenomenon has been compared with the ripening of viscose. However, it is not known whether this change of the viscosity of the nitrocellulose solution is the result of hydrolysis, i.e., partial restoration of hydroxyl groups, or other causes. As will be seen later, such changes take place in viscose.

So-called "gelatinization," which has been observed to take place with nitrocellulose solutions exposed to light,[139] is probably a phenomenon different from structural viscosity.

The change which the viscosity of nitrocellulose undergoes in solution seems to depend largely upon the experimental conditions. Kanamaru[140] allowed samples of nitrocellulose with 12.61 per cent nitrogen to stand in air and in a number of organic liquids (ethyl alcohol, carbon tetrachloride, benzene and

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[135] Nisizawa, *Kolloid-Z.*, **56**, 59, 179, 317 (1931); Hess, *Ber.*, **64**, 408 (1931); Gluckmann, *Kunststoffe*, **25**, 25, 120 (1935); Scheiber and Baier, *Kolloid-Z.*, **43**, 363 (1936).

[136] Mark, "Physik und Chemie der Cellulose," p. 88; Staudinger, "Die hochpolymeren organischen Verbindungen," p. 509; Berl, Karrer, and Umstätter, *Z. physik. Chem.*, **152**, 150 (1931); Staudinger and Sorkin, *Ber.*, **70**, 2003 (1937).

[137] Mark and Guth, *Ergeb. exakt. Naturw.*, **12**, 118 (1933); Sakurada, *Kolloid-Z.*, **63**, 311 (1933); Philippoff and Hess, *Ber.*, **70**, 639 (1937); Staudinger and Sorkin, *Ber.*, **70**, 1993, 2000, 2011 *ff.* (1937).

[138] Weltzien, "Chemische und physikalische Technologie der Kunstseiden," p. 251; Hess, "Chemie der Cellulose," p. 373; Piest, *Z. angew. Chem.*, **24**, 970 (1911); Mark, "Physik und Chemie der Cellulose," p. 270.

[139] Mark, *loc. cit.*

[140] Kanamaru, *Kolloid-Z.*, **87**, 191 (1939).

petroleum ether) as well as in water for 200 to 500 days in a cool, dark place and determined the viscosity of the samples in acetone (1 per cent concentration) and their x-ray patterns at intervals. It was found that the viscosity of the samples which had been allowed to stand in air or in weakly polar liquids (carbon tetrachloride and petroleum ether) remained practically unchanged or increased only slightly, whereas the viscosity of the samples stored in the polar liquids (water and alcohol) increased rather steeply and then decreased again, thus passing through a maximum.

This behavior of the samples was found to coincide with a change in the x-ray pattern. As the viscosity of the samples increased, the parallel arrangement of the crystallites became intensified. It is postulated that this increased orientation, resulting in an increase of the crystalline portion (with corresponding decrease of the amorphous portion) of the micellar system, leads to densification of the gel structure and thus seems to account for the increased viscosity of the dispersions prepared from such samples.

Kanamaru has compared this phenomenon with the reorientation which takes place when cellulose hydrate is heated in glycerin and other liquids at elevated temperature (p. 103). Such a reorientation, followed by recrystallization, occurs particularly in liquids which have a pronounced solvating effect (i.e., are strongly polar). It is likely that the polar liquid penetrates the noncrystalline portion of the micellar system and thus favors the tendency to crystallization. A nonpolar liquid, however, having only little or no affinity for nitrocellulose, fails to create conditions favorable to reorientation and recrystallization. As a result, the viscosity of the corresponding nitrocellulose samples increases either very little or not at all.

The decrease in viscosity after the maximum has been passed is difficult to explain. The degree of orientation and crystallization, once attained, does not change. Nor is it likely that, during standing in solution, the cellulose constituent suffers degradation. Among other possibilities, it is suggested that the viscosity measurements might be influenced by remainders of the polar liquid which are difficult to remove even by intensive drying, or by the dissolving action of the polar liquid upon some (undefined) intermicellar substance. Because these explanations are rather vague, it is hoped that further research will furnish a more satisfactory explanation.

Changes of Viscosity on Addition of Nonsolvents. More information is available on those nitrocellulose-solvent systems in which the composition of the solvent is gradually changed. As has been seen, in such systems (for example, ether-alcohol with increasing amounts of aqueous alcohol or acetone with increasing amounts of water) the optimum solvent power is reached when the viscosity is at its minimum. No doubt, in this case, as when the solvent composition is not changed (i.e., on mere standing of a nitrocellulose solution), solvation and desolvation play an essential part in bringing about viscosity changes. However, whereas the changes of the colloidal system of a nitrocellulose solution on mere standing extend over a very long period of time, those brought about by altering the solvent composition proceed within minutes or, at the most, hours.

The changes in viscosity which take place in a solution of nitrocellulose in acetone to which increasing quantities of water are added are illustrated diagrammatically in Fig. 55. When no water is present, the viscosity is very high; it falls as the percentage of water is increased, reaching a minimum with 7.8 per cent water whereafter it increases.

Highfield[141] has explained this phenomenon as follows: "When nitrocellulose is dispersed in acetone-water mixtures, the molecular aggregates of nitrocellulose can be presumed to absorb solvent. In the case of the sol in the optimum solvent, the composition of the absorbed liquid must be approximately the same as that of the solvent, as otherwise the composition of the optimum solvent should vary with the concentration of the nitrocellulose. Some of the solvent is to be regarded as more or less bound to the nitrocellulose aggregates and as a result the free flow of the molecules of liquid is restricted. The sols therefore have a high viscosity compared with the solvent.

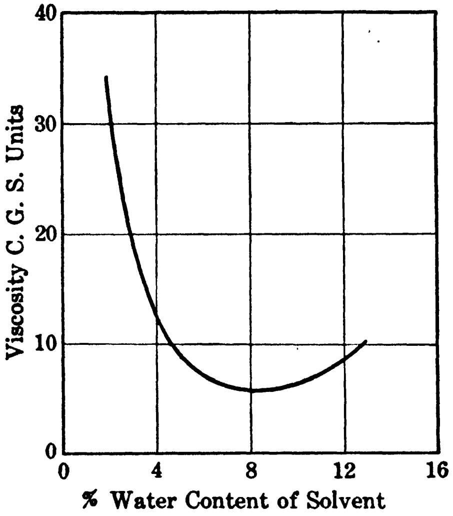

FIG. 55. Viscosity of 4 per cent nitrocellulose solutions in acetone-water mixtures. Highfield.

"With less water than the optimum solvent, the absorbed liquid will be richer in water than the remaining unabsorbed solvent. The molecular aggregates will therefore be surrounded, not only with absorbed liquid as in the case of the optimum solvent, but with a liquid whose composition alters progressively from the nitrocellulose molecular ag-

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[141] Highfield, *Trans. Faraday Soc.*, **22**, 74 (1926).

gregate outwards. The viscosity will therefore be expected to be higher. In this way the steep left-hand limb of the 'U' curve is accounted for.

"With excess of water the absorbed solvent will be richer in acetone than the remaining solvent. Since these solvent mixtures contain a large proportion of acetone, the difference between the absorbed solvent and the unabsorbed solvent will not be so great as in the previous case. The right-hand limb of the 'U' curve is hence less steep than the left-hand limb."

The development of structural viscosity in binary and ternary nitrocellulose systems has been investigated by Nisizawa[142] and by Scheiber and Baier.[143] Some data are also available on the changes in viscosity of the nitrocellulose-acetone-water system at very low nitrocellulose concentration (0.062 per cent).[144] In numerous other systems, no change of the viscosity was observed; examples are nitrocellulose solutions in butyl acetate to which increasing quantities of the following liquids had been added: petroleum ether, cyclohexanone, ethyl alcohol, chloroform, carbon tetrachloride, and chlorobenzene. Also, in the nitrocellulose-butyl acetate-benzene system the viscosities remained constant up to 50 per cent benzene addition, but 15 per cent more benzene caused the nitrocellulose to precipitate in the form of a swollen mass. Further research is required to elucidate these observations.

Influence of the Degree of Polymerization of the Cellulose upon Viscosity. The influence of certain pretreatments of degrading nature of cellulose upon the viscosity of its nitrate derivative was probably first recognized by Berl and Klaye.[145] They found that the more severe the pretreatment, the lower the viscosity of the nitrate. Even less severe treatments, such as may result from the mercerization or the bleaching of cellulosic materials, were observed to be reflected in the viscosities of the nitrates.[146]

Gibson and co-workers[147] established this relation more firmly and concluded that "the property inherent in cellulose to which viscosity is due is transmitted to the nitrated derivative."[148]

The possibility of obtaining nitrocellulose solutions of low viscosity without too much sacrifice in concentration is important in view of various commercial

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[142] Nisizawa, *Kolloid-Z.*, **56**, 61, 179, 181, 317 (1931).

[143] Scheiber and Baier, *Kolloid-Z.*, **43**, 363 (1936).

[144] Staudinger and Sorkin, *Ber.*, **70**, 2007 (1937).

[145] Berl and Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 381 (1907); **4**, 81 (1909); Berl and Bütler, *ibid.*, **5**, 82 (1910).

[146] Piest, *Z. angew. Chem.*, **24**, 968 (1911).

[147] Gibson, *J. Chem. Soc.*, **117**, 479 (1920); Gibson, Spencer, and McCall, *ibid.*, p. 484.

[148] See also Robertson's summary in *Kolloid-Z.*, **28**, 480 (1920).

uses of such solutions, for example, in the preparation of lacquers. Reference is made to various patents (for example, those of Chardonnet and of Berl), according to which cellulose is heated in air, in carbon dioxide, nitrogen, or hydrogen up to a temperature of 150–170° or in glycerin at 100° and higher to obtain low viscosity nitrocellulose solutions from such pretreated cellulosic materials.[149] Today, most low viscosity nitrates are prepared by heating the nitrate suspended in water at elevated temperature and pressure (see later).

The relationship between the viscosity of the original cellulose and that of its nitrate has also been demonstrated by Krüger,[150] who utilized this relationship for following the depolymerization of cellulose which occurs under the influence of alkali in the process of aging. On the assumption that the process of nitration does not degrade the cellulose, the results obtained with the nitrates reveal the state of depolymerization of the alkali cellulose, the underlying idea being the same as in the investigations of Schieber and co-workers and of Mark cited in Chapter IV, p. 131.

Influence of the Degree of Substitution upon Viscosity. The question arises whether or not the nitrogen content as such has an influence upon the viscosity of the nitrate in solution. We have seen from the work of Schiemann and Kühne that, with decreasing nitrogen content, the viscosity decreased; this decrease, however, was due to the increasing water content of the nitration acid which caused the cellulose to become degraded. Therefore, in such cases[151] it is difficult to tell whether the change in the nitrogen content has any direct influence upon the viscosity. However, cases are known in which the degradation of cellulose during the nitration process is practically eliminated and in which the change in viscosity thus appears to be caused by a change in the degree of substitution. Krüger[152] found that the radical drop in viscosity, i.e., from 203 seconds for a nitrate with 11.96 per cent nitrogen to 27 seconds for a nitrate with 11.05 per cent nitrogen, was not accompanied by a change in particle size (measured by the diffusion method). Moreover, when a nitrate was renitrated several times under carefully controlled conditions, the viscosity increased after each renitration. These findings confirm earlier results of Berl and Klaye[153] and of Berl and Hefter.[154]

Additional results demonstrating the direct influence of the degree of substitution upon the viscosity were reported by Rogowin and

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[149] Reistötter, *Kolloid-Z.*, **41**, 362 (1927).

[150] Krüger, *Cellulosechem.*, **8**, 1 (1927).

[151] See also Ishiwasa, *Cellulose Ind.* (Tokyo), **9**, 19 (1933); Leysieffer, *Kolloid-Beihefte*, **10**, 145 (1918); Berl and Klaye, *loc. cit.*, **2**, 381 (1907); Lunge, *Z. angew. Chem.*, **19**, 2051 (1906).

[152] Krüger, *Cellulosechem.*, **15**, 85 (1934).

[153] Berl and Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 403 (1907).

[154] Berl and Hefter, *Cellulosechem.*, **14**, 70 (1933).

Schlachover.[155] They nitrated and renitrated cotton linters by the method of Bouchonnet, Trombe, and Petitpas, using acetic anhydride as a catalyst and acetic acid as a diluent, a method which, as has been pointed out, involves hardly any degradation of the cellulose. The viscosity of the resulting nitrates was determined in acetone solution, both as absolute viscosity (concentration 2 per cent) and as specific viscosity (concentration 0.25 per cent). The results are shown in Table 24. It is seen from these data that the viscosity increases considerably with the degree of substitution.

TABLE 24

INFLUENCE OF THE DEGREE OF SUSTITUTION UPON THE VISCOSITY OF NITROCELLULOSE

No.	Materials	Nitrogen %	Absolute Viscosity, 2% Acetone Solution, Seconds	Specific Viscosity, 0.25% Acetone Solution
1	Original nitrate	11.40	93	0.78
2	Renitrated	13.39	348	1.75
3	Original nitrate	11.28	186	0.95–1.0
4	Renitrated	12.40	510	1.30
5	Renitrated	13.40	910	2.85
6	Original nitrate	11.21	51	0.6
7	Renitrated	13.41	153	1.4

It would appear that an explanation of the dependence of the viscosity upon the degree of substitution is found in the changes in the nitrate of the ratio of nitrated to unnitrated hydroxyl groups. This ratio, as has been seen, governs the solubility of nitrates of the same degree of polymerization, and it is conceivable that it controls the extent to which a nitrate is capable of becoming solvated by the solvent or solvent mixture. The degree of solvation—for example in acetone—increases with the degree of substitution and, with increased solvation, the viscosity increases.[156]

It is surprising that Staudinger and Mohr,[157] in commenting on Rogowin and Schlachover's results, still hold that "differences in the nitrogen content influence the viscosity of nitrocellulose solutions very little" and that, if such differences are observed, they are a result of different nitration methods. Evi-

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[155] Rogowin and Schlachover, *Angew. Chem.*, **48**, 649 (1935); see also Wannow, *Kolloid-Z.*, **102**, 29 (1943). Regarding renitration of cellulose nitrates, see also Fabel and Fritzsche, *Nitrocellulose*, **10**, 24 (1939).

[156] It must also be considered that cellulose nitrates tend to form addition compounds with organic solvents—for example, with nitroaniline [see Meyer, Schuster, and Bülow, *Melliand Textilber.*, **7**, 29 (1926)] and with acetone [see Tomonari, Trogus, and Hess, *Z. physik. Chem.*, **B16**, 241, 351 (1932)].

[157] Staudinger and Mohr, *Ber.*, **70**, 229 (1937).

dently, Staudinger and Mohr overlook the fact that Rogowin and Schlachover did not use different nitration methods; the only change was in the concentration of the nitric acid.

Obviously, the existence of a relationship between degree of substitution and viscosity cannot be denied and must be taken into consideration, particularly if viscosity data are to be used for calculating the molecular weight of cellulose nitrates and other cellulose derivatives (see Chapter XV).

Influence of After-Treatments upon Viscosity. The viscosity of nitrocellulose may be lowered, without the nitrogen content entering into the relationship between viscosity and chain length, by certain after-treatments. The simplest treatment consists in boiling the nitrate with water under pressure.

Commercially, this method has replaced almost all other methods which were previously used to adapt the viscosity of nitrocellulose to its particular use (see above). The method of boiling the nitrate with water under pressure probably originates from O. R. Schulz to whom a German patent on this process was granted in 1899, the object of which, however, was to effect stabilization of the nitrate.[158] That at the same time the viscosity was lowered without impairing other properties of the nitrate, provided the process is carefully controlled, was discovered later.

Schulz's method for producing low viscosity nitrocellulose has been used for various purposes.[159] Fritze[160] employed it for the preparation of a polyhomologous series of nitrates. It is interesting to note that on such treatment, carefully controlled, the nitrogen content of the nitrates remains practically the same, so that this method appears to be superior to that applied by Staudinger and co-workers for the same purpose (p. 200).

Fritze's method consists in heating nitrocellulose in the presence of water, first to the boiling point of water for a short time under normal pressure, and then for increasing lengths of time (up to 430 minutes) at a temperature of 134° in an autoclave equipped with a stirrer. The viscosity of nitrates thus treated was determined in butyl acetate at a concentration of 2 per cent, with the results shown in Table 25.[161] These results (which were also expressed in terms of molecular weight) may be interpreted to mean that, by the water-boiling method, glycosidic linkages are broken, resulting in shorter-chain

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[158] H. Schulz, *Kolloid-Z.*, **64**, 252 (1933).

[159] Craik and Miles, *Trans. Faraday Soc.*, **27**, 759 (1931); see also Highfield, *ibid.*, **22**, 72 (1926), and Inoue, Nakazawa, and Kimura, *Cellulose Ind.* (Tokyo), **16**, 5 (1940).

[160] Fritze, doctoral dissertation, Darmstadt (1938).

[161] Fritze, *loc. cit.*, p. 56.

molecules, whereas the degree of substitution remains unchanged within a certain range of temperature and time of treatment.

Wehr[162] has carried out similar experiments with a solution of nitrocellulose in butyl acetate (10 per cent concentration) at a temperature of 60° and for times up to 360 days. He found that, with increasing time, the viscosity decreased rather uniformly. Similar results were obtained when the nitrocellulose was dissolved in methylethylketone. It would appear, however, that in Wehr's experiments some hydrolysis (due to remainders of acid in the organic liquids) participated in the viscosity decrease.

TABLE 25

DECREASE OF VISCOSITY OF NITROCELLULOSE BY BOILING IN WATER UNDER PRESSURE

Materials	Nitrogen Content %	Time of Heating at 134°, Minutes	Time of Flow, Seconds		Absolute Viscosity (η abs)
			Capillary I	Capillary II	
Original	12.12	...	...	370	1.220
I	12.01	15	...	110	0.360
II	12.02	40	480	63	0.190
III	11.98	90	254	32	0.100
IV	11.98	165	178	16	0.050
V	11.97	295	75	...	0.029
VI	11.87	430	54	...	0.021

Stability of Nitrocellulose. As has been pointed out on several occasions, the stability of nitrocellulose depends upon various factors, particularly upon the presence or absence of combined sulfuric acid.

On standing, sulfuric acid is liberated and subsequently cleaves off nitrate groups. The nitric acid thus set free oxidizes the cellulose constituent, giving rise to the formation of unstable products. In fact, Kumichel[163] has extracted nitrated degradation products from nitrocellulose solutions.

The presence of such cellulose degradation products favors the decomposition of the rest of the nitrate. In addition, noncellulosic substances, especially those present in wood pulp, are said to exert an unfavorable influence upon the stability of the nitrocellulose (see p.

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[162] Wehr, *Kolloid-Z.*, **88**, 290 (1939).

[163] Kumichel, *Kolloid-Beihefte*, **26**, 175 (1928).

225). It is claimed that even cotton linters may contain such noncellulosic impurities, and that their effect upon the stability is quite noticeable.[164]

Decomposition is accelerated by external influences, especially by temperature and light; for this reason it is essential that nitrocellulose (usually kept in an aqueous or alcoholic suspension) be stored in dark, cool places.

Light seems to diminish the viscosity of nitrocellulose considerably. Donald [165] found that this change occurred even under the influence of the diffused light in the laboratory, after about a week. Similar observations were made by McBain, Harvey, and Smith.[166] Ultraviolet light has a very marked effect. This may be demonstrated by exposing nitrocellulose, either as such or dissolved in an organic solvent, to irradiation with a quartz lamp for a certain period of time. Thus, Kumichel [167] found that the viscosity of nitrocellulose in solution dropped to about one-half of its original value after 5 hours of exposure. Clément, Rivière, and Beck [168] observed a simultaneous increase of the solubility of nitrocellulose exposed in ether-alcohol. Since under these conditions the nitrogen content also decreased, the increase in solubility may be due to both loss of nitrogen and degradation. It is interesting to note that Clément and co-workers found that the viscosity decreased only with nitrates of the high viscosity type, those of lower viscosity being unaffected.

Montana [169] has confirmed the decrease in viscosity and the increase in solubility, but otherwise observed no chemical changes, except a very slight decrease of the nitrogen content on long exposure. That decomposition of both cellulose and nitrate groups occurs is seen from the work of Berthelot and Gaudechon [170] who reported the evolution of carbon dioxide, carbon monoxide, nitrogen, and nitrous oxide (N_2O).

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[164] Berl and Rueff, *Cellulosechem.*, **14**, 113 (1933).

[165] Donald, *J. Soc. Chem. Ind.*, **30**, 785 (1911).

[166] McBain, Harvey, and Smith, *J. Phys. Chem.*, **30**, 322 (1926).

[167] Kumichel, *Kolloid-Beihefte*, **26**, 177 (1928). See also Devore, Pfund and Cofman [*J. Phys. Chem.*, **33**, 1837 (1929)] who exposed nitrocellulose in the form of very thin films and found that they had become acid, brittle, and discolored and that their solution viscosity had considerably decreased.

[168] Clément, Rivière, and Beck, *Chimie & industrie*, Special Number, 702 (1932).

[169] Montana, International Congress of Chemistry, Rome (1938); *Chimica e industria (Italy)*, **20**, 237 (1938).

[170] Berthelot and Gaudechon, *Compt. rend.*, **154**, 201 (1912); see also Guilbaud, *ibid.*, **161**, 212 (1915).

The viscosity of nitrocellulose decreases also under the action of *ultrasonic* waves.[171] The effect is more pronounced with long- than with short-chain nitrocelluloses and comes practically to a standstill after some time, even if the time of treatment is lengthened considerably. This seems to indicate that the shorter chains are attacked very little. Such an equalization is noticeable even after a relatively short time of treatment.[172]

When the viscosities of a 0.10 per cent solution of a nitrocellulose preparation (nitrogen content of 13.23 per cent) were converted into molecular weights, using Staudinger's equation and extrapolating the viscosities to zero concentration, a decrease from an initial value of 123,000 to 70,000–80,000 was observed.[173]

No evidence could be produced which would indicate that the shortening of the chain molecules was caused by a chemical reaction, and the hypothesis is advanced that the effect is of a purely mechanical nature. It is suggested that the chain molecules are stretched and eventually broken by the forces of friction produced on contact between them and the violently oscillating particles of the liquid.

If this were true, it certainly would be of considerable interest, because it is one of the apparently rare cases of rupture of primary valences by mechanical forces. Such rupture need not necessarily occur on the glycosidic linkages. By analogy with results obtained with other linear polymers, it appears possible that —C—C— linkages are broken. A similar hypothesis was invoked when it was found that the viscosity of cellulose and wood was decreased by disintegration in the ball mill without any indication of a chemical reaction.[174]

The nitrates having nitrogen contents corresponding to the "di-" and "mononitrate" stage and to intermediate stages are easily inflammable; they burn very quickly, whereas the higher nitrates and the trinitrate are highly explosive when detonated by a blow or by means of an auxiliary substance (for example, mercury fulminate). The products of ignition are nitrogen dioxide, carbon dioxide, and water vapor. On detonation, additional gases are produced, such as nitrogen, hydrogen, and sometimes methane and ethylene.

The degree of stability of a nitrate is indicated by its behavior on

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[171] Sollner, *J. Phys. Chem.*, **42**, 1071 (1938).

[172] Schmid and Rommel, *Z. Elektrochem.*, **45**, 659 (1939); see also *ibid.*, **43**, 408 (1937).

[173] Schmid and Rommel, *Z. physik. Chem.*, **A185**, 97, 114 (1939).

[174] Staudinger, Heuer and Dreher, *Ber.*, **67**, 1159 (1934); Staudinger and Dreher, *ibid.*, **69**, 1091 (1936). See also Hess, Kiessig and Gundermann, *Z. physik. Chem.*, **B49**, 64 (1942).

gradual heating, by which a point is reached at which the temperature becomes high enough to cause the nitrate to burn with or without explosion (ignition point). A high ignition point indicates a stable nitrate and *vice versa*. A stable nitrate should stand a temperature of 180° before ignition occurs.

Commercially, the stability of cellulose nitrate is determined from the rate of decomposition of the sample. This rate is accelerated to a measurable amount by heat (65–135°). It is measured either as the time to react in part or fully with a test paper,[175] or as the amount of nitrous gas evolved over a given time.

Numerous investigations have been published on the decomposition of cellulose nitrates and the gaseous products of reaction. The reader is referred to the literature, as given below.[176] A summary of the tests in use may be found in the publications of the American Society for Testing Materials[177] and elsewhere.

Hydrolysis (Saponification) of Nitrocellulose. Since nitrocellulose is an ester, it may be hydrolyzed or saponified. However, no agent has thus far been found which is capable of completely regenerating the inorganic constituent of the nitrate without affecting the cellulose. If information on the nature of the regenerated cellulose is not essential and only on the degree of substitution is desired, hydrolysis may be achieved by means of strong sulfuric acid. Under these conditions, the nitrate groups are completely converted into nitric acid. For analytical purposes the nitric acid may be reduced to nitric oxide, which can be determined volumetrically in the Lunge nitrometer (method of Lunge and Lubarsch[178]). Other acids (for example, nitric acid) also

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[175] For example, Methyl Violet paper, this test paper losing its violet color under the influence of the acid fumes liberated from the sample.

[176] Berl and Delpy, *Z. ges. Schiess- u. Sprengstoffw.*, **8**, 129 (1913); Berl and Kunze (microchemical method), *Angew. Chem.*, **45**, 669 (1932); Berl and Rueff, *Cellulosechem.*, **14**, 43, 44, 109 (1933); Hill and Webber, *J. Soc. Motion Picture Engrs.*, **27**, 677 (1936); Berl, Rueff, and Carpenter, *Ind. Eng. Chem., Anal. Ed*, **10**, 219 (1938). The latter article gives a comprehensive list of literature. See also Fritze, doctoral dissertation, Darmstadt (1938), p. 47; Marshall, "Explosives," Blakiston's Son & Co., Philadelphia (1917 and 1932); Thorpe, "A Dictionary of Applied Chemistry," Vol. III, pp. 1–98, Longmans, Green & Co., London and New York (1928), Supplement (1934), pp. 437–454; Worden, "Technology of the Cellulose Esters," Vol. I, Part III, Eschenbach Printing Co., Easton, Penn. (1921). See also Wiggens and Goodyear, *Ind. Eng. Chem., Anal. Ed.*, **4**, 77 (1932); Ryan and Lautz, *Ind. Eng. Chem.*, **20**, 40 (1925).

[177] American Society for Testing Materials, "Standard Methods"; Philadelphia (1939), Vol. II, p. 790.

[178] Lunge-Berl, "Technische Untersuchungs-Methoden," Vol. III, p. 1266, Springer, Berlin (1932); see also Dorée, "Methods of Cellulose Chemistry," p. 229.

split off the nitrate groups. In all cases, the cellulose is degraded, usually so completely that it can no longer be regenerated.[179]

Saponification with alkalies is unsuitable, because the nitrate groups are regenerated only incompletely; again, the cellulose is degraded. Among the products of decomposition have been found formic, oxalic, and hydroxypyruvic acid [$CH_2(OH)COCOOH$],[180] aldehydes,[181] and various other substances. It is very probable that these products are formed from cellulose under the influence of the oxygen liberated from the nitrate groups.[182] Simultaneously, these decomposition products exert a reducing effect upon the sodium nitrate resulting from saponification, so that the latter is converted partly into nitrite[183] and partly into ammonia and nitrogen.[184]

The indirect oxidizing effect of the alkalies is diminished by the presence of certain reducing salts, such as ferric, copper, and tin salts, and the cellulosic constituent is regenerated in fibrous form, although the yield is not quantitative.[185] The nitrate groups are reduced to ammonia. Such methods were previously used for ascertaining the degree of substitution but have been abandoned in favor of the sulfuric acid method or modifications.[186] The same is true with regard to Lunge and Weintraub's method, in which alcoholic sodium ethylate solution is used.[187]

If the main object is to regenerate the cellulose as completely as possible and with the least amount of degradation, those chemicals which are used for "denitrating" nitrocellulose rayon (and thus depriving it of its inflammability),[188] seem to be the only suitable agents at the present time. These are alkali sulfides, polysulfides, and thiocarbonates, but more particularly alkali and ammonium hydrosulfides.

Ammonium hydrosulfide (NH_4SH) was widely used commercially

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[179] Häussermann, *Chem.-Ztg.*, **29**, 421 (1905); *Ber.*, **36**, 2956 (1903).

[180] Will, *Ber.*, **24**, 400 (1891); Berl and Smith, *J. Soc. Chem. Ind.*, **27**, 537 (1908).

[181] Häussermann, *Ber.*, **36**, 3956 (1903).

[182] Hess, "Die Chemie der Cellulose," p. 379; Kenyon and Gray, *J. Am. Chem. Soc.*, **58**, 1422 (1936).

[183] Silberad and Farmer, *J. Chem. Soc.*, **89**, 1759 (1906); Carlson, *Ber.*, **40**, 4192 (1907).

[184] Häussermann, *Chem.-Ztg.*, **29**, 421 (1905).

[185] Hess, "Die Chemie der Cellulose," p. 380.

[186] Schiemann and Kühne, *Cellulosechem.*, **15**, 79 (1934).

[187] Lunge and Weintraub, *Z. angew. Chem.*, **12**, 473 (1899).

[188] Süvern, "Die künstliche Seide," Springer, Berlin (1926). See also Weingand, *Papier-Fabr.*, **35**, 93 (1937).

as a denitrating agent[189] when nitrocellulose rayon was still manufactured. Similar effects are obtained with sodium, potassium,[190] and calcium hydrosulfide.[191]

A more systematic study of the effect of various denitrating agents upon the properties of the regenerated cellulose was made by Rassow and Dörr.[192] They found the hydrosulfides of potassium and of ammonia more effective in alcoholic than in aqueous solutions. At a temperature of 20–40°, denitration was practically complete after 2–6 hours, depending upon the type of nitrocellulose under investigation. The authors point out, however, that the nitrate groups cannot be eliminated entirely, the sulfuric acid-diphenylamine test[193] indicating in all cases the presence of greater or smaller residues of nitrogen.

Obviously, the extent to which the nitrate groups may be removed by denitrating agents depends not only on the conditions of the treatment but on other factors as well, the influence of which, however, has not been fully elucidated. According to Hess,[194] who found that the denitrated fibers retained as much as 1–2 per cent nitrogen, it is essential that the denitrating agent be well distributed. This is facilitated by the use of a high liquid-nitrocellulose ratio, but probably not by the use of an alcoholic rather than an aqueous solution, because, in the former, nitrocellulose swells less than in the latter. This difference was demonstrated by Frey-Wyssling.[195] Under the microscope, it may be observed that denitration in alcoholic ammonium sulfide solution begins in spots on the surface of the fiber and proceeds into the inner layers.[196] In aqueous solution, however, the reaction proceeds much more uniformly, that is, as a uniform band from the outside to the center of the fiber.

Staudinger and Mohr,[197] studied a number of variations of the ammonium hydrosulfide method but found that the regenerated cellulose

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[189] Piest, "Die Cellulose," Ferdinand Enke, Stuttgart (1910), p. 36; Piest, *Z. angew. Chem.*, **23**, 1009 (1910).

[190] Piest, "Die Cellulose," p. 36.

[191] Schwalbe, *Z. angew. Chem.*, **21**, 2404 (1908); Piest, *loc. cit.*, p. 36.

[192] Rassow and Dörr, *Z. angew. Chem.*, **108**, 121, 163 (1924); see also Hess, "Die Chemie der Cellulose," p. 383; also Atsuki, *J. Soc. Chem. Ind., Japan*, **45**, 1336 (1925).

[193] Dorée, "The Methods of Cellulose Chemistry," p. 235.

[194] Hess, "Die Chemie der Cellulose," pp. 380 and 381, footnote 3.

[195] Frey-Wyssling, *Protoplasma*, **26**, 45 (1936); see also Spurlin, *Trans. Electrochem. Soc.*, **73**, 106 (1938).

[196] See also Tomonari, *Z. Elektrochem.*, **40**, 1207 (1934).

[197] Staudinger and Mohr, *Ber.*, **70**, 2306 (1937).

still contained 0.5–1.0 per cent nitrogen. The results of Davidson[198] seem to indicate that the time of treatment is the essential factor; more than 20 hours were necessary to reduce the nitrogen content to 0.5 per cent, whereas 10 hours resulted in a nitrogen content of 1.43 per cent. Fritze,[199] who employed a modification of Rassow and Dörr's technique, ascertained the degree of denitration by observing the preparation under the polarization microscope. The fiber, when completely denitrated, shows the same refractive index as the original fiber (see also p. 188).

Earlier claims that cellulose is regenerated from the denitration treatment without degradation were based merely upon the observation that it retains its fibrous structure. The results of later studies, however, revealed that the cellulose is attacked during denitration even under the mildest conditions. Staudinger and Mohr found the degree of polymerization of the regenerated cellulose to be as low as 120–300 (corresponding to molecular weights of 20,000–50,000), figures which are in agreement with the degree of polymerization of 200 for nitrorayon.[200] Similar results were obtained by Rogowin and Schlachover[201] and by Davidson.[202] Since cellulose itself is scarcely affected by the alkali hydrosulfides under the conditions of denitration, it is very probable that the degrading effect is due to liberation of oxygen from the nitrate groups and subsequent oxidation of the cellulose, in much the same way as during the saponification of the nitrate with aqueous alkalies.

The degradation of the cellulose is reflected in the relatively low yield of regenerated cellulose, 95 per cent[203] and 90–96 per cent[204] being reported. Since the latter values were obtained with cellulose nitrates which had been subjected to boiling in water under pressure, the low yields on denitration may be due in part to some degradation and loss of short-chain material during the pressure-boiling procedure.

The inorganic reactions involved in the process of denitration may be expressed by the following equations:

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[198] Davidson, *J. Textile Inst.*, **29**, T208 (1938).

[199] Fritze, *loc. cit.*, p. 45.

[200] Staudinger and Feuerstein, *Ann.*, **526**, 97 (1937).

[201] Rogowin and Schlachover, *Angew. Chem.*, **48**, 649 (1935); see also Lenze and Rubens, *Kunststoffe*, **21**, 3 (1931).

[202] Davidson, *loc. cit.*, p. T214; see, however, Okada, *Cellulosechem.*, **10**, 120 (1929).

[203] Hess, "Chemie der Cellulose," p. 380.

[204] Fritze, *loc. cit.*, p. 59.

$$C_6H_8O_3(ONO_2)_2 + 2NaSH \rightarrow C_6H_{10}O_5 + 2NaNO_2 + 2S$$

$$2NaSH + 2S \rightarrow Na_2S_3 + H_2S$$

Thus, simultaneously with the saponification, the nitrate groups are reduced to the nitrite step. This reduction may even extend to ammonia.

Kinetically, the reaction of denitration follows the law of a first order reaction.[205]

Aminocellulose

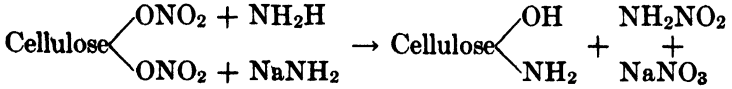
Recently, Scherer and Feild,[206] succeeded in introducing the amino group into cellulose by allowing sodium or potassium amide to act upon nitrocellulose in liquid ammonia.

If it is assumed that the reaction takes place according to the equation

$$C_6H_8O_3(ONO_2)_2 + 2NaNH_2 \rightarrow C_6H_8O_3(NH_2)_2 + 2NaNO_3$$

each nitrate group in the chain should contain (since nitrocellulose, corresponding to the dinitrate stage was used as the starting material) 17.5 per cent amino nitrogen. Analysis, however, showed only 8.35 per cent nitrogen, practically all of which was amino nitrogen. This amount corresponds to only 1 amino group per glucose residue (8.6 per cent theoretically required). It follows, therefore, that one-half of the nitrogen originally present in the nitrocellulose reacted in some manner in order to be replaced by a hydroxyl group and only one-half reacted to form the amino group. Scherer and Feild offer the following mechanism to account for the result obtained:

It is possible that two reactions take place. The first is a methathetic removal from the nitrocellulose of one nitrate and the introduction of one amino group. The second reaction might consist of aminolysis of the remaining nitrate group by the solvent in the presence of sodium amide, just as nitrate groups are removed by water in the presence of sodium hydroxide. If both reactions occurred to a nearly equal extent, the result should be a monoamine of cellulose. Thus:



$$\text{Cellulose}\begin{cases} ONO_2 + NH_2H \\ ONO_2 + NaNH_2 \end{cases} \rightarrow \text{Cellulose}\begin{cases} OH \\ NH_2 \end{cases} + \begin{matrix} NH_2NO_2 \\ + \\ NaNO_3 \end{matrix}$$

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[205] Nádai, *Z. physik. Chem.*, **136**, 289 (1928).

[206] Scherer and Feild, *Rayon Textile Monthly*, **22**, 607 (1941).

The aminocellulose which was obtained in the form of a reddish yellow powder was very easily soluble in water, so much so that, when once dissolved, it could not be precipitated from solution by the addition of alcohol. If the aqueous solution was evaporated, a gummy reddish solid remained which was exceedingly hygroscopic. The aminocellulose was soluble in alkalies and in concentrated and dilute mineral acids, but was insoluble in methyl alcohol, ethyl alcohol, ether, and acetone.

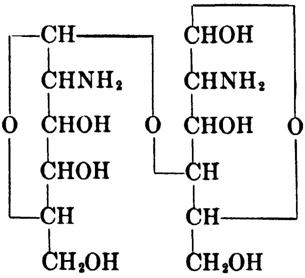
It would appear that the cellulose was considerably degraded but the extent was not determined.

When acetyl chloride was added to the water solution of the aminocellulose which had been prepared with the use of potassium amide, an acetylaminocellulose was obtained, the analysis of which designated it as a monoacetylmonoaminocellulose.

Aminocellulose was also obtained by allowing metallic sodium—without first being converted into sodium amide—to react with nitrocellulose. This preparation also yielded an acetyl derivative. The reaction involved in the action of sodium alone is still unexplained.

Aminocellulose was diazotized by treatment with nitrous acid and coupled with resorcinol to give a reddish dye. In view of the aliphatic nature of cellulose, it appears remarkable that its amino derivative could be diazotized and coupled in a manner analogous to the aromatic series.

Aminocellulose, being a polymeric glucosamine, might be compared with chitin. On the acetolysis of the chitin from lobster shells, chitobiose was obtained. It is a diglucosamine:[207]



The similarity of chitin and cellulose is also derived from the results of x-ray studies on chitin, chitosan, and their derivatives.[208] Regarding earlier attempts to prepare aminocellulose see p. 299.

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[207] Bergmann, Zervas, and Silberkweit, *Ber.*, **64**, 2436 (1931).

[208] Clark and Smith, *J. Phys. Chem.*, **40**, 863 (1936).

The Nature of the Cellulose Regenerated from the Nitrate

The question whether cellulose is regenerated from the nitrate in the form of a physically unchanged fiber or in the form of its mercerized modification has not as yet been clearly answered. Considering that the cellulose fiber becomes mercerized with strong mineral acids in much the same way as on treatment with strong alkalies, one would expect it to undergo this change while in contact with the nitration acid mixture. On denitration, this change would either be enhanced or remain unaltered, depending upon the concentration and temperature of the denitrating agent. Whereas Herzog[209] found that the x-ray pattern of cellulose fibers, regenerated by means of alkali hydrosulfide from nitrocotton and nitroramie (which had been prepared with sulfuric acid as the dehydrating agent) was the same as that of the original fiber, Miles and Milbourne[210] identified it in all cases in which it was sharp enough for evaluation as that of mercerized cellulose. Likewise, Berl and Rueff's investigation reveals erratic results,[211] whereas later on no discrepancies were observed,[212] the x-ray pattern of the regenerated cellulose in all cases being characteristic of the cellulose hydrate modification. Possibly, more or less degradation of the cellulose during nitration is responsible for the erratic results.[213]

The commercial uses of nitrocellulose are numerous, a considerable portion being consumed by the explosives and the motion picture film industries. An equally considerable quantity is used by the lacquer and the plastics industry. The useful commercial range of nitrogen contents is from approximately 10.5 to 13.9 per cent. The nitrates employed in explosives (under such terms as guncotton and pyroxyline) vary in nitrogen content from approximately 12.2 to 13.8 per cent, those in lacquers from 11.5 to 12.2 per cent, and in plastics from 10.5 to 11.5 per cent nitrogen.[214] The products also differ widely as to

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[209] Herzog, *J. Phys. Chem.*, **30**, 466 (1926); Herzog and Jancke, *Z. physik. Chem.*, **139**, 255 (1928).

[210] Miles and Milbourne, *J. Phys. Chem.*, **34**, 2606 (1930); Miles and Craik, *ibid.*, **34**, 2611 (1930).

[211] Berl and Rueff, *Cellulosechem.*, **12**, 56 (1931).

[212] Berl and Hefter, *ibid.*, **14**, 75 (1933).

[213] Miles and Craik, *loc. cit.*, p. 2613.

[214] Conaway, *Ind. Eng. Chem.*, **30**, 518 (1938). In addition, the following references pertain to commercial uses of nitrocellulose: Brown and Crawford, "A Survey of Nitrocellulose Lacquer," Chem. Catalog Company Inc., New York (1928); Robinson, "The Application of Cellulose Lacquers and Enamels," Scott, Greenwood & Son, London (1929); "A History of the duPont Company's Relations with the U. S. Government (1802–1927)," Smokeless Powder Dept., E. I. duPont de Nemours & Company, Inc., Wilmington, Delaware (1928)

molecular size. According to Kraemer,[215] dynamite-type nitrocellulose has an average degree of polymerization of 3000 to 3500, the plastics type approximately 500 to 600, and the lacquer type about 175. Celluloid, a compound containing nitrocellulose and camphor, has been an outstanding plastic for many years. Today, however, much of it is being replaced by cellulose acetate and other simple or mixed esters of cellulose, which are not inflammable. Many attempts have been made to substitute the noninflammable esters and ethers for nitrocellulose in motion picture films but with little success. Recently, the German government prohibited the use of nitrocellulose films in motion pictures and stipulated the use of acetate films instead.[216]

The chief raw material for nitrocellulose is cotton linters, but today much of it is being replaced by the cheaper wood pulp.[217] Considerable quantities of bleached sulfite pulp from spruce were used during World War I, particularly in countries which were cut off from cotton and cotton linters supplies. In the meantime, in this country also, bleached sulfite pulp as well as other types have become a more regular source of raw material for the manufacture of nitrocellulose to be used in the lacquer, plastics, and explosives industries.

Wood pulp contains a number of noncellulosic substances which are practically absent in cotton linters, particularly xylan and mannan, and resin and fatty acids. On nitration of the wood pulp, the noncellulosic carbohydrates are also converted into nitrates[218] and the resins and acids possibly into nitro compounds. These reaction products decompose more easily under the influence of moisture, light, and temperature than cellulose nitrate itself. In addition, wood pulp contains more degraded cellulose than cotton linters, and this increases the amount of more easily decomposable nitrates. Although most of these reaction products are removed by the process of stabilization, those which are retained (possibly the resinous nitro compounds) may constitute a certain hazard. However, since today considerable quantities of wood pulp are employed in the nitrocellulose industry, it would appear that stabilization difficulties have been overcome or that the presence of nitrates of noncellulosic carbohydrates and other impurities is less harmful than has been assumed heretofore.[219]

(this gives an interesting account of the development of smokeless powder prepared from nitrocellulose); see also *J. Am. Chem. Soc., News Edition,* **16,** 647 (1938), dealing with the life of Charles E. Munroe; Carver [*J. Soc. Motion Picture Engrs.,* **28,** 594 (1937)] discusses the use of nitrocellulose in the manufacture of motion picture films. See also the books of Marshall and Thorpe mentioned earlier, as well as Davis, "Chemistry of Powder and Explosives," John Wiley & Sons, Inc., New York (1941).

[215] Kraemer, *Ind. Eng. Chem.,* **30,** 1200 (1938).

[216] *Nitrocellulose,* **11,** 39 (1940).

[217] Schwalbe and Schrimpf, *Z. angew. Chem.,* **27,** 662 (1914); Schwalbe and Schrimpf, "Nitrocellulose aus Holzzellstoff," Lehmann's Verlag, Munich (1919); Wells and Edwardes, *Paper,* **23,** 780 (1919), Convention Number, p. 180; Schwarz, *Oesterr. Chem.-Ztg.,* Nos. 7, 9 (1919); Atsuki, *J. Fac. Eng. Chem.* (Tokyo), **15,** 117 (1924); Naiman and Troitzky, *J. Soc. Chem. Ind.,* **54,** T255 (1935).

[218] Rassow and Dörr, *J. prakt. Chem.,* **108,** 113 (1924).

[219] Wells and Edwardes, Technical Association Papers, **2,** 59 (1919); Olsen, *Ind. Eng. Chem.,* **21,** 354 (1929).

In cases in which the demands are more strict, refined wood pulp, having an *alpha*-cellulose content between 90 and 95 per cent, is being recommended. More recently, wood pulp has been purified to such an extent that its *alpha*-cellulose content and other characteristics approach those of cotton linters.[220] *Alpha* pulp of this degree of purity is expected to find its application in the manufacture of high grade nitrocellulose, such as that which is being used in the guncotton and motion picture industries.[221] The use of such a pulp would scarcely be cheaper than cotton linters, but is said to have the advantage of being a more uniform raw material than cotton linters.[222]

Nitrocellulose was the first raw material for the manufacture of artificial silk (rayon), its inventor being the Count de Chardonnet (1884).[223] It was chiefly manufactured in France, Belgium, Germany, and Hungary and, to a limited extent, also in this country. About three or four years ago it ceased to be manufactured and has since left the field to the more lucrative and less hazardous cellulose derivatives, such as cellulose xanthate (viscose), cellulose acetate, and cuprammonium cellulose.

The principle of manufacture consisted briefly in dissolving the nitrocellulose in a mixture of ether and alcohol or in acetone and forcing the solution through the fine openings of a spinning nozzle (spinnerette). When the solution leaving the spinnerettes came into contact with the air, the solvent evaporated and the filaments thus formed solidified so that they could be wound around a spool. The endless thread thus obtained had to be washed with water, denitrated, bleached, washed again, and finally dried. Owing to small residues of nitrogen, nitrocellulose rayon may be identified and distinguished from other types by the sulfuric acid-diphenylamine test (see above).[224]

CELLULOSE ACETATES

Acetic acid as such reacts rather reluctantly with cellulose as was shown by Cross, Bevan, and Traquair.[225] Even on boiling for a few hours, only 3.4–4.2 per cent acetic acid could be introduced. Somewhat higher acetyl contents were obtained by Malm and Clarke.[226]

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[220] Olsen, *Ind. Eng. Chem.*, **30**, 524 (1938).

[221] Schur and Hoos, *Ind. Eng. Chem.*, **29**, 26 (1937).

[222] Steude, *Nitrocellulose*, **7**, 161 (1936).

[223] See, for example, Rheinthaler, "Artificial Silk," Van Nostrand Company, New York (1930); Wheeler, "The Manufacture of Artificial Silk," Van Nostrand Company, New York (1931); Zart, "Herstellung und Eigenschaften der Kunstseide und Stapelfaser," Akad. Verlags-Ges., Leipzig (1935); "Rayon and Synthetic Yarn Handbook," Rayon Publishing Co., New York (1934); Schwarz, "Rayon and Staple Fiber Handbook," Rayon Handbook Co., New York (1939).

[224] Dorée, "Methods of Cellulose Chemistry," p. 235; A. Herzog, "Die mikroskopische Untersuchung der Seide und Kunstseide," Springer, Berlin (1924), p. 138.

[225] Cross, Bevan, and Traquair, *Chem.-Ztg.*, **29**, 528 (1905).

[226] Malm and Clarke, *J. Am. Chem. Soc.*, **51**, 274 (1929).

The following figures pertain to the refluxing of surgical cotton with glacial acetic acid for different lengths of time:

Time, hours	0	1	2	4	8	16	24	48	72	96
Acetyl, %	0.6	0.8	1.3	2.4	2.9	3.7	4.5	5.5	6.0	6.2

However, longer time (even 500 hours) did not increase the acetyl content and resulted in considerable degradation. About the same results were obtained with cotton linters, whereas 5.1 per cent acetyl could be introduced into commercial sulfite pulp after 24, and 7.5 per cent after 300 hours. In sealed glass tubes, the reaction was found to be more efficient; under these conditions, 4.6 per cent acetyl could be introduced into surgical cotton after 8, and 7.5 per cent after 48 hours. Again, the longer time led to degradation of the sample. The favorable influence of a lower degree of polymerization upon the degree of substitution, which is seen when the above results obtained with cotton and with wood pulp are compared, becomes still more obvious with cellulose in regenerated form, such as viscose and cuprammonium rayon and cellulose regenerated from nitrocellulose and from cellulose acetate. In all these cases, treatments for 300–400 hours resulted in an acetyl content of about 21 per cent (corresponding to about 30 per cent combined acetic acid or to 1.0 acetyl group per glucose residue). The same beneficial effect was observed with samples which had been mercerized with 18 and with 40 per cent sodium hydroxide solutions.

Analogous effects were obtained when propionic acid and *n*-butyric acid were allowed to react with surgical cotton. Within 200 hours, 8–8.2 per cent propionyl and 10.9 per cent butyryl could be introduced.

Malm and Clarke's results were confirmed by Bernoulli, Schenk, and Hagenbuch.[227] Whereas surgical cotton gave, after 500 hours, an acetyl content of 6.3 per cent, mercerized cellulose showed, after the same time of treatment, an acetyl content which corresponded to that of a monoacetate. The same degree of substitution was obtained with viscose rayon.

The use of *acetic anhydride* instead of acetic acid originates from Schützenberger[228] who in 1866 allowed the anhydride to react with cellulose in a sealed tube at 180° for some hours. Possibly, Schützenberger obtained the triacetate, although it is very probable that the cellulose was considerably degraded under these severe conditions. In

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[227] Bernoulli, Schenk, and Hagenbuch, *Helv. Chim. Acta,* **13**, 539, 550, 557 (1930).

[228] Schützenberger and Naudin, *Z. für Chemie,* 264 (1869).

fact, Bernoulli, Schenk, and Hagenbuch[229] found that cellulose (surgical cotton) was considerably degraded when it was heated with acetic anhydride at 118° (the boiling point of the anhydride) for 250–270 hours. After 261 hours, the combined acetic acid content was 38.26 per cent (corresponding to 1.57 acetyl groups per glucose residue). Still higher acetyl contents were obtained with viscose rayon, particularly after pretreatment with aqueous caustic soda solution, but the products were much degraded. The highest combined acetic acid content was 63.20 per cent, i.e., even above the theoretical requirement for the triacetate (62.51 per cent).

Acetylation in the Presence of Catalysts

Acetylation is essentially facilitated by the use of so-called catalysts, which actually are dehydrating agents, such as sulfuric acid and other acids and zinc chloride and other salts, although, as will be seen later, it is doubtful whether they act as such when acetic anhydride is the acetylation agent. The beneficial effect of sulfuric acid upon the result of acetylation is said to have been first recognized by Franchimont,[230] although his conditions of treatment were those of acetolysis rather than of acetylation.

At about the time that Franchimont's experiments were resumed by Skraup[281] and carried to the discovery of cellobiose octaacetate, sulfuric acid as a catalyst for acetylation was commercially introduced through two important patents.[232] From then on, acetylation of cellulose was carried out commercially and has developed into an important branch of the manufacture of cellulose derivatives.

Salts of dehydrating properties were probably first suggested as catalysts by Cross and co-workers. Cross, Bevan, and Briggs[233] used zinc chloride and Cross and Bevan[234] sodium acetate. Ost[235] and his school have contributed much to the clarification of the course of the reaction.

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[229] Bernoulli, Schenk, and Hagenbuch, *loc. cit.*

[230] Franchimont, *Compt. rend.*, **89**, 711 (1879); *Ber.*, **12**, 1941 (1879); *Rec. trav. chim.*, **18**, 472 (1899).

[281] Skraup, *Ber.*, **32**, 2413 (1899); Skraup and König, *Ber.*, **34**, 1115 (1901); *Monatsh.*, **22**, 1011 (1901).

[232] Lederer, German patent 163,316 (1901); Eichengrün and Becker, German patent 159,524 (1909), assigned to Elberfelder Farbenfabriken.

[233] Cross, Bevan, and Briggs, *J. Soc. Dyers Colourists*, **23**, 250 (1907).

[234] Cross and Bevan, "Researches on Cellulose," Longmans, Green and Co., London (1903), 2nd ed., Vol. I, p. 40; (1895), Vol. II, p. 11.

[235] See the compilation by Ost, *Z. angew. Chem.*, **32**, 66, 76, 82 (1919).

Acetylation in the Presence of Sulfuric Acid. The usual mixture for acetylation contains, besides acetic anhydride and sulfuric acid, a certain amount of glacial acetic acid as a solvent. At the usual temperature (which is seldom higher than 30–40°), substitution becomes complete after 7–8 hours.[236] Depending upon the degree of polymerization of the cellulosic material, the time may be shorter or longer. To insure completion of the reaction within the time mentioned, it is necessary to subject the cellulosic material to a pretreatment with a mixture of acetic acid and a small amount of sulfuric acid for some time; this results in considerable swelling of the fiber and thus facilitates acetylation.

Under the influence of the acetylation mixture (with continuous mechanical agitation, which is necessary for insuring a homogeneous mixture of the reactants), the cellulosic material loses its fibrous structure and gradually changes into a thick, viscous paste. Usually at this point, acetylation has been completed. However, it is desirable to dilute the mass with a fresh quantity of glacial acetic acid and continue the mechanical agitation for some time. The paste or colloidal solution is poured into cold water which precipitates the acetate in the form of white opaque flocks. Under these conditions, the flocks retain appreciable amounts of anhydride and acids, as well as of low molecular degradation products. For this reason, it is necessary to subject the flocks to thorough disintegration and washing with water and subsequent boiling with water.

Washing the acetate in the form of disintegrated flocks requires large quantities of water and a rather long time. In the laboratory more efficient methods of precipitation may be applied. Ost[237] recommends adding the water in portions to the diluted paste or solution under steady grinding (mortar). This ground material is more easily freed of acids on washing and subsequent boiling. Another way consists in allowing the solution, after considerable dilution with glacial acetic acid, to flow from a fine capillary into cold water while a current of compressed air from another capillary is being directed against the outflowing solution. Thus, a finely divided precipitate is obtained which, after the air has escaped, settles to the bottom of the vessel and may be easily washed and filtered.

It is important that all acid residues, particularly the sulfuric acid, as well as the cellulose degradation products, be removed as com-

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[236] For the influence of temperature upon the rate of acetylation, see Atsuki and Shinoda, *J. Soc. Chem. Ind., Japan,* **31,** 9711B (1928).

[237] Ost, *loc. cit.*, p. 66.

pletely as possible, otherwise the acetate tends to decompose on standing. Lack of stability is indicated by a gradually increasing odor of acetic acid.

In commercial practice various modifications of precipitation and stabilization are in use.[238]

Theoretically, 100 grams of cellulose require 189 grams of acetic anhydride for conversion into cellulose triacetate. Actually, a considerable excess is necessary, ranging between 250 and 400 per cent (calculated on the weight of cellulose).[239] About the same quantity of glacial acetic acid is employed, whereas the amount of sulfuric acid is only 2–5 per cent (in commercial practice somewhat greater quantities are the rule).

The Functions of the Sulfuric Acid. Whereas the chemical reaction between cellulose and acetic acid may be viewed as a condensation with the loss of water, different possibilities present themselves in the case of acetic anhydride.

The reaction may be expressed by either of the following equations:

$$C_6H_7O_2(OH)_3 + 3(CH_3CO)_2O = C_6H_7O_2(OCOCH_3)_3 + 3CH_3COOH$$

$$2C_6H_7O_2(OH)_3 + 3(CH_3CO)_2O = 2C_6H_7O_2(OCOCH_3)_3 + 3H_2O$$

According to the first equation, the by-product of the reaction is acetic acid and no water is formed, whereas an equivalent quantity of water appears in the second equation.

The theoretical anhydride requirement in the first case is 189 per cent, whereas in the second case it is only one-half this amount. Since a considerable excess of anhydride over 189 per cent is actually required for accomplishing complete substitution (even if thorough penetration of the reagent into the cellulosic material is insured by considerable dilution with acetic acid), it is probable that the reaction is more truly expressed by the first equation. The question is difficult to decide. The end effect of the dilution of the anhydride with acetic acid or with the water formed during the reaction is the same, because the 3 molecules of water formed would decompose an equivalent quantity of anhydride, resulting in 3 molecules of acetic acid for each molecule of cellulose acetate, i.e., as in the first equation.

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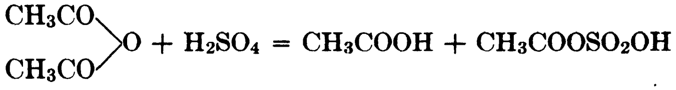
[238] See, for example, Krüger, "Zelluloseazetate," Steinkopf, Dresden and Leipzig (1933), pp. 172, 188.

[239] See Atsuki and Shinoda, *J. Soc. Chem. Ind., Japan*, **31**, 97B (1928); Atsuki and Ishii, *ibid.*, **34**, 331 (1931); **35**, 79 (1932); Sakurada, *ibid.*, **36**, 78 (1932).

Depending upon which of the two reactions occurs, the rôle of the sulfuric acid (and other auxiliary agents) would also differ. The dehydrating properties of these agents serve no purpose if water is not formed. Their function then must be of a different nature.

A limited justification for viewing the effect of the sulfuric acid as catalytic may be derived from the work of Franchimont,[240] which was subsequently substantiated by Stillich,[241] by Thiele and Winter,[242] and by Peski.[243] Since sulfuric acid is capable of reacting with the anhydride to form acetylsulfuric acid according to the equation



$$(CH_3CO)_2O + H_2SO_4 = CH_3COOH + CH_3COOSO_2OH$$

it is claimed that this acid functions as the acetylation agent, whereby the sulfuric acid is regenerated. Thus:

$$C_6H_9O_4OH + HOSO_2OCOCH_3 = C_6H_9O_4OCOCH_3 + H_2SO_4$$

Considering that acetylation of cellulose is a time reaction which proceeds gradually through the fiber, it is possible that a relatively small amount of sulfuric acid will suffice to accomplish complete substitution: While continuously small portions of the fiber are being acetylated, sulfuric acid is regenerated from the acetyl sulfate and subsequently combines with an equivalent fresh amount of anhydride. The latter effects further acetylation, setting free its sulfuric acid constituent which again reacts with anhydride to form fresh quantities of the acetylating agent, and so forth. However, part of the sulfuric acid is eliminated from the cycle because it enters the cellulose molecule to form esters.

Acetylsulfuric acid rearranges itself into sulfoacetic acid, HO_3SCH_2COOH, at a slow rate at room temperature, but more easily at higher temperature. However, according to Stillich, it possesses no acetylating power. On the other hand, sulfoacetic acid has been suggested as a catalyst.[244]

Indeed, most of the facts are against attributing a true catalytic effect to sulfuric acid and, for that matter, to other "catalysts" used in acetylation mixtures. Only the fact that the rate of acetylation increases with increasing quantities of the "catalyst"—not only with

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[240] Franchimont, *Compt. rend.*, **92**, 1054 (1881).

[241] Stillich, *Ber.*, **38**, 1241 (1905).

[242] Thiele and Winter, *Ann.*, **311**, 341 (1900).

[243] Peski, *Rec. trav. chim.*, **40**, 103 (1921).

[244] French patent, quoted by Krüger, *loc. cit.*, p. 148.

sulfuric[245] but also with perchloric acid[246] would seem to rule out this view.

No doubt the chief function of the sulfuric acid is to aid in the swelling of the cellulosic material and to degrade it. It would appear that the swelling effect which sulfuric acid exerts upon cellulose is considerably diminished by the simultaneous presence of the diluting acetic acid in the acetylation mixture. However, it is to be considered that glacial acetic acid itself is a swelling agent for cellulose. Moreover, a combination of the two compounds is even more powerful.[247]

Swelling is followed by peptization, the state prior to dissolution. It is probable that the cellulose becomes degraded long before an adequate acetyl content causes the reaction product to dissolve in the acetylation mixture.

The degradation of cellulose during acetylation in the presence of sulfuric acid acquires considerable proportions. The degree of polymerization derived from viscosity measurements of cellulose acetates, prepared either commercially or in the laboratory, following commercial recipes, ranges as low as 250 to 400, whereas that of the original cellulose might have been between 1200 and 3000. Although in commercial cellulose acetates the degradation thus revealed is, no doubt, in part due to the procedure of "partial hydrolysis" (see later), much of it must be attributed to the effect of the sulfuric acid or to its more powerful combination with acetic acid in the acetylation mixture. This degrading effect becomes very obvious if the temperature during esterification is increased slightly. At 50–60° instead of 30–40°, acetylation acquires the character of acetolysis.[248] With a sufficient quantity of sulfuric acid and after a sufficient length of time, all the cellulose is degraded to cellodextrin acetate and further to cellobiose octaacetate and glucose pentaacetate.

The Formation of Sulfoacetates. As mentioned above sulfuric acid takes part in the esterification reaction, resulting in the formation of mixed esters—cellulose sulfoacetates. This function of the sulfuric acid was apparently first recognized by Ost,[249] although sulfoacetates of cellulose had been prepared and analyzed earlier by Cross, Bevan,

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[245] Elöd and Schmidt-Bielenberg, *Z. physik. Chem.*, **B25**, 37 (1934).

[246] Krüger, Lüdtke, and Oberlies, *Angew. Chem.*, **47**, 806 (1934).

[247] Davidson and McAlister, *J. Am. Chem. Soc.*, **52**, 507 (1930); Davidson, *Chem. Rev.*, **8**, 175 (1931); Hall, *ibid.*, **8**, 191 (1931); Frey and Elöd, *Ber.*, **64**, 2556 (1931).

[248] Atsuki and Shinoda, *J. Soc. Chem. Ind., Japan*, **31**, 97B (1928).

[249] Ost, *Z. angew. Chem.*, **32**, 66 (1919).

and Briggs.[250] They used much greater quantities of sulfuric acid than would be employed for acetylation, and consequently their products were highly degraded, as indicated by their alcohol and water solubility. A product prepared by the action of acetic anhydride and about 30 per cent of sulfuric acid (calculated on cellulose) contained 8.76 per cent sulfuric and 52.20 per cent combined acetic acid. In a later publication,[251] the same investigators described sulfoacetates of varying acetyl and sulfuric acid content which were prepared by increasing the amount of sulfuric acid in the acetic anhydride. The results are shown in Table 26.

TABLE 26

CELLULOSE SULFOACETATES OF INCREASING COMBINED SULFURIC-ACID CONTENT

H_2SO_4 Employed, % on Cellulose	42.5			61.0			150	
Combined H_2SO_4 in sulfoacetate, %	5.00	5.96	6.13	10.08	8.46	8.58	25.8	24.5
Combined CH_3COOH in sulfoacetate, %	52.8	49.8	52.6	45.0	51.9	54.0	49.2	49.8

Ost[252] followed the acetylation process with acetic anhydride and 5 per cent sulfuric acid (calculated on the weight of cellulose) by analyzing samples, taken at intervals, for acetyl and sulfate content and found that the initially high sulfate content decreased with progressing acetylation, whereas the acetyl content increased:

Time of Acetylation, Days	Combined Acetic Acid, %	Combined Sulfuric Acid, %
3	59.5	1.15
4	61.8	0.23

When samples taken from acetylations with limited quantities of anhydride (240 per cent) and 10 per cent of sulfuric acid (calculated on the weight of the cellulose) were analyzed, the data shown in Table 27 were obtained. (The temperature was 20–22°.)[253]

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[250] Cross, Bevan, and Briggs, *Ber.*, **38**, 1859 (1905).

[251] Cross, Bevan, and Briggs, *loc. cit.*, p. 3531.

[252] Ost, *loc. cit.*, p. 69.

[253] Ost, *loc. cit.*, p. 77.

TABLE 27

DECREASING COMBINED SULFURIC-ACID AND INCREASING COMBINED ACETIC-ACID CONTENTS DURING ACETYLATION

Time of Acetylation, Days	Combined Acetic Acid, %	Combined Sulfuric Acid, %
1	49.1 and 49.2	2.22
2	53.8	2.10
4	61.1 and 61.2	trace
8	63.9	0.13 (ash 0.23)
2	48.8	2.2
4	61.0 and 60.9	0.8

More data are available from experiments in which methylamine sulfate was used as catalyst.[254] Ost found this salt to act in much the same way as sulfuric acid with the difference that, since it is a combination of sulfuric acid with a weak base, it exerts a more moderate action on the cellulosic material at a relatively low temperature. At 65–70°, far-reaching degradation occurs. The data in Table 28 pertain to experiments during which such a temperature was employed.

TABLE 28

THE FORMATION OF SULFOACETATES ON ACETYLATION WITH METHYLAMINE SULFATE AS CATALYST

Time of Acetylation, Hours	Combined Acetic Acid, %	Combined Sulfuric Acid, %
3	56.7	3.2
7	61.1	1.0
10	61.5	0.47
24	62.9	0.13

It would appear from Ost's results that esterification of cellulose with sulfuric acid is the primary process. In view of the fact that the quantity of sulfuric acid used was much less than that required for the esterification of all available hydroxyl groups, only a limited number of hydroxyl groups can be esterified. The reaction would be limited further by the interaction between the sulfuric and the acetic acids with the formation of acetyl sulfate, if such a reaction actually took place.

The presence of sulfate groups in cellulose acetate could explain why, with sulfuric acid as a catalyst, the theoretical value for the triacetate is never reached; it usually amounts to about 61 per cent combined acetic acid (Ost). But even if the combined sulfuric is subsequently replaced by combined acetic acid, the total combined

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[254] Ost, *loc. cit.*, p. 70.

acetic acid content is 1.5 per cent below the theoretical value. Ost has explained this fact on the assumption that during acetylation the sulfuric acid exerts a hydrolyzing influence upon the acetyl groups and that, thus, the system tends to reach an equilibrium. Against this explanation, other investigators[255] have advanced the argument that the elimination of water (by its interaction with an equivalent quantity of acetic anhydride) makes it rather improbable that acetyl groups are removed.

It might be of interest to mention in this connection that the interaction between acetic anhydride and water proceeds rather slowly. Lumière and Barbier[256] have shown that acetic anhydride may be dissolved in cold water to the extent of 12 per cent without a reaction taking place, unless the temperature is raised. The interaction at room temperature is favored by the presence of mineral acid, however.

Ost's findings on the participation of the sulfuric acid in the process of esterification and the replacement of sulfate by acetyl groups have been confirmed many times. Of more recent investigations, the results of Deripasko[257] may be mentioned; they show that acetates prepared by the usual method of acetylation may contain up to 5 per cent of combined sulfuric acid, the combined acetic acid content ranging from 55 to 61 per cent. No doubt, the combined sulfuric acid content depends upon the quantity of sulfuric acid used in the acetylation mixture. This relationship, also recognized by Ost,[258] is seen from data taken from the work of Deripasko (Table 29). Although the slightly higher temperature probably favored the replacement of sulfuric acid by acetyl groups, the main difference is, no doubt, due to the quantity of sulfuric acid used in the acetylation mixture.

TABLE 29

INFLUENCE OF THE AMOUNT OF SULFURIC ACID IN THE ACETYLATION MIXTURE UPON THE COMBINED SULFURIC ACID CONTENT OF THE ACETATE

H_2SO_4 Used, %	Temperature of Acetylation, °C.	Time of Acetylation, Hours	Combined Acetic Acid Content, %	Combined Sulfuric Acid Content, %
15	25	7	55	4
7.5	30	5	61.0–61.5	1–1.2

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[255] Smith and Orton, *J. Chem. Soc.*, **93**, 1242 (1908).

[256] Lumière and Barbier, *Bull. soc. chim.*, [3] **33**, 783 (1905); *Chem. Zentr.*, 1905, II, p. 466.

[257] Deripasko, *Cellulosechem.*, **12**, 255 (1931); see also Araki, *ibid.*, **18**, 109 (1940).

[258] Ost, *loc. cit.*, p. 69.

The greater part of the sulfuric acid content of the acetate is removed on stabilization, i.e., by boiling, for a long period of time, with water, dilute mineral acid or other agents capable of splitting off sulfate groups.[259] Yet, even after such treatments, small quantities of sulfuric acid remain combined with the acetate (0.2–0.7 per cent).[260] The stabilization procedure gives rise to a further, although small, reduction of acetyl, occurring under the hydrolyzing influence of the sulfuric acid which has dissolved in the water. According to Ost, the combined acetic acid content of the stabilized acetate is 1.5–3 per cent below the theoretical value.[261]

Higher combined acetic acid contents, and particularly those above the theoretical value, indicate that considerable degradation (acetolysis) has occurred. In other words, on the cleavage of glycosidic linkages additional hydroxyl groups are produced and are subsequently acetylated.[262] Moreover, it is probable that, even in an incompletely substituted acetate (provided a cellulose-degrading catalyst was used), a small portion of its acetyl content is due to acetylation of such regenerated hydroxyl groups.[263] However, it may be demonstrated by calculation that cleavage of glycosidic linkages must occur very frequently before it is reflected in an acetyl content which would range above the theoretical triacetate value.

An interesting observation made by Clément and Rivière,[264] throws further light upon the relation between the acetyl and the sulfate content of cellulose acetate. It was found that the ratio between combined acetic and combined sulfuric acid changes if the acetate paste is diluted with acetone and allowed to stand for 15 to 18 hours at 20°. The acetate, isolated from the mixture by precipitation with water, followed by washing and drying, showed 62.2 per cent combined acetic and 0.28 per cent combined sulfuric acid, whereas, when isolated from the acetone-diluted paste without standing, it had 61.7 per cent combined acetic and 1.02 per cent sulfuric acid. Obviously, the gradual decrease of sulfate and the increase of acetyl groups which occurs on acetylation continues on standing.

Likewise, Clément and Rivière observed that the acetyl content of an acetate which had been precipitated from the acetylation mixture and washed with water was raised and the sulfuric acid content was reduced when the moist product was redissolved in acetic acid. This

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[259] Jeanny, *Rev. gén. mat. plastiques,* **14**, 7 (1938).

[260] Ost, *loc. cit.*, p. 69.

[261] Ost, *loc. cit.*, p. 89.

[262] Ost, *Z. angew. Chem.*, **25**, 1996 (1912); Schliemann, doctoral dissertation, Hanover (1910), p. 57.

[263] Atsuki and Shinoda, *J. Soc. Chem. Ind., Japan,* **31**, 97B (1928).

[264] Clément and Rivière, *Bull. soc. chim.*, [5] **4**, 874 (1937).

observation is in agreement with results obtained by Sindl[265] with a fibrous acetate. Sindl's product contained 59.6 per cent combined acetic and 3 per cent sulfuric acid but, after it was heated in a mixture of benzene and some acetic acid, the combined acetic acid content had increased to 61.9 per cent, whereas the sulfuric acid content had decreased to 0.01 per cent. Thus, after-treatment of an acetate short of the theoretical triacetate value with acetic acid in the presence of a diluent serves as a means of bringing the acetyl content nearer to the theoretical and at the same time of reducing the sulfate content to a rather low level.

Acetylation in the Presence of Other Catalysts. In addition to sulfuric acid, which in commercial practice is still the most used agent, other catalysts have been employed, one of the oldest of which is zinc chloride. As in the case of sulfuric acid, extensive and fundamental studies on the action of zinc chloride originate from Ost and his school.[266]

It is probable that zinc chloride was first used in acetylation mixtures by Franchimont.[267] It exerts, as we have seen (p. 139), a considerable swelling effect upon cellulose, followed by peptization and eventual dissolution. The quantities of zinc chloride used in the acetylation mixture are large enough (50–100 per cent of the cellulose) to bring about such effects before the acetyl content is high enough for the product to be soluble in the anhydride-acetic acid mixture. After dilution of the solution with glacial acetic acid, the acetate may be obtained by precipitation with water. If prepared according to Hess and Schultze,[268] it represents the triacetate, having a combined acetic acid content of 62.61 per cent.

The swelling, peptizing, and dissolving action of the zinc chloride upon cellulose is accompanied by degradation. Until recently, it was generally believed that the degrading effect of zinc chloride is due to the liberation of hydrochloric acid, a process of decomposition which is furthered by the presence of moisture and, particularly, by elevation of temperature. Since the temperature during acetylation is kept rather low (20° or less), one would expect degradation to be rather limited. However, the degree of polymerization of acetates prepared with zinc chloride, even under rather mild conditions, indicates that the cellulose is considerably degraded. Therefore, it appears more

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[265] Sindl, French patent 755,981 (1933).

[266] Ost, *Z. angew. Chem.*, **32**, 66 (1919).

[267] Franchimont, *Ber.*, **12**, 2059 (1879); see also Cross, Bevan, and Briggs, *J. Soc. Dyers Colourists*, **23**, 250 (1907); Law, *Chem.-Ztg.*, **32**, 365 (1908).

[268] Hess and Schultze, *Ann.*, **455**, 91 (1927).

plausible to attribute the hydrolyzing effect of zinc chloride, in accordance with the view of Meerwein,[269] to the formation of a complex compound with acetic acid, namely, $ZnCl_2[COOCH_3]H$ which forms at ordinary temperature and shows a dissociation constant similar to strong mineral acids (see also p. 140).

Frey and Elöd[270] observed on the esterification of cellulose with formic acid, using zinc chloride and hydrochloric acid as catalysts, that the reaction proceeded at a much faster rate when these two catalysts were present than with either one alone. The effect is explained on the assumption that zinc chloride forms with hydrochloric acid the complex acid $[ZnCl_2 \cdot Cl]H$. Its dissolving power for cellulose is many times greater than that of hydrochloric acid alone. For example, 38 per cent hydrochloric acid dissolves cellulose only after many hours, whereas acid of the same concentration to which 6 per cent zinc chloride has been added dissolves cellulose within a few minutes. The strength of the complex acid corresponds very nearly to that of 68 per cent sulfuric acid. This parallel between the strength of the "catalyst" and its dissolving power is another argument against the concept of a true catalytic action of the auxiliary agents. Frey and Elöd attribute the essential effect of these substances to their specific swelling and dissolving power for cellulosic materials and point out that most acid catalysts and some of the bases used in esterification, as pyridine, quinoline and alkyl amines, are, indeed, effective swelling agents.

Ost, in his attempts to limit the hydrolizing effect of the zinc chloride as much as possible, employed rather low reaction temperatures, such as 20° or even only 10–20°. Under these conditions, a high degree of substitution required relatively long times—at 20° several weeks and at 10–12° even several months. But even under such mild conditions, the cellulosic material is considerably degraded. Thus, Staudinger and Freudenberger[271] found the degree of polymerization of a triacetate, prepared according to Ost at room temperature (reaction time, 4 months), to be as low as 260 (molecular weight of 74,000); other preparations,[272] obtained at 30° after 7 to 10 days, showed degrees of polymerization of 200 and 165, and 120 to 87 if prepared at 60° in 4 to 9 hours.

From these data it would appear that the degrading effect of zinc chloride is almost as great as that of sulfuric acid. When the latter was used as a catalyst (at 30°, 3 hours) for the acetylation of the

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[269] Meerwein, *Z. angew. Chem.*, **39**, 1191 (1926); *Ann.*, **453**, 16 (1927); **455**, 250 (1927).

[270] Frey and Elöd, *Ber.*, **64**, 2556 (1931).

[271] Staudinger, "Die hochmolekularen organischen Verbindungen," pp. 470–484. The highest degree of polymerization of a triacetate prepared according to Ost at 30° is given as 359.

[272] Staudinger, *loc. cit.*, p. 473.

same cellulosic material, the degree of polymerization was found to be 140 (molecular weight of 40,000).[273]

It is claimed that, owing to the absence of sulfuric acid groups, the acetates prepared with zinc chloride are more stable than those resulting from the use of sulfuric acid.

In addition to zinc chloride, other salts have been suggested, for example, antimony chloride, calcium chloride, and other chlorides.[274] It is probable that the degrading effect of these catalysts upon cellulose is due to their ability to form complex compounds with acetic acid in much the same way as does zinc chloride.

Neutral and acid sulfates, sulfates of organic bases (such as methylamine sulfate, Ost), or aromatic sulfonic acids may also be used as catalysts. The last are said to degrade cellulose very little, even if acetylation is carried out at a temperature as high as 80°,[275] a statement which, however, in the light of results obtained by modern methods for ascertaining the degree of degradation of cellulose, can hardly be supported. The action of these catalyzers, in some instances, is comparable to that of sulfuric acid, although the neutral salts may exert a somewhat less degrading effect than the acid salts.

A catalyst frequently used in scientific studies is sulfuryl chloride (SO_2Cl_2); it is formed when sulfur dioxide and chlorine are added to acetic anhydride in glacial acetic acid.[276] Esterification is carried out at 65°. It is claimed that this catalyst, being used in relatively small amounts, is more efficient than others and that it is helpful in cases in which difficulties are encountered in reaching the triacetate stage. However, the claim that it has a less degrading effect upon cellulose than other catalysts must be taken with the same reservation as other statements to this effect. In fact, Hess reports that, under the influence of this catalyst, cellulose is considerably degraded.[277] Sulfur dioxide and chlorine were employed also by Irvine and Hirst [278] and by Haworth and Machemer.[279]

According to Krüger and Tschirsch [280] the most powerful catalyst

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[273] Staudinger, *loc. cit.*, p. 470; in these and previous calculations a K_m constant value (see Chapter XV) of 11×10^{-4} was used, whereas more recent and somewhat higher degrees of polymerization are based upon $K_m = 6.3 \times 10^{-4}$ (see Staudinger and Daumiller, *Ann.*, **525**, 246 (1937).

[274] Knoevenagel, *Z. angew. Chem.*, **27**, 505 (1914); Schwalbe, *ibid.*, **21**, 2405 (1908); **23**, 433 (1910).

[275] Escales and Levy, *Kunststoffe*, **13**, 52, 64 (1923).

[276] Barnett, *J. Soc. Chem. Ind.*, **40**, T8 (1921).

[277] Hess, "Die Chemie der Cellulose," p. 390.

[278] Irvine and Hirst, *J. Chem. Soc.*, **121**, 1585 (1921).

[279] Haworth and Machemer, *J. Chem. Soc.*, 2270 (1932).

[280] Krüger and Tschirsch, *Ber.*, **64**, 1879 (1931); *Melliand Textilber.*, **13**, 541 (1932).

for the acetylation of cellulose is perchloric acid ($HClO_4$). In fact, it produces a high degree of substitution within a much shorter time than sulfuric acid. This conclusion is derived from experiments in which acetylation was carried out on the same cotton linters sample, sulfuric acid being used in one case and perchloric acid in the other. Both acetylations were carried out at 0° and in benzene, thus maintaining a fibrous structure (see later). The results are listed below:

Catalyst	Time of Acetylation, Hours	Combined Acetic Acid, %
H_2SO_4	20	24.6
$HClO_4$	2	60.0

As would be expected as a result of the relatively high rate of reaction, the acetate prepared with perchloric acid had a higher viscosity. On the other hand, it must be considered that perchloric acid is a very powerful oxidizing agent—a drop of this acid inflames filter paper on gentle heating.[281]

Studies on acetylation with perchloric acid and perchlorates in the presence of acids led Krüger to establish a hypothesis on the effect of the various catalysts in acetylation mixtures to which the reader is referred.[282]

Preparation of Fibrous Acetates. The cellulosic material retains its fibrous structure if a nonsolvent, such as benzene or carbon tetrachloride, is added to the acetylation mixture.[283] It is likely that the nonsolvents counteract the swelling and peptizing effect exerted by the catalysts and by the acetic acid, but degradation is by no means eliminated and occurs to a greater or lesser extent, depending upon the temperature and the amount of acid catalyst used. Since the methods developed from the various patents call for the use of relatively high temperatures, degradation may be expected to be considerable.[284] In fact, Staudinger[285] found that the molecular weight of a triacetate prepared according to Hess[284] was only 9550.

Considerably higher figures, although still rather low compared with

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[281] Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 139; see also Craik, *Chemistry & Industry,* **43**, 171T (1924).

[282] Krüger and Roman, *Angew. Chem.,* **47**, 58 (1934).

[283] Benzene was suggested by Bad. Anilin- und Sodafabrik in German patent 184,201 (1904), and carbon tetrachloride by Lederer in German patent 185,151 (1905).

[284] Hess, "Die Chemie der Cellulose," p. 411; Hess, Trogus, and Osswald, *Z. physik. Chem.,* **B5**, 165 (1929).

[285] Staudinger, "Die hochmolekularen organischen Verbindungen," p. 473, footnote 1.

the molecular weight of the original cellulose, were obtained by Elöd and Schmidt-Bielenberg.[286] With a reaction temperature of 45° and a time of 16 days, using benzene as the nonsolvent, they obtained an acetate (59.3 per cent combined acetic acid) which showed an average molecular weight of 43,000. Under milder conditions, the highest average molecular weight observed was 92,000. The raw materials were cotton and ramie.

Less degradation is claimed to occur with a mixture of sulfur dioxide and a small amount of perchloric acid as a catalyst in toluene. This method, also derived from a patent,[287] was used by Dorée and Healey.[288] The degree of degradation was not ascertained except by determination of the copper number which, however, would appear not to be a reliable test in this case. Werner[289] observed that for complete substitution it is essential that the cellulose material be subjected to a swelling pretreatment and that a large excess of anhydride be used.

By omitting the catalyst and by using acetic anhydride in the presence of pyridine, degradation is avoided.[290] To facilitate substitution the cellulosic material is subjected to a swelling pretreatment in strong caustic soda solution (16 per cent concentration for cotton linters and wood pulp and 8 per cent for viscose and cuprammonium rayon) for 1 hour at room temperature. After removal of the sodium hydroxide by washing with water, the water is displaced by pyridine. In the presence of acetic anhydride, the quantity of which amounts to only 100 per cent calculated on cellulose,[291] acetylation proceeds rather slowly, even at 50–70°, as may be seen from the data in Table 30.

TABLE 30

ACETYLATION OF CELLULOSIC MATERIALS WITH ACETIC ANHYDRIDE AND PYRIDINE

Materials	Temperature, °C.	Time, Days	Combined Acetic Acid, %
Cotton linters	55	43	61.50
Wood pulp	70	52	61.13
Viscose rayon	55	30	62.77
Cuprammonium rayon	55	34	61.61

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[286] Elöd and Schmidt-Bielenberg, *Z. physik. Chem.*, **B25**, 41 (1934).

[287] Böhringer and Söhne, British patent 387,533.

[288] Dorée and Healey, *J. Textile Inst.*, **29**, T31 (1938).

[289] Werner, *Angew. Chem.*, **50**, 127 (1937); see also Araki, *Cellulosechem.*, **18**, 109 (1940); Araki and Tadenuma, *Cellulose Ind.*, **17**, B1 (1941).

[290] Hess and Ljubitsch, *Ber.*, **61**, 1460 (1928); see also Wilson and Hughes, *J. Soc. Chem. Ind.*, **58**, T74 (1939).

[291] The quantity of pyridine amounts to 2 to 3 times that of the anhydride.

Cellulose (cotton linters) carefully regenerated from an acetate which had been prepared according to Hess and Ljubitsch's method from purified cotton was found to have a degree of polymerization of 1150, whereas the original cellulose showed 1200.[292] Thus the degree of polymerization remained practically unchanged.

The stability of cellulose to the anhydride-pyridine mixture is in agreement with the fact that the acetate was insoluble in organic solvents. On the other hand, acetates prepared with this acetylation mixture from cellulosic materials with a low degree of polymerization [such as viscose and cuprammonium rayon (D.P. 150 and 300)] were soluble in organic solvents, for example, chloroform, tetrachloroethane, formic acid, and *m*-cresol. The resistance of these materials to degradation during acetylation with acetic anhydride and pyridine was not different from that of cotton.[293] The upper limit of solubility of the acetates thus obtained seems to be reached with a degree of polymerization of 500.[294]

Pyridine is a swelling agent and as such may be expected to facilitate the acetylation reaction.[295]

The use of pyridine in acetylation mixtures goes back to Wohl's[296] method in which acetyl chloride and pyridine, instead of the stronger sodium hydroxide, constitutes the acetylation mixture, the base being used to eliminate the effect of the hydrochloric acid formed as by-product of reaction. Pyridine was used by early investigators for the acetylation of simpler organic compounds, such as alcohols and phenols. With acetyl chloride it forms an addition compound[297] and thus acts as a "reservoir," liberating the acetylating agent only as it is being used for the substitution of hydroxyl groups.

It is probable that, in the acetylation of organic compounds with acetic anhydride, the pyridine fulfills the same other purpose as when acetyl chloride is used; i.e., it neutralizes the acid formed in the substitution reaction.[298] Verley

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[292] Staudinger and Daumiller, *Ann.*, **529**, 219 (1937).

[293] Staudinger and Eilers, *Ber.*, **68**, 1613 (1936).

[294] Staudinger and Daumiller, *loc. cit.*, p. 226. Soluble acetates may be obtained from cellulose which has been regenerated from its cuprammonium solution (degree of polymerization 500 to 2000); see also Staudinger and Sohn, *J. prakt. Chem.*, **155**, 181 (1940).

[295] Bernoulli, Schenk, and Hagenbuch, *Helv. Chim. Acta*, **13**, 564 (1930); Thilo, doctoral dissertation, University of Berlin (1930).

[296] Wohl, *Z. angew. Chem.*, **16**, 285 (1903); Heuser and Schlosser have employed acetic anhydride and pyridine in the acetylation of xylan, *Ber.*, **56**, 392 (1923).

[297] Dennstedt and Zimmermann, *Ber.*, **19**, 75 (1886); Abderhalden, "Handb. Biochem. Arbeitsmeth.," Urban and Schwarzenberg, Berlin (1910), IV, Vol. 2, p. 1300.

[298] Frey and Elöd, *Ber.*, **64**, 2561 (1931).

and Bölsing[299] have explained the function of the pyridine in the reaction between alcohols or phenols and acetic anhydride by the following equation:

$$\mathrm{ROH} + \left.\begin{matrix}\mathrm{R'CO}\\ \mathrm{R'CO}\end{matrix}\right\rangle\mathrm{O} + \text{pyridine} = \mathrm{ROCOR'} + [\mathrm{R'COOH}, \text{pyridine}]$$

That part of the anhydride which is liberated in the substitution reaction combines at once with the pyridine to form a neutral salt.

If the cellulosic material is not subjected to an alkaline pretreatment as prescribed in the original Hess and Ljubitsch method, a longer time is required to reach the same degree of substitution.[300] For cotton (rag paper stock) three months were necessary to reach an acetyl content of 25 per cent (39 per cent combined acetic acid). The preservation of the original chain length is seen from the following figures:[301]

Original rag stock	Mol. wt. 233,000, D.P. 1440
Acetate (25% acetyl)	Mol. wt. 215,000, D.P. 1330*

* Calculated as cellulose.

Factors Influencing the Rate of Acetylation. Reference to the various factors which control the rate of acetylation of cellulose have been made at various points in the previous sections of this chapter. Additional information may be summarized as follows.

The rate of acetylation is distinctly influenced by the *moisture* content of the cellulosic material. This influence, known from early patents,[302] was systematically studied by Elöd and Schmidt-Bielenberg.[303] They measured the time of reaction to reach a certain degree of substitution of (1) dried cotton (0.1 per cent water), (2) air-dry cotton (6.7 per cent water), and (3) cotton which had been moistened to a water content of 24.4 per cent.

The curves in Fig. 56 show that the rate of reaction increases with increasing moisture content of the material. Acetylation was carried out with acetic anhydride and sulfuric acid in benzene, i.e., with the preservation of the fibrous structure.

When the relationship between the moisture content of cotton and the rate of reaction was followed over a wider range of moisture content, S-shaped curves were obtained as shown in Fig. 57. It is seen that the rate increases with increasing moisture content of the two samples rather rapidly until a certain moisture content is reached,

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[299] Verley and Bölsing, *Ber.*, **34**, 3354 (1901).

[300] Bernoulli, Schenk, and Hagenbuch, *loc. cit.*, p. 564.

[301] Bletzinger, doctoral dissertation prepared under the direction of E. Heuser at the Institute of Paper Chemistry, Appleton, Wis.; *Ind. Eng. Chem.*, **35**, 474 (1943).

[302] See Ost, *Z. angew. Chem.*, **32**, 76 (1919).

[303] Elöd and Schmidt-Bielenberg, *Z. physik. Chem.*, **B25**, 31 (1934); Elöd, Schmidt-Bielenberg, and Thoria, *Angew. Chem.*, **47**, 465 (1934).

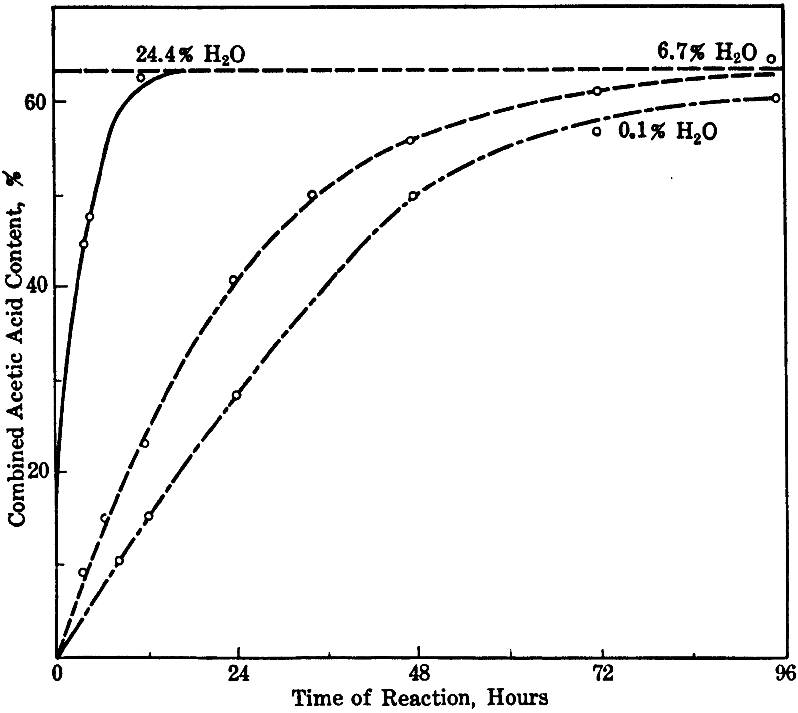

FIG. 56. Influence of moisture content of cotton upon rate of acetylation. Elöd and Schmidt-Bielenberg.

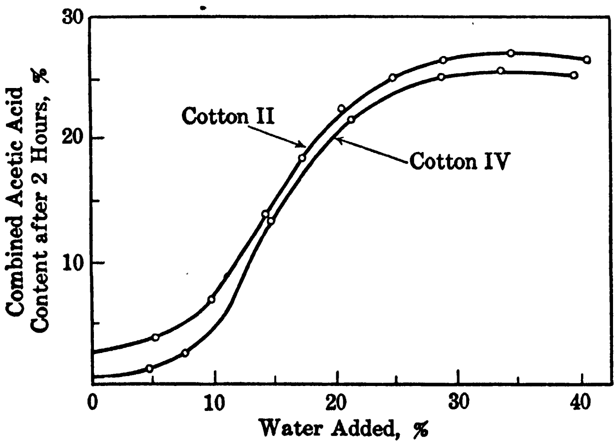

FIG. 57. Moisture content of cotton and rate of acetylation. Elöd and Schmidt-Bielenberg.

after which further increased moisture of the samples results in a decrease and eventually in a cessation of the reaction.

Obviously, with increasing water content, the capillaries of the fibers are enlarged; this favors the diffusion of the acetylating mixture into the inner parts of the fibers. That the rate of reaction reaches a maximum with samples containing about 25 to 30 per cent water is explained by the fact that, at this point, the fibers have reached saturation, i.e., all capillaries are filled with water, so that further increase of the water content is without influence upon the diffusion and hence upon the rate of reaction.

Water has been found to be a means of leveling the reactivity of fibers which are morphologically as different as are cotton, ramie, and hemp. In dried or air-dried condition, these show a marked difference in the rate of acetylation, chiefly because of the difference in parallel orientation of their micelles, flax exhibiting highest orientation and consequently lowest diffusion and reaction velocity. Preswelling in water equalizes these differences, and the various fibers, after 2 hours of acetylation at 25°, have the same combined acetic acid content, namely, 24–26 per cent (corresponding to a substitution of about 40 per cent of the available hydroxyl groups).

On the other hand, drying may destroy even the pronounced reactivity usually displayed by fibers of a relatively low degree of polymerization. Thus it was found[304] that the usual acetylation mixtures were incapable of penetrating viscose rayon fiber which had been dried at 80° for 2 hours. Reaction took place only superficially. Small particles, separated from the surface, were found to be considerably degraded, their combined acetic acid content being 68.3 per cent.

The influence of preswelling in water upon the rate of reaction was also observed when various cellulosic materials were acetylated without preservation of the fibrous structure.

Acetic acid as a preswelling agent acts in the same way as water, this effect being noticeable both in acetylation with retention of fibrous structure and in acetylation in solution. On acetylation in the presence of benzene, Elöd, *et al.*,[305] found that cotton which had been preswollen with 200 per cent of its weight of glacial acetic acid reacted about 10 times faster than without the pretreatment.

The beneficial effect of the pretreatments of the cellulosic material with water or with acetic acid is reflected in the degree of polymeri-

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[304] Bernoulli, Schenk, and Hagenbuch, *Helv. Chim. Acta*, **13**, 566, 567 (1930).

[305] Elöd, Schmidt-Bielenberg, and Thoria, *loc. cit.*, p. 466.

zation of the resulting acetates. Since these pretreatments shorten the time necessary to reach a certain acetyl content, the cellulose becomes less degraded and the molecular weights of the acetates are higher.[306]

This beneficial effect may, however, be diminished if a certain quantity of sulfuric acid is added to the acetic acid used for the pretreatment. The degrading effect of the mixture, depending upon the time it is allowed to act and the temperature, may thus become noticeable, in spite of the fact that the mixture exerts a greater preswelling effect and consequently shortens the time of reaction still further than acetic acid alone.[307]

Instead of sulfuric, perchloric acid may be used to aid the swelling of cellulose in glacial acetic acid. Perchloric acid, according to Andress and Reinhardt,[308] causes cellulose to undergo intramicellar swelling.

It is noteworthy that the beneficial effect of a pretreatment with glacial acetic acid is gradually neutralized by the simultaneous presence of increasing quantities of acetic anhydride,[309] which would suggest that the anhydride as such exerts a contracting rather than a swelling effect.

The rate of acetylation is also accelerated by a pretreatment of the cellulosic material with *aqueous alkali,* particularly of mercerizing strength[310] (p. 116). However, this effect is obtained only when the mercerized fiber is not dried. As mentioned previously, the surface of the mercerized fiber on drying becomes indurated and rather resistant to penetration by esterifying agents. The original reactivity of the mercerized fiber may be restored by boiling the dried material in acetic acid or subjecting it to the hot vapors of this acid.[311]

Liquid ammonia, although exerting a considerable swelling effect upon cellulosic materials, does not seem to increase the rate of acetylation.[312] It is probable that the effect is lost on the fast evaporation of

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[306] Elöd and Schmidt-Bielenberg, *loc. cit.,* p. 38; Elöd, Schmidt-Bielenberg, and Thoria, *loc. cit.,* p. 467.

[307] Hägglund, Löfman, and Färber, *Cellulosechem.,* **3,** 13 (1922); Sheppard and Eberlin, *J. Phys. Chem.,* **34,** 1041 (1930); Werner, *Cellulosechem.,* **12,** 320 (1931); Scheidegger, doctoral dissertation, Zürich (1931).

[308] Andress and Reinhardt, *Z. physik. Chem.,* **A151,** 425 (1930).

[309] Scheidegger, *loc. cit.*

[310] Scheidegger, *loc. cit.*

[311] Heuser and Haskins, unpublished data.

[312] Clark and Parker, *J. Phys. Chem.,* **41,** 785 (1937). With regard to the beneficial effect of pretreatments with other swelling agents, see Araki, *Cellulosechem.,* **18,** 109 (1940).

the ammonia, because, under these conditions, the micellar system seems to contract to a considerable extent (p. 138).

As with mercerized cellulose, the greater reactivity of *regenerated cellulose* with the acetylating agents is observed only in the undried state. Staudinger and co-workers prepared a highly reactive form of cellulose hydrate (regenerated from its cuprammonium solution) by displacing the water of the moist preparation with pyridine. The acetates (prepared according to the method of Hess and Ljubitsch) were soluble in organic solvents—for example, in tetrachloroethane and *m*-cresol and, in sufficient dilution, also in the acetic anhydride pyridine mixture—even if the degree of polymerization was above 500.[313]

With regenerated cellulose of such improved reactivity, the rate of reaction was considerably increased, acetylation of longer-chain material being completed within 6 to 8 days, and that with lower degrees of polymerization within 3 to 4 days, compared with 34 days for the original cotton linters.[314] In this way, Staudinger and Daumiller prepared soluble acetates ranging in degree of polymerization from 500 to 2000.

Those pretreatments which result in the formation of hydrocellulose also accelerate the rate of acetylation. Ost[315] showed that hydrocellulose may be converted into cellulose acetate more easily than the original material. However, in most cases the acetates prepared from hydrocellulose give products (e.g., films or fibers) which are too brittle to be of commercial value. The same may be said of acetates prepared from oxycellulose.[316]

Vandyke, Staud, and Gray[317] observed that the pretreatment with oxidizing agents diminished the reactivity of the cellulosic material. The most vigorously oxidized cellulose showed the least acetyl content; i.e., the esterification was in inverse ratio to the severity of the oxidizing conditions employed. It would appear that this result was due to the oxidation of hydroxyl groups which therefore were no longer available for esterification.

The Influence of the Fibrous Structure upon the Course of the Reaction. Depending upon the conditions, acetylation may proceed in

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[313] Staudinger and Daumiller, *Ann.*, **529**, 226 (1937). In a later publication, Staudinger and Sohn, *J. prakt. Chem.*, **155**, 181 (1940), claimed that the rate of acetylation is lower with regenerated than with fibrous cellulose. Apart from the fact that no data are given to substantiate this claim, it would appear improbable in the light of the previous findings.

[314] Staudinger and Eilers, *Ber.*, **68**, 1613 (1935).

[315] Ost, *Z. angew. Chemie*, **32**, 77 (1919); Rassow and Weber, *Papier-Fabr.*, **27**, Special Number, p. 88 (1929).

[316] Hibbert and Parsons, *J. Soc. Chem. Ind.*, **44**, 473T (1925); de Nyman, *Chimie & industrie*, **15**, 349 (1926).

[317] Vandyke, Staud, and Gray, *J. Am. Chem. Soc.*, **53**, 2725 (1931).

different ways. In the presence of sulfuric acid and without a nonsolvent for the acetate, the initial phase of the reaction takes place in a heterogeneous system. As the fibrous structure is lost, the reaction becomes less heterogeneous and, after dissolution of the partially acetylated cellulose in the acetylation mixture, the reaction continues in a homogeneous system. In contrast, the reaction is entirely heterogeneous if benzene or another nonsolvent for the acetate is added to the acetylation mixture. The same is true, and even to a greater extent if acetylation is carried out without sulfuric acid in the presence of pyridine.

In general, acetylation proceeds at a much slower rate than nitration. It will be recalled that only minutes or even seconds are required to substitute about two-thirds of the hydroxyls with nitrate groups. After such a short time, less than 1 acetyl per glucose unit has entered the cellulose. Whereas nitration may be regarded as a permutoidal and acetylation as a topochemical reaction, the line of demarcation between the two types of reaction is by no means sharp. By altering certain conditions, a topochemical may be converted into a permutoidal reaction and *vice versa.*

Karrer[318] showed that regenerated cellulose may be converted into its triacetate within 4 to 5 minutes by displacing the water content of the moist regenerated preparation with alcohol and the alcohol with ether before subjecting it to acetylation (acetic anhydride containing a small quantity of zinc chloride at 60°). Apparently, the ether fills the inter- and intramicellar spaces of the loose structure thus produced. On contact with the acetylation mixture, the ether evaporates and makes room for the acetylating agents which penetrate the whole micellar system.

Another example was furnished by Hess and Trogus.[319] Under the influence of sulfoacetic acid as catalyst and benzene as diluent, purified ramie fiber could be acetylated to the extent of 61.2 per cent combined acetic acid content within 15 minutes. Unfortunately, no details of this experiment are given. Also, perchloric acid as a catalyst speeds up the reaction considerably (see above).

The usually topochemical nature of the acetylation reaction in the earlier stages of acetylation in solution and throughout acetylation under retention of the fibrous structure was recognized by many investigators. Thus, Herzog and Londberg[320] showed that an outer

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[318] Karrer, "Polymere Kohlenhydrate," Akad. Verlags-Ges., Leipzig (1925), p. 176.

[319] Hess and Trogus, *Z. physik. Chem.*, **B15**, 219 (1931).

[320] Herzog and Londberg, *Ber.*, **57**, 329 (1924); see also *J. Phys. Chem.*, **30**, 457 (1926).

layer may be removed from a partially acetylated fiber with a solvent for acetylcellulose—e.g., nitrobenzene—the layers beneath consisting of unchanged cellulose. A similar experiment was performed by Möhring,[321] who used aniline for separating the acetylated from the unacetylated fiber. Likewise Elöd and co-workers,[322] following the process of acetylation of cuprammonium rayon fibers under the microscope, observed the formation of a cylindrical shell of acetylated cellulose around an unchanged cellulose nucleus. With cotton and ramie fibers, the development of the acetylcellulose shell was less regular; acetylated spots were found to alternate with unaffected cellulose.

Kanamaru's[323] photomicrograph (Fig. 58) of a partially acetylated cellulose fiber (acetic anhydride and benzene) and his schematic picture (Fig. 59) of the gradually proceeding acetylation reaction may serve as a good illustration of what takes place. In the photomicrograph, the gray parts of the fiber represent acetylated portions, whereas the white portions consist of unacetylated cellulose.

Fig. 58. Photomicrograph of partially acetylated cellulose fiber. Kanamaru.

The schematic picture (Fig. 59) may be interpreted as follows: The reaction starts at a few spots of the fiber. It is seen that the spots gradually enlarge to form bands around the fiber and that the bands extend in the upper and lower directions, more and more of the cellulose being attacked until it is completely acetylated. According to Kanamaru, the reaction on the surface proceeds to the triacetate stage, and layers beneath still consist of unchanged cellulose.

The phenomenon of attack at seemingly regular distances has been related to Lüdtke's[324] concept of the fiber structure according to which, as has been seen

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[321] Möhring, *Wissenschaft und Industrie,* **1,** 70 (1923); *Faserstoffe u. Spinnpflanzen,* **5,** 78 (1923).

[322] Elöd, Schmidt-Bielenberg, and Thoria, *Angew. Chem.,* **47,** 465 (1934). Special acetate rayon dyestuffs for making acetylated and unacetylated portions visible were used by Chippendale, *J. Soc. Dyers Colourists,* **50,** 142 (1934); see also Krüger, Lüdtke, and Oberlies, *Angew. Chem.,* **47,** 809 (1934).

[323] Kanamaru, *Helv. Chim. Acta,* **17,** 1436 (1934).

[324] Lüdtke, *Biochem. Z.,* **233,** 1 (1931); *Cellulosechem.,* **10,** 84 (1932); 14, 1 (1933)

earlier in this book, the fiber is thought to be subdivided by transverse elements into fragments of regular length. Since, however, the existence of such transverse elements is rather doubtful, it appears more probable that the attack at regular distances is a phenomenon similar to that involved in the enzymatic activity of certain wood-destroying fungi, as has been shown by Bailey and Vestal.[325] These fungi seem to follow the fiber along certain planes (planes of hydrolysis), leaving behind them hollow spaces of corrosion of distinct geometrical forms. Bailey and Vestal found that the pointed angle of these figures of corrosion (Fig. 60) amounted to 22.3°.[326]

This value has suggested to Frey-Wyssling[327] a possible connection between the enzymatic activity of the fungi and the cleavage of glycosidic linkages in cellulose fibers when boiled with dilute sulfuric acid and subsequently dried (formation of hydrocellulose). When the dry hydrocellulose fibers were subjected to the action of 10–15 per cent sodium hydroxide solution, they separated in transverse direction at regular distances into segments a few microns long (Fig. 61). This disintegration obviously was the result of the swelling of the fiber which simultaneously brought about contraction in its length. The hydrolyzed, weakened fiber was not able to stand the strain of the contracting forces, and broke at points where the glycosidic linkages had undergone cleavage under the influence of the acid.

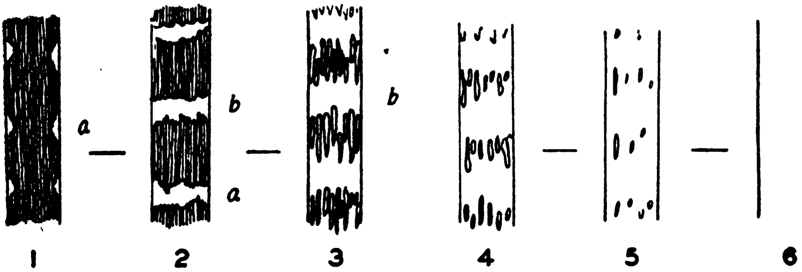

FIG. 59. Schematic picture of gradually proceeding acetylation. Kanamaru.

Frey-Wyssling calculated from x-ray data the possible planes of the micellar system of the fiber along which hydrolysis could occur and arrived at the conclusion that only one of the possible planes would permit hydrolysis to occur in a direction transverse to the fiber axis. Because of the position of the chains with respect to each other in the micellar system, hydrolysis would follow a zigzag line drawn in lateral direction through glycosidic linkages of neighboring chains. It was found that the angle (*Neigungswinkel*) of this plane of hydrolysis amounted to 22° 55′, which is very close to Bailey and Vestal's value of 22.3°.

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[325] Bailey and Vestal, *J. Arnold Arboretum,* **18,** 196 (1937); Bailey, *Ind. Eng. Chem.,* **30,** 40 (1938).

[326] Similar observations were recently made on the attack of the cell wall by bacteria of the *Cytophaga* group by Stanier, *Bact. Reviews,* **6,** 171 (1942).

[327] Frey-Wyssling, *Protoplasma,* **25,** 261 (1936); *Papier-Fabr.,* **36,** International Number, 215 (1938).

It thus would appear that hydrolysis, indirectly by way of enzymatic action or directly under the influence of acids, follows certain planes of hydrolysis which are predetermined in the micellar arrangement of the fiber.

Kanamaru's photomicrograph of a partially acetylated fiber would suggest that acetylation in the presence of a hydrolyzing catalyst would follow the same planes, thus breaking a path along which substitution would subsequently occur. This could be interpreted to mean that acetylation first replaces hydroxyl groups closest to the glycosidic linkages. It would also explain the rôle of the "catalyst" as a means of increasing the rate of reaction.

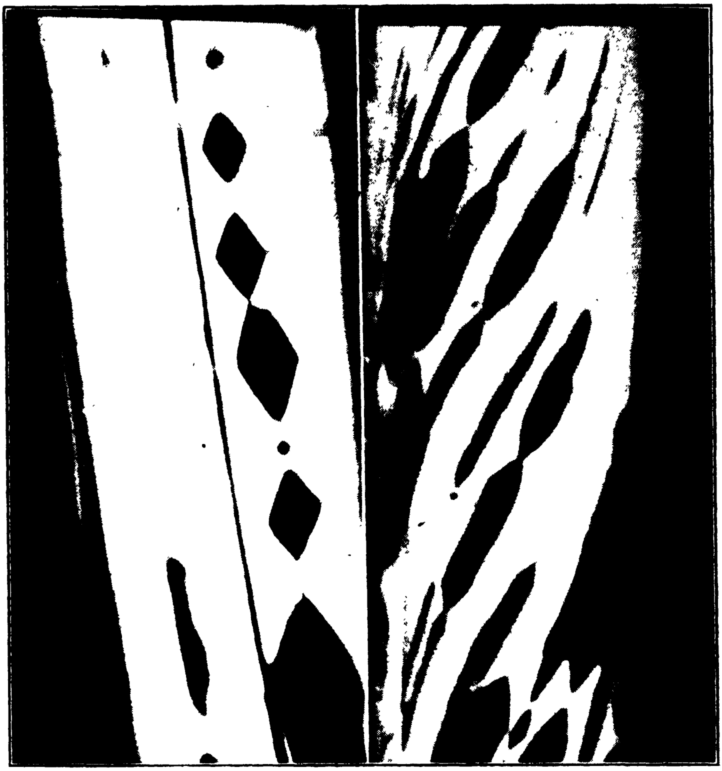

Fig. 60. Geometrical figures produced by wood-destroying fungi. Bailey and Vestal.

The conclusion that acetylation follows distinct planes seems to be in agreement with an earlier observation of Hess and Schultze.[328] It was found that, after the acetylated portions had been dissolved away

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[328] Hess and Schultze, *Ann.*, **456**, 55 (1927).

from a partially acetylated fiber (acetic anhydride, sulfuric acid, and benzene), fiber fragments of distinct geometrical forms remained. These fragments (0.05 to 0.1 mm. long) have the appearance of crystals (Fig. 62) and show a striking similarity with Bailey and Vestal's figures of corrosion.[329]

FIG. 61. Silver-dyed ramie hydrocellulose fibers in 15 per cent sodium hydroxide solution. Separation in transverse direction. Frey-Wyssling.

The pointed angle of Hess and Schultze's fiber fragments would make it seem probable that acetylation under their conditions proceeds along Bailey and Vestal's and Frey-Wyssling's planes of hydrolysis. It may be added that Hess has observed a similar phenomenon in the case of hydrocellulose.

The heterogeneous course of the acetylation reaction may also be recognized by observing the changes which the fiber undergoes with respect to double refraction.[330] The positive double refraction which the cellulose fiber exhibits when exposed to polarized light changes on acetylation through zero into the negative value. On interruption of the reaction, the various stages of esterification may be observed, i.e., fibers with unchanged double refraction, others which appear only slightly positive, and still others showing slightly negative to completely negative double refraction. These various stages of acetylation may be made more distinct by employing an acetylcellulose solvent to individual fibers: In aniline, for example, that portion of the fiber which shows negative double refraction dissolves, whereas the rest only swells.

The Process of Acetylation When Followed by X-ray Analysis

Many attempts have been made to elucidate the course of the acetylation reaction by x-ray analysis. Changes in the x-ray pattern may be followed if the fiber retains its physical structure during acetyla-

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[329] See also Rocha and Michaelis, *Kolloid-Beihefte,* **30**, 230 (1930).

[330] Möhring, *Wissenschaft und Industrie,* **1**, 70 (1923); *Faserstoffe u. Spinnpflanzen,* **5**, 78 (1923). See also Spence, *J. Phys. Chem.,* **43**, 865 (1939).

tion. Early investigations were made by Herzog and Londberg[331] and von Náray-Szabo and von Susich[332] and were followed by those of Trillat, Hess and co-workers, and of Sisson and various others of more recent date.

A review of the results available reveals the following picture. The x-ray pattern of the original cellulose does not change until a rather high combined acetic acid content has been reached. In the case of acetylation of ramie fibers with acetic anhydride and potassium acetate,[333] this value is about 43 per cent. Between 43 and 53 per cent combined acetic acid, both the original and the triacetyl cellulose pattern exist side by side, and with further increase in acetyl content the pattern becomes exclusively that of the triacetate. In general, the same observations are made if other methods of acetylation are employed—for example, with acetic anhydride and sulfoacetic acid or perchloric acid.

As in nitration, the first phase of the reaction, during which the combined acetic acid content reaches 43 per cent, is obscured. In other words, although about two-thirds of the total hydroxyl groups have been substituted, x-ray analysis furnishes no evidence of chemical reaction; except that the sharpness and intensity of the interferences diminish. Therefore, it is rather difficult to say whether, at any of the stages until distinct changes of the x-ray pattern occur, entirely unacetylated cellulose exists together with acetylated portions, and whether the latter consist of the triacetate or of lower stages of substitution or mixtures of both. It is argued that, if the reaction resulted in the formation of homogeneous mono- and diacetates before the triacetate is formed, one would expect to observe patterns characteristic of these intermediates. However, the frequently ad-

FIG. 62. Ramie fiber fragments after dissolving of acetylated portions. Hess and Schultze.

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[331] Herzog and Londberg, *Ber.*, **57**, 329 (1924); *J. Phys. Chem.*, **30**, 457 (1926).

[332] von Náray-Szabo and von Susich, *Z. physik. Chem.*, **134**, 268 (1928); see also Mark, "Physik und Chemie der Cellulose," p. 276.

[333] Hess and Trogus, *Z. physik. Chem.*, **B5**, 161 (1929); **7**, 10 (1930); **9**, 161 (1930).

vanced claim, namely, that the only product at any stage of the reaction is the triacetate, is only a probability and still has to be proved. This view is hardly altered if the results of Sakurada[334] and co-workers are considered. Partially acetylated cellulose (41.4 per cent combined acetic acid), which showed the mixed cellulose-cellulose triacetate diagram, was extracted with chloroform, a typical solvent for triacetylcellulose, and yielded 6.2 per cent chloroform-soluble material. The result of this experiment merely shows that probably triacetate was present among the products of reaction.[335] The same conclusion must be drawn from another experiment, in which a completely chloroform-soluble triacetate was deacetylated and again partially acetylated to about the same acetyl content as before; this also gave a mixed cellulose-cellulose triacetate x-ray diagram, although this time 17.6 per cent of the partially acetylated material was soluble in chloroform.

On the other hand, some results make it seem probable that, under special conditions, triacetate may be formed on the surface of the fiber at a rather early stage of the reaction. As mentioned earlier, Bernoulli and co-workers found that dried viscose rayon fiber reacted only on the surface and that portion of the outer layer which was separated from the fiber contained 68.3 per cent combined acetic acid, that is, about 6 per cent more than that theoretically required for the triacetate (62.5 per cent).

The x-ray findings can be evaluated intelligently only if they are considered in the light of the results revealed by chemical analysis and by microscopical observations as the reaction proceeds. On this basis, the x-ray findings can be interpreted merely to show that acetylation, in general, proceeds gradually from the surface of the fiber and that of the micelles or chain bundles to the interior without the formation of homogeneous intermediates being detectable (according to Hess and co-workers,[336] a "micellar-heterogeneous" reaction).

Some investigators have interpreted the x-ray data to indicate that, under usual conditions, acetylation proceeds in a permutoidal fashion.[337] However, a recent critical review of the results again shows that it is difficult to arrive at an unequivocal answer to the question

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[334] Sakurada, Hutino, and Matusita, *J. Soc. Chem. Ind., Japan*, 41, 383 (1938).

[335] See also Rassow, Röst-Grande, and Koch, *Z. angew. Chem.*, 42, 618 (1929).

[336] Hess, Trogus, Eveking, and Garthe, *Ann.*, 506, 260 (1933); Hess and Trogus, *Kolloid-Z.*, 68, 168 (1934).

[337] Trillat, *Trans. Faraday Soc.*, 29, 85 (1933); *Chimie & industrie*, 31, 175 (1934); Krüger, Lüdtke, and Oberlies, *Angew. Chem.*, 47, 809 (1934).

of how acetylation actually takes place.[338] The situation is best summarized in the words of Lorand and Georgi,[339] who stated: "There is evidence to support the view that cellulose reactions do not follow a single pattern, and that the type varies, depending upon the reaction partner, its concentration, the reaction medium, temperature, etc. It is quite probable that all the reaction models, worked out for microheterogeneous systems, such as surface reactions, topochemical macroheterogeneous reactions, permutoid or quasi-homogeneous reactions as well as the previously mentioned micellar heterogeneous reactions, may apply to cellulose in one case or another, depending on circumstances." [340]

Various attempts have been made to find a mathematical expression for the rate of acetylation. In view of the many uncontrollable factors involved, no great success was to be expected. The reader may be referred particularly to the publications of Hess and Trogus,[341] Atsuki and Ishii,[342] Sakurada,[343] as well as to the comments made on these attempts by Krüger.[344]

Lower Stages of Acetylation. In the light of what has been said in the section introductory to this chapter and of the experimental evidence produced thus far in the preceding pages, the claims made now and then in the literature regarding the homogeneity of di- and monoacetates [345] can hardly be maintained. Ost has shown that, with the usual acetylation methods, homogeneous lower-substituted acetates cannot be obtained.

Ost studied the preparation of the lower stages of substitution by interrupting the reaction or by the use of limited amounts of acetic anhydride. With zinc chloride as a catalyst, an insufficient quantity of anhydride or the interruption of the reaction, mixtures of unacetylated cellulose and acetylated portions were obtained, the analysis of which showed an average acetyl content approaching that of the diacetate. With sulfuric acid as catalyst, the resulting products were

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[338] Sisson, *Ind. Eng. Chem.*, **30**, 530, 532 (1938).

[339] Lorand and Georgi, *J. Am. Chem. Soc.*, **59**, 1166 (1937); the sentence was quoted by Sisson, *loc. cit.*

[340] See also Spurlin, *Trans. Electrochem. Soc.*, **73**, 95 (1938).

[341] Hess and Trogus, *Z. physik. Chem.*, **B15**, 157 (1931).

[342] Atsuki and Ishii, *J. Soc. Chem. Ind., Japan*, **34**, 331 (1931); **35**, 79 (1932).

[343] Sakurada, *Cellulosechem.*, **15**, 6 (1934); see also Hess, *Angew. Chem.*, **47**, 31 (1934); Sakurada and Morita, *J. Soc. Chem. Ind., Japan*, **41**, 381 (1938).

[344] Krüger, "Zelluloseazetate," pp. 9 and 140.

[345] For example, Barnett, *J. Soc. Chem. Ind.*, **40**, 8 (1921); Malm and Clarke, *J. Am. Chem. Soc.*, **51**, 274 (1929); Clarke and Gillepsie, *ibid.*, **54**, 2083 (1932); Bernoulli, Schenk, and Hagenbuch, *Helv. Chim. Acta*, **13**, 534 (1930); Reiner, *Angew. Chem.*, **46**, 675 (1933).

sulfoacetates with a rather high sulfate content—for example, 2 to 3 per cent combined sulfuric acid—and a combined acetic acid content of 48.8 per cent.[346] Similar products were prepared by Weltzien and Singer.[347]

Still lower stages of substitution, corresponding to a monoacetate, were prepared by Cross and Bevan [348] by boiling with acetic anhydride in the presence of potassium acetate and, more recently, by Reiner, by acetylation in the presence of zinc chloride at room temperature, in which, if the reaction was interrupted after about 12 hours, the fibrous structure was retained. Hess showed that Reiner's product cannot be regarded as a homogeneous monoacetate.[349]

The usual method of preparing partially substituted cellulose acetates consists in subjecting the triacetate to *partial hydrolysis.* The discovery of this method has been attributed to Miles.

> Miles was granted a patent [350] in 1904 for the manufacture of acetates which are soluble in acetone, a cheap and more practical solvent than chloroform which, up to Miles's invention, was regarded as almost the only solvent for commercial acetates. The adoption of Miles's method designates a remarkable upswing in the manufacture of cellulose acetates.

The method is as follows: When the formation of the triacetate ("primary" acetate) is complete, dilute sulfuric and acetic acids are added to the acetylation mixture, and the charge, without isolating the primary acetate, is heated for a number of hours at a temperature not higher than 50° C.

It should be mentioned that Miles's patent does not explain the conversion of the acetone-insoluble triacetate into an acetone-soluble product ("secondary" acetate) on the basis of partial deacetylation. Rather vaguely, the assumption is made that the effect is due to "hydration," that is, the formation of (hypothetical) "acetate hydrates." Subsequent research, particularly by Ost, revealed that the effect is always accompanied by partial deacetylation.

The original method of Miles may be modified in various ways.

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[346] Ost, *Z. angew. Chem.*, **32**, 76, 89 (1919); see also Cross, Bevan, and Briggs, *Ber.*, **38**, 1859, 3531 (1905); Stillich, *ibid.*, **38**, 1241 (1905); Briggs, *Farben-Ztg.*, **24**, 73 (1913).

[347] Weltzien and Singer, *Ann.*, **443**, 93 (1925); see also Araki, *Cellulosechem.*, **18**, 109 (1940), who showed that directly prepared partial acetates may be completely soluble in acetone.

[348] Cross and Bevan, "Researches on Cellulose," 2nd ed., Vol. I, p. 40; Vol. II, p. 11.

[349] Hess, *Angew. Chem.*, **47**, 30 (1934).

[350] Miles, U. S. patent 838,350 (1904).

Ost[351] made a comparative study of numerous commercial suggestions, most of which aimed at a less severe treatment than that of the original method. Instead of dilute sulfuric acid, aqueous solutions of sulfates (potassium sulfate, methylamine sulfates, etc.) or dilute acetic acid at 90 to 95° may be used. The effect may be obtained also by heating the primary acetate (in solution or in isolated form) in the presence of aniline, phenol, amyl alcohol or glycerin. Ost found that in all cases the combined acetic acid content was lowered by 3 to 10 per cent, the corresponding secondary acetates having a combined acetic acid content of between 57.6 and 50.8 per cent.[352] Below 50 per cent, the acetates were insoluble in acetone. If the primary acetate had been prepared with sulfuric acid as catalyst, the process of partial hydrolysis reduced the sulfate content to a low figure,[353] from which it follows that the secondary acetate requires less "stabilization" than the primary product. According to Deripasko,[354] the hydrolysis of the sulfate groups precedes that of the acetyl groups and, provided the anhydride has not been entirely destroyed, the restored hydroxyl groups are reacetylated to a certain extent.

Kita *et al.*[355] confirmed Ost's findings and, moreover, produced numerous experimental data to show the relationship which exists between the conditions of acetylation and the sensitivity of the primary acetate to partial hydrolysis. The results of Ost and Kita and coworkers leave no doubt that, whatever the conditions of partial deacetylation were, the primary acetate suffered, besides a loss in combined acetic acid content, degradation to a greater or smaller extent. This result was confirmed by subsequent investigators—for example, Hess and co-workers.[356] Indeed, these investigators isolated cellobiose and glucose from the methyl alcoholic sodium hydroxide solution used for the saponification of a secondary acetate. These and other low molecular products of degradation may be removed from the acetate by dissolving it in a 1 : 1 benzene-alcohol mixture at 65–70° and by separating the solution from the precipitate which forms on cooling.[357]

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[351] Ost, *Z. angew. Chem.*, **32**, 82 (1919).

[352] Ost, *loc. cit.;* see also Letters, doctoral dissertation, Berlin, quoted in Yarsley, "Über die Herstellung und physikalischen Eigenschaften der Zelluloseazetate," Berlin (1927).

[353] Ost, *loc. cit.*, p. 83.

[354] Deripasko, *Cellulosechem.*, **12**, 254 (1931); Clément and Rivière, *Bull. soc. chim.*, [5] **4**, 869 (1937).

[355] Kita, Asami, Kato, and Tomihisa, *Z. angew. Chem.*, **37**, 414 (1924).

[356] Hess and Schultze, *Ann.*, **444**, 277 (1925).

[357] Hess, Schultze, and Messmer, *Ann.*, **444**, 266, 268, 279 (1925); Hess, "Die Chemie der Cellulose," p. 402.

Numerous additional data are available to show the influence of the various factors, such as temperature, time, and composition of the hydrolyzing mixture,[358] as well as the addition of salts[359] and other conditions.

During the years which followed the appearance of Miles's method and its subsequent modifications,[360] the question of what causes the primary acetate to become soluble in acetone was widely discussed; a definite answer has not even yet been found. Knoevenagel,[361] who devoted much thought to the question, was inclined to believe that the primary acetate undergoes a sort of rearrangement, which, however, remained undefined and today appears rather doubtful.[362] Other investigators have expressed the opinion that the effect is due to a "decrease in particle size" of the dispersed acetate (i.e., degradation).[363] However, the results of later investigations show that degradation is not indispensable, for acetone-solubility has been produced under conditions which do not seem to cause degradation as, for example, the heating of the primary acetate in 95 per cent acetic acid at 100°.[364] Table 31 gives some of the results obtained by Elöd and Schrodt.

It is seen from Table 31 that, on heating the secondary acetate with acetic acid at 100°, the degree of polymerization remains practically unchanged, whereas the acetate loses acetyl and eventually becomes completely acetone-soluble.

Therefore, the essential prerequisite of acetone-solubility would appear to be that the triacetate must be deacetylated to a certain extent The loss of acetyl groups changes the ratio of acetyl to hydroxyl groups and, hence, the polarity of the acetate. As a result, the solubility characteristics of the secondary acetate are different from those

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[358] Kita and Kanuo, *J. Soc. Chem. Ind., Japan*, **31**, 176B (1928); Atsuki and Shinoda, *ibid.*, **31**, 98B (1928); Atsuki and Ishii, *ibid.*, **34**, 331 (1931); **35**, 79 (1932); Sakurada, *ibid.*, **35**, 78 (1932); Deripasko, *loc. cit.;* Clément and Rivière, *loc. cit.;* Kita, Sakurada, and Nakashima, *Cellulosechem.*, **9**, 13 (1928); Pringsheim and Schapiro, *ibid.*, **9**, 80 (1928).

[359] Fuess and Staud, *J. Am. Chem. Soc.*, **53**, 1934 (1931).

[360] Eichengrün in Ullmann, "Enzyclopädie der technischen Chemie," Urban and Schwarzenberg, Berlin (1928), 2nd ed., Vol. 1, p. 116.

[361] Knoevenagel, *Z. angew. Chem.*, **27**, 505 (1914).

[362] Gray, Murray, and Staud, *J. Am. Chem. Soc.*, **51**, 1810 (1929).

[363] Pringsheim, "Polysaccharide," 3rd ed., pp. 76, 77; Pringsheim, Kusenack, and Weinreb, *Papier-Fabr.*, **25**, 785 (1927); Hess and Schultze, *Ann.*, **450**, 65 (1926).

[364] Elöd and Schrodt, *Angew. Chem.*, **49**, 935 (1931); see also Staudinger and Daumiller, *Ann.*, **529**, 250 (1937); Werner and Englemann, *Z. angew. Chem.*, **42**, 443 (1929).

TABLE 31

ACETONE-SOLUBILITY AND DEGREE OF POLYMERIZATION OF CELLULOSE ACETATES

Time of Treatment, Hours	Combined Acetic Acid, %	Acetone-Solubility, %	Viscosity	Degree of Polymerization (Calculated for Cellulose)
0	60.6	18.2	163.3	266
1	60.1	36.7	163.4	265
3	59.8	75.2	163.6	266
6	59.4	92.4	163.4	262
9	58.4	100.0	164.8	272
12	57.0	100.0	165.6	274

of the triacetate. Thus, this explanation of the acetone solubility rests on the hypothesis which, as has been seen, Highfield has developed for nitrocellulose (see p. 205). On the other hand, it should not be overlooked that in cases in which the conversion of the primary into the secondary acetate is, by virtue of the nature of the agent and the conditions employed, accompanied by degradation of the cellulose constituent, such a degradation is likely to aid in accomplishing acetone-solubility. In fact, it will be seen that under certain conditions, the shortening of the average chain length may be the only cause (see p. 266).

This, no doubt, is true, when the solubilization is brought about by heating the triacetate according to Pringsheim and co-workers[365] in molten naphthaline, in boiling tetraline (207°), in acetyl acetate (under pressure), or in boiling benzyl acetate (boiling point 216°). The degradation of the cellulose constituent, obviously due to the high temperatures, is indicated by a considerable drop in viscosity of the solubilized acetate and by the brittleness of the films prepared therefrom.

Effect of Partial Hydrolysis upon Distribution of Hydroxyl Groups. The question arises whether, on partial hydrolysis, acetyl groups are removed from both the primary and secondary positions or from only one of the two positions: Sakurada and Kitabatake[366] determined the amount of triphenylmethyl chloride which condensed with a secondary, acetone-soluble (commercial) acetate dissolved in pyridine. Assuming that, of the free hydroxyl groups, only those in the primary 6-position would react under these conditions, one-third of the total

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[365] Pringsheim, Leibowitz, Schreiber, and Kasten, *Ann.*, **448**, 163 (1926); Pringsheim, Lorand, and Ward, *Cellulosechem.*, **13**, 124 (1932).

[366] Sakurada and Kitabatake, *J. Soc. Chem. Ind., Japan*, **37**, *Supplementary Binding*, **604** (1934).

was found to be in this position. Similar results were obtained by Schorigin, Veitsman, and Makarowa-Semlyanskaja.[367]

Such studies were extended in various directions by Cramer and Purves[368] by allowing *p*-toluenesulfonyl chloride (tosyl chloride) to react with a (commercial) secondary acetate in dilute pyridine solution at 20°. Since no acetyl was removed in this reaction, and shifting of acetyl groups into other positions was unlikely, the tosyl groups were regarded as being attached to the carbon atoms in those positions in which the free hydroxyl groups found themselves after partial hydrolysis. The nature of these positions could be ascertained by utilizing a reaction which has given unequivocal results in the case of *p*-toluenesulfonyl esters of glucose; namely, on heating with an excess of sodium iodide in acetone, the tosyl groups exclusively in the primary position are replaced by iodine to form a 6-iodotosyl glucose. In applying this reaction to cellulose tosyl acetate, it was found that 0.197 tosyl group per glucose residue was in the 6-position. Accordingly, of the hydroxyl groups originally free in the secondary acetate, 0.197 or 35 per cent (of 0.56 hydroxyl groups per glucose residue) were of a primary nature. Considering analytical errors, this figure is regarded as a minimum value and the true figure might probably be close to 50 per cent. When the cellulose tosyl acetate was reacted with pyridinium chloride in pyridine solution at 100°, a chlorotosyl cellulose acetate was obtained, whose chlorine atoms, as in the result obtained with methyl glucoside, were assumed to be in the primary position. In this case, 43 per cent of the original hydroxyl groups of the secondary acetate could be assigned to this position.

Considering the relatively good agreement of the two results, it follows that the partial hydrolysis of the secondary acetate involves the removal of acetyl from the primary and secondary positions in approximately the same proportion.

When the iodine reaction was applied to a tosyl cellulose acetate which had been isolated after about one-third of the original free hydroxyl groups had been tosylated, it was found that at least 84 to 90 per cent were in the primary position. Moreover, the form of the tosylation rate curve, which showed a marked slowing down after 3 hours, was definitely shown to be determined by the eleven- or twelvefold superiority in reaction velocity of the primary in contrast to the combined rates of the two secondary hydroxyls.

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[367] Schorigin, Veitsman, and Makarowa-Semlyanskaja, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 430 (1937); see also Spurlin, *J. Am. Chem. Soc.*, **61**, 2222 (1939).

[368] Cramer and Purves, *J. Am. Chem. Soc.*, **61**, 3458 (1939).

Cramer and Purves drew a parallel between the break in the tosylation rate curve and the break which was observed by Hess and Trogus in the heterogeneous acetylation of cellulose in benzene. Hess and Trogus interpreted this break to indicate that the reaction slowed down after one-third to one-half of the hydroxyl groups had been esterified. It appears quite probable that it is the primary nature of the one-third of the hydroxyl groups available in cellulose which is responsible for the initially rapid rate of acetylation in contrast to the slower rate involving the substitution of the remaining two-thirds, which are secondary in nature. Thus, an acetate produced by direct partial acetylation might have the same acetyl content as a secondary acetate obtained by partial hydrolysis of the triacetate but the distribution of acetyl and hydroxyl groups would be quite different, because free primary hydroxyls would be present in the latter and only secondary hydroxyls in the former.[369]

In pursuing this line of thought, Cramer and Purves concluded that free primary hydroxyl groups may prove to be necessary for solubility in acetone. This view appears to be supported by the observation that a secondary acetate loses its acetone-solubility when heated with glacial acetic acid.[370] It is probable that, on this treatment, the primary hydroxyl groups are preferentially re-esterified. On the other hand, by protecting some of the primary hydroxyl groups in cellulose —for instance, by allowing them to react with an aldehyde—prior to acetylation, and by liberating the aldehyde thereafter, Cramer and Purves believe that acetone-soluble acetates may possibly be obtained without resorting to partial hydrolysis.

Further studies have thrown some light also on the distribution of the *secondary* hydroxyl groups in a partially hydrolyzed (secondary) acetate.[371] On the assumption that the free hydroxyls in the second and the third positions are distributed at random, one would expect some of the glucose residues of the secondary acetate to be devoid of acetyl in both these positions. Thus, these units would contain the —CHOH—CHOH— or glycol grouping. Such groupings in many cases have been found to be oxidized quantitatively to 2 aldehyde groups by the consumption of 1 molecule of lead tetraacetate.

On the basis of such deliberations, the consumption of lead acetate by an acetone-soluble (commercial) acetate, dissolved in glacial acetic acid, was determined at intervals. From the fact that cellulose triacetate consumed no lead

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[369] See also Sakurada and Morita, *J. Soc. Chem. Ind., Japan, Supplementary Binding,* **41,** 381B (1938).

[370] See also Deripasko, *Cellulosechem.,* **12,** 261 (1931); Kita, *Z. angew. Chem.,* **37,** 414 (1924); Kita, Sakurada, and Nakashima, *Cellulosechem.,* **9,** 13, 27 (1928).

[371] Cramer, Hocket, and Purves, *J. Am. Chem. Soc.,* **61,** 3463 (1939); Gardner and Purves, *ibid.,* **64,** 1539 (1942).

acetate, it follows that the glycol groupings are protected by acetyl groups against oxidation in a satisfactory manner. With the partially acetylated preparation, the lead acetate consumption was found to decrease with time, but a break in the curve plotted from both values could be taken to indicate the end of the true glycol oxidation. On this assumption, it was found that 1 glycol grouping was present in every 100 to 150 glucose residues. Since this value is very different from a calculation based upon the assumption of a purely random distribution of hydroxyl groups between the two positions, the conclusion is drawn that the distribution is by no means a matter of chance. It remains to be seen whether this interesting conclusion, which deviates from the common view, can be further substantiated.

In the light of the work of Purves and co-workers, it may be assumed that, on partial hydrolysis, the acetyl groups are not always removed from the same but from different original positions, depending upon the agent used and the conditions employed. This assumption may possibly explain the differences which have been observed with respect to acetone-solubility of secondary acetates having the same acetyl content. Thus Elöd and Schrodt[372] observed that secondary acetates, prepared by allowing the triacetate to stand in dilute nitric acid at room temperature until the desired lower acetyl content was obtained, were insoluble in acetone, whereas secondary acetates prepared by partial hydrolysis in the usual way and having the same acetyl content were soluble. The opposite result was found by Sakurada and Morita,[373] partial hydrolysis of cellulose triacetate with dilute nitric acid resulting in acetone solubility. Of course, it is difficult to say to what extent degradation participated in the conversions to the acetone-soluble stage.

Acetone-solubility of secondary acetates has also been related to their combined sulfuric acid content. Caille[374] found that, on dissolution and reprecipitation, the acetone-solubility of a primary acetate increased, while the combined sulfuric acid content decreased. This observation was confirmed by Deripasko.[375] A primary acetate, having 2 per cent combined sulfuric acid, showed, after solution in acetic acid and precipitation with water, only 0.5 per cent combined sulfuric acid. Similar observations were made with secondary acetates on corresponding treatments. Such treatments were found to convert acetates which were insoluble or only partially soluble in acetone into fully acetone-soluble products.

It appears possible that the increase of the acetyl content which, as we have seen, follows a decrease in the sulfate content changes the proportion of substituted and free hydroxyl groups in a way which favors the affinity for acetone. However, it would be premature to draw definite conclusions, because the experimental data available are still insufficient.

Secondary acetates may be converted into the higher stages and into the triacetate in various ways, some of which were mentioned previously. It may be added that Hess and Schultze[376] employed the

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[372] Elöd and Schrodt, *Angew. Chem.*, **44**, 934 (1931).

[373] Sakurada and Morita, *J. Soc. Chem. Ind., Japan, Supplementary Binding,* **41**, 385B (1938).

[374] Caille, *Chimie & industrie,* **19**, 402 (1928); **25**, 276 (1931).

[375] Deripasko, *Cellulosechem.,* **12**, 261 (1931).

[376] Hess and Schultze, *Ann.,* **444**, 284 (1925).

zinc chloride method; Kita, Sakurada, and Nakashima[377] used both sulfuric acid and zinc chloride as catalysts; Bernoulli and co-workers[378] and Staudinger and Daumiller[379] dissolved or suspended the secondary acetate in pyridine and allowed it to react with acetic anhydride at room temperature.

The fact that on reacetylation, regardless of cellulose degradation, the acetates became insoluble in acetone seems to support the view that acetone-solubility is primarily a matter of substitution.

The Fractionation of Cellulose Acetates

Considering the fact that cellulose consists of chain molecules of varying lengths, the triacetate must also be regarded as heterogeneous with respect to chain length. Since, however, all three hydroxyl groups which are available for substitution per glucose residue are substituted by acetyl groups, the triacetate is homogeneous as regards the degree of substitution. In contrast, the intermediate stages, being incompletely esterified, are heterogeneous in respect to both chain length and degree of substitution. Hence, one encounters the same situation as obviously exists with cellulose nitrates, and this similarity extends through all treatments which aim at a separation of the constituents.

Data pertaining to the fractionation of cellulose *triacetate* are scarce. Some results are found in the work of Elöd and Schmidt-Bielenberg.[380] Various triacetate preparations were dissolved in chloroform and subjected to stepwise precipitation with methanol. The various fractions thus obtained were analyzed for specific viscosity (at a concentration of 1 : 200 in *m*-cresol). The specific viscosities were converted into molecular weights; Staudinger's equation was used. The data of Table 32 show that the molecular weights vary considerably (maximum and minimum values). It is also seen that all acetates are considerably degraded. Acetates 1 to 6 were prepared with retention of fibrous structure.

Most of the work published on fractionation refers to *acetone-soluble acetates* and, in almost all cases, the method of fractionation employed was that of fractional precipitation, using an acetone solution of the acetate and water or alcohol or a mixture of water and alcohol for precipitation.

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[377] Kita, Sakurada, and Nakashima, *Cellulosechem.*, **9**, 27 (1928).

[378] Bernoulli, Schenk, and Hagenbuch, *loc. cit.*, p. 571.

[379] Staudinger and Daumiller, *loc. cit.*, p. 248.

[380] Elöd and Schmidt-Bielenberg, *Z. physik. Chem.*, **B23**, 38 (1934).

TABLE 32

ACETYL CONTENTS AND MOLECULAR WEIGHTS OF VARIOUS CELLULOSE TRIACETATES

No.	Acetates from	Combined Acetic Acid, %	Molecular Weights and Yields				
			Average	Maximum	Yield, %	Minimum	Yield, %
1	Purified ramie	....	58,000	65,500	25	23,800	6
2	Purified cotton	60.2	62,300	67,000	33	19,300	5
3	Raw cotton	60.9	68,000	73,800	65	19,300	...
4	Wood pulp	60.2	63,000	67,500	70	25,400	6
5	Hemp	60.5	63,000	69,000	34	10,500	2–3
6	Flax	61.2	53,500	58,200	15	9,400	3
7	Commercial triacetate	60.0	34,800	42,000	44	8,200	7
8	Cotton acetylated in solution	....	30,700	36,000	..	6,400	...

The results of these investigations are very much the same as those obtained by the fractionation of nitrates: The fractions show great variation in chain length but very little or none in acetyl content. This result seems to indicate that the acetyl groups are more uniformly distributed along the chains (regardless of their length) than could be anticipated.

The investigations in question may be summarized as follows:

Fractional precipitation with water from acetone solutions was probably first applied by Mardles,[381] who demonstrated the heterogeneity of commercial acetates by viscosity determinations on the various fractions; the first fraction contained the most ash. Just as, from a solution of such polymers as polyvinyl acetate,[382] polystyrene,[383] and the like, the highest polymers are precipitated first. McNally and Godbout[384] found that the first fraction precipitated from an acetone-soluble acetate showed the highest and the last fraction the lowest viscosity, whereas the acetyl contents were fairly constant. The first fractions were also more insoluble in solvents than those precipitated later.

Rocha[385] applied the same method of fractional precipitation. Three fractions were obtained, of which the first contained most of the inorganic impurities and

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[381] Mardles, *J. Soc. Chem. Ind.*, **123**, 1951 (1923); *Kolloid-Z.*, **49**, 4 (1929).

[382] Whitby, McNally, and Gallay, *Trans. Royal Soc. Can.*, **22**, 27 (1928).

[383] Staudinger, *Ber.*, **59**, 3019 (1926).

[384] McNally and Godbout, *J. Am. Chem. Soc.*, **51**, 3095 (1929).

[385] Rocha, *Kolloid-Beihefte*, **30**, 230 (1930).

coloring matter, the second the acetate in its "purest" form, and the last the shorter chains and the acetolytic by-products. Further fractionation resulted in eleven smaller fractions, the acetyl content of which varied only from 39.8 to 38.2 per cent, whereas the relative viscosities, determined in acetone, varied from 7.3 to 1.97.

Herzog and Deripasko[386] extended the work of Rocha and determined the molecular weights of the various fractions by specific viscosity and osmotic pressure measurements. A fair agreement between the molecular weights derived from the two sets of data was established, provided the concentrations of the solutions measured were not too high. The molecular weights derived from osmotic pressure measurements (0.5 per cent concentration) are shown in Table 33. Similar results were obtained by Herz[387] and by Ohl.[388]

TABLE 33

MOLECULAR WEIGHT AND ACETYL CONTENT OF FRACTIONS OBTAINED FROM A SECONDARY ACETATE

Fractions	Combined Acetic Acid, %	Molecular Weight (Osmotic Pressure)
Original	51.9	....
I	52.5	68,000
II	52.5	52,000
III	52.3	37,000
IV	52.5	21,000

Diversion of a commercial secondary acetate into a greater number of fractions (15) was accomplished by Sookne, Rutherford, Mark, and Harris,[389] who used precipitation with ethyl alcohol from an acetone solution. The degree of polymerization varied from 380 to 30, whereas the acetyl contents were approximately that of the starting material (38.5 per cent) with the exception of the fractions of very low degree of polymerization. The difference in chain length distribution in cotton linters and wood pulp and their acetates was demonstrated by Lachs and co-workers[390] and the greater heterogeneity of wood pulp was established. The influence of chain length distribution upon the physical properties of acetate rayon was shown by Mark,[391] and of films by Sookne and Harris.[392] It was found that a fraction of D.P. 30 would not form a coherent film, but fractions of higher D.P. showed a rapid improvement

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[386] Herzog and Deripasko, *Cellulosechem.*, **13**, 25 (1932). The viscosity data of Herzog and Deripasko were criticized by Ubbelohde, *Cellulosechem.*, **14**, 169 (1933). But Herzog showed, *ibid.*, **15**, 99 (1934), that the correction omitted in the original data caused a change of these data of less than 10 per cent.

[387] Herz, *Cellulosechem.*, **15**, 95 (1934).

[388] Ohl, *Kunstseide*, **14**, 3 (1932).

[389] Sookne, Rutherford, Mark, and Harris, *J. Research Natl. Bur. Standards*, **29**, 123 (1942).

[390] Lachs, Kronman, and Wajs, *Kolloid-Z.*, **79**, 91 (1937); *ibid.*, **87**, 199 (1938); Lachs, Kronman, and Zurawicki, *ibid.*, **87**, 195 (1939); see also Mark below.

[391] Mark, *Paper Trade J.*, **113**, No. 33, 34 (1941).

[392] Sookne and Harris, *J. Research Natl. Bur. Standards*, **30**, 1 (1943).

of mechanical properties with increase in D.P. Above 150, further improvement was slight. Folding endurance and ultimate elongation were found to be more sensitive than tensile strength to changes in D.P. and heterogeneity with respect to D.P.

Fractional solution as a means of ascertaining the degree of homogeneity of cellulose acetates was employed by Sakurada and Taniguchi.[393] The solvents consisted of mixtures of benzyl and methyl acetate with increasing amounts of methyl acetate. The result of these studies were much the same as those obtained by the method of fractional precipitation; that is, the fractions varied widely in viscosity but scarcely at all in acetyl content.

The Solubility of Cellulose Acetates

As with nitrocellulose, the solubility of acetyl cellulose depends chiefly upon the degree of polymerization, the physical form (whether fibrous, nonfibrous, prepared from regenerated cellulose, etc.), the degree of substitution, and the nature of the solvent. As was shown when the behavior of the secondary acetates with acetone was discussed, it is often difficult, if at all possible, to decide whether solubility is a function of the degree of polymerization or that of substitution, for reliable methods for ascertaining each influence without interference by the other are lacking. Quite often the acetyl content seems to have no influence upon the solubility, and the degree of polymerization and, moreover, the physical form of the acetates are the predominating factors.

An example showing that solubility may be a function solely of the degree of polymerization is derived from the observation [394] that, under the influence of ultraviolet light, and provided the influence of the air is carefully excluded, cellulose acetate changes in both viscosity and solubility without a change in the degree of substitution.[395] When a solution of cellulose triacetate in acetic acid in the absence of air oxygen was exposed to ultraviolet rays emitted from a mercury vapor lamp, the viscosity of the acetate decreased 50 per cent after 6 hours

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[393] Sakurada and Taniguchi, *J. Soc. Chem. Ind., Japan,* **35**, 249B (1932).

[394] I. G. Farbenindustrie and Bincer, German patent 601,478 (1934); see also Clément, Rivière, and Beck, *Chimie & industrie,* **27**, 702 (1932); Montana, *Chimica e industria (Italy)*, **20**, 237 (1938); Montonna and Winding, papers presented before the American Chemical Society, Pittsburgh, Pa. (1936), and at Chapel Hill (1937); see also Winding, doctoral dissertation, University of Minnesota, Minneapolis (1936).

[395] Irradiation in the presence of air caused the combined acetic acid content to drop from 63.2 to 53.2 per cent (German patent 601,478). The treatment in the absence of air seems to offer a method for preparing a polymer-homologous series of cellulose acetates (see Chapter XV).

and, on longer irradiation, to 2 per cent of its original value. Simultaneously, the acetate had become acetone-soluble for the greatest part, but the acetyl content had not changed. Likewise, triacetate, prepared by the pyridine method and insoluble in all usual solvents, had become soluble in glacial acetic acid, in chloroform, and in acetone after exposure to ultraviolet light for only 4 hours; again the acetyl content remained unchanged. Thus, in these cases, the cleavage of glycosidic linkages, as indicated by the drop in viscosity, seems to be solely responsible for the change in solubility. Why, in the presence of air, the acetyl content drops is still to be explained.

The increase in solubility with decreasing chain length of the cellulosic constituent [396] is not yet fully understood, except that it is conceivable that shorter acetate chain molecules become more easily solvated than longer ones.[397]

Omitting from further deliberations the influence of the degree of polymerization and the influence of the physical form discussed earlier in this chapter, the solubility or nonsolubility of cellulose acetates has been explained in various ways. The most satisfactory explanation is based upon the ideas which Highfield has developed for cellulose nitrates and which have been discussed earlier in this chapter. As with cellulose nitrates, optimum solubility appears to be the result of striking a balance between polar and nonpolar groups in the acetate and in the solvent or solvent mixture. The results of a number of investigations support this concept quite satisfactorily. Thus, Sheppard, Carver, and Houck [398] observed maximum solvent power when a certain quantity of water had been added to the solvent. Similarly, Sheppard and Sweet [399] found that, when a certain quantity of a nonsolvent (diluent) was added to an acetone acetate solution, a point was established at which the nonsolvent developed solvent properties in conjunction with the acetone. Further, Werner and Engelmann [400] showed that an acetone-insoluble acetate (containing 50 per cent combined acetic acid) was soluble in a mixture of acetone and alcohol or acetone and water. Likewise, a secondary acetate of 58.9 per cent which was insoluble in chloroform became soluble therein when a

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[396] See also Sookne *et al.*, *loc. cit.*

[397] Staudinger and Fritschi, *Helv. Chim. Acta*, **5**, 785T (1922); see also *Ber.*, **63**, 3132 (1930).

[398] Sheppard, Carver, and Houck, "Colloid Symposium Monograph V," 243 (1928).

[399] Sheppard and Sweet, *J. Phys. Chem.*, **36**, 819 (1932); see also Whitby, "Colloid Symposium Monograph IV," 203 (1926).

[400] Werner and Engelmann, *Z. angew. Chem.*, **42**, 443 (1929).

certain quantity of ethyl alcohol was added to the chloroform. The influence of a change in polarity of the solvents upon the solubility of the acetate was also recognized when mixtures of acetone with benzene or ethyl alcohol were used. Similar observations were made by Atsuki and Shinoda.[401]

The studies of Ostwald and co-workers on the effect of the dipole moment of numerous liquids upon the swelling and solubility of cellulose acetates may be regarded as the application and extension of Highfield's ideas. Ostwald and Ortloff[402] divided a great number of liquids into three groups: (1) inactive liquids, comprising simple and halogenized hydrocarbons; (2) liquids possessing swelling effect; and (3) liquids possessing solvent activity. The last two groups are difficult to characterize from a chemical viewpoint; they comprise esters, ketones, alcohols, and amines. All three groups, however, may be classified on the basis of a dielectric function, namely, μ^2/ϵ. In this expression, μ is the dipole moment and ϵ the dielectric constant. The value of this quotient was found to be very small for the inactive liquids (0 to 0.105), whereas for the liquids having swelling activity it was 0.115 to 0.235, and for the liquids having solvent activity, 0.251 to 0.528.

A relationship was found to exist between the dielectric function (solvent power) and the viscosity of the acetate in single solvents and in mixtures: The viscosity was low in liquids possessing high solvent activity and *vice versa*, and the maximum solvent power of a mixture of solvents corresponded to the minimum viscosity. The various aspects of this relationship[403] have been discussed more recently by Moll[404] and by Takei and Erbring.[405]

Knoevenagel was inclined to believe that the solvent forms an addition compound with the acetate. Subsequent investigators adopted similar ideas.[406] In this connection the influence of low temperatures upon the solvent power of organic liquids for cellulose nitrates and acetates appears of interest. Berl and Körber[407] observed that

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[401] Atsuki and Shinoda, *Rep. Aeronaut. Research Inst., Tôkyô Imp. Univ.*, III (Feb., 1928).

[402] Ostwald and Ortloff, *Kolloid-Z.*, **59**, 25 (1932); see also Ostwald and Ortloff, *ibid.*, **58**, 295 (1932); **58**, 215 (1932).

[403] See also von Fischer, *Kolloid-Z.*, **29**, 260 (1921).

[404] Moll, *Kolloid-Z.*, **85**, 335 (1938); *Kolloid-Beihefte*, **49**, 1 (1939).

[405] Takei and Erbring, *Kolloid-Z.*, **94**, 312 (1941).

[406] Mardles, *J. Soc. Chem. Ind.*, **42**, 129 (1923); *Kolloid-Z.*, **49**, 11 (1929); McBain, *J. Phys. Chem.*, **30**, 239 (1926); McBain, Harvey, and Smith, *J. Phys. Chem.*, **30**, 312 (1926); see also Moll, *Kolloid-Beihefte*, **49**, 60 (1938).

[407] Berl and Körber, *J. Am. Chem. Soc.*, **61**, 154 (1939).

solvents or mixtures of solvents which exert no dissolving effect upon these cellulose derivatives at room temperature become good solvents when applied at such low temperatures as −50° and the like. This effect is attributed to the formation of soluble addition compounds, assuming that these compounds are stable only at very low temperatures and dissociate into their constituents at elevated temperatures.

The methods for determining the solubility of cellulose acetates in various solvents and solvent mixtures are, in general, the same as for nitrocellulose. They are discussed by Krüger.[408]

Whereas the primary chloroform-soluble acetate is, in general, not soluble in acetone, the secondary acetone-soluble acetate is usually soluble in chloroform. The chloroform-solubility is often improved by small amounts of alcohol.

The triacetate also dissolves in acetylene tetrachloride and other chlorine-substituted hydrocarbons; likewise, aniline, phenol, formic acid, glacial acetic acid, and some formic and benzoic acid esters are solvents. Solubility has also been observed in formamide and in liquid sulfur dioxide.[409]

The solvents and solvent combinations are more numerous for secondary acetates than for the triacetate. Acetates may also be dissolved in some concentrated salt solutions.[410]

The acetone-solubility range of commercial secondary acetates comprises an acetyl content between 35.8 and 41.5 per cent. All commercial acetates fall within this range; those for plastics range between 36.5 and 38, for rayon between 38 and 39.4, and for films between 39.4 and 41.6 per cent acetyl.[411] The rayon industry consumes 70 to 80 per cent of all acetate manufactured.[412]

Until recently, the opinion has prevailed that only secondary acetates yield high grade conversion products, such as threads and films, and that the products originating from primary acetates are commercially unsuitable. One of the probable reasons for this view may be found in the difficulty in the early periods of manufacture in the preparation of triacetates of sufficient stability. Residues of sulfuric acid caused the products to become brittle within a short period of time. Today, such deficiency is easily overcome. In addition, cheap

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[408] Krüger, "Die Zelluloseazetate," p. 85.

[409] Fenton and Berry, *Proc. Cambridge Phil. Soc.*, **20**, Part I, 16 (1920). See also Whitby, "Colloid Symposium Monograph IV," 205 (1926); Lee, *J. Soc. Chem. Ind.*, **49**, 226 (1931).

[410] Herzog and Schweiger, *Z. physiol. Chem.*, **117**, 61 (1921); Herzog, *Kolloid-Z.*, **39**, 101 (1926). See also Williams, quoted in Cross and Bevan, "Researches on Cellulose (1910–22)," Vol. 4, p. 60. For x-ray diagrams of secondary cellulose acetates swollen in lithium thiocyanate see Katz and Derksen, *Rec. trav. chim.*, **50**, 746 (1931).

[411] Conaway, *Ind. Eng. Chem.*, **30**, 52 (1938).

[412] See also the statistical data published by *Rayon Organon*, Textile Economics Bureau Inc., New York, for example, **11**, No. 2 and No. 7 (1940).

and commercially feasible solvents—for example, methyl chloride or mixtures of this solvent with others—are available. Water resistance and physical properties of films and threads prepared from the primary acetate are said to be excellent.[413] The suitability of the triacetate for commercial uses would do away with the necessity of subjecting it to partial hydrolysis. Likewise, the tripropionate and the tributyrate are said to be commercially useful preparations.[414]

Many organic liquids exert a pronounced swelling effect upon cellulose acetate without, however, dissolving it. The reader may refer to the numerous studies on this subject by Knoevenagel and co-workers.[415] More recently, results have been reported[416] which are explained on the assumption that the swelling in certain organic liquids is primarily due to hydrogen bond formation between acid radical and liquid. Thus, the uptake of phenol by cellulose acetate is explained by hydrogen bond formation between the phenolic hydroxyl group and one of the oxygen atoms of the carbonyl group of the acid radical.

The Viscosity of Cellulose Acetate Solutions

Acetylcellulose may be expected to produce solution viscosities dependent upon the factors which govern this characteristic in the case of other lyophilic colloids. As with nitrocellulose, the viscosity of cellulose acetates in organic solvents is influenced by pressure,[417] temperature,[418] and concentration,[419] and shows similar anomalies. On standing, for example, acetate solutions tend to develop structural viscosity, although the observations are to a certain extent contradictory.[420]

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[413] Werner, *Angew. Chem.*, **50**, 127 (1937); *ibid.*, **51**, 681 (1938).

[414] Werner, *Chem.-Ztg.*, **65**, 467 (1941).

[415] Knoevenagel and co-workers in *Kolloid-Beihefte*, 1921 and 1923; also Ostwald and Orloff, *Kolloid-Z.*, **59**, 25 (1932).

[416] Mardsen and Urquhart, *J. Textile Inst.*, **23**, T105 (1942).

[417] Mardles, *J. Chem. Soc.*, **123**, 1951 (1923); Sheppard, Carver and Houck, "Colloid Symposium Monograph V," 243 (1927); Phipps, *ibid.*, **5**, 259 (1927); Sakurada and Hess, *Ber.*, **64**, 1174, 1183 (1931); Eisenschitz and Rabinowitsch, *ibid.*, **64**, 2522 (1931); see also Rabinowitsch, *Z. physik. Chem.*, **145**, 1 (1929); Hess and Rabinowitsch, *Ber.*, **65**, 1407, 1856 (1932).

[418] Mardles, *loc. cit.*; Staudinger and Schweitzer, *Ber.*, **63**, 2317 (1930); Meyer and Mark, *ibid.*, **64**, 1999 (1931); Berl and Umstätter, *Z. physik. Chem.*, **148**, 471 (1930); Berl, Umstätter and Karrer, *ibid.*, **152**, 284 (1931); *Kolloid-Beihefte*, **34**, 22 (1931); Fickentscher, *Cellulosechem.*, **13**, 71 (1932).

[419] Mardles, *loc. cit.*; Staudinger and Freudenberger, *Ber.*, **63**, 2331 (1930); Berl, Rau, Berkenfeld, Djang and Dillenius, *Kolloid-Beihefte*, **34**, 12 (1931); Barthelemy, *Chimie & Industrie*, **25**, 819 (1931); Berl and Umstätter, *Kolloid-Beihefte*, **34**, 12 (1931); Suida, *Cellulosechem.*, **12**, 310 (1931); Fickentscher, *ibid.*, **13**, 58, 71 (1932); Sakurada, *J. Soc. Chem. Ind., Japan*, **35**, 445B (1932).

[420] See, for example, Mardles, *loc. cit.*; Yarsley, "Über die Herstellung und physikalischen Eigenschaften der Zelluloseazetate."

Likewise, the phenomena which occur on the addition of a nonsolvent to a solution of acetylcellulose are evidently the same as those which are involved in the nitrocellulose solution-nonsolvent system. For example, when increasing quantities of water are added to a solution of acetylcellulose in acetone, the viscosity decreases first, reaches a minimum, and then gradually increases again. Similar observations were made when, instead of water, ethyl or methyl alcohol was added to the solution in acetone.[421] This change in viscosity may be explained in the same way as in the case of nitrocellulose. Thus it would appear that here also the decrease in viscosity is due to a gradual desolvation of the acetylcellulose particles, until a point is reached at which the total volume is smallest. When so much water is added that the particles become entirely dissolvated, they approach each other so closely that a new structure is built up; i.e., the viscosity increases until gelation occurs.[422] In certain systems, for example, when benzene is added to a solution of acetylcellulose in acetone, syneresis of the gel has been observed.[423]

Gelation may be prevented by subjecting the solution to stirring while the nonsolvent is being added. Under these conditions, precipitation occurs when a certain quantity of nonsolvent has been added. In this way it is possible to divide the acetate into various fractions, in much the same way as this may be done with nitrocellulose.

The change in viscosity which acetylcellulose sometimes undergoes during storage has been explained[424] on the assumption that even the small quantities of water which may be taken up by the preparation when stored in sealed bottles through loose stoppers, etc., may exert its influence upon the viscosity of the solution. Likewise, small variations in the moisture content of freshly prepared and dried acetylcellulose may be responsible for the difficulty in reproducing the same viscosity values under otherwise equal conditions. The same observations were made on ethylcellulose, a solution of which in benzene appears to be even more sensitive to water.

In some cases, deviations from the ordinary behavior seem to occur which are not yet fully understood. For example, on the addition of benzene to the solution of a secondary acetate in acetone no decrease and only a steady increase of the viscosity was observed.[425] Moreover, the second liquid evidently

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[421] Barr and Bircumshaw, *Kolloid-Z.*, **28**, 223 (1921); von Fischer, *ibid.*, **29**, 260 (1921); Mardles, *loc. cit.;* Dechiens, *Chimie & industrie*, **20**, 175T (1928); *Kolloid-Z.*, **49**, 11 (1929); Sheppard and Houck, *J. Rheol.*, **1**, 20 (1929); Barthelemy, *Chimie & industrie*, **25**, 819 (1931); Herzog and Deripasko, *Cellulosechem.*, **13**, 25 (1932).

[422] Mark, "Physik und Chemie der Cellulose," pp. 271, 280.

[423] Nisizawa, *Kolloid-Z.*, **56**, 323 (1931).

[424] Suida, *Cellulosechem.*, **12**, 310 (1931).

[425] Barr and Bircumshaw, *loc. cit.*

does not always need to be a nonsolvent. An acetate solvent, such as cyclohexanone, was found to cause a minimum in viscosity when 75 per cent of it had been added to a solution of the acetate in benzyl alcohol.[426]

The phenomenon which manifests itself in an initial decrease of viscosity and subsequent increase followed by gelation and syneresis is obviously different from what has been termed "gelatinization" and which is sometimes observed when cellulose is acetylated in the presence of sulfuric acid as catalyst. Although in the beginning of the reaction peptization of the cellulosic material might seem to take a normal course, in later stages the dispersion coagulates to form a gelatinous mass.

That the presence of sulfuric acid is possibly instrumental in achieving this effect seems to follow from an observation of Knoevenagel and König,[427] that the solution of a secondary acetate in acetone was found to "gelatinize" when very small amounts of sulfuric acid or sulfoacetic acid were added to the solution. The mechanism of this phenomenon has not yet been explained.

As with nitrocellulose, the degree of polymerization of the original cellulosic material is reflected in the acetate. In other words, high viscosity cellulosic materials yield high viscosity acetates and *vice versa*. This relation, which also extends to the secondary acetate, was known to the early investigators in the field and has been frequently mentioned in later studies.[428] Conceivably, if degradation during acetylation and during partial hydrolysis acquired considerable proportions, the viscosity of the final products would be found much lower than could have been anticipated from the viscosity of the original cellulosic material.

Whether or not a relationship exists between the viscosity and the *degree of substitution* of the acetate cannot be stated with certainty. The relatively few data which are available are contradictory. Thus Elöd and Schrodt[429] found that the specific viscosity (concentration of 0.014 per cent in *m*-cresol) of a series of acetates of decreasing acetyl content remained constant. On the other hand, Staudinger and Daumiller[430] found that the viscosity of secondary acetates was about 20 per cent higher than that of the triacetates into which the former had been converted by the pyridine method, both types of preparations being dissolved at the same concentration in the same solvent (1 per cent in *m*-cresol). Likewise, the viscosity of a secondary acetate was higher than that of a triacetate when the former had been obtained by partial hydrolysis of the latter. This conversion was accomplished

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[426] Mardles, *Kolloid-Z.*, **49**, 11 (1929).

[427] Knoevenagel and König, *Cellulosechem.*, **3**, 113 (1922).

[428] Kita, *Z. angew. Chem.*, **37**, 414 (1924); Hess, Schultze, and Messmer, *Ann.*, **444**, 281 (1925); Letters, doctoral dissertation, Berlin (1926).

[429] Elöd and Schrodt, *Angew. Chem.*, **44**, 933 (1931).

[430] Staudinger and Daumiller, *Ann.*, **529**, 250 (1937).

by heating the primary acetate in 95 per cent acetic acid at 100°, i.e., by a method which was found not to change its degree of polymerization (see p. 258).

That the viscosity of the lower substituted acetate should be higher than that of the triacetate is surprising in view of the contrasting observations made on nitrocellulose. It will be recalled (see p. 212) that the viscosity of nitrocellulose in acetone was found to increase with increasing degree of substitution.

As we have seen, the viscosity of nitrocellulose may be lowered by certain *after-treatments*, e.g., by boiling in water under pressure (p. 214). Few data are available to show that the same effect is obtained with cellulose acetate under similar treatment. Wehr[431] found that the viscosity of a commercial secondary acetate was lowered to about half of its original value by heating in methyl glycol at 60° for 120 days. No doubt, the drop in viscosity was due to degradation. The acetyl content was not ascertained.

The Stability of Cellulose Acetates

As has been mentioned previously, the stability of cellulose acetates prepared with sulfuric acid as catalyst depends chiefly upon its sulfuric acid content, both chemically combined and merely absorbed. In addition, the stability is influenced by the amount of degradation products of low molecular weight which might be retained. The sulfuric acid tends to decompose the acetate even at room temperature. When a bottle in which a poorly stabilized acetate had been kept for a certain length of time is opened, the odor of acetic acid is noticed. Simultaneously, the free sulfuric acid exerts a degrading influence upon the cellulosic constituent. Both these effects become quite noticeable when the acetate is heated. Carefully stabilized preparations, however, may be heated to 200° and higher before showing signs of decomposition. The first indication of decomposition is a discoloration to yellow and brown.

The point at which the acetate begins to decompose lies near its melting point. The latter is not sharp, however. In general it decreases with the acetyl content, but it is also influenced by its sulfate content. Thus Ost[432] found that a combined sulfuric acid content of more than 0.5 per cent depressed the melting point. Such preparations underwent discoloration at a temperature of 100°.

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[431] Wehr, *Kolloid-Z.*, **88**, 185 (1939).

[432] Ost, *Z. angew. Chem.*, **19**, 67 (1919).

Under the influence of heat, other volatile products, in addition to acetic acid, are formed. Although their nature is not known, they may be determined quantitatively.[433] The total of the volatile products (including the acetic acid liberated) may be oxidized (over red-hot copper oxide) to carbon dioxide; this is a measure of the stability of the acetate at a given temperature. Berl and Rueff found a carefully stabilized triacetate to withstand a temperature of 235° for 3 hours before showing signs of discoloration and substantial liberation of acetic acid, whereas an unstable triacetate began to decompose at a temperature of 195°. A stable acetone-soluble secondary acetate (55 per cent combined acetic acid) showed the same behavior as the stable triacetate.[434]

Here, another effect of heat upon cellulose acetates (and other cellulose derivatives) may be mentioned. Baker, Fuller, and Pape[435] showed that the ratio of crystalline to disordered regions in the micellar system may be changed by subjecting cellulose derivatives to the action of heat under certain conditions. These changes may be followed by x-ray analysis. Various stages from crystalline to disordered were produced in cellulose triacetate, cellulose acetate containing a small amount of butyryl, and cellulose tributyrate by subjecting them to "quenching" (cooling from the temperature of their melting points to 20° and −75°) and to "annealing" (heating the dry quenched samples in an oven at temperatures below their softening or deforming points in the dry-hydrogen atmosphere). These studies are of considerable interest in view of the relationship which, as has been seen, exists between the ratio of the crystalline to the noncrystalline portions of cellulose and cellulose derivatives and their physical properties.

The absorption of ultraviolet light by cellulose acetate and other cellulose derivatives in solution has been studied by Rassow and Aehnelt[436] to which the reader is referred. The effect of ultraviolet light upon the properties of cellulose acetates has been discussed on p. 266.[437]

The optical properties of the cellulose acetates are of considerable commercial interest in view of the many uses which cellulose acetate has found in

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[433] Berl and Rueff, *Cellulosechem.*, **14**, 44 (1933).

[434] Regarding other heat stability tests for acetyl cellulose see, for example, Dorée, "Methods of Cellulose Chemistry," p. 281; Krüger, "Zelluloseazetate," p. 205. See also Nat. Bur. Standards (U. S.), *J. Franklin Institute*, **234**, 492 (1942); Schröder, *Kunststoffe*, **32**, 82 (1942).

[435] Baker, Fuller, and Pape, *J. Am. Chem. Soc.*, **64**, 776 (1942).

[436] Rassow and Aehnelt, *Cellulosechem.*, **10**, 169 (1929); see also Davey and Duncan, *Phys. Rev.*, [2] **35**, 1423 (1930). For fluorescence of cellulose acetates in the ultraviolet light, see McNally and Vanselow, *J. Am. Chem. Soc.*, **52**, 3846 (1930).

[437] See also Montana, *Holz Roh- u. Werkstoff*, **1**, 438 (1938).

the plastics and safety glass industries. It is noteworthy that cellulose acetate transmits a relatively high percentage of ultraviolet light.

For the sorption of water by cellulose acetates see Chapter II.

Optical Rotation of Cellulose Acetates

Solutions of cellulose acetates show the phenomenon of optical rotation. Ost[438] found that triacetates prepared by various methods showed levorotation values in chloroform ranging from −24° to −20° and, furthermore, that these values decreased and then changed into dextrorotation as the molecular weight of the acetates decreased. The same observation was made when the triacetates were subjected to partial hydrolysis. Measured in chloroform under the same conditions, secondary acetates[439] showed values ranging from −13° to +2°. Since optical rotation also depends upon the acetyl content of the acetate, the change in specific rotation observed to occur on partial hydrolysis cannot be interpreted solely as being indicative of a decrease in chain length.

Hess, Schultze, and Messmer's[440] specific rotation values for secondary acetates, prepared by partial hydrolysis according to Ost's method, were considerably lower (mostly between −2.02° and +3.14°). In view of the fact that the acetyl contents were about the same as those of Ost's secondary acetates, the lower specific rotation values seem to indicate that these products were degraded to a considerable extent. Indeed, Hess and co-workers isolated cellobiose and glucose from the methyl alcoholic sodium hydroxide solution used for saponification of the secondary acetate. With less degraded preparations, the optical rotation values are independent of the method of preparation.[441]

Gray, Murray, and Staud[442] believe to have demonstrated that the acetyl content influences the optical rotation values of cellulose acetates. It was found that an acetate when heated to 183° in aniline according to a method suggested by Knoevenagel[443] lost acetyl while the rotation value decreased.

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[438] Ost, *Z. angew. Chem.*, **19**, 67 (1919).

[439] Ost, *ibid.*, **19**, 88 (1919).

[440] Hess, Schultze, and Messmer, *Ann.*, **444**, 277 (1925).

[441] Ost, *loc. cit.*; Hess and Schultze, *Ann.*, **455**, 94 (1927); see also Hess, Trogus, and Osswald, *Z. physik. Chem.*, **B3**, 165 (1929); Dziengl, Trogus, and Hess, *Ann.*, **491**, 52 (1931).

[442] Gray, Murray, and Staud, *J. Am. Chem. Soc.*, **51**, 1810 (1929).

[443] Knoevenagel, *Z. angew. Chem.*, **27**, 505 (1914).

After 100 hours of treatment the acetyl content had dropped from 44.2 to 2.2 per cent. On reacetylation to the former degree of substitution the rotation had assumed the original value (−26°). It is surprising that the cellulose constituent should have withstood degradation under the severe treatment.

The Reducing Power of Cellulose Acetates

The determination of the copper number is not a reliable method of ascertaining the degree of degradation of cellulose acetates. Tollens[444] showed that fully acetylated glucose does not react with Fehling solution; this indicates that one of the acetyl groups is located on the potential reducing group and is not saponified by the alkali of the Fehling solution. If the same is assumed to occur on acetylation of cellulose, cellulose triacetate should exhibit no reducing power at all. Indeed, the copper number of cellulose triacetate is very low; Letters[445] found figures ranging from 0.08 to 0.12. On the other hand, secondary acetates prepared by subsequent partial hydrolysis of the triacetate in acid media ought to exhibit reducing power because reducing groups are restored—not only those which were present in the original cellulosic material but also those which were produced as a result of the cleavage of glucosidic linkages during acetylation as well as during partial hydrolysis. The copper number of such secondary acetates should therefore be higher than that of the original cellulose. This has been found to be true. Letters' figures for commercial secondary acetates range from 0.96 to 1.86. However, these figures appear rather low in view of the fact that the degradation, at least that which takes place during the usual process of acetylation, is considerable. The copper number of such acetates would thus indicate a higher degree of polymerization than the viscosity or any other data from which the molecular weights may be calculated.[446]

Again, such incompletely substituted acetates, which are prepared by adjusting the process of acetylation to a limited acetyl content, ought to exhibit no reducing power because the assumption may be made that all reducing groups originally present and subsequently produced by the action of the acetylating mixture are covered by acetyl groups.

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[444] Tollens, "Handbuch der Kohlenhydrate," J. A. Barth, Leipzig (1914), 3rd ed., p. 199.

[445] Letters, doctoral dissertation, Berlin (1926), p. 29.

[446] While this book was in the press, a publication appeared by Montonna and Winding [*Ind. Eng. Chem.*, **35**, 782 (1943)] who found the copper number of commercial acetates to be inversely proportional to their viscosities.

Saponification of Cellulose Acetates

As with other cellulose esters, the saponification of acetylcellulose serves two purposes, namely, to ascertain the acetyl content and to regenerate the cellulosic constituent. As with cellulose nitrates, it is difficult to accomplish both these aims simultaneously. The methods devised for the determination of the acetyl content tend to degrade the cellulosic constituent unless special precautions are taken.

Alkaline methods, using strong aqueous sodium or potassium hydroxide solutions, were developed by Knoevenagel and Eberstadt[447] and by Schwalbe,[448] and an acid method, applying strong sulfuric acid with subsequent dilution and liberation of the acetic acid by distillation, was developed by Ost.[449] Freudenberg[450] has suggested saponification with *p*-toluenesulfonic acid.

Since with both types of methods the cellulosic constituent is more or less affected, the possibility exists that other volatile organic acids are formed and are determined together with the acetic acid, thus unduly increasing the expected value.

For a long time, Ost's method was regarded as more reliable than any of the alkaline methods, provided that the analyst strictly adhered to the standardized conditions.[451] However, other drawbacks of the method, as the time required, the number of operations, etc., caused investigators, particularly in commercial practice, to give preference to the alkaline methods. The sources of error involved in the alkaline methods in their original form have since been largely reduced.[452] Earlier comparative studies on the accuracy and reproducibility of the various methods established the so-called Eberstadt method as the most accurate and reliable way for the estimation of the acetyl content.[453] In a recent survey and study of the subject,

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[447] Eberstadt, doctoral dissertation, Heidelberg (1909); Gatsche, doctoral dissertation, Heidelberg (1910); Knoevenagel, *Z. angew. Chem.*, **27**, 505 (1914).

[448] Schwalbe, *Z. angew. Chem.*, **23**, 433 (1910).

[449] Ost and Katayama, *Z. angew. Chem.*, **19**, 995 (1906); **25**, 1468 (1912).

[450] Freudenberg, *Ann.*, **433**, 230 (1923).

[451] See also the modification worked out by Hess and Weltzien, *Ann.*, **435**, 65 (1923); Weltzien and Singer, *ibid.*, **443**, 110 (1923).

[452] Knoevenagel and König, *Cellulosechem.*, **3**, 119 (1922); Murray, Staud, and Gray, *Ind. Eng. Chem., Anal. Ed.*, **3**, 269 (1931).

[453] Fenton and Berry, *Proc. Cambridge Phil. Soc.*, **20**, Part I, 16 (1920); Torii, *J. Soc. Chem. Ind., Japan*, **25**, 110 (1922). See also Krüger, "Die Zelluloseazetate," p. 225. Krüger gives a comprehensive survey on numerous modifications of the two types of methods (pp. 218–232). See also Robertson, *J. Soc. Chem. Ind.*, **26**, 624 (1906), who found that sulfate groups left in the acetates are not removed with aqueous alkali.

Genung and Mallatt[454] arrived at the same conclusion, although they state that, in special cases, Ost's method also may be reliably applied.

The Eberstadt method provides for a pretreatment of the acetate with ethyl alcohol as a swelling agent in accordance with Knoevenagel's findings,[455] namely, that the rate of saponification is considerably increased if the acetate had been preswollen with such agents as aqueous acetic acid, aqueous alcohol, aqueous acetone, or a mixture of acetic acid and alcohol. The conditions of treatment with alkali are mild, a slightly elevated temperature (50°) being applied only for a short time in the beginning, after which the mixture is left standing for 24 hours at room temperature.

If the object of saponification is the regeneration of the cellulose component, the use of sodium methylate or ethylate, dissolved in the corresponding alcohols, has proved more suitable than the use of aqueous alkali. In the absence of water, the reaction is, of course, no longer that of saponification,[456] the acetic acid being regenerated in the form of its ester (methyl or ethyl acetate).

Zemplén and co-workers[457] suggested a modification in which the sodium is reduced to a very small amount. This method was successfully applied to the regeneration of acetyl from acetylated sugars, for example, cellobiose octoacetate. The very small amount of sodium, for example, 0.023 gram for 2 grams of acetylcellulose, is, no doubt, a safeguard against degradation.

Aqueous solutions of sodium hydroxide in the presence of methyl or ethyl alcohol also have been recommended for the regeneration of the cellulose component.[458] However, according to Staudinger[459] these methods will give rise to degradation of the cellulosic constituent, unless the procedure is carried out in the nitrogen atmosphere,

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[454] Genung and Mallatt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941); see also Malm, Nadeau, and Genung, *ibid.*, **14**, 292 (1942).

[455] Knoevenagel, *Kolloid-Beihefte*, **13**, 207 (1921).

[456] Woodbridge, *J. Am. Chem. Soc.*, **31**, 1067 (1909); see also Whistler and Jeanes, *Ind. Eng. Chem., Anal. Ed.*, **15**, 317 (1943); Cramer, Gardner, and Purves, *ibid.*, **15**, 319 (1943).

[457] Zemplén, Gerecs, and Hadácsy, *Ber.*, **69**, 1827 (1936); see also Zemplén, *ibid.*, **59**, 1254 (1926).

[458] Schultze and Hess, *Ann.*, **450**, 15 (1926); see also Zemplén and Pacsu, *Ber.*, **62**, 1613 (1929); Sakurada and Tukahara, *J. Soc. Chem. Ind., Japan*, **41**, 384B (1938); see also Genung and Mallatt, *loc. cit.*

[459] Staudinger, "Die hochmolekularen organischen Verbindungen," p. 484; Staudinger and Eilers, *Ber.*, **69**, 819 (1936); Staudinger and Daumiller, *Ann.*, **529**, 264 (1937).

i.e., with careful exclusion of air. With this precaution, the degree of polymerization remains practically unchanged.

Saponification also may be accomplished without degradation by dissolving the acetate in cuprammonium hydroxide in the nitrogen atmosphere and by regenerating therefrom the cellulose with salt solutions under the same precautions.[460]

Aqueous ammonium sulfate was used for the deacetylation of fibrous cellulose acetate by Möhring.[461]

As a matter of interest we may mention that cellulose acetate may also be saponified by means of liquid ammonia.[462] In their studies on ammonia cellulose, Clark and Parker[463] observed that cellulose acetate lost its combined acetic acid content under the influence of liquid ammonia.

Aqueous solutions of aniline and pyridine do not saponify cellulose acetate, whereas an aqueous solution of triethanolamine has been found suitable.[464]

In addition to determining the acetyl (acyl) content, the unsubstituted hydroxyl groups in partially acetylated (acylated) preparations may be estimated, for example, with acetic anhydride in pyridine, and thus a check on the acetyl (acyl) determination may be obtained.[465]

A method for differentiating between very small amounts of salt sulfate and combined sulfate in acetates and other cellulose derivatives has been suggested by Malm and Tanghe.[466]

Saponification of *fibrous* cellulose acetate is likely to proceed in the same heterogeneous fashion as does acetylation, because the cause of the heterogeneity remains practically the same. Some experimental evidence is available to support this view.[467] On the other hand, it may be expected that saponification of an acetate in solution proceeds more homogeneously.[468]

Cellulose triacetate passes through a limited acetone solubility while it is being saponified, as shown in Fig. 63. Saponification was carried out with dilute alcoholic potassium hydroxide.[469] It is seen that the

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[460] Staudinger and Daumiller, *loc. cit.*, **529**, 256.

[461] Möhring, *Deut. Faserstoffe Spinnpflanzen*, **5**, 78 (1923).

[462] Taft and Starck, *J. Phys. Chem.*, **35**, 578 (1931).

[463] Clark and Parker, *J. Phys. Chem.*, **41**, 785 (1937).

[464] Meunier and Revillon, *Chimie & industrie*, **27**, 251 (1932).

[465] Malm, Genung, and Williams, *Ind. Eng. Chem., Anal. Ed.*, **14**, 935 (1942).

[466] Malm and Tanghe, *ibid.*, **14**, 940 (1942).

[467] Haller and Ruperti, *Leipzig. Monatschr. Textil-Ind.*, **40**, 353, 399 (1925); Herzfeld, *Z. physik. Chem.*, **119**, 377 (1926); Krüger, *Melliand Textilber.*, **10**, 208 (1929); Hess and Trogus, *Z. physik. Chem.*, **B15**, 157 (1931); Colthof, Waterman, and Wolf, *Z. angew. Chem.*, **44**, 163 (1931).

[468] Hess and Trogus, *Z. physik. Chem.*, **B15**, 180 (1932); Seki, *J. Soc. Chem. Ind., Japan, Supplementary Binding*, **42**, 253B (1939).

[469] Sakurada and Tukahara, *J. Soc. Chem. Ind., Japan, Supplementary Binding*, **41**, 384B (1938).

acetone solubility increases in the beginning and reaches a maximum when about 1 per cent combined acetic acid is split off and that the acetate becomes practically acetone-insoluble again when the combined acetic acid content has dropped to about 56 per cent. The different behavior of a preparation resulting from partial hydrolysis (with acid agents) is evident: Such a preparation, having the same acetyl content, would still be acetone soluble. The difference may possibly be explained on the assumption that the acetyl groups are removed from different positions.

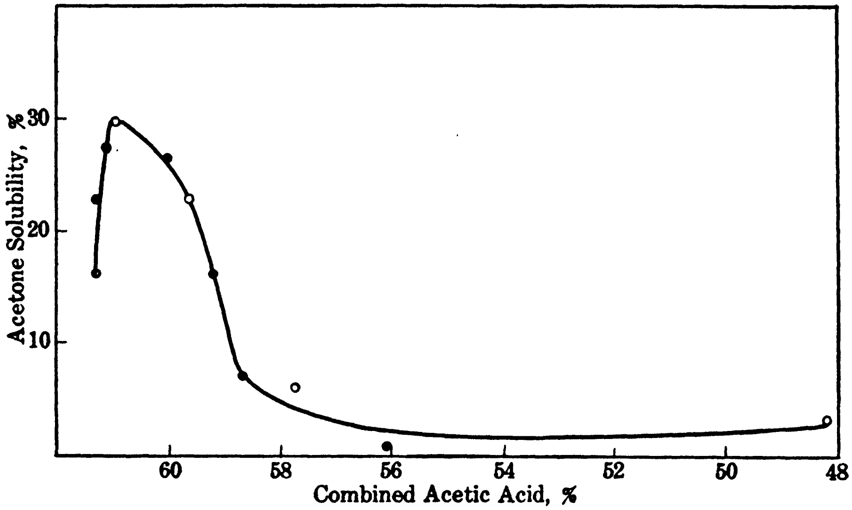

FIG. 63. Saponification of triacetylcellulose with alcoholic potassium hydroxide. Combined acetic acid and acetone solubility. Sakurada and Tukahara.

The Nature of the Regenerated Cellulose

The cellulose regenerated from triacetates and secondary acetates (which have been prepared in the usual way) is chemically characterized by its low degree of polymerization as shown by its low solution viscosity. The reducing power is not always a reliable indication, because it might have been partly eliminated during the process of regeneration; this elimination depends chiefly upon the type and concentration of the alkali used. Thus, the copper number of the regenerated cellulose is subject to considerable variation, values between 3.21 and 0.88 being reported.[470]

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[470] Letters, doctoral dissertation, Berlin (1926), p. 16.

Physically, the change which cellulose undergoes on acetylation and subsequent procedures may consist of a conversion of the original cellulose into its hydrate modification. Again, whether such a change takes place will depend upon the nature of the methods employed for acetylation, partial hydrolysis, and regeneration. Whereas the presence of sulfuric acid or zinc chloride in the acetylation mixture or the use of strong alkali for regeneration will give rise to the formation of cellulose hydrate, the cellulose may emerge in its original form if these agents which cause intramicellar swelling are omitted.

Letters found that cellulose which had been carefully regenerated from commercial acetates showed the characteristics typical for cellulose hydrate: increased hygroscopicity (28.2 to 40 per cent, native cellulose usually ranging within 8 to 12 per cent); increased absorptivity for dyestuffs and increased reactivity, indicated by a greater susceptibility to hydrolysis, for example, with dilute sulfuric acid.[471]

The results of x-ray analysis of the regenerated cellulose are ambiguous. The x-ray pattern of cellulose preparations originating from the same acetate, and seemingly regenerated in the same way, may be that of cellulose hydrate,[472] a mixed diagram of cellulose and cellulose hydrate,[473] or a diagram of unchanged cellulose.[474] Probably, alterations of the conditions of regeneration or of subsequent procedures are responsible for the variations.

Acetylation with Other Acetylating Agents

Acetylcellulose may also be obtained by allowing *acetyl chloride* to act upon alkali cellulose or cellulose in the presence of alkali or other bases. These agents serve to obviate, at least partly, the action of the hydrochloric acid which appears as the second product of reaction.

The action of an acid chloride upon cellulose in the presence of aqueous alkali may be regarded as an analogy to the well-known Schotten-Baumann reaction which serves to introduce the benzoic acid and other acid radicals into various hydroxy compounds. For this purpose, the solution of the hydroxy compound in aqueous sodium

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[471] Letters, *loc. cit.*, p. 15; regarding increased hygroscopicity of cellulose regenerated from superficially acetylated rayon fibers, see Elöd and Etzkorn, *Angew. Chem.*, **51**, 45 (1938).

[472] Centola, *Gazz. chim. ital.*, **65**, 1230 (1935); Trillat, *Rev. gén. colloïdes*, **6**, 177 (1928).

[473] Sakurada and Hess, *Ber.*, **64**, 1174 (1931).

[474] Sisson, *Ind. Eng. Chem.*, **30**, 536 (1938).

hydroxide is shaken with the acid chloride. The reaction with cellulose may be formulated as follows:

$$C_6H_9O_4OH + ClCOCH_3 + NaOH = C_6H_9O_4OCOCH_3 + NaCl + H_2O$$

If less alkali is used than is required for the neutralization of the entire quantity of hydrochloric acid formed, more than enough acid remains in its free form to cause considerable degradation of the cellulose. This is even greater than that produced by acetic acid anhydride in the presence of sulfuric acid or other degrading catalysts, as may be seen from the results obtained by Hess and Weltzien.[475] Their method consisted in allowing a large excess of acetyl chloride to act upon cellulose in the absence of any base at 17–20° until the cellulose had completely dissolved (this took 4 to 8 days). The combined acetic acid content of the isolated product was 62.22 per cent but the yield was very poor (60 per cent of the theoretical). Likewise, the low viscosity and the brittleness of the films prepared from the acetate as well as the complete solubility of the regenerated cellulose ("cellulose A") in 8 per cent sodium hydroxide solution indicated that the cellulose had suffered considerable degradation.

Cross and Bevan used acetyl chloride in the presence of zinc acetate.[476]

As mentioned earlier (p. 242), Wohl's[477] method provides for the use of pyridine or quinoline instead of sodium hydroxide. Simultaneously, a solvent for the ester, e.g., nitrobenzene, is added to the acetylation mixture. The reaction is carried out at 150°. Even with an excess of pyridine the cellulose may be expected to become degraded to an appreciable extent, because at this high temperature the equilibrium involved in the reaction between the pyridine and the hydrochloric acid formed would shift to the left-hand side.[478] At room temperature, however, all hydrochloric acid could be expected to remain neutralized. As a result, the cellulose of the acetate thus prepared should show hardly any degradation, in much the same way as the acetate prepared with acetic anhydride and pyridine, according to the method of Hess and Ljubitsch (p. 241). Without the use of a

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[475] Hess and Weltzien, *Ann.*, **435**, 44 (1923); *Ber.*, **54**, 2867 (1921); Hess, "Die Chemie der Cellulose," pp. 388 and 413; Hess and Schultze, *Ann.*, **455**, 97 (1927).

[476] Cross and Bevan, *Chem.-Ztg.*, **20**, 221, 411 (1896); see also Ost, *Z. angew. Chem.*, **19**, 993 (1906).

[477] Wohl, German patent 139,669 (1899), *Z. angew. Chem.*, **16**, 285 (1903); see also Thile, doctoral dissertation, University of Berlin (1930).

[478] See Hlasko, *Roczniki Chem.*, **17**, 11 (1937); *Chem. Zentr.*, **II**, 1150 (1937).

solvent in the acetylation mixture, the acetate should retain fibrous structure.

Another method of acetylation consists in allowing *ketene* (CH_2CO) to act upon cellulose.[479] Ketene, which is a gas and may be prepared from acetone,[480] reacts with water, with alcohols, and with amines to give acetic acid, esters, and amide derivatives, respectively. Van Alphen[481] studied the reaction with phenolic hydroxyl compounds, and Bergmann and Stern[482] and, more recently, Mearl, Kise, and Carr[483] with *alpha*-amino acids and with silk fibroin. The latter investigators employed ketene to avoid the degradation of the protein, which occurs when the usual acetylating mixtures are used.

Attempts to introduce *chloroacetyl*, into cellulose by allowing the chloroacetyl chlorides to act upon cellulose were not successful,[484] whereas the action of chloroacetic anhydride in the presence of zinc chloride at 120° upon hydrocellulose led to a chloro-substituted cellulose acetate with a chlorine content corresponding to cellulose monochlorotriacetate, $C_6H_7O_4(OCOCH_2Cl)_3$, which, however, contained the cellulose constituent in a highly degraded form. It is noteworthy that in spite of this fact the ester showed no reducing power (see p. 276). Trichloroacetic anhydride reacted without the use of a catalyst but the degree of substitution was limited to the diester stage, $C_6H_8O_3(OCOCCl_3)_2$ (cellulose trichlorodiacetate), its chlorine content ranging beween 44.3 and 46.04 per cent (theoretically 44.87 per cent).

The triester stage may, however, be obtained by allowing phosphorus pentachloride to act upon cellulose triacetate at 130° for about 10 hours. The reaction may be expressed by the following equation:

$$C_6H_7O_2(OCOCH_3)_3 + 9PCl_5 = C_6H_7O_2(OCOCCl_3)_3 + 9HCl + 9PCl_3$$

Again the cellulose constituent is considerably degraded, and still more so when, instead of phosphorus pentachloride, chlorine is introduced into a solution of cellulose triacetate in chloroform in the presence of phosphorus trichloride and under the influence of natural or artificial sunlight at temperatures from 75–140°.

It is noteworthy that the chloro-substituted cellulose acetates strongly resisted all attempts of saponification and of even very severe hydrolysis and acetolysis, a result which Rudy explains by the protecting influence of the chloroacetyl groups.

Attempts to exchange the acetyls in cellulose triacetate against monochloroacetyls by allowing monochloroacetic anhydride to act upon the triacetate in the presence of some concentrated sulfuric acid at 70° for 5–7 hours were not successful. Most of the cellulose underwent far-reaching degradation to di- and monosaccharide derivatives, among which a crystalline compound, probably

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[479] British patent 237,591 (1925); U. S. patent 1,604,471 (1924), Ketoid Co.; U. S. patent 1,685,220 (1925), du Pont de Nemours & Co.

[480] Rice *et al.*, *J. Am. Chem. Soc.*, **56**, 1760 (1924).

[481] Van Alphen, *Rec. trav. chim.*, **44**, 838 (1925).

[482] Bergmann and Stern, *Ber.*, **63**, 437 (1930).

[483] Mearl, Kise, and Carr, *Textile Research*, **7**, 103 (1936).

[484] Barnett, *J. Soc. Chem. Ind.*, **40**, T253 (1921); Rudy, *Cellulosechem.*, **13**, 49 (1932); Brass and Kurz, *ibid.*, **15**, 99 (1934).

α-1,6-di(monochloroacetyl)-2,3,4-triacetyl-glucose, was identified (Brass and Kurz).

In the presence of alkali, the action of chloroacetic acid on cellulose takes a different course. The chlorine reacts with a hydroxyl group of the cellulose, and the result is an ether, more correctly an acid ether (glycolic acid ether). (See Chapter IX.) Thus:

$$C_6H_9O_4OH + ClCH_2COOH + NaOH = NaCl + C_6H_9O_4OCH_2COOH + H_2O$$

As mentioned previously, cellulose acetates are of considerable commercial interest—for example, for the manufacture of acetate rayon, lacquers, and plastics. Numerous attempts have been made to replace cotton linters by the cheaper wood pulp as a raw material for the commercial manufacture of cellulose acetates. Since, however, cotton linters are still almost exclusively used, the problem has, evidently, not yet been solved completely.

CELLULOSE ESTERS WITH OTHER ORGANIC ACIDS

Formyl Cellulose (Cellulose Formates)

Whereas glacial acetic acid esterifies cellulose, only if severe conditions of temperature and time are chosen (see p. 226), formic acid is capable of esterifying cellulose at room temperature. This property is a specific of formic acid and seems to be in line with the exceptional position which this acid holds in the homologous series.

Unfortunately, formic acid, when used for esterification, simultaneously degrades cellulose to a great extent, particularly if an attempt is made to increase the formyl content above the mono stage.

Depending upon its degree of polymerization, cellulose dissolves in formic acid to different degrees. For example, hydrocellulose or cellulose regenerated from its solution in sulfuric acid or in the form of viscose rayon fiber dissolves in formic acid of 90 to 100 per cent at room temperature, either completely or to a great extent. The products obtained from these solutions on precipitation with water are esters but with formyl contents below that required for a monoformate.

Higher degrees of substitution are reached if "catalysts" are used. Under these conditions, the formic acid may be less concentrated (95 to 90 per cent). When cellulose formates were first prepared, sulfuric acid was used as a catalyst.[485] However, this acid would not appear to be very suitable, because it tends to decompose formic acid into carbon monoxide and water. Nevertheless, Uyeda and Kato[486] and

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[485] Berl and Smith, *Ber.*, **40**, 903 (1907); Woodbridge, *J. Am. Chem. Soc.*, **31**, 1067 (1909); Cross and Bevan, *J. Chem. Soc.*, **99**, 1450 (1911).

[486] Uyeda and Kato, *Cellulose Ind.*, **4**, 23 (1928); Uyeda, *ibid.*, **8**, 33 (1932); Uyeda and Shimada, *ibid.*, **15**, 77 (1939).

Uyeda[486] succeeded in introducing almost 3 formyl groups by applying 10 times the amount of formic acid on the weight of the cellulosic material and about 8 per cent of the formic acid of sulfuric acid at 25° for 16 hours. In some cases, the combined formic acid content was higher (more than 45 per cent) than theoretically required for the triformate (42.8 per cent), indicating that the cellulose had been considerably degraded.

Of the many other catalysts which have been suggested, hydrogen chloride, zinc chloride, and phosphorus oxychloride are preferred. The function of these agents is similar to that of the sulfuric acid in the process of nitration—namely, to dehydrate the esterifying acid and to absorb the water formed on substitution.

The degrading effect of the formic acid is much enhanced at elevated temperature and, for this reason, most formulas for the preparation of formyl cellulose call for room temperature or below. Degradation is limited by diluting the formylation mixture with nonsolvents for the formate, such as benzene and chloroform. These liquids also counteract the dissolving effect of the formic acid upon the formate.

Whereas none of the above-mentioned catalysts, with the exception of sulfuric acid, allows the introduction of more than 2 formyl groups per glucose residue,[487] a combination of hydrochloric acid and zinc chloride (p. 238) resulted in a combined formic acid content of 42 per cent.

The triformate was also obtained by the use of acetyl chloride as catalyst and by reformylating the initially formed "diformate." Acetyl chloride permits the use of 95 and 90 per cent formic acid for the lower stages, but an acid of 99 per cent concentration is needed for reformylation.[488]

The cellulose formates are rather unstable. When they are isolated from the formylation mixture (by precipitation with water) and subsequently washed with water or alkalies, formic acid is liberated, and on standing in the air for a few weeks, as well as on dry heating, all formic acid is liberated.[489] The decomposition of the formate on heating recalls the sensitivity of the formates of polyvalent alcohols. For instance, the monoformate of glycerol decomposes on heating with the

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[487] Rassow, *Z. angew. Chem.*, **35**, 594 (1922); Döge, doctoral dissertation, Leipzig (1914); Noyer, *Kunststoffe*, **4**, 207, 227 (1914); Frey and Elöd, *Z. angew. Chem.*, **43**, 579 (1930); Frey and Elöd, *Ber.*, **64**, 2556 (1931).

[488] Montonna and Heinemann, *Paper Trade J.*, **65**, No. 23, T332 (Dec. 3, 1936).

[489] Rassow and Döge, *loc cit.*

loss of carbon dioxide and water (see also the section on the formation of cellulose methyl carbonate, p. 376).

Cellulose formates are soluble in a great number of solvents, including those for cellulose acetates.[490] No doubt, the low degree of polymerization of the formates favors their solubility in organic liquids. Likewise, their solubility in aqueous acid solutions, concentrated zinc chloride, and aqueous solutions of potassium and ammonium thiocyanate[491] is, to a considerable extent, due to their low degree of polymerization.

On heating with alcoholic sodium or potassium hydroxide, the cellulose constituent is degraded to fragments of low molecular weight and to acids. For this reason this method is unsuitable for both the regeneration of the cellulose component and the determination of the combined formic acid content. The latter objective may, however, be achieved in various other ways—for example, by decomposing the formate with concentrated sulfuric acid and measuring the resulting carbon monoxide volumetrically[492] or by complete oxidation of the formate with potassium chromate solution and determination of the amount of oxygen consumed.[493]

Up to the present time cellulose formates have not been made or used on a commercial scale.

Propionyl and Butyryl Cellulose (Cellulose Propionates and Butyrates)

These may be prepared by either of the methods (or their modifications) which are used for the acetylation of cellulose. For example, propionic anhydride in the presence of sulfuric acid or zinc chloride was used for the preparation of cellulose tripropionate.[494] Malm and Clarke[495] studied the reactions with the two acid anhydrides without using a catalyst. Maximum esterification occurred after a reaction time of about 100 hours at boiling point temperature (or after shorter

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[490] Clément and Rivière, "Matières Plastiques," Baillière et Fils, Paris (1924), p. 276.

[491] Cross and Bevan, *J. Soc. Chem. Ind.*, **99**, 1450 (1911).

[492] Berl and Smith, *loc. cit.*

[493] Tocco and Nyssens, *Giorn. chim. ind. applicata*, **12**, 14 (1930); for other methods, see Schmitt, doctoral dissertation, Karlsruhe (1927); Uyeda and Hata, *Cellulose Ind.*, **4**, 1 (1928).

[494] Woodbridge, *J. Am. Chem. Soc.*, **31**, 1067 (1909); see also Stein, *Z. angew. Chem.*, **26**, 673 (1913), Faust, *Celluloseverbindungen*, Springer, Berlin (1935), Vol. I, p. 1277, as well as von Frank and Cohn, *Cellulosechem.*, **12**, 68 (1931).

[495] Malm and Clarke, *J. Am. Chem. Soc.*, **51**, 274 (1929).

time when pressure was applied), the combined propionic acid content being 6 to 7 per cent and the combined butyric acid content 8.6 per cent. Even under such conditions, fibrous structure was retained, but the fibers were weak and friable.

Acid chlorides in the presence of pyridine and diluents were used by Hagedorn and Möller,[496] and Hess and Trogus[497] obtained a tripropionate (67.4 per cent combined propionic acid, theoretical 67.28 per cent) and a highly substituted butyrate (66.5 per cent combined butyric acid, theoretical 71.05 per cent) by using a mixture of chloroacetic acid and chloroacetic anhydride as catalyst.

Cellulose propionates and butyrates have properties similar to those of the acetates and are of ever-increasing commercial interest.[498]

Esters of Cellulose with Higher Fatty Acids

These esters may be prepared with the respective acid chlorides in the presence of alkali[499] or pyridine[500] or similar bases, such as quinoline,[501] according to the Schotten-Baumann reaction. In this way, the following esters were prepared: valerates, caproates, pelargonates (nonylates), laurates, palmitates, and stearates.

The difficulties involved in preparing the higher esters increase with the molecular weight of the radicals to be introduced. Whereas as much acyl as would correspond to the mono stage may be introduced comparatively easily, severer conditions are required for reaching the higher stages of substitution, particularly the tri stage. But the fibrous structure may be maintained.[502] With increasing chain length of the fatty acid radical, the water resistance of the esters increases, and a smaller quantity of acyl groups per glucose residue suf-

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[496] Hagedorn and Möller, *Cellulosechem.*, **12**, 29 (1931).

[497] Hess and Trogus, *Z. physik. Chem.*, **B15**, 171 (1931); see also Thilo, doctoral dissertation, Berlin (1931).

[498] Wiggam and Goor, *Ind. Eng. Chem.*, **26**, 551 (1934); Malm, Fordyce, and Tanner, *ibid.*, **34**, 430 (1942).

[499] Kita *et al.*, *Cellulose Ind.*, **1**, 23 (1925), *Cellulosechem.*, **7**, 125, 130 (1926); *Cellulose Ind.*, **2**, 30 (1926); *Cellulosechem.*, **8**, 105 (1927); Sakurada and Nakashima, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **6**, 197 (1927).

[500] Grün and Wittka, *Z. angew. Chem.*, **34**, 645 (1921); Gault and Ehrmann, *Compt. rend.*, **177**, 124 (1923); Thilo, doctoral dissertation, Berlin (1930); Engelbrecht, doctoral dissertation, Berlin (1927); Pringsheim, Lorand, and Ward, *Cellulosechem.*, **13**, 119 (1932); Lorand, *ibid.*, **13**, 185 (1932).

[501] Karrer, Peyer and Zega, *Helv. Chim. Acta*, **5**, 853 (1922); Karrer and Zega, *ibid.*, **6**, 822 (1923).

[502] Kita *et al.*, *Cellulosechem.*, **7**, 125 (1926).

fices to produce this effect. Cellulose laurates of medium degree of substitution are practically indifferent to water.[503] It would appear that the higher fatty acid esters lose more and more of the properties of the cellulose fiber and acquire more and more those of the fatty acids as the chain of the radical increases. For the same reason the number of solvents for the higher fatty acid esters in general increases with increasing chain length of the acid radical. But it must be borne in mind that the solubility of the esters is markedly influenced by their degree of polymerization. In fact, fibrous trilaurates and tripalmitates are insoluble in ordinary solvents if prepared without substantial degradation.[504]

Such insoluble esters may be rendered soluble by being subjected to treatments in high boiling liquids, etc., as described earlier in this chapter (p. 259).[505]

Data pertaining to the saponification of the higher fatty acid esters and to the properties of the regenerated cellulose are scarce. Alcoholic potassium hydroxide has been used for this purpose by Kita *et al.* and by Sakurada.[506] Sakurada also made an attempt to find a mathematical expression for the saponification reaction. In contrast to the acetates, the acid groups in the higher fatty acids are more resistant to heating with absolute alcohol.

A question arises as to how the long carbon chains of the higher fatty acids arrange themselves within the spaces available between the primary valence chains of the cellulose system. One could imagine that these spaces eventually become too narrow for the very long carbon chains to arrange themselves perpendicularly to the fiber axis and that they thus would tend to assume a position more parallel to the fiber axis. It is difficult to answer this question, because the esters of the fatty acids above the butyrate are no longer of a crystalline nature when observed under x-rays; rather, the internal cellulosic structure appears to be entirely masked by the diagram of the fatty acid radical.[507]

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[503] Hagedorn and Möller, *loc. cit.;* Fordyce, Salo, and Clarke, *Ind. Eng. Chem.*, **28**, 1312 (1936).

[504] Grün and Wittka, *loc. cit.;* Hess and Messmer, *Ber.*, **54**, 499 (1921); Hess and Trogus, *Z. physik. Chem.*, **B15**, 204 (1931); Kita *et al.*, *Cellulosechem.*, **14**, 13 (1928); see also Abd El Shahid, doctoral dissertation, Berlin (1930); Engelbrecht, doctoral dissertation, Berlin (1931).

[505] See also Hagedorn and Möller, *loc. cit.*, p. 29.

[506] Sakurada, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **8**, 21 (1928); see also Genung and Mallatt, *Ind. Eng. Chem., Ann. Ed.*, **13**, 370 (1941).

[507] Nowakowsky, *Compt. rend.*, **191**, 411 (1930); Trillat, *ibid.*, **197**, 1616 (1933); *J. phys. radium*, **5**, 207 (1934).

The higher fatty acids possess such interesting properties that they ought to be of considerable commercial interest. In fact, numerous suggestions have been made in connection with the manufacture of films and artificial threads, or to use the esters as moisture repellents in textile and paper coatings, lacquers and paints, and as a basis for the manufacture of plastics.[508]

Esters of cellulose with *hydroxy acids* and with *unsaturated acids* of the aliphatic series have also been prepared. Most of the references to the preparation and properties of these esters are confined to patents.[509]

A gluconic acid ester derivative was prepared and investigated by Wolfrom and Morgan.[510] It was obtained by allowing *o*-pentaacetyl-*d*-gluconyl chloride to act upon mercerized cellulose in the presence of nitrobenzene at 80° for 16 hours. The product was fibrous but the degree of substitution amounted to only 0.45 pentaacetyl gluconyl group per glucose residue. This value could be raised to 0.75 when the starting material was a secondary acetate. The reaction may be formulated as follows:

$$C_6H_9O_4ONa + ClCO(CHOCOCH_3)_4CH_2OCOCH_3 = C_6H_9O_4OCO(CHOCOCH_3)_4CH_2OCOCH_3 + NaCl$$

The ester was soluble in a number of cellulose acetate solvents.

Hagedorn and Möller[511] mention some interesting properties of esters of unsaturated acids such as oleic, linoleic, ricinoleic, and higher acids which were obtained in fibrous form and were for the greater part insoluble in all solvents. The sensitivity of some of the unsaturated aliphatic acids to oxidation was reflected in the esters. Thus, it is said that the linoleic esters of cellulose tend to become spontaneously ignited when exposed to the air; for this reason such esters can be preserved only in moist condition. Likewise, the difference in the physical properties of the *trans*- and *cis*-isomeric forms of the oleic acids is said to be reflected in the cellulose esters. This claim is based upon the observation that cellulose oleate is insoluble in all solvents, whereas the elaidate is soluble in some organic liquids.

Esters of Cellulose with Dibasic Acids

The possibilities of reaction inherent in organic dibasic acids attracted early cellulose research workers.[512] However, the attempts of these investigators to introduce, for example, the oxalic acid radical into cellulose, have not been very successful; they have resulted only in more or less superficial esterification.

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[508] Krüger, "Die Zelluloseazetate," p. 360; Montonna, *Paper Trade J.*, **65**, No. 23, T332 (Dec. 3, 1936); Fordyce, Salo, and Clarke, *Ind. Eng. Chem.*, **28**, 1312 (1936).

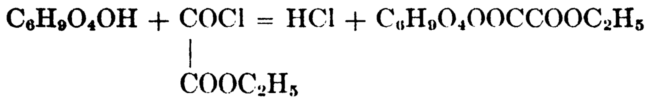
[509] Marsh and Wood, "Introduction to Cellulose Chemistry," pp. 225 and 228; Worden, "Technology of Cellulose Esters."

[510] Wolfrom and Morgan, *J. Am. Chem. Soc.*, **64**, 2026 (1942).

[511] Hagedorn and Möller, *loc. cit.*, p. 32.

[512] Knecht, *7th Intern. Congr. Applied Chem., London* (1909); Briggs, *J. Soc. Chem. Ind.*, **31**, 521 (1912); Levy, *Ind. Eng. Chem.*, **12**, 743 (1920); see also Montgomery, *J. Am. Chem. Soc.*, **53**, 2701 (1931).

The problem of preparing higher substituted oxalic acid esters of cellulose was resumed by Frank and Caro[518] who succeeded in introducing an oxalic acid radical in which one of the 2 carboxyl groups was blocked by an alkyl group so that only 1 carboxyl group reacted with cellulose. The reaction was achieved by allowing the chloride of an alkyl oxalic acid ester to act upon cellulose in the presence of pyridine, with nitrobenzene as a diluent, at temperatures between 40 and 100°. The reaction leading to the ethyl oxalic ester of cellulose may be formulated thus:



$$C_6H_9O_4OH + \underset{\substack{|\\ COOC_2H_5}}{COCl} = HCl + C_6H_9O_4OOCCOOC_2H_5$$

Frank and Caro prepared, in addition to the ethyl derivative, the allyl, isoamyl, cyclohexyl, menthyl, and cetyl oxalic esters of cellulose and found that the physical properties of these dibasic half-esters changed quite distinctly with the nature of the alkyl group. Thus, the density, softening point, film-forming properties, stability, and resistance to saponification were increased with increasing size of the alkyl group. Likewise, with increasing size of the alkyl group, the solubility increased in nonpolar liquids and decreased in polar liquids. The viscosity of the esters in a mixture of acetone and petroleum ether showed a minimum at a certain proportion of the two liquids, and the larger the size of the alkyl group, the more petroleum ether was required for producing the viscosity minimum (solubility optimum).

Frank and Caro's attempt to prepare the free oxalic acid ester by careful elimination of the alkyl radical was not successful. By this procedure, the ester linkage between the free carboxylic group and cellulose was cleaved.

The degree of substitution of these esters ranged within the di- and the triester stage. Only the ethyl oxalic ester corresponded to the full triester stage with 57.97 per cent combined oxalic acid (theoretical value, 58.00 per cent). This ester, which was prepared from fibrous ramie, completely retained its fibrous structure, whereas the other esters, because of their solubility in nitrobenzene, dissolved partly or entirely in the esterification mixture.

The esters may be saponified with 0.5 *N* alcoholic aqueous sodium hydroxide at room temperature. Judged by the low copper number and the low alkali-solubility of the regenerated cellulose in 2 *N*

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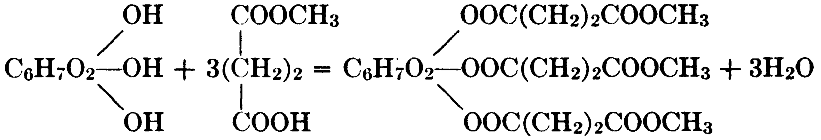
[518] Frank and Caro, *Ber.*, **63**, 1532 (1930).

sodium hydroxide solution, little degradation seems to have taken place during esterification and saponification.

Other varieties of dibasic acid esters of cellulose were described by Malm and Fordyce.[514] They prepared methyl, ethyl, propyl, and butyl succinates of cellulose. These esters were obtained by allowing the corresponding alkyl esters of succinic acid to act on cellulose in the presence of chloroacetic anhydride as catalyst, according to procedures laid down in patents.[515] An example of the reactions is represented by the following equation:

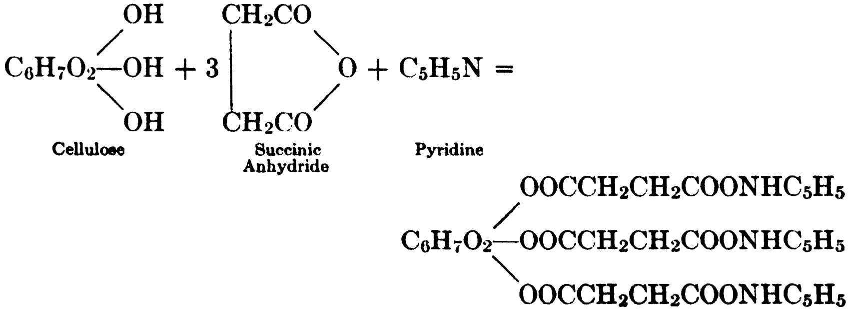


$$C_6H_7O_2\begin{cases}OH\\OH\\OH\end{cases} + 3\begin{matrix}COOCH_3\\|\\(CH_2)_2\\|\\COOH\end{matrix} = C_6H_7O_2\begin{cases}OOC(CH_2)_2COOCH_3\\OOC(CH_2)_2COOCH_3\\OOC(CH_2)_2COOCH_3\end{cases} + 3H_2O$$

The chloroacetic anhydride takes part in the reaction only in so far as it is converted into chloroacetic acid by the water of the reaction.

The esters thus prepared exhibit a wide range of solubility, a high degree of resistance to moisture but, in general, a low melting point which limits their commercial utilization. Also, a number of mixed esters were prepared by allowing the unoccupied hydroxyl groups of an incompletely substituted cellulose acetate to react with the dibasic acid half-esters (see later).

Dibasic acid esters of cellulose, in which 1 of the carboxyl groups remains unesterified, may be prepared by allowing cellulose to react with dibasic acid anhydrides in the presence of pyridine.[516] The first phase of the reaction consists of the formation of the pyridinium salt of the ester, but the latter, on acidification, liberates the free acid (the dicarboxylate). The reaction with succinic anhydride may be expressed by the following equation:



$$C_6H_7O_2\begin{cases}OH\\OH\\OH\end{cases} + 3\begin{matrix}CH_2CO\\|\\CH_2CO\end{matrix}\!\!>O + C_5H_5N = C_6H_7O_2\begin{cases}OOCCH_2CH_2COONHC_5H_5\\OOCCH_2CH_2COONHC_5H_5\\OOCCH_2CH_2COONHC_5H_5\end{cases}$$

Pyridine-Succinic Acid Ester of Cellulose

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[514] Malm and Fordyce, *Ind. Eng. Chem.*, **32**, 405 (1940).

[515] Strachfield, U. S. patent 1,704,306 (1929); Clarke and Malm, U. S. patent 1,880,808 (1932).

[516] Malm and Waring, U. S. patents 2,093,462 and 2,093,464 (1937); Schulze, U. S. patent 2,069,974 (1937).

The pyridine salt is decomposed by hydrochloric acid to form the free acid ester, $C_6H_7O_2(OOCCH_2CH_2COOH)_3$, and pyridinium chloride (C_5H_5NHCl).

The free ester is insoluble in water but soluble in dilute alkali solutions (salt formation). In organic solvents, the solubility of the acid dicarboxylates is very limited; but mixed esters, containing both acetyl and dicarboxylic groups (see later), have even a wider range of solubility than cellulose acetate. However, their melting point is lower than that of the acetates.

Naphthenic Acid Esters of Cellulose

Various attempts have been made to esterify cellulose with acids of cyclic paraffins, ($C_nH_{2n-1}COOH$)—for example, naphthenic acid. Whereas the action of the anhydride in the presence of pyridine resulted only in a low degree of substitution, that of naphthenic acid chloride and pyridine yielded esters with between 2 and 3 acid radicals per glucose unit. However, very little acid radical could be introduced when the base was sodium hydroxide instead of pyridine.[517]

Hagedorn and Möller[518] employed the chloride in the presence of pyridine without, however, giving details of the preparation. Their product, probably the triester prepared from cotton linters, was soluble in a number of organic liquids, such as ether, ethylacetate, benzene and homologues, and chlorinated hydrocarbons, whereas Kita *et al.* found their products in general to be insoluble when prepared from cotton or cotton linters. A wider range of solubility was observed when the starting material was hydrocellulose. In all cases, the degree of substitution influenced the solubility of the esters. The esters partly or entirely retained the fibrous structure of the original cellulosic material.

Hagedorn and Möller have prepared also mixed esters containing naphthenic acid and higher fatty acid radicals—for instance, a naphthenate-laurate and a naphthenate-oleate-laurate of cellulose.

Esters of Cellulose with Aromatic Acids

The chief interest has been devoted to the preparation of cellulose esters with benzoic acid (*cellulose benzoates*, benzoyl cellulose) as the

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[517] Kita, Mazume, Sakurada, and Nakashima, *Mem. Coll. Eng. Kyoto Imp. Univ.*, **4**, 1 (1925); *Cellulose Ind.*, **2**, 31 (1926); *Kunststoffe*, **16**, 41, 167, 199 (1926); *Cellulosechem.*, **9**, 13 (1928).

[518] Hagedorn and Möller, *Cellulosechem.*, **12**, 30 (1931).

first representative of the monobasic acids of the aromatic series. Early investigators, as Cross and co-workers[519] and later Ost and Klein,[520] made use of the Schotten-Baumann reaction and allowed benzoyl chloride to act upon cellulose in the presence of aqueous sodium hydroxide. The highest degree of substitution reached under favorable conditions with this method corresponded to about 2.5 benzoyl groups per glucose residue. It is probable that the alkali exerts a saponifying influence upon higher stages of substitution and that the system tends to establish an equilibrium between the esterification and the saponification reactions. Similar observations have been made with the benzoylation of sugars.

To insure thorough reaction, the cellulosic material must be present in a particularly reactive form because benzoyl chloride reacts readily with sodium hydroxide to form free benzoic acid which scarcely attacks cellulose. Dried fibrous cellulose cannot be esterified at all, but rather catalyzes the reaction between sodium hydroxide and benzoyl chloride.[521] The benefit of having the cellulosic material in a reactive form seems to be confirmed by the observation that the benzoyl content of the cellulosic material increases up to a certain point with increasing alkali concentration.[522] Obviously, the maximum swelling degree which the cellulosic material thus acquires increases its reactivity considerably. The reaction is also facilitated with cellulose in a finely ground state,[523] with cellulose in its mercerized modification,[524] with hydrocellulose,[525] and with aged alkali cellulose.[526]

On the other hand, a higher degree of substitution is obtained by using a base with less saponifying power as, for example, pyridine,[527] particularly in combination with an excess of benzoyl chloride (the so-called acidic pyridine mixture), first suggested by Wohl.[528] The sa-

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[519] Cross and Bevan, *Ber.*, **34**, 1514 (1901); Cross, Bevan, and Beadle, *J. Chem. Soc.*, **63**, 838 (1907); Briggs, *Z. angew. Chem.*, **26**, 255 (1913).

[520] Ost and Klein, *Z. angew. Chem.*, **26**, 437 (1927).

[521] Briggs, *loc. cit.*

[522] Cross and Bevan, "Researches on Cellulose, 1895–1900, I," Longmans, Green and Co., London (1907), p. 34; Vieweg, *Ber.*, **40**, 3881 (1907); Ost and Klein, *loc. cit.*; Kita *et al.*, *Cellulose Ind.*, **2**, 30 (1926). See also Hess, "Die Chemie der Cellulose," p. 424.

[523] Ost and Klein, *loc. cit.*

[524] Wichelhaus and Vieweg, *Ber.*, **40**, 442 (1907).

[525] Hauser and Muschner, *Z. angew. Chem.*, **26**, 137 (1913).

[526] Ost and Klein, *loc. cit.*; Atsuki and Shimoyama, *Cellulose Ind.*, **2**, 35 (1926).

[527] Ost and Klein, *loc. cit.*

[528] Wohl, *Z. angew. Chem.*, **26**, 285 (1903); German patent 139,669 (1899).

ponifying influence of the base is evidently so diminished that the tribenzoate (77.2 per cent combined benzoic acid) is obtained.

The ester retains fibrous structure unless a solvent is added—for example, nitrobenzene. In this case, the tribenzoate may be precipitated from its solution with alcohol. It may be purified by dissolving in chloroform and precipitating with ether.

Data from which conclusions can be drawn as to the extent of the degradation during esterification are scarce. Under the influence of sodium hydroxide, air present in the system or introduced through mechanical agitation of the mixture may oxidize the cellulosic constituent to a certain extent. On the other hand, hydrolysis will scarcely occur in the presence of sufficient alkali. Likewise, if the amount of pyridine is equivalent to that of the benzoyl chloride (resulting in the formation of benzoyl-pyridinium chloride) and the temperature is low, no hydrolysis of cellulose should occur, for all hydrochloric acid formed on the exchange reaction remains neutralized in the form of pyridinium chloride. If, however, an excess of benzoyl chloride is used, this excess may give rise to the presence of free hydrochloric acid which will tend to attack the cellulose, particularly at an elevated temperature (Ost and Klein used 120–130°).

Instead of pyridine, similar bases which form weak compounds with benzoyl chloride and which break up during the reaction may be used. Whereas pyridine may be replaced by quinoline, acridine is less suitable because its benzoyl chloride compound is rather stable.[529]

When benzene (a nonsolvent) is added to the benzoylation mixture, the process of substitution takes a longer time, and the degree of substitution is limited as compared with the results when nitrobenzene is used. Allowing 3 hours at 120° for the reaction, cellulose took up only 70.5 per cent combined benzoic acid (corresponding to 2.35 benzoyl groups per glucose residue), whereas in the presence of nitrobenzene under the same conditions the triester was produced.[530]

Benzoylation is greatly facilitated when it is allowed to take place with cellulose in solution. It was found[530] that cellulose in the form of viscose rayon, dissolved in a mixture of benzyl chloride and pyridine at 100–120°, was completely benzoylated with benzoyl chloride within 1 hour. When the chloride was replaced by benzoic anhydride, complete esterification occurred after 3 hours at 94°.

It appears of considerable interest that the incompletely substituted benzoates may be separated into fractions of varying degree of sub-

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[529] Montonna and Katz, *Paper Trade J.*, **103**, No. 23, 36 (1936); Katz, master's thesis, University of Minnesota (1934).

[530] Bernoulli, Schenk, and Rohner, *Helv. Chim. Acta*, **17**, 897 (1934).

stitution, for this result is quite different from those obtained with nitrates and acetates. Using the fractional solution method, Ost and Klein obtained the following fractions:

Fraction Soluble in	Combined Benzoic Acid Content, %
Aniline-phenol (1 : 1)	0–59
Aniline	61–65
Chloroform	68–70

These results may be interpreted to indicate that the aniline-phenol fraction contains chiefly the monoester stage (theoretically, 46 per cent combined benzoic acid), the aniline fraction the diester stage (theoretically, 66 per cent), and the chloroform fraction the triester stage (theoretically, 77.2 per cent).

Briggs[531] claimed to have separated the residue remaining from the extraction of partially benzoylated cellulose with chloroform into "dibenzoate" and unesterified cellulose by repeated extraction with cuprammonium hydroxide solution. However, it is probable that the presence of unesterified cellulose was the result of the saponification of part of the benzoate by the basic cuprammonium hydroxide,[532] although it is surprising that, on repeated treatment, the benzoate was not completely saponified. It will be recalled that this is the case with cellulose acetate.

The x-ray pattern of the incompletely substituted cellulose benzoate is that of unchanged cellulose.[533] However, in the light of the negative results obtained with partially substituted nitrates and acetates, these x-ray findings are no proof that unchanged cellulose was actually present.

Although numerous suggestions have been made in the patent literature for the preparation and the use of cellulose benzoates,[534] it is doubtful whether they are commercially manufactured.

A number of esters with other aromatic acids are known. Levy[535] has described a *phthalic acid ester* which was obtained by allowing phthalic anhydride in glacial acetic acid, or diethyl phthalate in the presence of zinc chloride, to act upon cellulose. However, the ester contained only a fraction of a phthalate group per glucose unit; it was thus only slightly soluble in any of the usual solvents.

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[531] Briggs, *loc. cit.;* Cross and Bevan, "Researches on Cellulose, I," 35 (1895).

[532] See also Kita *et al., Cellulose Ind.,* **2,** 30 (1926), and Ost and Klein, *loc. cit.*

[533] Herzog and Londberg, *Ber.,* **57,** 329, 750 (1924).

[534] Krüger, "Die Zelluloseazetate," p. 376.

[535] Levy, *Ind. Eng. Chem.,* **12,** 743 (1920).

Obviously, the reaction is facilitated with cellulosic materials of a low degree of polymerization. By heating low viscosity cotton linters with phthalic anhydride and pyridine at 100° for 12 hours, Malm and Fordyce[536] obtained a uniform solution from which, after dilution with acetone, a cellulose phthalate was precipitated with dilute hydrochloric acid. The product contained 66 per cent phthalyl, which corresponds to somewhat more than 2 phthalyl groups per glucose residue (theoretically, 61.45 per cent). Since one of the two carboxylic groups of the phthalic acid remained free, the ester was capable of forming salts—for example, with sodium and ammonium and with the heavy metals. The heavy-metal salts and those of other polyvalent cations are insoluble in water, possibly because the cation forms a cross link between the esterified cellulose chains.[537]

A completely substituted *cinnamic acid ester* of cellulose was prepared by Frank and Mendrzyk[538] with cinnamyl chloride ($C_6H_5CH{=}CHCOCl$) and pyridine. The ester, which was nonfibrous, was soluble in many organic solvents and quite resistant to heating and saponification. When heated in trichloroacetic acid or in phenol, it was converted into a product which was soluble in cold benzene and in hot acetone; this solubility was evidently due to considerable degradation of the cellulosic component.

On treatment with bromine in chloroform, the cinnamic acid ester was almost quantitatively converted into the dibromohydrocinnamic acid ester.

The p-toluenesulfonyl ester seems to be the only ester of cellulose with an aromatic sulfonic acid which has been investigated more closely. It was first prepared by allowing *p*-toluenesulfonyl chloride to act upon the solution of (alkali-soluble) cellulose in aqueous sodium hydroxide.[539]

Esterification is generally accomplished by allowing a great excess of *p*-toluenesulfonyl chloride ("tosyl" chloride[540]) to act upon fibrous cellulose in the presence of aqueous sodium hydroxide or of pyridine at room temperature. The reaction is slow. Sakurada and Nakashima[541] found under these conditions a maximum of about 1 tosyl

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[536] Malm and Fordyce, *Ind. Eng. Chem.*, **32**, 407 (1940).

[537] Yackel and Kenyon, *J. Am. Chem. Soc.*, **64**, 126 (1942).

[538] Frank and Mendrzyk, *Ber.*, **63**, 875 (1930). About veratric acid ester of cellulose see Freudenberg and Dürr, *Ber.*, **63**, 2719 (1930).

[539] German patent 200,334, Akt. Ges. für Anilin-Fabrikation, 1907.

[540] According to a suggestion made by Hess and Pfleger, *Ann.*, **507**, 48 (1933), "tosyl" is used for *p*-toluenesulfonyl.

[541] Sakurada and Nakashima, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **6**, 214 (1927); *Kunststoffe*, **17**, 269 (1927); Kita, Sakurada, and Nakashima, *Cellulose Ind.*, **2**, 30, 47 (1926).

group per glucose unit. Only by frequently repeated operation did they succeed in introducing a quantity corresponding to 1–2 tosyl groups.

As with benzoylation and other esterification reactions carried out according to Schotten-Baumann, the concentration of the aqueous alkali has to be high; the rate of reaction increases with increasing alkali concentration. It appears of interest that, in general, the rate of substitution seems to follow Vieweg's curve representing the formation of alkali cellulose (p. 68). Using benzenesulfonyl chloride, Sakurada and Nakashima found that the monoester stage was reached at the first inflection point of the Vieweg curve, that is, at an alkali concentration of 25 per cent. With tosyl chloride, this stage was reached when the Vieweg curve showed its second inflection point, that is, at 40 per cent alkali concentration. It is doubtful, however, whether this coincidence is to be interpreted to mean that the formation of alkali cellulose compounds of these compositions is a prerequisite for the formation of the esters.

The tosylation reaction may be represented by the following equation:

$$C_6H_9O_4OH + ClSO_2C_6H_5CH_3 = C_6H_9O_4OSO_2C_6H_5CH_3 + HCl$$

Hess and Ljubitsch[542] observed that cellulose subjected to tosylation also takes up a certain quantity of chlorine. With increasing temperature (from 20 to 100°), the chlorine content of the reaction product increased while, in accordance with Sakurada and Nakashima's observation, the sulfur content decreased. When a temperature of 70° was reached, nitrogen was also taken up by the cellulose, probably because of a combination of part of the pyridine with the chloroester. Hence, if a tosyl ester with as little chlorine and nitrogen as possible is to be obtained, the temperature must be low, i.e., below 20°, preferably at 15° or even at 0°. At low temperature, substitution reaches a maximum with about 2 tosyl groups per glucose residue; this seems to indicate that 2 hydroxyl groups per glucose residue are more easily substituted than the third. The appearance of greater quantities of chlorine in the reaction product after the maximum of tosylation has been passed is obviously due to the exchange of hydroxyl for chlorine, as in observations made on the tosylation of starch and of simple sugars.[543]

The products which were prepared at low temperatures from cotton,

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[542] Hess and Ljubitsch, *Ann.*, **507**, 62 (1933).

[543] Hess and Pfleger, *Ann.*, **507**, 50 (1933); Hess and Kinze, *Ber.*, **70**, 1139 (1937); Bernoulli and Stauffer, *Helv. Chim. Acta*, **23**, 615 (1940).

ramie, and cuprammonium rayon contained from 0.2 to 0.5 per cent chlorine and about 0.7 per cent nitrogen. The sulfur content corresponded to 2 tosyl groups (theoretically, 13.46 per cent sulfur). The preparations originating from rayon were amorphous and soluble in nitrobenzene, pyridine, and cyclohexanone, whereas those prepared from cotton and ramie were fibrous and not or only sparingly soluble in these and other solvents. The tosyl esters also seem to be rather resistant to saponification. The esters prepared by Bernoulli and Stauffer[544] from viscose rayon were those of considerably degraded cellulose.

The introduction of tosyl into partially hydrolyzed (secondary) cellulose acetates by Cramer and Purves[545] has been discussed on p. 260.

The action of *p*-toluenesulfonyl chloride upon cellulose has been and is possibly still being used commercially in the manufacture of the so-called "Immune Yarn," i.e., immune to dyeing with direct dyes.[546] For this purpose, the yarn or fabric is first mercerized and then subjected to a limited action of tosyl chloride. These materials refuse to take up direct dyes, whereas their affinity to basic dyes is increased. Under the conditions of the treatment with tosyl chloride, only an outer layer of the cotton fiber is esterified. Chippendale[547] demonstrated this by microscopical pictures of cross sections dyed with those dyestuffs which dye the esterified portion and leave the rest of the fiber undyed. The dyed portion appeared as a dark ring around the unchanged center of the cross section. Chippendale explains the failure of the tosylated fiber to take up direct dyes on the assumption that the colloidal particles of the direct dye cannot penetrate beyond the ester layer.

In this connection, the behavior of the esterified portion to cuprammonium is of interest. This reagent attacks the tosylated fiber at first only in those parts where the fiber has been cut; the cellulose then swells beneath the esterified coat. As a result, the layer bursts and, on sufficiently long contact, the cellulose dissolves completely, leaving the coating as a relatively wide spiral tape.[548] Conversely, the outer esterified layer may be dissolved in pyridine and the unesterified center left as a somewhat thinner fiber.

The tosylated yarn is also repellent to acid dyes. However, as Karrer and Wehrli[549] have shown, it may be dyed with such dyes after it has been treated

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[544] Bernoulli and Stauffer, *loc. cit.*, p. 627.

[545] Cramer and Purves, *J. Am. Chem. Soc.*, **61**, 3458 (1939); Gardner and Purves, *ibid.*, **64**, 1539 (1942); see also **65**, 444 (1943).

[546] Tagliani, *J. Soc. Dyers Colourists*, **41**, 165 (1925); *Z. angew. Chem.*, **39**, 835 (1926).

[547] Chippendale, *J. Soc. Dyers Colourists*, **50**, 144 (1934).

[548] This behavior reminds us of that of cellulose superficially esterified with stearic acid (see p. 12).

[549] Karrer and Wehrli, *Helv. Chim. Acta*, **9**, 591 (1926); *Z. angew. Chem.*, **39**, 1509 (1926); Karrer and Kwong, *Helv. Chim. Acta*, **11**, 525 (1928).

with ammonia. The dyeing appears to be genuine in much the same way as, for example, with vat dyes. The ammonia-treated yarn has been given the trade name Amine Yarn.

Karrer and Wehrli have explained this effect on the assumption that the tosyl groups are replaced by amino groups in much the same way as the toluenesulfonyl ester of 2,4-dinitrophenol is converted into 2,4-dinitroaniline, as has been shown by Ullmann.[550] Thus it was thought that tosylated cellulose, when treated with ammonia, was converted into "aminocellulose."

It is doubtful, however, whether the ammonia content of tosylated cellulose is actually due to an exchange of tosyl groups against ammonia. In fact, Hess and Ljubitsch,[551] applying the ammonia treatment to much higher substituted tosyl esters, found that more nitrogen was not taken up than by a surface-tosylated fiber containing only 1–2 per cent sulfur. A similar result was obtained when, instead of ammonia, diethylamine was used. Hess and Ljubitsch's results are given in Table 34. The figures show that, with the small increase of the nitrogen content, disproportionately more sulfur was removed; this would indicate that the action of the amine consisted chiefly of the partial saponification of the tosyl groups. Thus, it appears probable that the small amounts of ammonia left in the fiber are due to a combination with the chlorine rather than to a substitution of hydroxyl groups.

TABLE 34

PER CENT OF SULFUR, CHLORINE, AND NITROGEN IN TOSYL CELLULOSE TREATED WITH DIETHYLAMINE (50% SOLUTION AT 90°)

	Sulfur	Chlorine	Nitrogen
Before treatment	13.97	1.61	0.16
	11.87	6.66	0.53
	11.52	5.91	0.55
After treatment	9.94	1.58	1.14
	9.89	6.55	1.37
	9.05	5.84	1.70

However, different results were obtained by Sakurada.[552] He heated cellulose tosyl ester in strong ammonia or in ethyl alcoholic ammonia for 90 hours in a sealed tube. When the reaction product was freed of unreacted tosyl groups by saponification and of unreacted cellulose by extraction with cuprammonium hydroxide, it contained a quantity of nitrogen corresponding to one NH_2 group (or one C_6H_5NH group when aniline was used instead of ammonia) per two glucose units. No data are given on the chlorine content of the "aminocellulose."

Nakashima and Sakurada[553] studied the action of hydrazine upon tosyl cel-

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[550] Ullmann, *Ber.*, **41**, 1870 (1905).

[551] Hess and Ljubitsch, *Ann.*, **507**, 68 (1933).

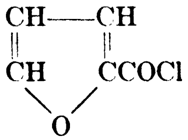
[552] Sakurada, *J. Soc. Chem. Ind., Japan, Supplementary Binding*, **32**, 11 (1929).

[553] Nakashima and Sakurada, *J. Soc. Chem. Ind. Japan, Supplementary Binding*, **32**, 9B (1929); *Bull. Inst. Phys. Chem. Research (Tokyo)*, **8**, 272, Abstracts **2**, 33 (1929).

lulose for the purpose of determining which of the 3 hydroxyl groups of cellulose has reacted with the tosyl chloride. Indications were that the secondary hydroxyl groups had reacted; however, the results are not conclusive.

Cellulose Furoates

Cellulose esters with *furoic acid* (cellulose furoates) were prepared by Kobe and Montonna[554] by allowing furoic acid chloride,



to act upon cellulose in the presence of pyridine. The products of reaction had a fibrous structure but a dark color, analyzing from 2.5 to 3 furoate radicals per glucose residue. They were insoluble in the usual solvents. In the triester, one furoate group appeared to be much more firmly bound than the other two; this was probably the one united with the primary alcohol group of the cellulose. Indications were that the cellulosic constituent was considerably degraded.

MIXED CELLULOSE ESTERS

The possibility of introducing different ester groups into cellulose and thus of combining the properties of single esters or creating entirely new properties has frequently attracted cellulose chemists.

Inorganic mixed esters, such as the sulfonitrates and inorganic-organic mixed esters, such as the sulfoacetates, have been discussed earlier. Other combinations of inorganic and organic acids have been prepared, mostly with the object of commercial utilization. Among them are some which also offer scientific interest.

Mixed esters of cellulose may be prepared either by successive esterification with different agents or by simultaneous action of a mixture of these agents, the former method being preferred because the latter seldom leads to the desired distribution of the different ester groups. But successive esterification does not always yield the expected result, for example, in cases where the secondary esterification mixture exerts a saponifying influence upon the ester groups resulting from the primary reaction. In such cases, the secondary reaction may even be applied to esters which have been completely esterified in the

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[554] Kobe and Montonna, *J. Am. Chem. Soc.*, **53**, 1889 (1931).

primary reaction. Usually it is more advantageous first to prepare the ester which is more stable to saponification and to cover the remaining hydroxyl groups with the less stable ester groups in the secondary procedure.

The cellulosic constituent in the mixed esters may, in general, be expected to be still more degraded than in the simple compounds, since the cellulose has to pass twice through a process of degradation.

Nitrocellulose Acetates

The preparation of nitroacetates and their composition and properties furnish an example of the generalization made above. Since nitrate groups are more stable to saponification by acids than are acetyl groups, one would expect the treatment of nitrocellulose with an acetylation mixture to be more suitable for preparing nitroacetates than the opposite procedure. However, neither of these methods leads to the desired result. On the acetylation of (incompletely) nitrated cellulose nitrate groups become saponified and both the originally free and the regenerated hydroxyl groups are acetylated. The result is an ester with a low nitrogen and a high acetyl content. Thus, for example, Berl and Smith,[555] using nitrocellulose with 12.4 to 12.9 per cent nitrogen, obtained products containing only 2.64 to 4.19 per cent nitrogen and 47.74 to 34.84 per cent combined acetic acid. One of their products showed 4.86 per cent nitrogen and 41.22 per cent combined acetic acid; this would correspond to 1 nitrate and 2 acetyl groups per glucose residue.

It must be pointed out, however, that the substantial loss of nitrate groups in the products described was probably due to the unusually high sulfuric acid content of the acetylation mixture. In fact, Krüger[556] showed that the higher substituted nitrates are rather resistant to acetylation mixtures containing the usual, i.e., a much smaller quantity of sulfuric acid, and only the lower nitrates lose their nitrate groups more easily. With such nitrates (11.1 per cent nitrogen), increasing amounts of sulfuric acid in the acetylation mixture give rise to a decrease of the nitrogen and an increase of the acetyl content.[557] If the sulfuric acid is omitted, the nitrogen content is

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[555] Berl and Smith, *Ber.*, **40**, **903** (**1907**); see also Nishida, *Kunststoffe*, **4**, **141** **1914**), and Cross and Bevan, "Researches on Cellulose, II," **90** (**1905**).

[556] Krüger, *Kunststoffe*, **20**, **73** (**1930**).

[557] Atsuki, *J. Faculty Eng., Tokyo Imp. Univ.*, **15**, **309** (**1925**); see also Oguri and Takei, *Cellulosechem.*, **18**, Abstracts, p. **65** (**1940**).

higher. Oddo[558] obtained "monoacetyl-dinitro" cellulose by treating an alcohol-ether-soluble nitrate with boiling acetic anhydride. This result is in contrast to a statement by Krüger,[559] namely, that acetylation of nitrocellulose without the use of a catalyst is impossible.

In the light of Oddo's results, the application of Hess and Ljubitsch's very mild method of acetylation to partially substituted nitrates would appear to be a possible means of preparing nitroacetates in which the original nitrogen content of the nitrate has not changed.[560]

The preparation of nitroacetates by nitration of acetylcellulose yields varying results.[561] The number of nitrate groups that are introduced and of acetyl groups that are saponified depends essentially upon the water content of the nitration acid. Nitration acid which contains an appreciable amount of water acts simply as a means of partial hydrolysis. However, with a nitration acid having a sufficiently low water content, Krüger[562] converted a fibrous acetate into a nitroacetate, with 10.8 per cent nitrogen.

The third method—subjecting cellulose to the action of a nitration acid mixture containing acetic anhydride—aiming at simultaneous nitration and acetylation, fails to produce any other ester but the nitrate. Obviously, the acetic anhydride loses its power of acetylation under these conditions. It either acts merely as a dehydrating agent, enhancing the effect of the sulfuric acid, or it reacts with nitric acid to form acetyl nitrate or other compounds whose effect upon the reaction is difficult to predict.[563] On the other hand, if the nitric acid content in the esterification mixture is very low (about 2 per cent), it loses all its nitration power and only acetates are produced (Krüger).

From a commercial point of view, the main object of preparing nitrocellulose acetates is to reduce the inflammability of nitrocellulose and thus to diminish the hazards of fire and explosion. Although this objective is accomplished to a considerable extent, the products fail to meet other essential requirements, possibly because the cellulose is too much degraded.

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[558] Oddo, *Gazz. chim. ital.*, **49**, 140 (1919).

[559] Krüger, "Die Zelluloseazetate," p. 322, footnote 1.

[560] See in this connection the experiments by Gault and Ehrman who describe a "mononitrocellulose dilaurate" and a "dinitrocellulose monolaurate" prepared by allowing lauroyl chloride to act upon cellulose nitrate in the presence of pyridine and a diluent, such as benzene or the like. The authors failed to observe any loss of nitrogen under these conditions [(*Caoutchouc & gutta-percha*, **24**, 13824 (1927), and **25**, 13868 (1928)].

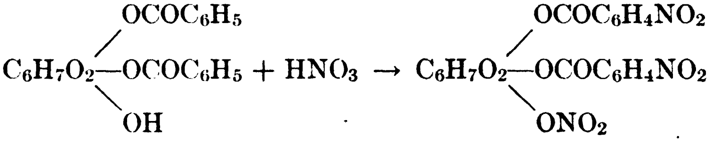
[561] Nishida, *Kunststoffe*, **4**, 141 (1914).

[562] Krüger, *Kunststoffe*, **20**, 73 (1930).

[563] Berl and Smith; Nishida, *loc. cit.*; Krüger, *Cellulosechem.*, **11**, 220 (1930).

Nitrocellulose Benzoates

Briggs[564] observed that, on nitration of benzoyl cellulose, not only are the hydroxyl groups which are free in the benzoate replaced by nitrate groups but nitro groups also enter the benzoyl radical. As a result, a nitrocellulose nitrobenzoate is obtained. The reaction may be visualized as follows:



$$C_6H_7O_2\begin{cases}OCOC_6H_5\\OCOC_6H_5\\OH\end{cases} + HNO_3 \rightarrow C_6H_7O_2\begin{cases}OCOC_6H_4NO_2\\OCOC_6H_4NO_2\\ONO_2\end{cases}$$

In the light of results obtained on the nitration of cellulose benzoate by Lottermoser and Gansel,[565] it would appear that the product of reaction represents a mixture of nitrocellulose and cellulose nitrobenzoate. These investigators stated that the reaction product could be separated into these two constituents by extraction with ether-alcohol, in which the nitrocellulose is soluble. Since no data are given regarding the composition, the possibility remains that the other component of the mixture had some nitrate groups in the cellulose constituent.

The nitrobenzoyl radical may be introduced into cellulose directly by treating cellulose with nitrobenzoyl chloride.[566] The nitrobenzoate may be represented by the formula $C_6H_9O_4OCOC_6H_4NO_2$.

Both products lend themselves to combination with dyestuffs. The nitro groups in the nitrocellulose nitrobenzoate and that in the cellulose nitrobenzoate may be reduced to amino groups; the latter diazotized and subsequently coupled with amines or phenols to yield azo dyestuffs in chemical combination with the ester groups and hence with cellulose. Briggs used the first method, i.e., the nitration of cellulose benzoate. The reduction of the nitro compound was carried out with ammonium sulfide[567] and the amino compound was diazotized and coupled with dimethylaniline.

Similar results were obtained[568] by subjecting cotton yarns to a superficial esterification with aminobenzenesulfonyl chloride, followed by diazotizing and coupling with β-naphthol or other compounds.

Other dyestuffs in actual chemical combination with cellulose may be produced by boiling cellulose with the acid chlorides of benzene-sulfonylsulfanilic acid, $C_6H_5SO_2NHC_6H_4SO_3Cl$, or of benzene-sulfonylnaphthionic acid, $C_6H_5SO_2NH$-

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[564] Briggs, *Z. angew. Chem.*, **26**, 255 (1913); Cross and Bevan, "Researches on Cellulose, I," 34 (1895); see also Sendo and Kondo, *Cellulose Ind.*, **6**, 27 (1930).

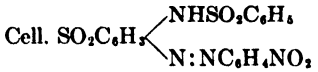
[565] Lottermoser and Gansel, *Melliand Textilber.*, **12**, 407 (1931).

[566] Karrer and Wehrli, *Z. angew. Chem.*, **39**, 1509 (1926).

[567] See also Lottermoser and Gansel, *loc. cit.*, and Karrer and Wehrli, *loc. cit*

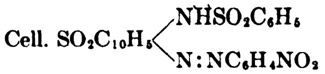
[568] Riesz, *Bull. Soc. Ind. Mulhouse*, **99**, 349 (1933).

$C_{10}H_6SO_3Cl$, dissolved in chloroform and in the presence of pyridine.[569] The former gives a cellulose ester, $C_6H_9O_4OSO_2C_6H_4NHSO_2C_6H_5$, containing 2.77 per cent sulfur, calculated on cellulose. If the esterified cotton is placed in a solution of *p*-nitrobenzenediazonium acetate, a yellow dyestuff appears on the fiber which may be formulated thus:



$$\text{Cell. }SO_2C_6H_3\begin{matrix}\diagup NHSO_2C_6H_5\\ \diagdown N{:}NC_6H_4NO_2\end{matrix}$$

The compound with the naphthionic acid derivative has an orange-yellow color and may be formulated as follows:



$$\text{Cell. }SO_2C_{10}H_5\begin{matrix}\diagup NHSO_2C_6H_5\\ \diagdown N{:}NC_6H_4NO_2\end{matrix}$$

It is obtained from mercerized cotton by shaking with a solution of the agent for several hours.

Since the attachment of a dyestuff molecule by means of an ester grouping would be of little value from a commercial point of view because of the ease with which such a molecule would be removed by hydrolysis, Peacock[570] chose the ether grouping as an intermediary. He prepared a benzyl ether of cellulose (see later) by allowing nitroleucotrope (nitrophenylbenzyldimethylammonium chloride) to act on cellulose in the presence of a slight excess of sodium carbonate at the boiling temperature, subjecting the ether to reduction with sodium hydrosulfite, diazotizing the amino group and coupling with β-naphthol. The dyeings thus created were fast to washing.

Similar results were obtained by Niethammer and König[571] by allowing 1-chloro-2,4-dinitrobenzene to act upon alkali cellulose. The cellulose ether thus produced, $C_6H_9O_5C_6H_3(NO_2)_2$, was reduced with sodium hydrosulfite or sodium sulfide to the amino compound; the latter was diazotized and coupled with the sodium salt of naphthoquinonesulfonic acid. A brownish dyestuff was thus produced which proved to be resistant to washing.

Miscellaneous Mixed Esters

Cellulose nitrates in combination with higher fatty acid ester groupings, such as nitrocellulose laurate and nitrocellulose palmitate, are described by Gault and Ehrman.[572] These esters are produced by the action of the acid chlorides upon nitrocellulose in the presence of pyridine.

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[569] Schröter, *Ber.*, **39**, 1570 (1906).

[570] Peacock, *J. Soc. Dyers Colourists*, **42**, 53 (1926).

[571] Niethammer and König, *Cellulosechem.*, **10**, 203 (1929). It should be borne in mind that in most of the cases described above the cellulose is only superficially esterified.

[572] Gault and Ehrman, *Caoutchouc & gutta-percha*, **24**, 13,748, 13,824 (1927); see also Lorand, *Cellulosechem.*, **13**, 185 (1932). As to further combinations of cellulose nitrates with other ester groupings, see Marsh and Wood, "Introduction to Cellulose Chemistry," p. 296.

Acetopropionates and acetobutyrates may be prepared by the action of the respective acid chlorides on cellulose in successive procedures.

The interesting solubility properties[573] of these mixed esters and their compatibility with plasticizers[574] seem to offer great commercial possibilities.

Cellulose acetates in combination with higher fatty acid ester groupings, such as acetolaurates and acetopalmitates, were prepared and investigated by Gault and Ehrman,[575] and particularly by Lorand.[576] Although the amount of lauroyl or palmitoyl which may be introduced into a secondary acetate is rather small, the change in solubility of the mixed esters is remarkable. An increase of the quantity of the higher fatty acid radicals by only a fraction widens the range of solubility very considerably. Somewhat larger quantities of higher fatty acid radicals (for example, 0.7 palmitoyl per glucose residue) may be introduced into secondary cellulose acetates if, instead of the chlorides, the anhydrides are used, according to the modification of a method suggested by Clarke and Malm.[577]

Cellulose acetates in combination with dibasic acids have been described by Malm and Fordyce,[578] such as the acetophthalates of varying acetyl and phthaloyl content. Such mixed esters may be obtained by heating a solution of cellulose acetate of the desired acetyl content with phthalic anhydride in the presence of pyridine at 100° for 12 hours, after which the solution may be precipitated by dilute hydrochloric acid. In this way, they prepared mixed acetylcellulose esters with 10, 15, 20, and 35 per cent phthaloyl.[579]

With increasing phthaloyl content, the solubility of the esters in organic solvents increases; other physical properties also change.

The presence in the phthaloyl radical of a free carboxyl group causes these mixed esters to form salts—for example, with ammonia, sodium, and the heavy metals. The ammonia and sodium salts are water-soluble, but those of the heavy metals are insoluble. Some of them are colored; the copper salt is blue, the cobalt salt purple, and the nickel and chromium salts green.

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[573] Hagedorn and Möller, *Cellulosechem.*, **12**, 29 (1931).

[574] Fordyce, Salo, and Clarke, *Ind. Eng. Chem.*, **28**, 1312 (1936); Fordyce and Meyer, *ibid.*, **32**, 1056 (1940); see also Malm, Fordyce, and Tanner, *ibid.*, **34**, 430 (1942), for extensive solubility data.

[575] Gault and Ehrman, *loc. cit.*

[576] Lorand, *loc. cit.*

[577] Clarke and Malm, U. S. patent 1,698,048 (1929).

[578] Malm and Fordyce, *Ind. Eng. Chem.*, **32**, 406 (1940).

[579] The acetyl contents are not mentioned in the publication.

Owing to their interesting properties the acetylcellulose phthalates seem to have a wide range of commercial application.

Phenylcarbamates (urethans) of cellulose were obtained by allowing phenylisocyanate (C_6H_5NCO) to act upon cellulose in the presence of anhydrous pyridine.[580] The reaction may be expressed by the following equation:

$$C_6H_9O_4OH + C_6H_5NCO \rightarrow C_6H_9O_4OCONHC_6H_5$$

By the same reaction, Hearon, Hiatt, and Fordyce[581] obtained a tricarbamate of good solubility, whereas the lower substituted carbamates were insoluble.

A mixed ester was prepared by allowing phenylisocyanate (or other isocyanates) to act upon the unsubstituted hydroxyl groups of a secondary acetate in the presence of pyridine. Fibrous but soluble products were thus obtained. No acetyl groups are removed in this reaction. However, they may be removed from the mixed ester by acid hydrolysis without attacking the carbamate groups. Thus, products are obtained which contain the free hydroxyl groups in the positions occupied by the acetyl groups in the original acetate. The fact that these products are soluble in organic solvents, in contrast to those prepared by direct (partial) esterification seems to indicate a more favorable distribution of the carbamate groups. (For phenylthiourethanes and similar derivatives see p. 376).

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[580] Goissedet, British patent 130,277 (1915); see also Marsh and Wood, "Introduction to the Chemistry of Cellulose," p. 302.

[581] Hearon, Hiatt, and Fordyce, *J. Am. Chem. Soc.*, **65**, 829, 833 (1943).

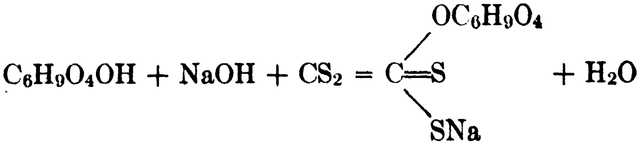
CHAPTER VIII

CELLULOSE XANTHATES

If the action of carbon disulfide upon alkali cellulose is viewed as a chemical reaction and not merely as a dispersion of highly swollen cellulose in a dispersing agent, this reaction may be classified as the formation of an ester, similar to the action of carbon disulfide upon an aliphatic alcohol in the presence of sodium hydroxide, resulting, for example, in the formation of sodium ethyl xanthate, $C_2H_5O{-}\underset{\text{SNa}}{\underset{|}{C}}{=}S$.

The first step of this reaction may be visualized as the formation of ethyl alcoholate. In the second step, the alcoholate reacts with carbon disulfide. As a matter of fact, alcoholates react directly with carbon disulfide to form xanthates.

The xanthate mentioned above is the sodium salt of xanthogenic acid but, because it may be considered as being derived from dithiocarbonic acid, $HO\underset{\text{SH}}{\underset{|}{C}}{=}S$, it should be termed the sodium salt of ethyldithiocarbonate. That the reaction of alkali cellulose with carbon disulfide is analogous to the formation of xanthates from simpler alcohols was postulated by Cross, Bevan, and Beadle,[1] who also were the first to prepare cellulose xanthates. Viewing cellulose as a polyvalent alcohol, they formulated the reaction thus:



$$C_6H_9O_4OH + NaOH + CS_2 = C\!\begin{array}{l}\diagup OC_6H_9O_4\\ =S\\ \diagdown SNa\end{array} + H_2O$$

The sodium salt of cellulose dithiocarbonate (sodium cellulose xanthate) thus formed is soluble in water, as are the alkali salts of the simple xanthates. Although the isolated cellulose xanthate tends to decompose on standing in aqueous solutions, it is relatively stable in the reaction mixture for some time.

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[1] Cross, Bevan, and Beadle, *Ber.*, **26**, 1090, 2524 (1893); **34**, 1513 (1901).

XANTHATE FORMATION WITH SIMPLE ALCOHOLS AND SUGARS

In view of the analogy which has been drawn between the reaction with cellulose and the formation of xanthates from simple hydroxy compounds a brief discussion of the latter would seem to be in order.

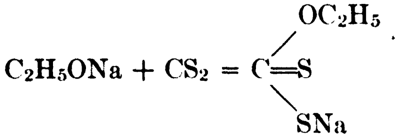
The xanthates of the simpler alcohols may be obtained by allowing carbon disulfide to react either upon the alcoholate prepared as such in a separate step or upon a solution of solid or strong aqueous sodium hydroxide in the respective alcohol.

With the use of solid or strong aqueous sodium hydroxide in alcohol, alcoholate formation represents an equilibrium reaction:

$$C_2H_5OH + NaOH \rightleftarrows C_2H_5ONa + H_2O \qquad [1]$$

The water formed, as well as the water present originally, tends to shift the reaction to the left, i.e., to decompose the alcoholate into its original constituents.

On the addition of carbon disulfide, the alcoholate present in the equilibrium system will react to form an equivalent quantity of xanthate:



$$C_2H_5ONa + CS_2 = C(OC_2H_5)(=S)SNa \qquad [2]$$

This reaction will shift the formation of alcoholate (equation 1) to the right-hand side; i.e., more alcoholate is formed which again reacts with carbon disulfide. This continues until all the alcoholate is transformed into xanthate.

This course of the reaction, however, is complicated by the fact that carbon disulfide also reacts with sodium hydroxide to form sodium carbonate and sodium trithiocarbonate, according to the equation:

$$3CS_2 + 6NaOH = 2Na_2CO_3 + 2Na_2CS_3 + 3H_2O \qquad [3]$$

In case the xanthate is prepared by using a solution of solid sodium hydroxide in alcohol, the water formed in reaction 3 will enhance the tendency of reaction 1 to shift to the left, so that less alcoholate, and consequently less xanthate, will be formed. The yield of xanthate will eventually depend upon which of these two competing reactions proceeds at the faster rate. With ethyl alcohol and other monovalent alcohols the velocity of the xanthate formation is generally so high that hardly any inorganic by-products are formed. However, the velocity is different with polyvalent alcohols.

Berl and Bitter[2] studied the xanthate reaction with simple polyvalent alcohols, such as glycol [$CH_2(OH)CH_2OH$] and glycerol [$CH_2(OH)CH(OH)CH_2OH$], expecting to throw some light on the mechanism of the reaction with cellulose. To exclude any hydrolyzing influence, they prepared the xanthates of the two alcohols directly from their alcoholates. It was found that sodium glycolate reacted much slower than sodium ethylate and that sodium glycerate did not react at all with carbon disulfide. In both cases, a certain quantity of byproducts was formed, the greater quantity in the case of glycerol. These results show that, contrary to expectation, the ability of the alcohols to react decreases as more hydroxyl groups are available and *vice versa.*

This result could be confirmed by the behavior of such alcohols in which part or all of their hydroxyl groups had been covered with ether groups and thus made incapable of alcoholate formation. Whereas the alcoholates of glycol monomethyl ether and of glycerol dimethyl ether reacted with carbon disulfide in much the same way as sodium ethylate, the alcoholate of the monomethyl ether of glycerol reacted slowly. The alcohols and their derivatives may thus be arranged with respect to their reactivity in a series in which the reactivity increases with the decreasing number of free hydroxyl groups thus:

$$HOCH_2CH(OH)CH_2OH \rightarrow HOCH_2CH(OH)CH_2OCH_3 \rightarrow CH_3OCH_2CH(OH)CH_2OCH_3$$

and

$$HOCH_2CH_2OH \rightarrow HOCH_2CH_2OCH_3$$

Thus, the conclusion was drawn that the xanthate reaction takes place with 1 hydroxyl group only and that the presence of more than one free hydroxyl group tends to retard the reaction.

Moreover it would appear that, in unmethylated glycerol, the 3 hydroxyl groups are in some state of mutual bondage which is strong enough to withstand the action of carbon disulfide under ordinary conditions. Only if the reaction is allowed to proceed under pressure does xanthation take place.[3] On the other hand, the introduction of methyl groups also seems to weaken the bondage and to render 1 hydroxyl group more susceptible to reaction under less severe conditions.

As we shall see later, with cellulose as the reacting alcohol similar difficulties are encountered in an attempt to introduce an appreciable number of xanthate groups unless especially favorable conditions are

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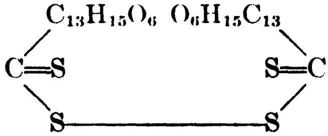
[2] Berl and Bitter, *Cellulosechem.*, **7**, 137 (1926).

[3] Lobisch and Loos, *Monatsh.*, **2**, 373 (1881); Berl and Bitter, *loc. cit.*

chosen. But the effect of alkylation of part of the hydroxyl groups is quite different from that which has been observed with the simpler polyvalent alcohols.

The difficulties encountered by Berl and Bitter in preparing a glycerol xanthate from glycerol alcoholate were confirmed by Lieser and Nagel.[4] However, the latter investigators succeeded in preparing the (mono) xanthate of glycerol and that of glycol by substituting barium hydroxide for sodium hydroxide.

Further information useful for the elucidation of the cellulose xanthate reaction is derived from the action of alkali and carbon disulfide on simple sugars. In contrast to the attempts of previous investigators,[5] Lieser and co-workers succeeded in preparing glucose xanthates in which either 1, or 2, or 3 hydroxyl groups are substituted by xanthate groups. Again, the monoxanthate is prepared more easily than the di and tri compounds. The former is obtained by allowing carbon disulfide to act upon α-methylglucoside in the presence of aqueous barium hydroxide.[6] In addition, small amounts of di-, tri-, and tetraxanthate are formed. α-Methyl xanthate is rather stable, and it may be heated to 140° or boiled in aqueous hydrochloric acid without decomposing. However, with weak alkali, it is easily decomposed, methyl glucoside being regenerated. The xanthate group is probably attached to the carbon atom in the 2-position of the glucose ring.[7] The glucoside group in methyl glucoside seems to influence the reaction essentially as has been observed in other cases.[8]

With iodine solution the xanthate of β-phenyl glucoside[9] is converted into xanthogen or disulfide,  which crystallizes. Another product is obtained by the action of iodine upon the xanthate of β-methyl glucoside, although in a lower yield.

Lieser and Hackl[10] prepared also xanthates of maltose, lactose, and cellobiose, with 1 xanthate group in each glucose residue, and those of

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[4] Lieser and Nagel, *Ann.*, **495**, 235 (1932).

[5] Dubski, *J. prakt. Chem.*, **103**, 109 (1922); see also Berl and Bitter, *loc. cit.*; Geiger, *Helv. Chim. Acta*, **13**, 293 (1930).

[6] Lieser and Nagel, *Ann.*, **495**, 235 (1932); Lieser and Hackl, *ibid.*, **511**, 121 (1934).

[7] Lieser and Leckzyck, *Ann.*, **519**, 279 (1935).

[8] Helferich and Strauss, *J. prakt. Chem.*, **142**, 15 (1935).

[9] Lieser and Thiel, *Ann.*, **522**, 48 (1936); Lieser and Leckzyck, *ibid.*, **522**, 56 (1936).

[10] Lieser and Hackl, *loc. cit.*

sucrose and raffinose having only 1 xanthate group. The reason for the limited substitution in sucrose and raffinose is that the furanose unit does not react to yield a xanthate.

XANTHATE FORMATION WITH CELLULOSE

Cellulose xanthates are prepared by allowing carbon disulfide to act upon alkali cellulose, either as such or after it has been subjected to a certain period of aging (see p. 126).

According to Cross and Bevan, cellulose, in loose form or in sheets, is steeped in aqueous sodium hydroxide of mercerizing strength and freed of excess solution by pressing or centrifuging until it has acquired about three times its original dry weight. The alkali cellulose thus obtained is defibered and subjected to the action of carbon disulfide in a closed vessel, the latter being frequently shaken by hand or slowly rotated on a mechanical device. Under the influence of the carbon disulfide, the mass swells considerably and changes from white to yellow and finally to deep orange. At this point (usually after about 2 hours), the mass is still crumbly. Xanthation is regarded as complete if the crumbs, when broken apart by hand, reveal no lighter colored portions. In this state, the crumbs are soluble in water or in dilute sodium hydroxide solution. During xanthation ("sulfidation"), the temperature tends to rise but only a few degrees. It may be kept constant by cooling. Elevated temperature decreases the degree of substitution. Unconsumed carbon disulfide may be removed by evacuation.

If the time of xanthation is extended, the crumbly mass tends to become peptized and gradually, particularly when stirred, loses its fibrous structure and becomes a more or less homogeneous paste.

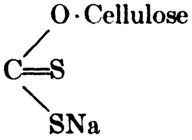
The solution of the crumbs in water or dilute alkali is an orange-colored, highly viscous liquid which Cross and Bevan have termed "viscose."

It is remarkable that cellulose loses its hydrophobic properties and becomes a highly hydrophylic substance as a result of the introduction of even a limited number of xanthate groups. The swelling which the alkali cellulose fiber undergoes by the action of carbon disulfide prior to dissolving is very considerable, as may be observed under the microscope. If further action of the carbon disulfide is arrested by submerging the highly swollen fibers in water and washing them on a Büchner funnel, swelling is somewhat reduced but still so pronounced that the regenerated fibers are highly reactive in the moist condition. Incidentally, their reactivity is much greater than that of the precipitate which may be obtained from viscose by the action of dilute mineral or organic acids.

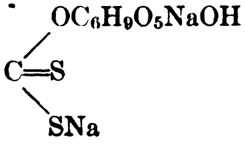
The aqueous (alkaline) solution of cellulose xanthate contains a number of inorganic sulfur compounds (by-products) which, as has been seen, are formed by the simultaneous interaction of carbon disulfide and sodium hydroxide, sodium trithiocarbonate (Na_2CS_3) being the chief by-product.

Isolation of Cellulose Xanthates

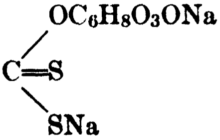
Cellulose xanthates may be isolated from their solution in various ways—for example, by precipitation with saturated aqueous sodium or ammonium chloride solution or with alcohol, acetone, or other organic liquids. After being washed with alcohol or acetone, a product is obtained which is fairly free of inorganic by-products but which shows an appreciably higher sodium content than required by the formula



This excess of sodium is probably present in the form of sodium hydroxide. Accordingly, Cross and Bevan, and later Westhoff,[11] ascribed to the xanthate, obtained by precipitation with alcohol, the formula



whereas Ost, Westhoff, and Gessner,[12] assuming that the second sodium atom is present in cellulosate form, formulated the xanthate thus:



Other investigators, for example, Rassow and Aehnelt,[13] have placed

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[11] Westhoff, doctoral dissertation, Hanover, 1911.

[12] Ost, Westhoff, and Gessner, *Ann.*, 382, 340 (1911).

[13] Rassow and Aehnelt, *Cellulosechem.*, 10, 177 (1929); see also Schwedler, doctoral dissertation, Leipzig, 1927.

the molecule of sodium hydroxide in combination with the C=S grouping of the xanthate.

Whereas, as will be seen later, experimental evidence does not favor a combination of sodium hydroxide with the C=S grouping, it is quite possible that it is combined with the cellulose radical of the xanthate. Fink, Stahn, and Matthes,[14] in subjecting viscose to the process of ultrafiltration, found that a certain quantity of alkali was retained by the xanthate on the ultrafilter, whereas the greater part passed into the filtrate. The retained portion was assumed to be combined with the xanthate. This portion, however, amounted to only one-fifth of a mole, in contrast to 1 mole per glucose residue as formulated by Cross and Bevan and the previously mentioned investigators.

Finally, it appears possible that part or all of the sodium hydroxide is merely adsorbed on the xanthate or the cellulose radical and that the stoichiometric formulations, as expressed in the formulas above. are to be regarded as incidental.

This conclusion seems to find support in the observation [15] that, with increasing alkali content of the viscose, the xanthates obtained by precipitation with alcohol show an increasing sodium hydroxide content.

TABLE 35

ALKALI CONTENT OF VISCOSE AND OF XANTHATES PRECIPITATED THEREFROM

NaOH added to viscose, %	4.5	7.0	11.0	14.0
Total NaOH in precipitate, %	12.5	12.6	13.2	14.1
NaOH "combined" with xanthate, %	6.09	5.82	8.84	8.97

Whether a certain quantity of sodium hydroxide is chemically combined with or merely adsorbed on the xanthate is evidently not important. This follows from the fact that the xanthate does not decompose into its constituents when the sodium hydroxide is removed. The removal may be accomplished by neutralizing the dilute viscose with weak organic acids. If precautions are taken, the sodium atom in the xanthate is attacked very little if at all. Such xanthates may be prepared by acidifying dilute viscose with dilute acetic acid and immediately precipitating with saturated sodium chloride solution.[16] Simultaneously, sodium trithiocarbonate (which is very sensitive even to weak acids) is completely decomposed. The precipitate, after thorough purification with alcohol, represents a xanthate free of sodium

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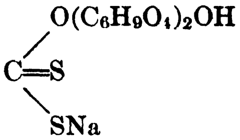
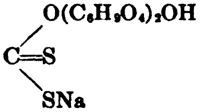
[14] Fink, Stahn, and Matthes, *Angew. Chem.*, **47, 606** (**1934**).

[15] Heuser and Schuster, *Cellulosechem.*, **7,** 27 (**1926**).

[16] Heuser and Schuster, *loc. cit.*, p. 21.

hydroxide. The ratio of sulfur to sodium to cellulose derived from analysis is in agreement with the formula  $\overset{\diagup O(C_6H_9O_4)_2OH}{\underset{\diagdown SNa}{C{=}S}}$

Another way to produce a purified xanthate has been suggested by Lieser.[17] It consists in treating the crude fibrous xanthate obtained from the process of xanthation with methyl alcohol (ethyl alcohol is said to be unsuitable[18]) at room temperature; the inorganic by-products are thus removed, together with most of the sodium hydroxide. However, the total sodium content of the purified xanthate is 7.0 to 7.5%, instead of 5.45% as required by the formula


$\overset{\diagup O(C_6H_9O_4)_2OH}{\underset{\diagdown SNa}{C{=}S}}$

The inorganic by-products may also be removed with sulfurous acid or alkali bisulfites, which are said to leave the xanthate unaffected.[19]

Eggert[20] and later Berl and Dillenius[21] recommended the isolation of the xanthate in the form of a film, because in this form it may be washed more easily. Fink, Stahn, and Matthes[22] have employed this technique in determining the sodium content of the xanthate.

Under certain conditions dialysis appears to be a suitable means of isolating the xanthate.[23]

The aqueous solution of the purified and alkali-free xanthate reacts slightly alkaline, indicating slight dissociation. If, after neutralizing with dilute acetic acid, using phenolphthalein as an indicator, the solution is allowed to stand for a while, it becomes slightly alkaline again. After a certain time, temporary equilibrium seems to be reached.[24]

If an aqueous iodine solution is added to viscose which has been slightly acidified with acetic acid, a precipitate is obtained which appears free of combined sodium, the latter having been converted into

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[17] Lieser, *Ann.*, **464**, 43 (1928).

[18] See, however, Staudinger and Daumiller, *Ber.*, **71**, 1997 (1938), who prefer ethyl alcohol.

[19] Hess, "Die Chemie der Cellulose," p. 331.

[20] Eggert, "Die Herstellung und Verarbeitung der Viscose," Springer, Berlin (1926), p. 51.

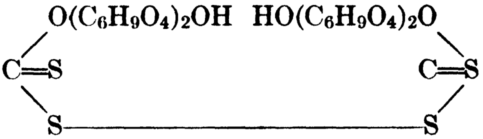
[21] Berl and Dillenius, *Cellulosechem.*, **13**, 8 (1932).

[22] Fink, Stahn, and Matthes, *Angew. Chem.*, **47**, 602 (1934); see also Bredée, *Kolloid-Z.*, **94**, 81 (1941).

[23] Karrer and Lieser, *Cellulosechem.*, **7**, 3 (1926); Hottenroth, *Chem.-Ztg.*, **39**, 119 (1915); see also Sokolow, *Rev. gén. mat. plastiques*, **13**, 199 (1937), and Herzog and Gaebel, *Kolloid-Z.*, **35**, 196 (1924).

[24] Heuser and Schuster, *loc. cit.*, p. 22; see also Rassow and Aehnelt, *Cellulosechem.*, **10**, 180 (1929), and Berl and Dillenius, *loc. cit.*, p. 10.

sodium iodide. Cross and Bevan showed that the removal of sodium does not cause the xanthate to decompose.[25] This fact is explained on the assumption that 2 molecules of xanthate unite to form a complex compound through a linkage between the 2 sulfur atoms to which the sodium had been attached. Thus, a disulfide which has been given the following hypothetical formula is formed:



The product is soluble in dilute caustic soda solution.[26] Cross and Bevan assumed that, in this solution, the disulfide is decomposed into the normal xanthate if a reducing agent is added. However, experimental evidence does not sufficiently support this conclusion, nor does it support the formula shown above. Doubts in this respect have been expressed by Geiger[27] and by Berl and Dillenius,[28] although, as will be recalled, a crystalline and, hence, well-defined disulfide was obtained from the xanthate of β-phenyl glucoside (Lieser and Hackl, see above).

Analytical Methods

The iodine reaction may be utilized for analytical purposes. Thus, one may determine the sodium in the purified xanthate by adding to its aqueous solution an excess of iodine solution and titrating the excess with thiosulfate solution.[29] If the xanthate contains sodium hydroxide, the latter must first be neutralized with dilute acidic acid.

Titration with iodine may also be used for determining the xanthate and the sodium trithiocarbonate (Na_2CS_3) contents in viscose.[30] In the presence of dilute acetic acid, the thiocarbonate is decomposed to yield carbon disulfide and hydrogen sulfide. Iodine attacks only the hydrogen sulfide. At the same time, a certain amount of iodine is consumed when the disulfide is formed. Thus, the total iodine consumption corresponds to the amounts of xanthate and thiocarbonate present in the viscose. Another sample of the viscose is titrated with iodine in the presence of sulfuric acid. Both the xanthate and the trithiocar-

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[25] Cross and Bevan, *Ber.*, **26**, 1096 (1893); **34**, 1517 (1901).

[26] Cross and Bevan, *loc. cit.;* Geiger, *Helv. Chim. Acta,* **13**, 290, 300 (1930).

[27] Geiger, *loc. cit.*

[28] Berl and Dillenius, *loc. cit.*, p. 9.

[29] Heuser and Schuster, *loc. cit.*, p. 21; Dorée, "The Methods of Cellulose Chemistry," p. 240; see also Eggert, "Die Herstellung und Verarbeitung der Kunstseide," Springer, Berlin (1926); see also Berl and Dillenius, *loc. cit.*, p. 8.

[30] The method was used by Rupp and Krais, *Ber.*, **35**, 4157 (1903), for the determination of xanthates of simple alcohols.

bonate are decomposed by the acid to yield carbon disulfide and hydrogen sulfide. The consumption of iodine in this case corresponds to the amount of sodium in the thiocarbonate only. By deducting the latter iodine consumption from the former, the amount of xanthate present in the viscose is obtained. This method is known as the Jentgen method.[31]

A modification of this method consists in precipitating the xanthate with saturated sodium chloride solution and titrating the filtrate with iodine. This yields the value for the thiocarbonate alone. By deducting this value from the iodine consumed in the presence of acetic acid (which yields the values for both the thiocarbonate and the xanthate), the value for the xanthate alone is obtained.[32]

The method of titrating viscose with iodine in the presence of acetic acid was improved by Geiger[33] and by Bernhardt.[34] These modifications seem to decrease the error caused by slight decomposition of the xanthate in the presence of acetic acid. However, Geiger's modification seems to introduce another error—the formation of thiosulfate.[35]

In this connection, De Wyss'[36] method may be mentioned. It consists in adding dilute acetic acid to a sample of viscose, extracting the solution with ether to remove the carbon disulfide and the hydrogen sulfide, decomposing the aqueous solution with dilute sulfuric acid, and converting the carbon disulfide, thus liberated from the cellulose xanthate, into potassium ethyl xanthate. The ethyl xanthate is converted into its copper salt, and the copper is determined by titrimetric methods.

The iodine reaction, which leads to the formation of the (hypothetical) disulfide, may also be utilized for determining in the viscose the sulfur content of the xanthate. On adding iodine solution in the presence of acetic acid to viscose, all xanthate sulfur is found in the precipitate, whereas the inorganic sulfur (resulting from the decomposition of the thiocarbonate by the acetic acid) is in the filtrate. By oxidizing the washed precipitate, the xanthate sulfur is obtained. The ratio of sulfur to cellulose (or xanthate groups per glucose residue) is the same in the disulfide as in the xanthate, and therefore this method also furnishes a way of determining the degree of substitution. Scherer and Miller[37] believe that any colloidal sulfur which may be formed and retained on precipitation is subsequently removed by washing with water. However, Geiger,[38] obviously for reasons of safety, subjected the disulfide precipitate to an extraction with carbon disulfide.

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[31] Jentgen, *Kunststoffe*, **1**, 165 (1911); Jentgen, "Laboratoriumsbuch für die Kunstseidenindustrie," Knapp, Halle (1923); Faust, Graumann, and Fischer, *Cellulosechem.*, **7**, 165 (1926); D'Ans and Jäger, *Kunstseide*, **8**, 17 (1926).

[32] Wheeler, quoted in Dorée, "The Methods of Cellulose Chemistry," p. 250.

[33] Geiger, *Helv. Chim. Acta*, **13**, 296 (1930).

[34] Bernhardt, *Kunstseide*, **8**, 173 (1926); see also Berl and Dillenius, *Cellulosechem.*, **13**, 5 (1932).

[35] Tanemura, *J. Soc. Chem. Ind., Japan*, **33**, B50 (1930); Fink, Stahn, and Matthes, *Angew. Chem.*, **47**, 602 (1934).

[36] De Wyss, *Ind. Eng. Chem.*, **17**, 1043 (1925); see also Bernhardt, *Kunstseide*, **8**, 259 (1926).

[37] Scherer and Miller, *Rayon Textile Monthly*, **19**, 478 (1938); Scherer and Lin, *ibid.*, **498** (1939); Scherer, *Rayon Textile Monthly*, **20**, 141 (1939).

[38] Geiger, *Helv. Chim. Acta*, **13**, 300 (1930).

The total sulfur of the viscose is best determined by oxidizing a sample with hypobromite solution and subsequently estimating the sulfuric acid as barium sulfate.[39]

Methods for determining the total alkali and the cellulose content of viscose are described in Dorée's book.[40]

The Formation of Heavy Metal Salts

The sodium atom linked to the acidic sulfur in the xanthate reacts in various other ways. It may be replaced by heavy metals, a reaction which again emphasizes the analogy to the xanthates of simpler alcohols. The heavy metal salts are obtained in the form of precipitates, because they are insoluble in water and dilute alkali.

The precipitates are of different color (with iron, brown; with lead, red; with mercury, yellow; with nickel, deep red; with bismuth, reddish brown; and with zinc, white). The colors, however, are not characteristic of the xanthate, but are due to the interaction of the metal salts with sodium trithiocarbonate.[41] In fact, the precipitates obtained from an aqueous solution of purified xanthate are either colorless or only slightly colored.[42] The copper salt seems to be an exception.

The reaction involved in the addition of aqueous copper sulfate to an aqueous ethyl sodium xanthate solution is well known and is used for the qualitative and quantitative estimation of ethyl and other simple xanthates.[43] The brown precipitate obtained soon changes to a deep yellow. For some time the brown precipitate was thought to consist of the unstable cupric xanthate which is spontaneously converted to the yellow, stable cuprous xanthate. Ragg,[44] however, showed that the brown color is due to the formation of copper thiocarbonate, the latter being present as an impurity, and that it is the copper thiocarbonate which reacts with ethyl sodium xanthate to form yellow cuprous xanthate (and sodium thiocarbonate). According to Ragg, cupric xanthate is not formed at all. Obviously, then, the yellow color of the final precipitate is a property of the copper xanthate itself and not caused by impurities.[45] The zinc salt of cellulose xanthate was investigated by Poznaski.[46]

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[39] Heuser and Schuster, *loc. cit.*, pp. 20, 47.

[40] Dorée, "The Methods of Cellulose Chemistry," p. 249.

[41] Seidel, *Ber.*, **35**, 2184 (1902); Margosches, "Die Viskose," Leipzig (1906); see also Gaebel in "Kunstseide" in R. O. Herzog's "Technologie der Textilfasern," J. Springer, Berlin (1927), Vol. VII, p. 140.

[42] Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 94; Karrer and Lieser, *Cellulosechem.*, **7**, 3 (1926). See, however, Atsuki and Takada, *Cellulose Ind.*, **15**, 73 (1939).

[43] Johnson, *J. Am. Chem. Soc.*, **28**, 1211 (1906); Heuser and Schuster, *loc. cit.*, p. 23.

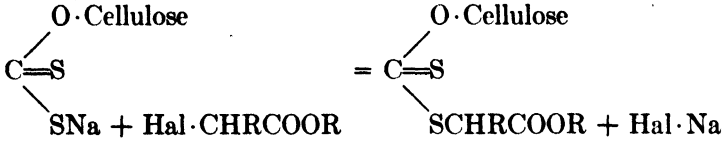
[44] Ragg, *Chem.-Ztg.*, **32**, 630, 654, 677 (1908).

[45] See also Karrer and Lieser, *Cellulosechem.*, **7**, 3 (1926).

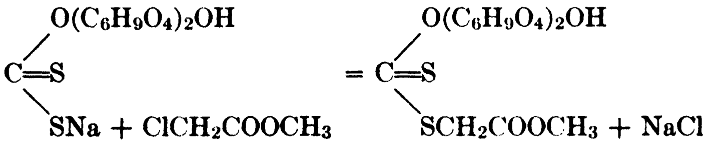
[46] Poznaski, *Rayon Textile Monthly*, **20**, 385, 437, 500 (1939).

The Reaction of Cellulose Xanthate with the Halides of Fatty Acids

The sodium atom attached to the acidic sulfur atom in cellulose xanthate also reacts with α-halogenated fatty acids according to the general equation:[47]

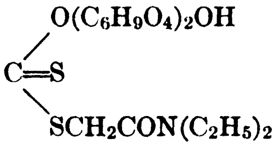


Most of these derivatives are unstable. However, with methyl chloroacetate a stable compound is obtained.[48] The reaction proceeds in the following way:



The methyl content of the reaction product was found to be in agreement with this formula. The product is obtained by adding methyl chloroacetate to viscose. Precipitation occurs almost immediately; the precipitate is powderous, stable, and insoluble in water.

With *N*-diethylchloroacetamide, $ClCH_2CON(C_2H_5)_2$, an analogous reaction occurs, the chlorine combining with the sodium of the xanthate to form sodium chloride and a xanthate derivative, thus:



In this product, diethylacetamide cellulose xanthate, 1 nitrogen atom corresponds to 1 xanthate group per 2 glucose residues. Its physical properties are similar to those of the methyl ester derivative; it is insoluble in water and entirely stable to hydrolysis with water.

These properties make these derivatives extremely useful for ascertaining the degree of substitution in the xanthate. The afore-mentioned difficulties in obtaining reliable analytical data encountered with the xanthate itself, resulting from its tendency to hydrolyze in aqueous solution, are entirely eliminated. If the nitrogen content of

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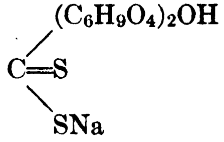
[47] Lilienfeld, German patent 448,984 (1927).

[48] Fink, Stahn, and Matthes, *Angew. Chem.*, **47**, 602 (1934).

the xanthate derivative is known, the degree of substitution may be easily calculated. Likewise, the degree of substitution of the xanthate in its original solution, i.e., in the viscose, may be ascertained by determining the nitrogen content of the (moist) xanthate derivative precipitated from an aliquot part of the viscose and calculating it on the basis of the weight of cellulose used for preparing the viscose.

The results of such determinations show that the composition of the xanthate precipitate prepared from fresh viscose under normal conditions is in agreement with the previously given formula, namely,



$$C(=S)\begin{cases}(C_6H_9O_4)_2OH \\ SNa\end{cases}$$

for it was found that the ratio of carbon disulfide to glucose residues was between 0.5 and 0.6 : 1, which corresponds very nearly to 1 xanthate group to 2 glucose residues; this is the same as was found when the xanthate was isolated and purified according to the method suggested by Heuser and Schuster.

The Function of the Alkali in the Formation of Cellulose Xanthate

In preparing alkali cellulose, an excess of sodium hydroxide is required in order to avoid poor xanthate yields. Cross and Bevan suggested the use of a quantity of sodium hydroxide which would correspond to at least 2 moles of alkali per mole of $C_6H_{10}O_5$. As a matter of fact, Berl and Bitter[49] found that, with 1 mole of NaOH per $C_6H_{10}O_5$, only a small portion of the cellulose was converted into xanthate. This result need not necessarily be explained on the assumption that 2 molecules of sodium hydroxide take part in the formation of the xanthate. The function of the excess alkali is probably merely physical because, as with other cellulose reactions, the degree of diffusion of the agents into the fibrous structure and the degree of swelling accomplished under the action of the alkali are essential prerequisites in approaching completeness of reaction.

Apart from the physical effects of the sodium hydroxide solution, experimental evidence seems to show that chemical combination between sodium hydroxide and cellulose is another prerequisite for the formation of the xanthate. If the chemical combination between sodium hydroxide and cellulose is prevented, xanthate formation fails to

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[49] Berl and Bitter, *Cellulosechem.*, **7**, 139 (1926).

occur.[50] This conclusion follows from two facts. First, it has not been possible to obtain a xanthate with alkylated cellulose of a certain degree of substitution. Methyl cellulose corresponding to the dimethyl ether stage does not (as has been seen in Chapter IV) undergo chemical combination with alkali; likewise, it does not form a xanthate, although it still contains one-third of its original hydroxyl groups uncovered.[51] Since, on the other hand, "monomethyl cellulose" yields a xanthate,[52] it would appear that, in "dimethyl cellulose," those hydroxyl groups, which in cellulose itself are capable of combining chemically with sodium hydroxide, are blocked by methyl groups. This conclusion implies that in the methylated products the methoxyl groups are rather unevenly distributed.

The results obtained with dimethylcellulose were confirmed with diethylcellulose.[52]

Second, xanthate formation is complete only if the concentration of the alkali used for the preparation of the alkali cellulose is such that chemical combination is complete. Heuser and Schuster found that "xanthates" prepared from alkali celluloses which were obtained from the action of caustic soda solutions below 16 per cent concentration dissolved only incompletely in dilute aqueous alkali, whereas alkali cellulose prepared with sodium hydroxide solution above 16 per cent yielded fiber-free viscose. These findings were later confirmed by other investigators.[53]

Likewise, alkali cellulose prepared with other alkalies, such as lithium, potassium, and rubidium hydroxide, exhibited the same behavior.[54] Only if the concentration of the alkali hydroxides was that required for chemical combination was xanthation complete.

Once the alkali cellulose is formed, the concentration of the surrounding alkali hydroxide solution is less important. In fact, the initially used concentration of the sodium hydroxide solution of 18 per cent may subsequently be decreased to 16, 14, 12, and 10 per cent without interfering with the formation of the cellulose xanthate. Only if the initial concentration is subsequently brought below 10 per cent, does the action of carbon disulfide fail to produce a xanthate soluble in dilute aqueous alkali.[55]

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[50] Heuser and Schuster, *Cellulosechem.*, **7**, 26 (1926).

[51] Heuser and Schuster, *loc. cit.*, p. 29.

[52] Berl and Bitter, *Cellulosechem.*, **7**, 140 (1926).

[53] Lottermoser and Radestock, *Angew. Chem.*, **42**, 1152 (1929); Atsuki and Kuvahara, *Cellulose Ind.*, **7**, 47 (1931).

[54] Heuser and Schuster, *loc. cit.*

[55] Schramek and Küttner, *Kolloid-Beihefte*, **42**, 359 (1935); see also Schramek, *Z. physik. Chem.*, **B20**, 214 (1933).

Carbon Disulfide Requirements

In their preparation of cellulose xanthate, Cross and Bevan used 1 molecule of carbon disulfide per $C_6H_{10}O_5$ unit, which is in accordance with their xanthate formula (which has a ratio of xanthate groups to glucose units of 1 : 1). However, on the assumption that the reaction results in the formation of a xanthate as formulated above, this quantity of carbon disulfide would mean a considerable excess, a xanthate with a xanthate-glucose residue ratio of 1 : 2 requiring only 23.4 per cent carbon disulfide (calculated on cellulose) against 46.9 per cent as used by Cross and Bevan. Actually, the smaller quantity of carbon disulfide (plus a small excess) is quite sufficient for complete xanthation, i.e., for preparing a xanthate which, in its crude form, is completely soluble in dilute caustic soda solution. Heuser and Schuster[56] found that the minimum amount is 30 per cent and, according to Berl and Bitter,[57] only 26 per cent is required. In commercial practice, 35–37 per cent of carbon disulfide is employed. Under these conditions, the xanthate, which may be isolated and purified as mentioned above, shows a composition which justifies the formula having a xanthate-glucose ratio of 1 : 2.[58]

A similar ratio was found by Scherer and Miller[59] in the disulfide isolated by means of iodine solution from fresh commercial viscose. The ratio of sulfur to cellulose was 0.237, which corresponds to a ratio of 0.6 carbon disulfide to 1 glucose residue or with very nearly 1 xanthate group to 2 glucose residues.

Cellulose Xanthates of Higher Degrees of Substitution

For a long time, the opinion prevailed that not more than 1 xanthate group per 2 glucose residues could be introduced into cellulose. The results of Wolffenstein and Oeser,[60] who believed that they had prepared a dixanthate from acetylcellulose, could not be confirmed by Heuser and Schuster.[61] Although Herzog and Hegel's[62] preparations were probably contaminated with inorganic sulfur, indications were

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[56] Heuser and Schuster, *loc. cit.*, p. 32.

[57] Berl and Bitter, p. 142.

[58] See also, Fink, Stahn, and Matthes, *loc. cit.*, pp. 603, 604. The authors express the ratio as moles CS_2 which combine with 100 $C_6H_{10}O_5$ units (γ value).

[59] Scherer and Miller, *Rayon Textile Monthly*, **20**, 141 (1939).

[60] Wolffenstein and Oeser, *Ber.*, **56**, 756 (1923).

[61] Heuser and Schuster, *loc. cit.*, p. 28.

[62] Herzog and Hegel, *Kolloid-Z.*, **35**, 196 (1924).

that the degree of substitution increased with the time of contact between the alkali cellulose and the excess of carbon disulfide. In fact, De Wyss[63] found that, under such conditions, the ratio of sulfur to $C_6H_{10}O_5$ in the trithiocarbonate-free viscose was 1.7 : 1.0, which corresponds to 0.85 xanthate groups per glucose residue. Faust,[64] using 180–200 per cent of carbon disulfide on the weight of the cellulose, arrived at a ratio of 1.8 xanthate groups per glucose residue. Geiger,[65] as well as Weeldenburg,[66] likewise using a large excess of carbon disulfide, found that 1 xanthate group per glucose residue had entered the cellulose. Scherer and Miller found slightly lower values, namely, a sulfur to cellulose ratio of 0.366 (theoretically, a ratio of 2 sulfur atoms to 1 $C_6H_{10}O_5$ unit is 0.395), equal to 0.93 xanthate groups per glucose residue. This ratio was obtained when more than 100 per cent carbon disulfide and a time of 200 hours were used.

The various results are summarized in Table 36. The figures may be interpreted to show that it is possible to introduce 1–2 xanthate groups per glucose residue into alkali cellulose; i.e., up to four times the number of xanthate groups found under normal conditions,[67] in which case the ratio is 0.5 : 1.

TABLE 36

DEGREE OF SUBSTITUTION IN CELLULOSE XANTHATES

Investigators	De Wyss	Faust	Geiger	Scherer and Miller
Ratio of xanthate groups: $C_6H_{10}O_5$ unit	0.85 : 1.0	1.8 : 1.0	1.0 : 1.0	0.93 : 1.0

Instead of a large excess of carbon disulfide being applied in the initial reaction, it may be incorporated into the viscose. By shaking viscose, prepared in the normal way, with carbon disulfide in a closed flask for a few hours, Geiger[68] observed that the carbon disulfide was entirely consumed. By this procedure, the number of xanthate groups per glucose residue was increased to 1.5. This increased substitution, reached after only a few hours, was obviously due to the fact that the partially xanthated cellulose was in solution, in which state it is more

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[63] De Wyss, *Ind. Eng. Chem.*, **17**, 1044 (1925).

[64] Faust, *Ber.*, **62**, 2572 (1929); *Kolloid-Z.*, **46**, 329 (1928).

[65] Geiger, *Helv. Chim. Acta*, **13**, 292 (1930).

[66] Weeldenburg, *Chem. Weekblad.*, **30**, 47 (1933); see also Bredée, *Kolloid-Z.*, **94**, 81 (1941).

[67] See also Lieser and Ebert, *Ann.*, **528**, 276 (1937), referring to the use of cuprammonium rayon as the cellulosic material.

[68] Geiger, *loc. cit.*, p. 284.

reactive than it is in fibrous form. Similar results (1.1 xanthate groups per glucose residue) were reported by Jimbo and Takada.[69]

The concentration of sodium hydroxide in the viscose, before fresh amounts of carbon disulfide are incorporated, is far below that which is necessary to enable cellulose to undergo alkali cellulose (cellulosate) formation. That xanthation does occur is explained on the assumption[70] that the negative dithiocarboxylic group in the xanthate exerts an influence upon the reactivity of uncovered hydroxyl groups similar to that of a nitro group in the ortho position upon nitrophenol. The acidic nature of the phenolic hydroxyl groups is enhanced and it is capable of forming salts which, even in aqueous solution, are not subject to hydrolysis. This could be interpreted to mean that the xanthate groups enable the cellulose radical in the xanthate to undergo cellulosate formation, in spite of the apparent lack of high sodium hydroxide concentration. On the other hand, and as would be expected, Geiger found that increasing quantities of freshly added carbon disulfide were consumed when the alkali concentration of the xanthate solution was increased.[71]

If the cellulosic constituent of the xanthate is capable of cellulosate formation and thus of an extended reaction with carbon disulfide, the same behavior should be observed with cellulose disulfide. Indeed, Geiger was able to increase the sulfur content of a disulfide preparation from 17.7 to 29.6 per cent by allowing carbon disulfide to act on an alkaline solution of the disulfide.

That the xanthates having a higher degree of substitution than normally obtainable are not merely lower stages contaminated with inorganic sulfur compounds is seen from the fact that the high degree of substitution is retained in the acetamide derivatives and that the solubility properties of these derivatives change with increasing number of modified xanthate groups. Whereas the acetamide derivatives with less than 1 xanthate group per glucose residue are soluble only in aqueous pyridine, those having 1.5 xanthate groups per glucose residue are also soluble in hot aqueous acetone, in a mixture of benzene and ethyl alcohol, and in glacial acetic acid. A derivative with 1.7 xanthate groups per glucose residue swells considerably in chloroform and is almost entirely soluble in acetone.

With these cellulose xanthate derivatives, we obviously encounter a similar behavior as with other cellulose esters, their solubility properties being essentially governed by the ratio of polar to nonpolar groups and by the balance between this ratio and that present in the solvent or solvent mixture. The xanthate derivatives in which free

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[69] Jimbo and Takada, *J. Soc. Chem. Ind., Japan*, Supplementary Binding, **38**, B252 (1935).

[70] Geiger, *loc. cit.*, p. 288.

[71] Schramek and Zehmisch, *Kolloid-Beihefte*, **48**, 93 (1938), came to the conclusion that even with a large excess of carbon disulfide the degree of substitution is not increased unless alkali is also added.

hydroxyl groups are still abundant are soluble in aqueous bases and even in water. As the number of free hydroxyl groups decreases, the products become soluble in organic solvents.

Finally, the degree of substitution of a xanthate may be increased by adding to ordinary viscose a xanthate with a higher degree of substitution.[72] Obviously, the two xanthates tend to establish a state of equilibrium; i.e., the product with the higher degree of substitution liberates carbon disulfide which thus becomes available for reacting with the xanthate with the lower degree of substitution. This explanation appears to be supported by the facts that ethyl xanthate actually decomposes with the liberation of carbon disulfide as such (that is, without passing through intermediate stages)[73] and that free carbon disulfide has been found to exist in viscose, particularly shortly after its preparation.[74]

Cellulose Trixanthate. The fact that the degree of substitution may be increased by incorporation into viscose of increasing quantities of carbon disulfide—with or without simultaneous increase of the alkali concentration—made it seem probable that similar results might be obtained by dissolving cellulose in a quaternary ammonium base and allowing a large excess of carbon disulfide to react with the cellulose in this solution.[75]

Because, as will be recalled, quaternary ammonium bases combine with cellulose as alkalies do, the former are evidently capable of replacing the latter in the cellulose xanthate reaction. In the light of the interpretation of the mechanism of the reaction suggested earlier, we may assume that the quaternary ammonium base reacts with cellulose to form a compound of the cellulosate type. The reaction—for example, with tetraethylammonium hydroxide—may then be expressed by the following equation:

$$C_6H_7O_2(OH)_3 + 3HON(C_2H_5)_4 \rightleftarrows C_6H_7O_2[ON(C_2H_5)_4]_3 + 3H_2O$$

and the action of carbon disulfide on the "cellulosate" may be formulated thus:

$$C_6H_7O_2[ON(C_2H_5)_4]_3 + 3CS_2 = C_6H_7O_2[OCSSN(C_2H_5)_4]_3$$

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[72] Geiger, *loc. cit.*, p. 285.

[73] Halban, *Z. physik. Chem.*, **82**, 325 (1913).

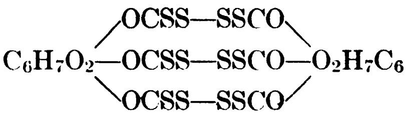
[74] Bernhardt, *Kunstseide*, **8**, 259 (1926). The carbon disulfide was isolated from viscose by removing it with a current of carbon dioxide-free air, also by extraction with ether following the method of De Wyss.

[75] Lieser and Leckzyck, *Ann.*, **522**, 56 (1936).

> For preparing tetraethylammonium cellulose xanthate, 1 part of cellulose is dissolved in 10–15 parts of a 3.7 *N* aqueous tetraethylammonium hydroxide solution. To the very viscous solution, which is cooled to 0°, a large excess of carbon disulfide (1500 per cent on the weight of the cellulose) is added, and the mixture is stirred intermittently for 1 hour, after which time the highest degree of substitution obtainable is reached. The solution, which has acquired a dark red color, is diluted with methyl alcohol, in which the higher substituted xanthates are soluble.

The tetraethylammonium cellulose trixanthate has not been isolated as such. On precipitation with ether, a product is obtained which contains less than 2 xanthate groups per glucose residue.

However, with iodine, the trixanthate may be obtained in the form of its "polyxanthogen" which is stable. As in the action of iodine on ordinary viscose, the sodium of the xanthate is eliminated as sodium iodide, the tetraethylammonium radical being removed in the form of tetraethylammonium iodide, $[(C_2H_5)_4NI]$. The polyxanthogen may be formulated as follows:



In this product, the ratio of sulfur to cellulose is the same as in the trixanthate, namely, 6 : 1.

The degree of substitution obtainable by Lieser and Leckzyck's method depends essentially upon the degree of dispersion of the cellulose in the tetraethylammonium base. Only if the dispersion is at its optimum is the highest degree of substitution accomplished. As with other esterification reactions, the triester stage is not reached completely; the highest sulfur content was 48.23 per cent, whereas the theory requires 49.7 per cent. No doubt, this is due to the tendency of the system to establish an equilibrium. In addition, the two equations given above show that the highest degree of substitution may be expected only if carbon disulfide is present in great excess. This condition, as well as a low temperature, shifts the reaction to the right and thus counteracts the tendency of the reaction product to decompose.

The Rate of Xanthation

The rate of xanthation may be ascertained by taking samples of the reaction product at intervals and determining the ratio of sulfur to cellulose. An extensive investigation of this kind was undertaken by Scherer and Miller.[76]

An excess of carbon disulfide (152 per cent calculated on the cellulose) was allowed to act on alkali cellulose prepared in the usual way (containing 31.5 per cent cellulose and 15 per cent sodium hydroxide, the rest being water) for a total time of 1020 minutes at 29.5°. In samples, taken every 10 minutes up to 300 minutes and thereafter at longer intervals, cellulose and sulfur were determined, the latter by precipitating the xanthate in the form of its disulfide with iodine solution (after acidification of the viscose with dilute acetic acid) and subsequently oxidizing the precipitated disulfide with nitric acid. The sulfuric acid thus formed was converted into barium sulfate, which was determined with a Parr turbidimeter as used for the determination of sulfates in boiler water. It is said that the results obtained with this quick method compare very well with the gravimetric results.

In the compilation of average data, shown in Table 37, for alkali cellulose which had been aged for different lengths of time (the aging having little influence), the ratio of sulfur to cellulose is expressed by a quotient (weight of sulfur divided by weight of cellulose). For 1 xanthate group per glucose residue the quotient is $^{64}/_{162} = 0.395$, so that figures below this theoretical value indicate a sulfur-cellulose ratio

TABLE 37

RATE OF XANTHATION AT 29.5

Time, Minutes	Ratio, Sulfur-Cellulose	Time, Minutes	Ratio, Sulfur-Cellulose
10	0.072	180	0.329
20	0.109	190	0.331
30	0.130	200	0.324
40	0.158	210	0.343
50	0.171	230	0.332
60	0.193	240	0.332
70	0.222	260	0.335
80	0.237	270	0.314
90	0.250	280	0.345
100	0.253	290	0.348
110	0.282	300	0.259
120	0.282	720	0.352
130	0.293	780	0.356
140	0.304	840	0.319
150	0.293	900	0.338
160	0.309	930	0.310
170	0.334	1020	0.309

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[76] Scherer and Miller, *Rayon Textile Monthly*, **19**, 478, 541 (1938).

equal to a degree of substitution below 1 xanthate group per glucose residue.

The data of Table 37 and those obtained when the temperature was increased to 35° or lowered to 25° are represented in Fig. 64. They show that the degree of substitution increases rather steadily. However, after 200 minutes of reaction time, the sulfur-cellulose ratio remains practically constant. On the other hand, the rate of reaction increases with the temperature.

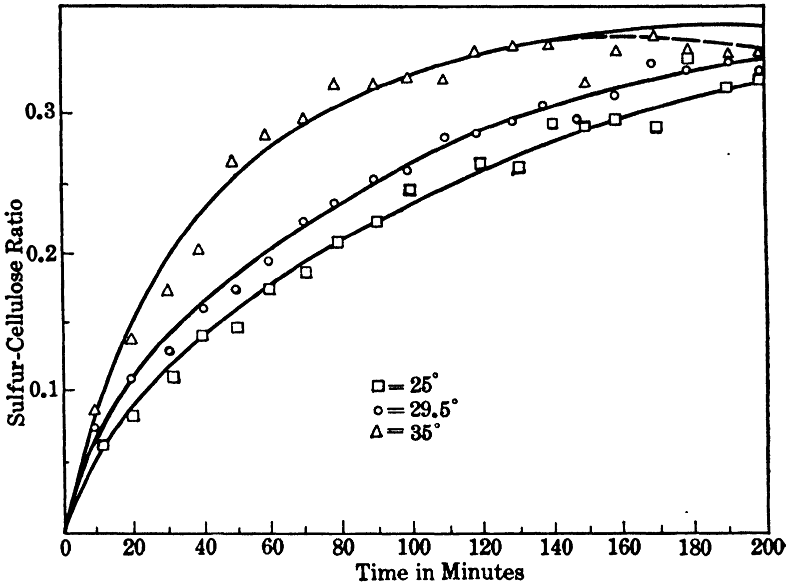
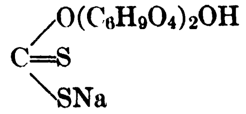


FIG. 64. Rate of xanthation at 29.5, 35, and 25° C. Scherer and Miller.

The mathematical treatment of the data revealed that the reaction curves obey the equations for a unimolecular reaction.

By determining the alkali-solubility of the samples taken at intervals, it was found that complete solubility occurred when the sulfur-cellulose ratio was close to 0.16. This ratio corresponds to 0.405 xanthate group per glucose residue, or to not quite 1 xanthate group per 2 glucose residues. The result appears to be in good agreement with previous observations, according to which xanthates which approach the formula  $C(=S)(O(C_6H_9O_4)_2OH)(SNa)$ are soluble in dilute sodium hydroxide solution and even in water.[77]

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[77] Heuser and Schuster, *Cellulosechem.*, **7**, 21, 25 (1926).

The time required to reach the 0.16 ratio decreased with increase in temperature. Thus:

Temperature of Xanthation	Time of Xanthation to Soluble
25°	50–60 minutes
29.5°	40 minutes
35°	30 minutes

After a period of 105 minutes, which corresponds to the time usually allowed for preparing viscose by the commercial method, the sulfur-cellulose ratio at 25° was very nearly 0.243 and at 29.5° about 0.268 (see Fig. 64). Assuming that the value at 27° would be the mean of these two values, the ratio should be 0.255 at 27°. When the commercial method was used for preparing a xanthate, using 37 per cent carbon disulfide (calculated on the weight of the cellulose) and a time of 105 minutes at 27°, the sulfur-cellulose ratio was 0.237, which is in good agreement with the values obtained from the curves. This ratio corresponds to 0.6 xanthate group per glucose unit, which is somewhat more than 1 xanthate group per 2 glucose units.

Another method of ascertaining the rate of xanthation consists in measuring the change in pressure exerted by the carbon disulfide.[78] The pressure would be expected to be high at the beginning of the reaction but to decrease gradually as more and more carbon disulfide is consumed and eventually to come to atmospheric pressure after all the carbon disulfide has been absorbed by the mixture of the reactants.

Side Reactions During Xanthation

As pointed out earlier, the formation of cellulose xanthate is accompanied by side reactions between carbon disulfide and sodium hydroxide, and it is generally believed that for the formation of the sodium trithiocarbonate the following equation holds:

$$6NaOH + 3CS_2 = Na_2CO_3 + 2Na_2CS_3 + 3H_2O$$

This equation, which was originally proposed by Berzelius,[79] also seems to express the formation of trithiocarbonate in viscose,[80] although results have been reported which make it seem probable that various reactions are involved in the formation of trithiocarbonate. Thus,

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[78] Scherer and Miller, *Rayon Textile Monthly*, **20**, 24 (1939).

[79] Berzelius, *Gilberts Ann. Phys.*, **48**, 159 (1814).

[80] Kita and Tomihisa, *Cellulosechem.*, **10**, 134 (1929); Geiger, *Helv. Chim. Acta*, **13**, 297 (1930).

sodium sulfide may be formed as an intermediate, which subsequently could react with 1 more molecule of carbon disulfide to form trithiocarbonate, according to the equation $Na_2S + CS_2 = Na_2CS_3$.[81] Indeed, sodium sulfide has been identified in viscose.[82] However, its presence has also been explained as the result of the decomposition of sodium trithiocarbonate rather than as an intermediate in its formation. Such a decomposition may take place in the presence of excess sodium hydroxide according to the equation

$$Na_2CS_3 + 6NaOH = Na_2CO_3 + 3Na_2S + 3H_2O$$

Whereas neither Geiger[83] nor Klauditz[84] could find an indication of the presence of sodium sulfide when sodium thiocarbonate, dissolved in aqueous sodium hydroxide, was allowed to stand for about 3 weeks, Moore[85] observed a slow but definite rise of the sodium sulfide content at the expense of that of the thiocarbonate when a thiocarbonate solution was treated with normal sodium hydroxide, samples being analyzed over a certain period. The data are shown in Table 38.

TABLE 38

Decomposition of Sodium Trithiocarbonate in Excess Alkali

Time *	0	23	29	38
Na_2S, %	0.05	0.09	0.33	0.29
Na_2CS_3, %	0.77	0.50	0.37	0.40

* The figures indicating time of contact are probably days.

That the presence of sodium sulfide is more probably a result of the decomposition of the trithiocarbonate is also deduced from the fact that the presence of sodium sulfite favors this decomposition. This was observed by Tanamura and co-workers and confirmed by Moore[86] as a result of the following comparative experiment. Two mixtures were investigated: (*a*) one containing 250 cc. carbon disulfide-saturated water and 100 cc. of 0.1 *N* sodium hydroxide and (*b*) the same mixture but for the addition of 3 grams of sodium sulfite. The results shown in Table 39 were obtained. It is seen from (*b*) that the pres-

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[81] Tanemura, Kohno, and Miyoshi, *J. Soc. Chem. Ind., Japan,* **33,** 4B (1930); Klauditz, *Papier-Fabr.,* **37,** 255 (1939); see also Leuchs, *Kunstseide,* **7,** 286 (1925), but also Geiger, *loc. cit.*

[82] Bernhardt, *Kunstseide,* **8,** 260, 314 (1926).

[83] Geiger, *loc. cit.,* p. 284.

[84] Klauditz, *loc. cit.,* p. 254.

[85] Moore, *Silk and Rayon,* **8,** 564 (1934).

[86] Moore, *loc. cit.,* p. 564.

TABLE 39

CHANGE OF Na_2S AND Na_2CS_3 IN AQUEOUS NaOH WITH AND WITHOUT Na_2SO_3

Time, Days	Mixture *a*		Mixture *b*	
	Na_2S, %	Na_2CS_3, %	Na_2S, %	Na_2CS_3, %
1	0.04	0.09	0.04	0.10
2	0.03	0.09	0.08	0.07
3	0.04	0.08	0.08	0.03

ence of sodium sulfite in a mixture of aqueous sodium hydroxide and carbon disulfide favors the formation of sodium sulfide at the expense of the sodium trithiocarbonate.

The presence of sodium sulfide and its tendency to dissociate probably account for the slight odor of hydrogen sulfide which emanates from viscose, particularly after the excess carbon disulfide has been removed by evacuation and the treated viscose has been allowed to stand for a while. The admission of air (carbon dioxide) seems to favor the development of the odor. Bernhardt[87] is inclined to believe that hydrogen sulfide may also result from the hydrolysis of carbon disulfide. According to the equation $CS_2 + H_2O = H_2S + COS$, the formation of an equivalent quantity of carbon oxysulfide could be expected. In fact, Bernhardt has identified this compound in viscose.

Competition between Xanthation and Formation of Thiocarbonate

The degree of substitution which cellulose eventually reaches within a certain set of conditions will depend upon the rate of substitution and by-product formation and thus will be the result of a competition between the two reactions.

The rate of the side reaction which results in the formation of sodium trithiocarbonate may be ascertained by titrating samples, taken at intervals, with iodine solution in the presence of dilute acetic acid as explained earlier in this chapter (p. 315). Under these conditions, the iodine consumption is equivalent to the amount of thiocarbonate present. This test may be combined with an iodine titration in the presence of dilute sulfuric acid, which yields values for both xanthate and thiocarbonate and, after deduction of the value for the thiocarbonate, for xanthate alone.

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[87] Bernhardt, *Kunstseide*, 8, 260, 314 (1926).

Judged by the results obtained by Kita and Tomihisa[88] and by Geiger[89] with mixtures of sodium hydroxide solutions and carbon disulfide, the time needed for the completion of trithiocarbonate formation is rather long. Geiger found that 95.35 per cent of the theoretically required carbon disulfide was present as trithiocarbonate after 40 hours[90] of contact, when an 8 per cent sodium hydroxide solution was shaken with an excess of carbon disulfide. The figures in Table 40 show the rate of formation.

TABLE 40

RATE OF SODIUM TRITHIOCARBONATE FORMATION WITHOUT THE PRESENCE OF CELLULOSE

Hours	1	2	3	4	5	6	7	8	9	10	20	40
%, Na_2CS_3 formed	15.85	31.0	42.95	55.3	61.15	68.15	73.7	78.3	81.85	84.95	93.2	95.35

It is seen that the rate is high at the beginning but slows down as the time of contact becomes longer. It therefore may be expected that, in the presence of cellulose, a considerable portion of the carbon disulfide (provided an appreciable excess is used) is consumed in the formation of sodium trithiocarbonate from the beginning. Bernhardt[91] found that, at the end of a normal xanthation period (after the crude xanthate had been dissolved), 18.67 per cent of the carbon disulfide used was present in the form of trithiocarbonate and 76.30 per cent as xanthate. The rest (5.03 per cent) was found distributed over sodium sulfide, hydrogen sulfide, carbon oxysulfide, and free carbon disulfide.

Geiger's results of the distribution of carbon disulfide between thiocarbonate and xanthate differ somewhat from those reported by Bernhardt; this is probably due to the difference in the analytical methods used. On the basis of a normally prepared viscose (probably with about 35 per cent carbon disulfide and a time of xanthation of about 2 hours), Geiger[92] found that 72.2 per cent of the carbon di-

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[88] Kita and Tomihisa, *Cellulosechem.*, **10**, 135 (1929).

[89] Geiger, *Helv. Chim. Acta*, **13**, 297 (1930).

[90] The table on page 297 of Geiger's publication does not indicate whether the figures represent hours or minutes. Comparing Geiger's data with those published by Kita and Tomihisa, it is probable that Geiger's figures represent hours.

[91] Bernhardt, *Kunstseide*, **8**, 316 (1926).

[92] Geiger, *loc. cit.*, p. 286.

sulfide was present as xanthate and about 30 per cent as thiocarbonate. When double the usual (commercial) amount of carbon disulfide was used and the time was extended to 6 hours at 22° the figures were: [93]

CS_2 as thiocarbonate	23.2	23.50%
CS_2 as xanthate	75.0	78.0%

The latter values approach Bernhardt's results more closely.

Summarizing the various findings, it appears fairly safe to conclude that, on xanthation of alkali cellulose, between one-fourth and one-third of the carbon disulfide employed is consumed for the formation of by-products.

The rate at which both reactions proceed was determined by Scherer and Lin [94] over a period of 3 hours at 25°, but the results obtained differ greatly from those discussed above. At the end of 3 hours, as much as 96.2 per cent of the carbon disulfide used was present in the form of xanthate and only 2 per cent in the form of by-products. After 2 hours, a period comparable with those investigated by Bernhardt and by Geiger, the values were 92.3 and 2.6 per cent. Although Scherer and Lin's methods of analysis differed from those used by the earlier investigators, it is difficult to explain the discrepancy merely by the difference in analytical procedure. It would appear as if the hydrolysis of the viscoses (see later) which were used by Bernhardt and by Geiger had advanced to such an extent that higher values for thiocarbonate and correspondingly lower values for xanthate would result. Further comparative investigations appear to be necessary.

In agreement with previous findings, Scherer and Lin observed that the rate of xanthation increases with temperature. With respect to the observations made on the influence of temperatures higher and lower than 25° upon the rate of the by-product formation, the original should be consulted.

As would be expected (p. 308), the completeness of the xanthation reaction depends upon the water present in the system. In this system, so much water is present from the start that the water resulting from the thiocarbonate formation has practically no effect upon the substitution reaction. However, the original water content, i.e., that introduced with the alkali cellulose, has a definite influence, inasmuch as a higher water content than usual (which is about 3 times the weight of the cellulose) tends to slow down the rate of xanthation and to favor the formation of thiocarbonate.

On the other hand, Geiger [95] found that alkali cellulose which had been dried over phosphorus pentoxide reacted only very slowly with carbon disulfide.

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[93] Geiger, *loc. cit.*, p. 292.

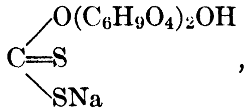
[94] Scherer and Lin, *Rayon Textile Monthly*, **20**, 498, 577 (1939).

[95] Geiger, *loc. cit.*, p. 293.

Indeed Kita *et al.*[96] observed that completely dried alkali cellulose had lost its reactivity.

Sakurada[97] studied the kinetics of the xanthation reaction and found the equation which had been previously developed for finding a mathematical expression for the nitration and acetylation reactions holds also in the case of xanthation.

The Distribution of Xanthate Groups in Cellulose Xanthates

The formula  $\mathrm{C}\begin{cases}\mathrm{O(C_6H_9O_4)_2OH} \\ {=}\mathrm{S} \\ \mathrm{SNa}\end{cases}$, ascribed to the product which is isolated from viscose shortly after its preparation, may be interpreted in different ways. It may mean that the xanthate groups are distributed regularly over the whole aggregate of chain molecules; i.e., every other glucose residue in all chain molecules has 1 hydroxyl group replaced by 1 xanthate group. Or, it may mean that only 50 per cent of all chain molecules are xanthated. Such an arrangement could result in three different ways: (*a*) all glucose residues in every other chain could have 1 hydroxyl group replaced by 1 xanthate group; (*b*) all glucose residues of those chains which are located on the surface of the micelles (assumed to represent closely to 50 per cent of all chains present in the system) could have 1 hydroxyl group replaced by 1 xanthate group; or (*c*) only 50 per cent of the cellulose is xanthated. Whereas the arrangements in (*a*) and (*b*) would represent a regular distribution of xanthate groups, that in (*c*) would be merely a mechanical mixture of xanthated and unxanthated cellulose.

Lieser[98] showed that cellulose xanthate groups are replaced by methyl groups when the xanthate is subjected to the action of diazomethane. This agent was supposed to leave the free hydroxyl groups practically unsubstituted. When this reaction was applied to a normally prepared xanthate (isolated according to Lieser's method), a partially substituted methylcellulose having 1 methoxyl group per 2 glucose residues was obtained. On hydrolysis with sulfuric acid, the methylcellulose yielded a mixture of monomethylglucose and unmethylated glucose.

If the xanthate contained 1 xanthate group in every other glucose residue of each chain, the same may be assumed to be true for the methylated cellulose. Thus, acetolysis of the methylated product

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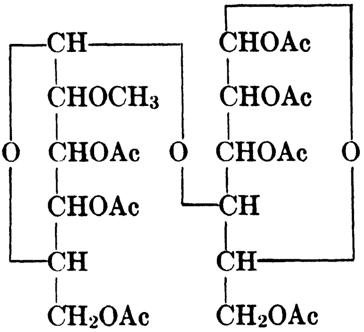
[96] Kita *et al.*, *Cellulosechem.*, **7**, 71 (1926).

[97] Sakurada, *Cellulosechem.*, **15**, 19 (1934).

[98] Lieser, *Ann.*, **470**, 104 (1929).

should result in the formation of monomethylcellobiose heptaacetate, such as:



Actually, no heptaacetyl monomethylcellobiose was obtained.[99] According to Lieser, any methylated cellobiose acetate is destroyed under the conditions of acetolysis. Hence, this result cannot be evaluated against the first possibility, namely, that 1 hydroxyl group in every other glucose residue of all chains is replaced by 1 xanthate group.

If only 50 per cent of the chains in the xanthate had been substituted, according to either (*a*) or (*b*), the same would be true of the methylated cellulose. The latter would then contain 1 methoxyl group per glucose residue or 2 methoxyl groups per 1 cellobiose residue in 50 per cent of all chains. Acetolysis then should yield 50 per cent dimethylcellobiose hexaacetate and 50 per cent unmethylated cellobiose octaacetate. Again, no dimethylcellobiose hexaacetate could be isolated but unmethylated cellobiose octaacetate was obtained at a yield of nearly 50 per cent of the xanthate.[99] This result—with the reservation that it was not possible to isolate the other half of the reaction products—seems to be in favor of the second possibility with its two alternatives (*a* and *b*).[100] However, the result could also be interpreted as supporting the arrangement in (*c*), according to which 50 per cent of the cellulose is substituted and 50 per cent is not substituted at all.

Lieser's hypothesis that only those chain molecules which are located on the surfaces of the micelles are xanthated, as expressed in (*b*), is based upon Meyer's assumption, namely, that the reaction of sodium hydroxide with cellulose is confined to hydroxyl groups of those chains which are located on the micelle surfaces. As has been

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[99] Lieser, *Ann.*, **483**, 135 (1930).

[100] Lieser found that the methoxyl content of the products of acetolysis decreased with the length of the reaction. Hence, the 50 per cent yield of unmethylated cellobiose could be an incidental result.

pointed out earlier, this assumption is in contrast to the general belief that alkali of mercerizing strength enters not only the spaces between the micelles but also those between the individual chain molecules within the micelles (intramicellar swelling). If it actually does—and x-ray analysis seem to prove it—it would be difficult to understand why the alkali should not also react with those hydroxyl groups which have become as accessible as those exposed on the micelle surfaces. Thus, the possibility as expressed in (*b*) appears to be improbable.

Unfortunately, the results of x-ray analysis of the xanthate do not enable us to decide between the various possibilities of arrangement. The observation that the x-ray patterns of cellulose xanthates (of low degree of substitution) do not differ from that of alkali cellulose I, $[(C_6H_{10}O_5)_2NaOH]$, has been regarded as supporting the view that xanthation occurs only on the surface of the fiber, in which event the xanthated layer would escape detection by x-rays.

The x-ray pattern obtained by Sakurada and Hutino,[101] which was interpreted as showing interference lines typical of a xanthate, could not be confirmed by Hess and Trogus.[102] These investigators found that alkali cellulose I, on suitable treatment, showed the pattern seen by Sakurada and Hutino even without being subjected to the action of carbon disulfide. On the other hand, the xanthates which were investigated by Hess and Trogus gave x-ray patterns which showed only the interference lines of alkali cellulose I.

The same conclusions were reached by Schramek and Küttner.[103] The x-ray patterns obtained with xanthates which had been purified by the method suggested by Heuser and Schuster were those of alkali cellulose I.

Unfortunately, no data are available on the x-ray analysis of higher substituted xanthates. The patterns of such products would be expected to show interference lines characteristic of xanthated chains, and, when the trixanthate is approached, as in Scherer and Miller's product prepared from trisodium cellulosate (see later), the x-ray pattern would be expected to show a very distinct change.[104]

The conclusions drawn from the investigations with x-rays (as far as they are known) are not in agreement with the results which were obtained on the fractionation of the diethyl chloroacetamide deriva-

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[101] Sakurada and Hutino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **17**, 294 (1932).

[102] Hess and Trogus, *Cellulosechem.*, **13**, 84 (1932).

[103] Schramek and Küttner, *Kolloid-Beihefte*, **42**, 347, 364 (1935); see also Schramek, *Papier-Fabr.*, **36**, 233 (1938).

[104] Recently Bredée, *Kolloid-Z.*, **94**, 81 (1941), has directed attention to an investigation by Centola, according to which the x-ray diffraction lines of alkali cellulose disappeared when an excess of carbon disulfide was allowed to act upon alkali cellulose for a long time.

tive of a normally prepared xanthate.[105] The fractions obtained by precipitation showed very little difference in degree of substitution, this being very close to 0.5 xanthate groups per glucose residue.[106] This result seems to indicate that the xanthate groups are uniformly distributed over all chains of the cellulose system and would thus rule out the possibility that the xanthate represents a mixture of equal parts of xanthated and unxanthated cellulose.

In judging the interpretation of the analytical evidence presented above, it should be borne in mind that this evidence was gained from the investigation of xanthates which revealed the ratio of 1 xanthate group to 2 glucose residues or thereabouts.

No doubt, before this ratio has been reached, the product must be regarded as a mixture of xanthated portions with still unreacted cellulose fibers. Crumbs broken apart in the early stages of xanthation reveal centers of unreacted cellulose. Scherer and Miller[107] showed that, with 37 per cent carbon disulfide at 25°, the sulfur-cellulose ratio which would correspond to 1 xanthate group per 2 glucose residues, ($64/324 = 0.2$), was reached after about 80 minutes. It may be assumed that, at this time, the carbon disulfide had penetrated the whole mass of fibers. When all the carbon disulfide was used up, the ratio approached 0.23, which corresponds to 1.2 xanthate groups per 2 glucose residues. It would appear that long before this ratio is attained, the carbon disulfide has penetrated the micelle surface, and has reacted with hydroxyl groups located in the interior of the micelles.

Scherer and Miller[107] showed that the normally prepared xanthate (the crude crumbs) became soluble in dilute sodium hydroxide solution when the sulfur-cellulose ratio was very close to 0.16 (which corresponds to about 0.4 xanthate groups per 2 glucose residues), i.e., long before the full ratio of 1 xanthate group per 1 glucose unit has been reached. Thus, a relatively small degree of substitution in cellulose seems to suffice to increase its hydrophilic properties considerably. Since at the time when the solubility ratio is reached (after 50–55 minutes) the carbon disulfide has hardly penetrated all the cellulose fibers, it would appear that the xanthated portions are capable of dispersing a certain quantity of unreacted alkali cellulose fibers when the crumbs come into contact with the dissolving alkali.

Indeed, Frenkel[108] succeeded in preparing such a dispersion by subjecting a

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[105] Fink, Stahn, and Matthes, *Angew. Chem.*, **47**, 604 (1934).

[106] Surprisingly, the authors' own interpretation of their results is that the degree of substitution varies distinctly with the different fractions.

[107] Scherer and Miller, *Rayon Textile Monthly*, **19**, 478, 541 (1938); **20**, 141 (1939).

[108] Frenkel, *Cellulosechem.*, **9**, 26 (1928); see also the reference to Centola on the dispersion of *alkali* cellulose in viscose in Bredée, *loc. cit.*, p. 90.

mixture of viscose, moist cellulose (which had been regenerated from the same viscose), and additional aqueous sodium hydroxide to a short treatment in the colloid mill. It is conceivable that such a dispersion is made possible by the highly swollen state of the regenerated cellulose, which is further increased by the presence of the alkali added to the viscose. In this connection, it would also be of interest to test an alkaline solution of the *isolated* and *purified* xanthate for its ability to disperse cellulose.

Summarizing the discussion on the distribution of the xanthate groups in the cellulose xanthate corresponding to a ratio of 1 xanthate group to 2 glucose residues, it would appear that the experimental evidence does not favor the micelle surfaces concept or the assumption that the xanthate represents a mere mixture of xanthated and unxanthated cellulose. On the contrary, the xanthate groups appear to be rather uniformly distributed over all chains of the cellulose system. However, the experimental evidence does not suffice to make a decision between the two possibilities—the location of 1 xanthate group in every second glucose residue of all chains or its location in all glucose residues of every other chain.

The Position of the Xanthate Groups in the Glucose Residues

In connection with the distribution of xanthate groups over the chain molecules, the question arises whether the primary hydroxyl group shows any preference in reaction over the two secondary groups or *vice versa* and whether, of the latter two, the one in the 2-position or the one in the 3-position is preferred.

Lieser[109] attempted to decide this question by applying the technique already mentioned above, namely, by methylating the xanthate with diazomethane, hydrolyzing the resulting monomethylcellulose, and subjecting the monomethylglucose to identification reactions. Its phenylhydrazone showed the same characteristics as the phenylhydrazone of a synthetically prepared 2-methylglucose. Thus, it would appear that the xanthate groups in the cellulose xanthate investigated were located in the 2-position. Unfortunately, the yield of 2-methylglucose obtained on the hydrolysis of the monomethylcellulose was very small.[110] Thus, it is not certain whether all xanthate groups in the original xanthate were located in the 2-position or in the latter as well as in other positions. Rassow and co-workers[111] have suggested that the hydroxyl groups in the 6-position are preferred but furnished

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[109] Lieser, *Ann.*, **470**, 104 (1929).

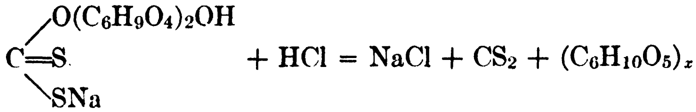
[110] Lieser and Leckzyck, *Ann.*, **522**, 56 (1936).

[111] Rassow, Vorster, and Wolff, *Papier-Fabr.*, Special Number, **28**, 83 (1930)

no experimental evidence of this assumption. Hence, all that can be said at present is that possibly a small percentage of the xanthate groups is located in the 2-position.

The Decomposition of Cellulose Xanthate

As has been seen on several occasions, cellulose xanthate is, to a limited extent, stable against dilute organic acids, such as acetic (and also lactic) acid. Under the influence of mineral acids, it decomposes very readily into its original constituents. Thus:



$$C(=S)(O(C_6H_9O_4)_2OH)(SNa) + HCl = NaCl + CS_2 + (C_6H_{10}O_5)_x$$

Practically all the sulfur present in the xanthate may thus be recovered in the form of carbon disulfide, which may be determined by conversion into potassium ethyl xanthate. A very small part of the sulfur appears in the form of hydrogen sulfide. This is due to the fact that the xanthate tends to dissociate in aqueous solution. The small amounts of sodium hydroxide and carbon disulfide thus liberated react to form sodium trithiocarbonate which, on addition of sulfuric acid, decomposes to regenerate carbon disulfide with the formation of hydrogen sulfide. The hydrogen sulfide may be estimated as copper sulfide. It was found that the total sulfur obtained by decomposition checked quite satisfactorily with the total sulfur which had been determined by oxidation of the xanthate with bromine solution.[112]

The same effect as with mineral acids is obtained with carbonic acid, but under these conditions decomposition proceeds at a much slower rate. For example, at the end of 24 hours, during which time a current of carbon dioxide was continuously passed through an aqueous solution of the purified xanthate, its original sulfur content had decreased by 42.6 per cent.[113]

It is characteristic of the xanthate that it decomposes in aqueous solution in the absence of an acid, even as weak an acid as carbonic (carbon dioxide from the air) being not necessary.[114] This process of decomposition may be visualized as hydrolysis. Thus:

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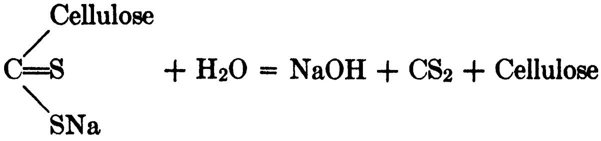
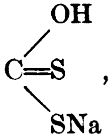
[112] Heuser and Schuster, *Cellulosechem.*, **7**, 23 (1926); see also, Berl and Dillenius, *ibid.*, **13**, 14 (1932).

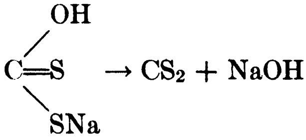
[113] Heuser and Schuster, *loc. cit.*, p. 49.

[114] Herzog and Hegel, *Kolloid-Z.*, **35**, 193 (1924).



$$\mathrm{C(Cellulose)({=}S)(SNa)} + \mathrm{H_2O} = \mathrm{NaOH} + \mathrm{CS_2} + \mathrm{Cellulose}$$

It is possible that the sodium dithiocarbonate,  $\mathrm{C(OH)({=}S)(SNa)}$, forms as an intermediate but, being unstable, decomposes to yield carbon disulfide and sodium hydroxide:



$$\mathrm{C(OH)({=}S)(SNa)} \rightarrow \mathrm{CS_2} + \mathrm{NaOH}$$

Cellulose xanthate also decomposes under the influence of the electric current. Under the conditions of electrophoresis, sulfur-free cellulose hydrate deposits at the anode;[115] this indicates that the cellulose particles have a negative charge. According to Hess,[116] it appears possible that, owing to the exhaustion of sodium hydroxide at the anode, primarily deposited cellulose xanthogenic acid quickly decomposes.

The decomposition of cellulose xanthates by oxidation will be discussed later.

THE RIPENING OF VISCOSE

The hydrolytic changes which viscose undergoes on standing are described by the term "ripening." The ripening process, which also plays an essential part in the preparation of viscose for commercial purposes, actually represents a sequence of rather complex phenomena, in which colloidal changes are also involved. The colloidal changes, particularly when viscose was first made the subject of research, have often been allowed to interfere with attempts to arrive at a clear understanding of the chemical reaction, and the opinion has been voiced quite often that the process of ripening is simply a change of the colloidal state of the solution. As will be seen, this is not so, however.

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[115] Karrer and Lieser, *Cellulosechem.*, **7**, 3 (1926).

[116] Hess, "Die Chemie der Cellulose," p. 342.

The Chemical Changes During Ripening

Chemically, ripening may be regarded as the reverse of xanthation. Whereas xanthation represents the substitution of hydroxyl groups, the ripening process embodies the regeneration of hydroxyl groups and, hence, of cellulose. The carbon disulfide and the sodium hydroxide liberated react to form sodium trithiocarbonate. Thus, as the xanthate loses more and more of its dithiocarbonic acid groups and approaches the composition of the original cellulose, the amount of trithiocarbonate increases until all regenerated carbon disulfide has been consumed.

Cross and co-workers[117] explained the transition of the xanthate into cellulose on the assumption that, while dithiocarbonic acid groups are cleaved off, the cellulose constituent polymerizes into multiples of the individual $C_6H_{10}O_5$ unit, until, when all dithiocarbonic acid groups are eliminated, cellulose is regenerated in its original molecular size. This concept would imply that on xanthation the reverse process takes place, that is, depolymerization of the cellulose to monomeric $C_6H_{10}O_5$ units. There is no experimental evidence to justify such an assumption. The depolymerization of cellulose, which, as will be seen later, takes place during xanthation, is relatively small, and whereas there has recently been ample speculation, there is as yet no experimental evidence available to prove that shorter cellulose chain molecules are capable of polymerizing into larger units through primary valences.

The transition of cellulose xanthate into cellulose may be followed by precipitating the xanthate from the ripening viscose at intervals with saturated salt solution or alcohol and analyzing the products thus obtained for cellulose, sulfur, and sodium. In this way, Cross, Bevan, and Beadle obtained a series of products with decreasing sulfur content. Their results were confirmed by Ost, Westhoff, and Gessner[118] and by Heuser and Schuster.[119]

As has been pointed out before, the products obtained on precipitation with saturated salt solution or with alcohol contain, even if thoroughly washed with alcohol, varying quantities of sodium hydroxide, which interferes with the consistency of the analytical results. For this reason and also to eliminate any interference by the by-products contained in viscose, Heuser and Schuster isolated the xanthate from viscose, purified it in the way earlier described, dissolved it in water, and subjected this solution to the ripening process. The transition was then followed by subjecting this solution, at intervals, to precipi-

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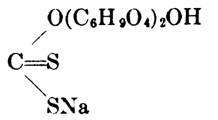
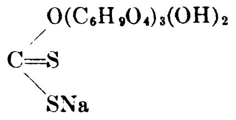
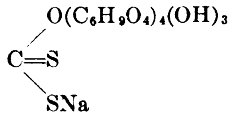
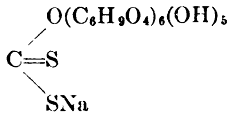
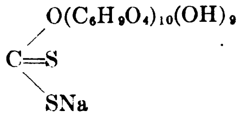
[117] Cross, Bevan, and Beadle, *Ber.*, **26**, 1090 (1893); **34**, 2513 (1901).

[118] Ost, Westhoff, and Gessner, *Ann.*, **382**, 340 (1911).

[119] Heuser and Schuster, *loc. cit.*, p. 19.

TABLE 41

Change of Composition of Purified Cellulose Xanthate during Ripening

Ripening Time, Hours	Sodium, %	Sulfur, %	Cellulose, %	Ratio $Na : S : C_6H_{10}O_5$	Ratio Expressed in Formula	Theoretical Requirements, %	Ratio Na : S : Cellulose
Before dissolving	4.9	13.3	77.4	0.90 : 1.70 : 2	 $O(C_6H_9O_4)_2OH$ $C{=}S$ SNa	Na 5.45 S 15.3 Cell. 76.9	1 : 2 : 2
12	4.3	11.4	81.9	1.05 : 1.95 : 3			
26	3.3	9.2	83.5	0.84 : 1.65 : 3	 $O(C_6H_9O_4)_3(OH)_2$ $C{=}S$ SNa	Na 3.94 S 10.96 Cell. 83.2	1 : 2 : 3
36	3.0	....	90.0	0.94 : .... : 4			
50	3.0	8.9	91.5	0.92 : 1.96 : 4	 $O(C_6H_9O_4)_4(OH)_3$ $C{=}S$ SNa	Na 3.1 S 8.6 Cell. 86.9	1 : 2 : 4
61	3.1	8.2	92.1	0.96 : 1.80 : 4			
106	2.32	5.6	94.6	1.08 : 1.80 : 6	 $O(C_6H_9O_4)_6(OH)_5$ $C{=}S$ SNa	Na 2.15 S 5.99 Cell. 90.84	1 : 2 : 6
112	1.19	4.22	96.1	0.80 : 2.20 : 10	 $O(C_6H_9O_4)_{10}(OH)_9$ $C{=}S$ SNa	Na 1.34 S 3.73 Cell. 94.30	1 : 2 : 10

tation with alcohol. The samples thus obtained were purified again and analyzed for cellulose, sulfur, and sodium. The results are shown in Table 41.

The figures show that the sodium and sulfur contents of the xanthates decrease and the cellulose content increases. This transition of the original xanthate into products richer in cellulose content is also expressed in the ratio Na : S : $C_6H_{10}O_5$. The formulas (with their theoretical requirements and their ratios) have been given in the table merely to show the degree of substitution.

The gradual loss of xanthate sulfur on the ripening of viscose has since been substantiated by a number of investigations in which widely differing analytical methods were employed. Some of these have also supplied data on the corresponding increase of trithiocarbonate and on other changes pertaining to the inorganic by-products in the ripening viscose.

The result of these investigations may be summarized as follows: From data supplied by Leuchs[120] and by Herzog and Hegel,[121] the impression is gained that, on ripening, the xanthate undergoes no chemical change at all. After Zart and Mönckemeyer[122] had pointed out that Leuchs' method of ascertaining the sulfur-cellulose ratio in the xanthate was unsuitable because it did not give due consideration to the by-products, De Wyss[123] was the first to develop a method (p. 316) with which it was possible to determine the sulfur-cellulose ratio in the xanthate without interference from the by-products.

This method, applied to samples taken at intervals from viscoses which were ripened at 18° over a total period of 200 hours, yielded results which showed a decided decrease of the sulfur-cellulose ratio with time. About 50 per cent of the total decrease occurred within the first third of the time of observation. It is apparent, then, that the initial rate of decomposition is faster. This may also be seen from Fig. 65. I represents viscose made with an excess of carbon disulfide to bring up the ratio S : $C_6H_{10}O_5$ as close as possible to 2 : 1. The other two curves were obtained with viscose made with less than the theoretical amount of carbon disulfide.

In Fig. 66 are shown results for xanthate-sulfur, thiocarbonate-sulfur, and hydrogen sulfide-sulfur, all of which were determined for the same viscose during ripening. It is seen that the curve representing

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[120] Leuchs, *Chem.-Ztg.*, **47**, 801 (1923).

[121] Herzog and Hegel, *Kolloid-Z.*, **35**, 196 (1924).

[122] Zart and Mönckemeyer, *Chem.-Ztg.*, **48**, 192 (1924); see also Leuchs' reply, *ibid.*, **48**, 192 (1924); also D'Ans and Jäger, *Kunstseide*, **8**, 18 (1926).

[123] De Wyss, *Ind. Eng. Chem.*, **17**, 1043 (1925).

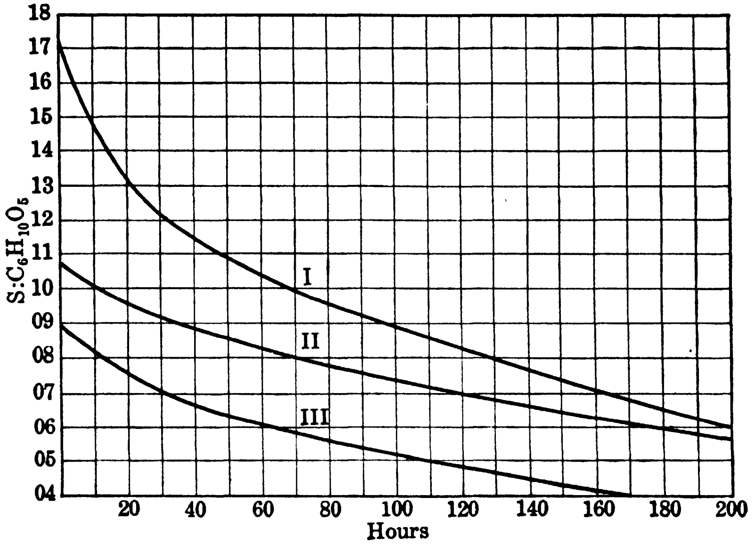

FIG. 65. Change of sulfur : cellulose ratio in xanthate on ripening of viscose. De Wyss.

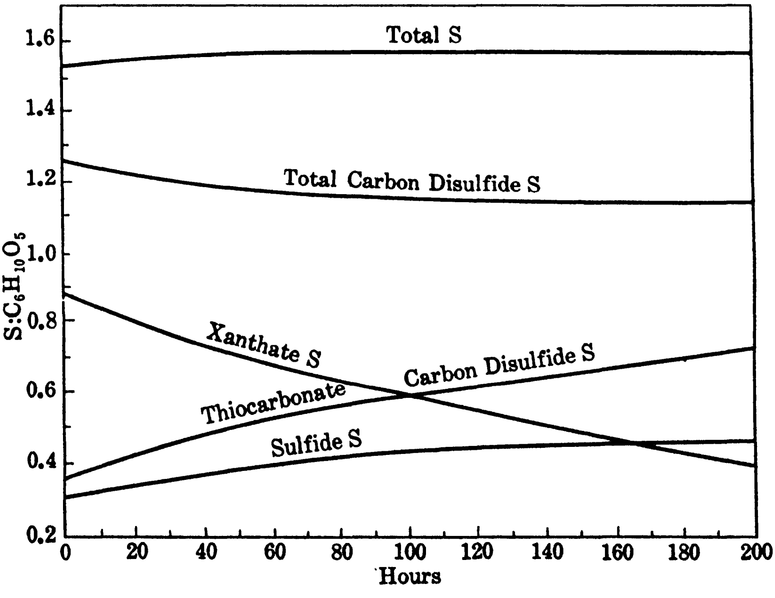

FIG. 66. Change of xanthate and by-product sulfur in viscose on ripening De Wyss.

the xanthate-sulfur shows a decided drop. Correspondingly, the values for the thiocarbonate-sulfur increase.

Since by the action of sulfuric acid part of the total carbon disulfide is converted into hydrogen sulfide, the values for total carbon disulfide may be expected to drop slightly and those for hydrogen sulfide to rise slightly. The curves in Fig. 66 show this to be true, whereas the values for total sulfur, obtained by adding the values of total carbon disulfide-sulfur and hydrogen sulfide-sulfur, remain constant.

Heuser and Schuster[124] followed the decrease of carbon disulfide-sulfur of xanthates isolated from viscose at intervals (and subsequently purified) by decomposing the aqueous solutions of these preparations with sulfuric acid and determining the carbon disulfide by converting it into copper ethyl xanthate. The small amounts of hydrogen sulfide which originated from the slight dissociation of the xanthate in aqueous solution were also determined. The values thus obtained for total xanthate-sulfur ($CS_2 + H_2S$) were then compared with the total xanthate-sulfur obtained by oxidizing a sample of the xanthate and determining the resulting sulfuric acid gravimetrically. The results are shown in Table 42. The rate of decrease in carbon disulfide-sulfur is faster in the beginning of the ripening period; this confirms De Wyss' results. The hydrogen sulfide remains practically constant, as could be expected. In view of the many analytical operations required, the agreement between total xanthate-sulfur (the sum of carbon disulfide and hydrogen sulfide) and total xanthate-sulfur (as sulfuric acid) appears quite satisfactory.

TABLE 42

CARBON DISULFIDE AND HYDROGEN SULFIDE FROM XANTHATES ISOLATED FROM RIPENING VISCOSE

Ripening Time, Hours	Carbon Disulfide-Sulfur, %	Hydrogen Sulfide-Sulfur, %	Total Xanthate-Sulfur ($CS_2 + H_2S$), %	Total Xanthate-Sulfur from $BaSO_4$, %
24	11.37	0.05	11.42	11.60
48	8.48	0.04	8.52	8.99
72	8.39	0.07	8.46	8.80
96	8.16	0.06	8.22	8.45
120	7.82	0.07	7.89	8.23

When the ripening process was followed by decomposing samples of viscose directly with sulfuric acid instead of by isolating the xan-

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[124] Heuser and Schuster, *loc. cit.*, pp. 23 and 24.

thates, it was found that the carbon disulfide-sulfur again decreased but that the hydrogen sulfide-sulfur increased. This result was to be expected in view of the fact that part of the carbon disulfide is converted into trithiocarbonate which, on decomposition with sulfuric acid, yields a definite amount of hydrogen sulfide. Since the amount of thiocarbonate increases on ripening, the values for hydrogen sulfide also increase. These results also agree with De Wyss' findings.[125]

The simplest way of ascertaining the changes in organic and inorganic sulfur during ripening appears to be the use of the iodine titration method with two samples of viscose: one in the presence of acetic acid, and the other in the presence of sulfuric acid. The two titrations supply the data from which the values for the xanthate and for the thiocarbonate may be calculated. Geiger and other investigators applied this method, with several modifications, to commercial viscose.[126]

Geiger's data show that more rapid decomposition takes place in the beginning of the ripening process, i.e., in agreement with the results of previous investigators, whereas the curves which were obtained by D'Ans and Jäger[127] indicate a more uniform decrease of the xanthate-sulfur. In view of the observations made with other cellulose reactions, it would appear that an initially rapid decrease and a slowing down (as ripening proceeds) is a more exact description.

The method developed by Fink, Stahn, and Matthes (see p. 318) seems to produce more exact results than can be ascertained through the use of the double iodine titration procedure. Samples of viscose, taken at intervals, are converted into the diethylchloroacetamide derivative, of which the nitrogen content is determined and related to the sulfur content. The curve which Fink, Stahn, and Matthes obtained by plotting the degree of substitution (γ-value) against time of ripening may be regarded as representing an average of the values as obtained by other methods—ranging between those which are too high or too low.

Fink and co-workers also developed another interesting method for estimating the xanthate-sulfur and its decrease during ripening. This method is based upon ultrafiltration. When ultrafiltration is applied to viscose, suitably diluted, only the inorganically combined "electrolytic" sulfur enters the ultrafiltrate, whereas the sulfur combined with the xanthate ("colloidal" sulfur) remains upon the filter. Thus, if the total sulfur content of the viscose is known, the xanthate-sulfur

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[125] See also Bernhardt, *Kunstseide*, **8**, 316 (1926).

[126] Geiger, *Helv. Chim. Acta*, **13**, 286, 299 (1930).

[127] D'Ans and Jäger, *Kunstseide*, **8**, 83 (1926).

may be calculated. The method was applied to viscose which was continuously stirred during the period of ripening in order to reduce inhomogeneity and consequently erratic results. The data obtained for xanthate-sulfur agree very well with those derived from the diethylchloroacetamide method, as shown in Fig. 67.

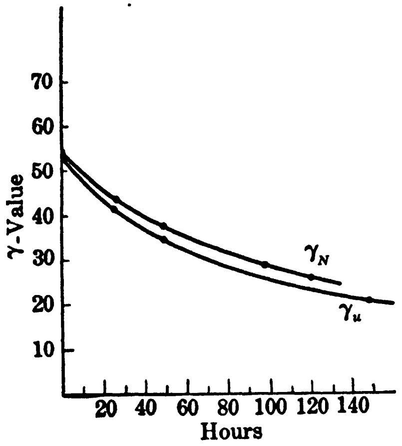
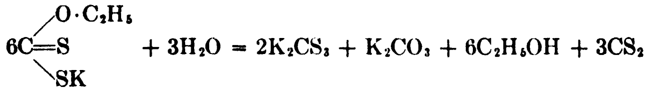


FIG. 67. Xanthate-sulfur determined by the acetamid (γ_N) and the ultrafiltration method (γ_u) during ripening of viscose. Fink, Stahn, and Matthes.

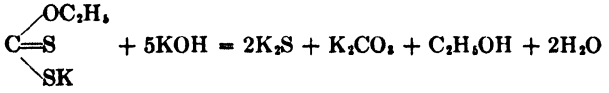
Although trithiocarbonate is the end product of the reaction between carbon disulfide and sodium hydroxide we are still in doubt whether trithiocarbonate is formed directly, as expressed in the equation $3CS_2 + 6NaOH = Na_2CO_3 + 2Na_2CS_3 + 3H_2O$, or indirectly through sodium sulfide as an intermediate (see p. 329).

In order to throw more light upon this question, Klauditz[128] subjected aqueous and alkaline solutions of potassium *ethyl* xanthate to the process of "ripening" and followed the decomposition of the xanthate by iodometric titration of the ethyl xanthate-sulfur and the thiocarbonate-sulfur. It was found that the iodine consumption of ethyl xanthate which was ripened in aqueous solution was definitely different from that in alkaline solution. The iodine consumption of the aqueous solution was in agreement with the equation:



$$6C\begin{cases}O\cdot C_2H_5\\=S\\SK\end{cases} + 3H_2O = 2K_2CS_3 + K_2CO_3 + 6C_2H_5OH + 3CS_2 \qquad [I]$$

whereas the higher iodine consumption of the xanthate in alkaline solution was interpreted to indicate that, besides trithiocarbonate, another sulfur compound must have been present. This compound could be only potassium sulfide. In fact, it could be identified in the alkali-containing solution and is probably formed according to the following equation:



$$C\begin{cases}OC_2H_5\\=S\\SK\end{cases} + 5KOH = 2K_2S + K_2CO_3 + C_2H_5OH + 2H_2O \qquad [II]$$

On the assumption that the potassium sulfide does not originate from the decomposition of the trithiocarbonate under the influence of potassium hydroxide as shown in the equation on p. 329, Klauditz concludes that the two products, tri-

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[128] Klauditz, *Papier-Fabr.*, **37**, 251 (1939).

thiocarbonate and sulfide, represent the final stages of two reactions which proceed side by side, namely, as hydrolysis (equation I) and as saponification (equation II). In a third reaction, the carbon disulfide from equation I and the sulfide from equation II combine to yield trithiocarbonate: $Na_2S + CS_2 = Na_2CS_3$.

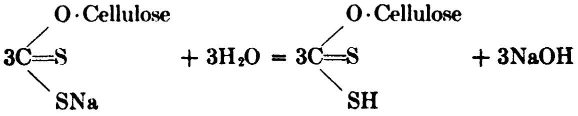
Moreover, it was found that, with increasing alkali concentration of the ethyl xanthate solution, the decomposition by saponification increases at the expense of the decomposition by hydrolysis. For example, whereas in aqueous solution 100 per cent of the ethyl xanthate was decomposed by hydrolyses, 55 per cent was decomposed by saponification in 0.5 *N* potassium hydroxide and 92.5 per cent in 3 *N* potassium hydroxide. Likewise, the rate of the hydrolysis (in water) is faster than that of the saponification (in alkaline solution). Obviously, then, the increase in alkali concentration retards the hydrolysis.

A similar situation was encountered with viscose, with the difference that hydrolysis predominated over saponification even at high alkali concentration. Yet, more sodium sulfide was formed at the higher than at the lower alkali concentration.

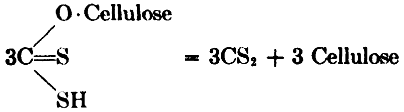
Klauditz calculated that, in ordinary viscose (containing about 6 per cent total alkali), only 15–20 per cent of the total decomposition of the cellulose xanthate was a result of saponification. Higher alkali contents in the viscose (13–15 per cent total alkali) increased the percentage due to saponification to one-third and 18–20 per cent total alkali to about one-half of the total.

According to Klauditz, the two reactions which comprise the viscose-ripening process may be expressed by the following equations:

Hydrolysis

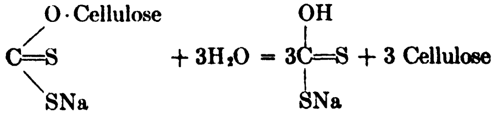


$$3\,\mathrm{C}\begin{array}{l}\diagup \mathrm{O\cdot Cellulose}\\ = \mathrm{S}\\ \diagdown \mathrm{SNa}\end{array} + 3H_2O = 3\,\mathrm{C}\begin{array}{l}\diagup \mathrm{O\cdot Cellulose}\\ = \mathrm{S}\\ \diagdown \mathrm{SH}\end{array} + 3NaOH \qquad [I]$$

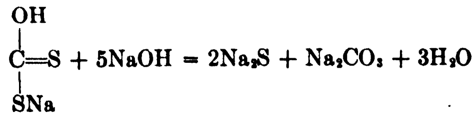


$$3\,\mathrm{C}\begin{array}{l}\diagup \mathrm{O\cdot Cellulose}\\ = \mathrm{S}\\ \diagdown \mathrm{SH}\end{array} = 3CS_2 + 3\ \mathrm{Cellulose} \qquad [II]$$

Saponification



$$\mathrm{C}\begin{array}{l}\diagup \mathrm{O\cdot Cellulose}\\ = \mathrm{S}\\ \diagdown \mathrm{SNa}\end{array} + 3H_2O = 3\,\overset{\mathrm{OH}}{\underset{\mathrm{SNa}}{\mathrm{C}}}{=}\mathrm{S} + 3\ \mathrm{Cellulose} \qquad [I]$$



$$\overset{\mathrm{OH}}{\underset{\mathrm{SNa}}{\mathrm{C}}}{=}\mathrm{S} + 5NaOH = 2Na_2S + Na_2CO_3 + 3H_2O \qquad [II]$$

As these two reactions proceed, the carbon disulfide and the sodium sulfide combine to form trithiocarbonate.

It remains to be seen whether Klauditz' results and the conclusions drawn therefrom can be confirmed by other investigators.

Other Side Reactions During Ripening

As ripening proceeds, the system contains partially xanthated alkali cellulose, carbon disulfide, sodium hydroxide, and water. Because this system tends to reach an equilibrium, we may expect part of the free carbon disulfide to react with the partially xanthated alkali cellulose and thus to increase the degree of substitution of the latter. Since, on the other hand, the equilibrium is continuously shifted in the direction of the decomposition reaction, because the free carbon disulfide is continuously eliminated in the form of thiocarbonate, we would expect that eventually all the carbon disulfide would be liberated from the xanthate. Actually, the end point is reached very slowly, if at all, for the product, even after a period of many days, still contains a small but definite amount of sulfur.[129]

It will be easily understood that, by adding a fresh amount of carbon disulfide to viscose which is in the state of ripening, the process of decomposition may be arrested for a certain period of time, depending on the quantity of carbon disulfide added. Likewise, an increase of the alkali content in viscose will tend to counteract the decomposition, because it will favor the formation of fresh cellulosate groups which react with carbon disulfide.

The ripening of cellulose xanthate dissolved in tetraethylammonium hydroxide solution (Lieser, see p. 324) was followed by determining the sulfur content of samples taken at intervals. It could be shown that the sulfur content of the xanthate gradually decreases.[130]

The Colloidal Changes During Ripening

Viscose represents a typical colloidal solution. It is, to use Wolfgang Ostwald's words [131] "naturally honey-combed with colloidal phenomena." The colloidal changes which viscose undergoes on ripening consist chiefly of changes in viscosity and in its behavior with electrolytes.

The viscosity of cellulose xanthate in solution, like that of a lyophylic colloid, is dependent upon concentration, temperature, and pressure. The investigations of Herzog and Gaebel, Mukoyama, and

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[129] Heuser and Schuster, *loc. cit.*, p. 22; D'Ans and Jäger, *Kunstseide*, **8**, 46 (1926).

[130] Lieser and Leckzyck, *Ann.*, **522**, 56 (1936).

[131] Ostwald, "Theoretical and Applied Chemistry," translation by M. H. Fisher, Wiley and Sons, New York (1917), p. 208.

others[132] have shown that the system is subject to the development of structural viscosity.

The characteristic changes which viscose undergoes on standing have been known for a long time and confirmed more recently.[133] Immediately after solution of the crude xanthate in dilute sodium hydroxide solution, the viscosity drops over a certain length of time. It reaches a minimum, then slowly increases over a longer period, and eventually increases rapidly. When this last state has been reached, the viscose coagulates. On still longer standing, the gel very distinctly shows the phenomenon of syneresis.

If viscose is allowed to stand in a flask for a few months, a dense and elastic cake, surrounded by a more or less yellow-to-brown colored liquor, is formed. The cake, which has assumed the shape of the flask, shrinks enormously on drying, becomes hard, and is workable as horn or ebony. It was temporarily manufactured under the trade name of Viscoid.[134]

A typical ripening curve[135] of viscose, indicating the changes just described (2 per cent cellulose concentration; viscosities measured in an Ostwald viscometer at 15° against water) is shown in Fig. 68. It is seen that the viscosity drops over a period of 2–3 days from about 52 to about 28 seconds, when the lowest point of the curve is reached. It then slowly increases up to about 40 seconds, a point which is reached after 14–15 days, when it rather suddenly increases sharply and very soon becomes so high that it cannot be measured.

The shape of this curve is subject to certain modifications, depending upon such factors as cellulose and alkali concentration, temperature, etc.

The viscosity changes may be explained in the following way:[136] In viscose, we are obviously dealing with a highly hydrated sol, i.e., a system in which the liquid surrounding the particles is highly immobilized so that the viscosity immediately after dissolving is high. However, on standing, the sol tends to dehydrate (desolvate) and thus

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[132] Herzog and Gaebel, *Kolloid-Z.*, **35**, 193 (1924); **39**, 252 (1926); Mukoyama, *Kolloid-Z.*, **41**, 62 (1927); Venable, *J. phys. Chem.*, **29**, 1239 (1925); Bredée and van Bergen, *Chem. Weekblad*, **30**, 223 (1933); Lieser and Ebert, *Ann.*, **533**, 94 (1937).

[133] Cross and Bevan, *loc. cit.;* Westhoff, doctoral dissertation, Hanover (1911); Mukoyama, *Kolloid-Z.*, **43**, 349 (1927); Kita *et al.*, *Cellulose Ind.*, **5**, 5 (1929); Berl and Dillenius, *Cellulosechem.*, **13**, 18 (1932); Compton, *Ind. Eng. Chem.*, **31**, 1754, 1757, 1758 (1939).

[134] Piest, "Die Zellulose," Ferd. Enke, Stuttgart (1910), p. 65; Hottenroth, *Chem.-Ztg.*, **39**, 119 (1915).

[135] Heuser and Schuster, *Cellulosechem.*, **7**, 45 (1926).

[136] Mark, "Physik und Chemie der Cellulose," p. 259.

to increase the free water and the mobility of the liquid. As a result, the viscosity decreases. Simultaneously, as the particles become dehydrated, they are drawn together more closely. When the lowest viscosity is reached, the particles have approached each other, through the activity of their forces of attraction, to such an extent that they arrange themselves to build up a new structure. This phenomenon is reflected first in a gradual rise of the viscosity and, as ripening proceeds, in the formation of a gel (autocoagulation). Under the influence of continued dehydration, the particles approach each other still further and eventually are so close together that the water held within the structure is squeezed out; i.e., syneresis occurs.

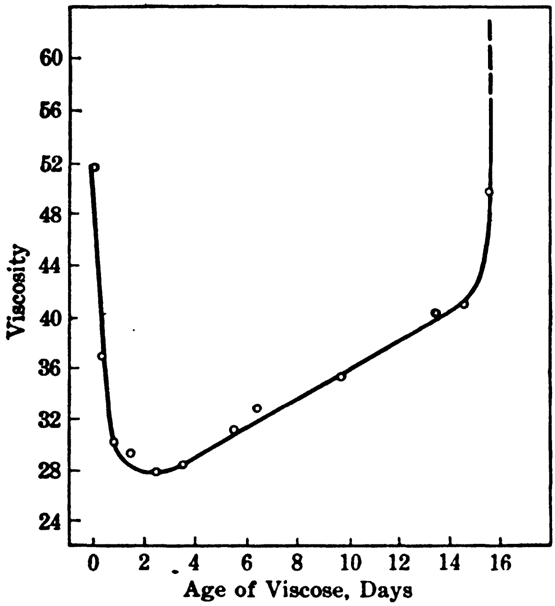

FIG. 68. Changes of viscosity of viscose on ripening. Heuser and Schuster.

Moore,[137] elaborating on the desolvation phenomenon in the early stage of ripening, suggested that the sodium hydroxide present in the solution exerts an osmotic pressure, thereby attracting the water from the internal into the external phase. This view seems to be supported by the fact that the viscosity of viscose, or of the purified xanthate dissolved in water, drops as the alkali concentration is increased.

The initial drop of the viscosity of the ripening viscose has also been explained on the assumption that it requires a certain period of time until the xanthate

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[137] Moore, *Silk and Rayon*, 8, 507 (1934).

particles are completely dispersed in the sodium hydroxide solution.[138] In fact, the lowest point of the viscosity curve is reached after a shorter time, if the viscose, during this period of ripening, is subjected to continuous stirring. Obviously, mechanical agitation favors and thus accelerates the dispersion of initially coarser to finer particles. This conclusion agrees with ultramicroscopical observations,[139] according to which the fibrous xanthate continues to disperse into smaller fragments during the first two days of ripening, until it yields a fairly homogeneous dispersion in which fewer larger fragments of fiber and fibrils are observed.

No doubt, mechanical agitation favors the decrease in viscosity but the phenomenon seems to be more satisfactorily explained by the desolvation concept.

It is noteworthy that the lowest point of the viscosity curve coincides with a change of the charge from negative to positive on the interface between viscose and water (*zeta*-potential).[140]

Microdiffusion experiments and ultramicroscopic studies were made in an attempt to ascertain whether the changes in the number and size of the dispersed particles are in accord with the colloidal changes of the system. However, the results which Herzog and Gaebel[141] obtained with the diffusion of viscose against aqueous sodium hydroxide over a certain period of ripening were not conclusive.

Under the ultramicroscope[142] only 20–30 per cent of the xanthate originally dispersed was found to be visible. In sufficiently diluted dispersions, the particles showed the Brownian movement. On ripening, the Tyndall effect increased but the number of particles remained the same.

In contrast, Berl and Bitter[143] (who also observed the Brownian movement at the beginning of the ripening process) found that the number of particles decreased with ripening and interpreted this observation to mean that smaller units had aggregated to larger particles.

Compton,[144] using the slit ultramicroscope, disclaimed any change in particle size on ripening, although he stated that after the fifth and sixth days the particles agglomerated and the Brownian movement came to a standstill.[145]

This divergency of results (which obviously exists, although Compton denies it[146]) may be due to various causes and could, no doubt, be eliminated by further studies. It is most probable that Berl and Bitter's observations come closest to the truth.

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[138] Heuser and Schuster, *Cellulosechem.*, **7**, 45 (1926).

[139] Compton, *Ind. Eng. Chem.*, **31**, 1254 (1939).

[140] Kanamaru, Kobaysi, and Seki, *Kolloid-Z.*, **87**, 62 (1939). Regarding the *zeta*-potential between cellulose and water, see Kanamaru and Nakamura, *Kolloid-Z.*, **76**, 83 (1936); Kanamaru, Shiratori, and Nakamura, *ibid.*, **84**, 50 (1938).

[141] Herzog and Gaebel, *Kolloid-Z.*, **35**, 194 (1924); **39**, 253 (1926).

[142] Herzog and Gaebel, *Kolloid-Z.*, **39**, 252 (1926).

[143] Berl and Bitter, *Cellulosechem.*, **7**, 143 (1926).

[144] Compton, *Ind. Eng. Chem.*, **31**, 1255 (1939).

[145] The Brownian movement in dilute viscose was also observed by Karrer and Lieser, *Cellulosechem.*, **7**, 3 (1926).

[146] Compton, *loc. cit.*, p. 1258.

The gel structure of viscose is, within a certain range of ripening, reversible.[147] The structure may be destroyed by shaking or other mechanical agitation, which results in a drop in viscosity. However, on standing, the structure builds itself up again, and the viscosity increases. This procedure of destroying the structure and allowing it to be restored may be repeated frequently with the same result. The phenomenon is noticeable even in the early stages of ripening but, as ripening proceeds, it becomes more difficult to destroy the structure. On the other hand, the time required for the restoration of the structure decreases considerably with the time of ripening. It is probable that continuous stirring during ripening will prevent gel formation altogether.[148]

In view of the fact that the gel is subject to syneresis, this reversibility of the gel structure formation must be classified as a characteristic of structural viscosity. Nevertheless, it appears possible that, at least temporarily, the phenomenon of thixotropy is involved.[149]

The phenomenon of syneresis has been investigated only to a very limited extent. The solid phase probably still contains some xanthate groups, although it is also possible that the small amounts of sulfur left result from by-products which are entrapped in the gel structure and which are possibly concentrated and retained on the surface of the particles when the liquid separates from the solid on contraction. The liquid was analyzed for alkali only. It was found that the alkali concentration increased as syneresis proceeded[150]; this may or may not be interpreted to mean that remaining xanthate groups were liberated while syneresis was in progress.

The Relation between the Chemical and the Colloidal Changes

If cellulose xanthate is viewed as a lyophilic colloid, the desolvation of particles and the development of a gel structure with subsequent syneresis could *a priori* be visualized to take place without the participation of chemical reactions. From this point of view, the chemical changes which do take place may be regarded as a factor which contributes to, or accelerates, the colloidal changes. Thus, Heuser and Schuster[151] have expressed the opinion that the accumulating by-

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[147] Herzog and Gaebel, *loc. cit.*

[148] Lottermoser and Schwarz, *Kolloid-Beihefte*, **42**, 426 (1935).

[149] As to other phenomena in the anomalous behavior of viscose see Philippoff and Krüger, *Kolloid-Z.*, **88**, 218 (1939); Philippoff, *Kolloid-Z.*, **75**, 146 (1936).

[150] Liepatoff, *Kolloid-Z.*, **49**, 444 (1929).

[151] Heuser and Schuster, *loc. cit.*, p. 55.

products tend to exert a salting-out effect upon the xanthate which results in increased particle size and, hence, in increased viscosity. Indeed, increasing amounts of by-products added to an alkaline solution of the purified xanthate resulted in increasing viscosity. The quantities of sodium carbonate and trithiocarbonate added were so calculated as to maintain the same proportions between these salts and the cellulose and the free alkali as they exist during the various stages of the ripening process. The "artificial" viscoses thus prepared were tested for viscosity (1) immediately after dissolving in sodium hydroxide solution, (2) after 7 and (3) after 15 days of standing at room temperature. The results are shown in Fig. 69. The figure shows that the viscosities increase with the presence of increasing amounts of sodium thiocarbonate (and sodium carbonate) and that this effect becomes more pronounced the longer the viscoses are allowed to stand.

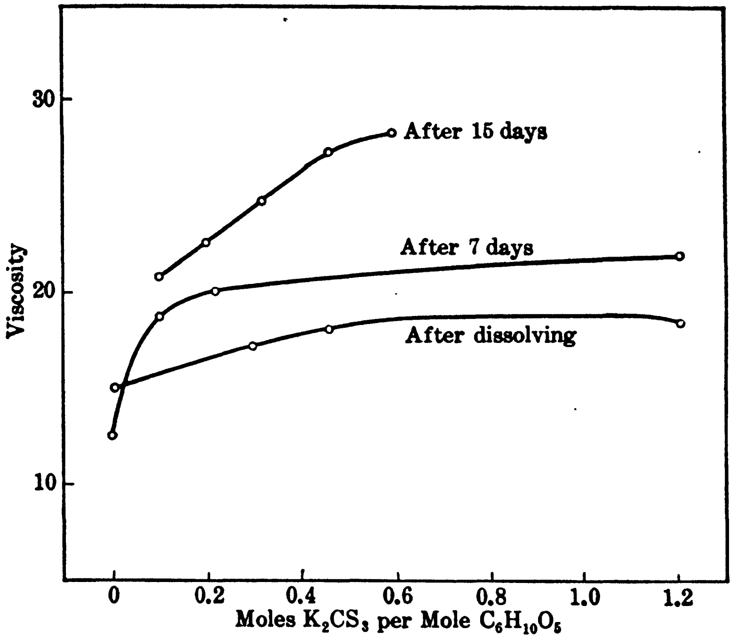

FIG. 69. Influence of by-products upon the viscosity of an alkaline xanthate solution. Heuser and Schuster.

Although the xanthate in the ripening viscose approaches more and more the composition of the original cellulose, it is rather stable to the precipitating power of the by-products formed. It will be recalled that regenerated cellulose may be dispersed in aqueous alkali in the presence of relatively small amounts of cellulose xanthate and that cellulose regenerated from viscose is soluble even in dilute alkali. Therefore, it is conceivable that no precipitation occurs.

Moore[152] has expressed the opinion that part of the cellulose xanthate which has not been decomposed acts as a protective colloid and thus keeps the cellulose, as it is being regenerated, in solution. This protective action of the cellulose xanthate is viewed as being due to the adsorption of a lyophilic substance, i.e., the undecomposed xanthate on the surface of a less lyophilic sol (the regenerated cellulose). The latter acquires, thus, the properties of a highly lyophilic substance and is rendered immune to precipitation.

Staudinger and Daumiller[153] have explained the initial decrease and the subsequent increase in the viscosity of viscose solely by the change in degree of substitution which the xanthate undergoes on ripening. This concept is based upon the observation that isolated xanthates of low degrees of substitution yield solutions of higher viscosity than those of higher degrees of substitution. This concept, which disclaims the occurrence of colloidal changes, can hardly be accepted.

Factors Influencing the Colloidal Changes

The rate of the colloidal changes is dependent upon such factors as temperature, cellulose, and, particularly, alkali concentration, as well as the presence of electrolytes.

Temperature. As would be expected, temperature is a very efficient means of increasing the rate at which the colloidal phenomena occur.[154] Viscose, and, to a still greater extent, an aqueous solution of the purified xanthate, may be made to coagulate quickly if heated to 50–60°. Under these conditions, coagulation is accompanied by decomposition of the xanthate. Conversely, low temperature retards both coagulation and decomposition, and viscose may be kept at 0° for many days without any change taking place.

Cellulose Concentration. This acts in the same direction and is illustrated by the data[155] in Fig. 70; the viscosities were determined by the falling ball method and are plotted against time of ripening.

The various curves show that, with increasing cellulose concentration, the viscosity of the viscose not only increases but also tends to increase at a faster rate. In other words, the time in which the viscose coagulates becomes shorter with increasing cellulose concentra-

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[152] Moore, *Silk and Rayon*, **8**, 507 (1934).

[153] Staudinger and Daumiller, *Ber.*, **71**, 2001 (1938).

[154] Berl and Lange, *Cellulosechem.*, **7**, 146 (1926); Liepatoff, *Kolloid-Z.*, **49**, 443, 444 (1929).

[155] Lottermoser and Wultsch, *Kolloid-Z.*, **83**, 185 (1938).

tion. Even an increase of only 0.1 per cent has a noticeable effect.[156] These results are in accord with commercial experience.[157]

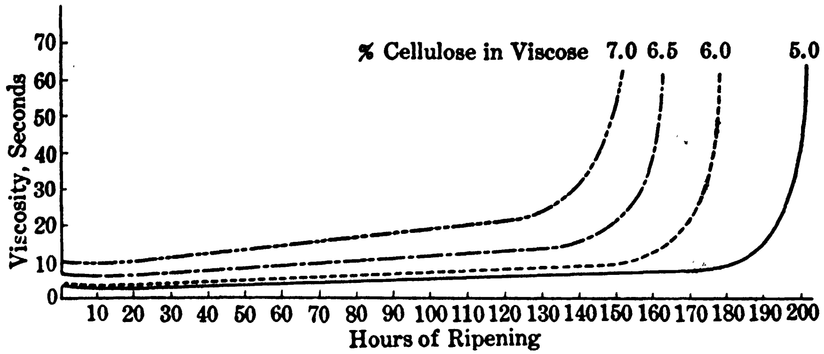

FIG. 70. Influence of cellulose concentration upon rate of ripening. Lottermoser and Wultsch.

Alkali Concentration. The alkali concentration in viscose influences the viscosity and the rate of ripening very definitely.

The viscosity of an aqueous solution of a purified xanthate, under otherwise identical conditions, is considerably higher than that of ordinary viscose. Likewise, the viscosity of viscose[158] or of an aqueous xanthate solution[159] drops with increasing alkali concentration. As an explanation we may consider the probability that the presence of alkali favors the dehydration of the hydrated xanthate particles, thus increasing the mobility of the system. The curve which may be plotted from alkali concentrations and viscosities reaches a minimum at 8–9 per cent alkali concentration. Further addition of alkali to the aqueous xanthate solution causes the viscosity to rise again slowly. This relationship is shown in Fig. 71. The data refer to portions of purified xanthate dissolved in sodium hydroxide solutions of increasing concentration. The cellulose content was kept constant at 3 per cent. That the viscosity-decreasing effect of the alkali concentration is limited may be explained by the assumption that the alkali, if added in sufficient amounts, causes a salting-out effect upon the xanthate.

If a purely aqueous solution of (purified) cellulose xanthate is allowed to stand at room temperature, we notice that it ripens much

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[156] See also D'Ans and Jäger, *Kunstseide*, **8**, 82, 110 (1926).

[157] See, however, Liepatoff, *Kolloid-Z.*, **49**, 443 (1929), who found the opposite result.

[158] Westhoff, doctoral dissertation, Hanover, 1911.

[159] Heuser and Schuster, *loc. cit.*, **7**, **26**.

faster than viscose; i.e., the solution coagulates much sooner. As an example, ordinary viscose, which was allowed to ripen at 20°, was found to coagulate after 230 hours, whereas an aqueous xanthate solution had reached this point after only 19 hours.[160] This effect of the alkali upon the behavior of viscose is probably due to its retarding influence upon the rate of hydrolysis. But again, it is limited, and viscose shows its greatest stability to coagulation at 8–9 per cent alkali concentration. This fact was first recognized by Ost, Westhoff, and Gessner,[161] and later on confirmed by other investi-

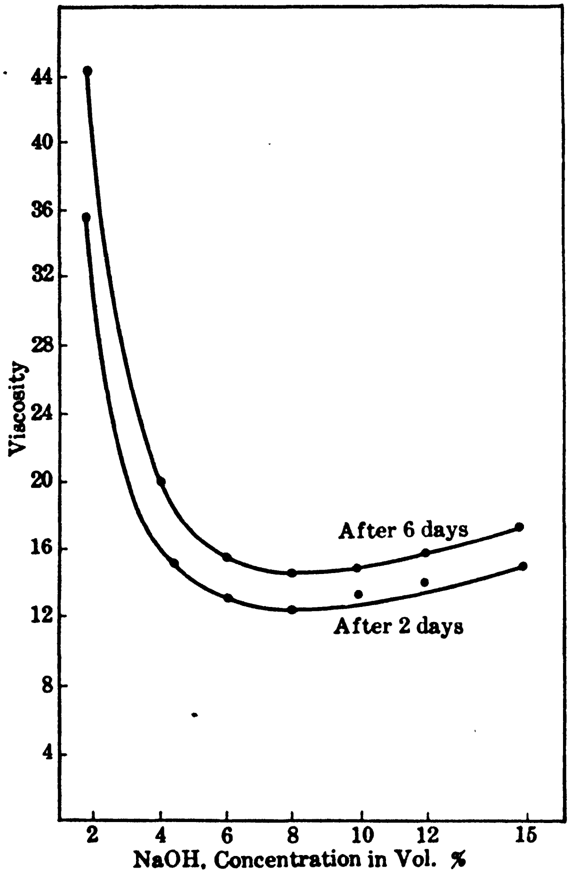

FIG. 71. Change of viscosity of a cellulose xanthate solution with alkali concentration. Heuser and Schuster.

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[160] Heuser and Charbonnier, *Ind. Eng. Chem.*, **33**, 402 (1941).

[161] Ost, Westhoff, and Gessner, *Ann.*, **382**, 340 (1911).

gators.[162] Fig. 72 shows this relationship in the case of an aqueous solution of purified cellulose xanthate. It is noteworthy that thus maximum stability coincides with minimum viscosity at the same alkali concentration (Heuser and Schuster).

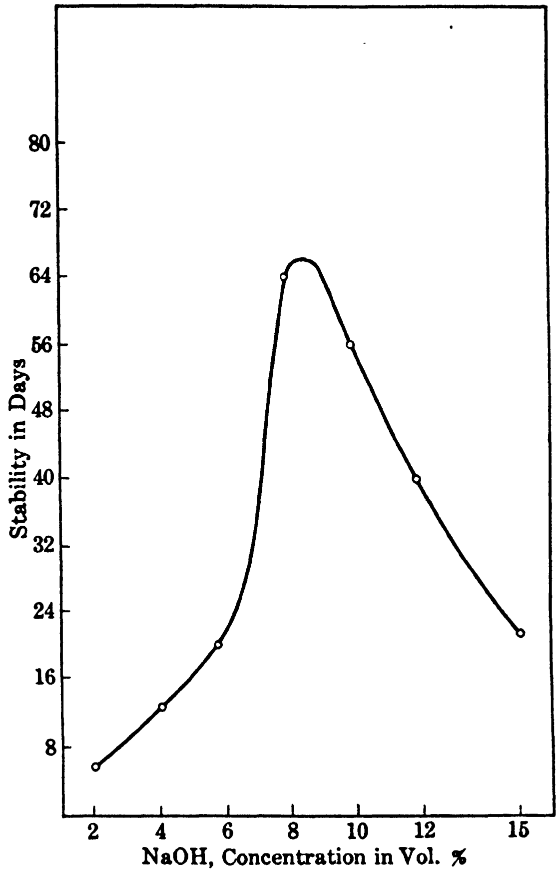

FIG. 72. Stability of an aqueous xanthate solution to coagulation at varying alkali concentrations. Heuser and Schuster.

Influence of Electrolytes. The behavior of viscose and of aqueous solutions of the purified xanthate containing the by-products formed during ripening would lead us to expect that other electrolytes pres-

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[162] D'Ans and Jäger, *Kunstseide*, 8, 19, 45, 57 (1926); Kita *et al.*, *Cellulose Ind.*, 4, 43 (1928); Geiger, *Helv. Chim. Acta*, 13, 290 (1930); Fink, Stahn, and Matthes, *Angew. Chem.*, 47, 607 (1934); Schramek and Küttner, *Kolloid-Beihefte*, 42, 344 (1935); Heuser and Schuster, *loc. cit.*, p. 26.

ent in the viscose would exert similar effects. Indeed, sodium sulfate and carbonate[163] or sodium chloride[164]—incorporated into viscose in relatively small amounts—accelerate the process of coagulation.

However, the opposite effect is observed with sodium sulfite.[165] Its retarding effect (which is also well known in commercial practice) has been explained by the fact that it impedes the chemical decomposition of the xanthate, probably because, as a reducing agent, it obviates the attack of air (oxygen) upon the xanthate. The oxygen of the air oxidizes sodium sulfite to sulfate, in which form it may be expected to have an accelerating effect upon the coagulation. That this effect is not observed might be explained on the assumption that only a relatively small portion of the sulfite is oxidized.

Staudinger and Daumiller[166] made the statement that the viscosity of viscose is considerably lowered by the presence of inorganic salts and that this phenomenon has long been common commercial experience. This effect is compared with the observation that the addition of sodium chloride to a solution of polyacrylic acid prevents the aggregation of particles which, if it had occurred, would have resulted in increased viscosity. It is doubtful, however, whether this parallel can be drawn and whether the above-mentioned statement can be made in such a general form.

The rate of ripening is also influenced by the presence of *organic substances* of various kinds. Some information on the influence of gelatin, tannic acid, glycerol, glucose, sucrose, and resorcinol is available from the work of D'Ans and Jäger.[167] Generally speaking, all these compounds (with the exception of resorcinol[168]) were found to have an accelerating influence upon the rate of ripening, that of gelatin being less pronounced than that of the other substances. However, the results are not always consistent. The addition of these substances and of many others, aiming at manifold effects, is the object of numerous patents.

The Investigation of the Ripening Process with Added Electrolytes

It was early recognized that the sensitiveness of viscose to coagulation under the influence of added salt solution increases with the time of ripening. In other words, the riper the viscose, the smaller is the quantity of electrolyte required to bring about coagulation and

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[163] D'Ans and Jäger, *Kunstseide, loc. cit.*, pp. 82 and 110.

[164] Liepatoff, *Kolloid-Z.*, **49**, 443 (1929).

[165] Moore, *Silk and Rayon*, **8**, 565 (1934).

[166] Staudinger and Daumiller, *Ber.*, **71**, 2001 (1938); Staudinger, "Die hochmolekularen organischen Verbindungen," pp. 333–337.

[167] D'Ans and Jäger, *loc. cit.*

[168] Eckert, Herr, and Swatek, *Papier-Fabr.*, **36**, 282 (1936), observed that the ripening process is accelerated by phenols, whereas British patent 328,044 (1928), granted to Johnson, claims that phenols retard it.

vice versa. Thus, the quantity of electrolyte added to the ripening viscose becomes a measure of its degree of maturity at any point of the process.

It is conceivable that, at the beginning of the ripening process, larger quantities of electrolyte are required than during the later stages in which the tendency for spontaneous coagulation is quite pronounced. Thus, on ripening, a point will be reached at which a minimum quantity of electrolyte suffices to bring coagulation to completion.

The viscose manufacturer makes use of either of two tests for ascertaining the ripening degree, these tests being based upon the above-mentioned observations. In the Hottenroth test,[169] the ripening degree of viscose is expressed as the number of cubic centimeters of a 10 per cent ammonium chloride solution which a sample of 20 grams of viscose, diluted with 30 cc. of water, requires for coagulation at room temperature. Unripened viscose usually requires 14–15 cc. ammonium chloride solution; accordingly, the ripening degree of this viscose is 14–15. The ripening degree of viscose at the time it is being spun into rayon is usually between 7 and 10.

The ripening degree of viscose is also expressed as "salt point," "salt number," or "salt index."[170] Solutions of sodium chloride of various concentrations, ranging from 2.5 to 4.5 per cent, are prepared. A drop of viscose is added to the various solutions at 15° with stirring, and the ability of the coagulate to form fiber-like strings is observed. The ripening degree is expressed as that concentration of the salt solution which produces the desired condition. If this concentration is 3.7 per cent, the salt point is 3.7.

A ripening degree of 7–10 (or a salt point of 3–4) represents the state in which the minimum quantity of electrolyte is required for complete coagulation of the viscose. It is in this state in which the viscose should be spun into the setting bath. This consists essentially of sodium sulfate and dilute sulfuric acid, and thus acts simultaneously as an electrolyte and a means of decomposing the coagulate. The filaments eventually obtained, therefore, consist of regenerated cellulose. The ripening degree of the viscose is thus adapted to the high velocity at which the viscose filaments pass through the setting bath. Young viscose, having a high ammonium chloride demand, would require reduced spinning speed or a longer time of contact with the setting bath to insure the desired coagulation effect.

Modifications of the Hottenroth test were suggested by Mukoyama,[171] Jentgen,[172] Eggert,[173] and Berl and Dillenius.[174]

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[169] Hottenroth, *Chem.-Ztg.*, **39**, 119 (1915).

[170] Eggert, "Die Herstellung und Verarbeitung der Viscose," p. 50; Berl and Dillenius, *Cellulosechem.*, **13**, 3 (1932); Ziegler and Schäfer, *ibid.*, **15**, 92 (1934); Dorée, "Methods of Cellulose Chemistry," p. 254.

[171] Mukoyama, *Kolloid-Z.*, **43**, 349 (1927).

[172] Jentgen, "Laboratoriumbuch für die Kunstseiden-Industrie."

[173] Eggert, "Herstellung und Verarbeitung der Kunstseide."

[174] Berl and Dillenius, *Cellulosechem.*, **13**, 19 (1932).

The greater stability of viscose in the presence of excess alkali is reflected in its behavior with ammonium chloride. As would be expected, the amount of ammonium chloride required to produce coagulation increases with increasing alkali concentration.[175]

Many other simple salts, as well as those of bi- and polyvalent ions, exert a coagulation effect. The coagulation power of the salts increases with the valency of their cations.[176]

The ripening degree may also be determined by following the change of the elastic properties which the viscose undergoes under the influence of ammonium chloride solution.[177]

The Relationship between the Degree of Maturity of the Viscose and the Degree of Substitution of the Xanthate

As would be expected, a relationship exists between the degree of maturity of the viscose and the degree of substitution of the xanthate contained therein.

Ziegler and Schäfer[178] determined the salt point of samples taken at intervals from the ripening viscose and the sulfur content of the isolated xanthate films, both by the iodine titration method (Geiger's modification[179]) and gravimetrically. The average values were converted into "molecular index numbers"; this is the degree of substitution expressed as number of carbon atoms in the cellulose constituent per xanthate group.

In Fig. 73 the salt points of numerous viscoses are plotted against "molecular index numbers." The shaded area indicates the magnitude of the variations. It is seen that (with the exception of the data for one viscose) all points fall within the relatively narrow shaded area. Thus it is possible to predict from the salt point the approximate degree of substitution which the xanthate possesses at any state of the viscose while ripening is in progress. As an example, a salt point of 2 coincides with an index number between C_{18} and C_{22}, i.e., a xanthate carrying 1 xanthate group per 3 to 3.5 $C_6H_{10}O_5$ units.

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[175] D'Ans and Jäger, *Kunstseide*, **8**, 45 (1926); Mukoyama, *Kolloid-Z.*, **43**, 352 (1927).

[176] Atsuki, *J. Faculty Eng., Tokyo Imp. Univ.*, **17**, 135 (1927); *Cellulosechem.*, **9**, 106 (1928); see also Rassow and Aehnelt, *ibid.*, **10**, 185 (1929).

[177] Gernert, *Zellwolle und Kunstseide*, **23**, 80 (1941).

[178] Ziegler and Schäfer, *Cellulosechem.*, **15**, 89 (1934).

[179] Geiger, *Helv. Chim. Acta*, **13**, 296 (1930).

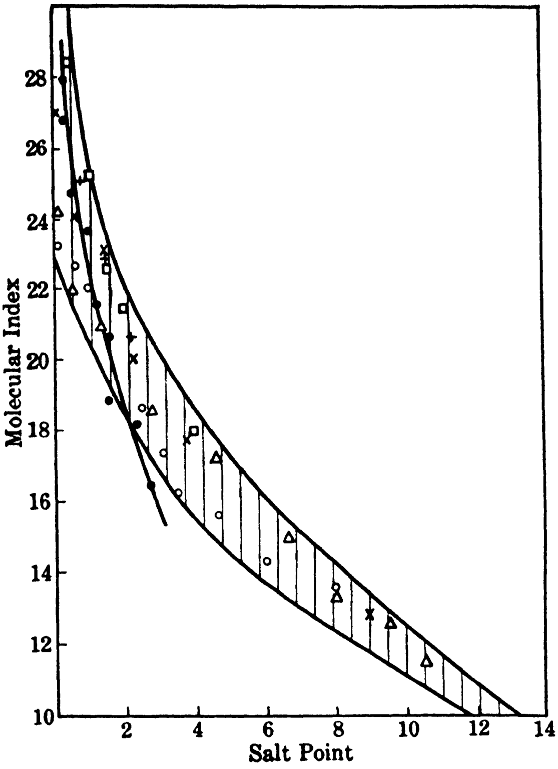

FIG. 73. Relationship between salt point of viscose and degree of substitution of cellulose xanthate. Ziegler and Schäfer.

The Influence of the Degree of Polymerization of the Original Cellulose and of the Aging of the Alkali Cellulose upon the Ripening Process

As with other cellulose derivatives, the degree of polymerization of the original cellulosic material is reflected in the cellulose xanthate. This relationship is expressed in the viscosity of the viscose, it being high if the viscose was prepared from cellulose of a high degree of polymerization and *vice versa.*[180] For example, cotton linters yield viscose of a higher viscosity than wood pulp.[181] Likewise,

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[180] Hess, "Die Chemie der Cellulose," p. 336; Rassow and Wadewitz, *J. prakt. Chem.*, **106**, 312, 314 (1923).

[181] Berl and Lange, *Cellulosechem.*, **7**, 146 (1926); Lottermoser and Radestock, *Z. angew. Chem.*, **42**, 1151 (1929).

the degree of polymerization of the original cellulose influences the colloidal changes during ripening. The higher the degree of polymerization, the more pronounced is the tendency of the viscose to develop gel structure; i.e., the faster is the rate of ripening. The opposite is true for viscose originating from cellulose of a low degree of polymerization.

As has been seen in an earlier section, the degree of polymerization of cellulose is lowered by the *aging of the alkali cellulose.* This process, therefore, supplies a means of influencing the ripening process and of adjusting the viscosity of the viscose. Both effects are of great importance in the commercial manufacture of rayon and cellophane.

Possibly Cross and Bevan, the inventors of the viscose process, were the first to observe that longer aging of the alkali cellulose produced a much lower viscose viscosity than a short aging time. This observation was subsequently confirmed by many other investigators.[182]

The influence of the age of the alkali cellulose upon the rate of ripening is shown in Fig. 74, which is taken from Ost, Westhoff, and Gessner and in which the viscosities of four viscoses, corresponding to two different aging times (1 and 6 days) of the alkali cellulose, are plotted against time of ripening. The xanthates from these two alkali celluloses were dissolved in (1) water and (2) in 3 per cent sodium hydroxide solution. Thus, four viscoses were obtained, and the four curves of Fig. 74 correspond to these four viscoses, as follows:

Curve 1.	Alkali cellulose, aged 1 day.	Xanthate dissolved in water.
Curve 2.	Alkali cellulose, aged 1 day.	Xanthate dissolved in 3% NaOH sol.
Curve 3.	Alkali cellulose, aged 6 days.	Xanthate dissolved in water.
Curve 4.	Alkali cellulose, aged 6 days.	Xanthate dissolved in 3% NaOH sol.

The curves clearly demonstrate the decreasing influence of aging upon the initial viscosity of the viscose and upon the rate of ripening. At the same time, we recognize again the influence of the alkali concentration, the rate of ripening being lower in alkali than in water.

The lower viscosity of viscose from wood pulp as compared with

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[182] See, for example, Ost, Westhoff, and Gessner, *Ann.*, **382**, 352 (1911); Rassow and Wadewitz, *J. prakt. Chem.*, **106**, 321 (1923); D'Ans and Jäger, *loc. cit.*, **8**, 57 (1926); Lottermoser and Radestock, *loc. cit.*, p. 1153; Lottermoser and Wultsch, *Kolloid-Z.*, **83**, 186 (1938); Staudinger and Reinecke, *Papier-Fabr.*, **36**, 559, Table 8 (1938).

that from cotton and cotton linters and the higher viscosity in all three cases when the aging of the alkali cellulose was omitted are shown in Table 43. The data refer to the specific viscosities of diluted viscoses (approximately 3 per cent cellulose and 5.4 per cent sodium hydroxide concentration).[183]

As would be expected, elevated temperature during aging accelerates the rate of ripening of viscose.[184]

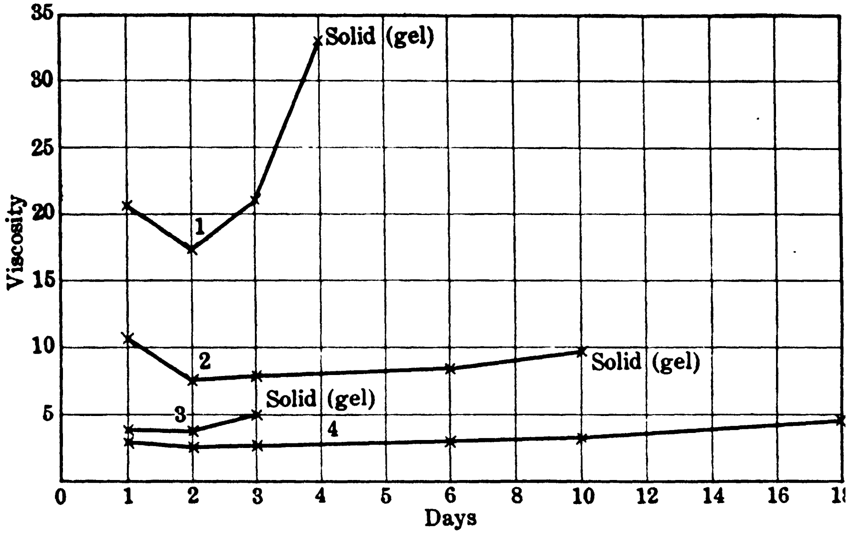

FIG. 74. Influence of time of aging of alkali cellulose upon the viscosity of viscose during ripening. Ost, Westhoff, and Gessner.

Since certain metals (particularly iron and manganese) catalyze the action of oxygen in the presence of alkali (p. 131), alkali cellulose which has been prepared in the presence of such metals enters the subsequent processes in a more degraded state. This is reflected in the viscosity and the rate of ripening of the viscose, as shown by Lottermoser and Wultsch.[185] The more iron present during the aging of the alkali cellulose, the lower was the viscosity of the viscose and the longer the time until coagulation occurred.[186]

In contrast, alkali cellulose which had been aged in the presence of copper metal yielded viscose of higher viscosity than alkali cellulose aged without cop-

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[183] Compton, *Ind. Eng. Chem.*, **31**, 1252, 1258 (1939).

[184] Rassow and Wadewitz, *loc. cit.*, pp. 302, 322.

[185] Lottermoser and Wultsch, *loc. cit.*, p. 186.

[186] See also Bartell and Cowling, *Ind. Eng. Chem.*, **34**, 607 (1942), on the catalytic action of manganese upon the process of xanthation.

TABLE 43

EFFECT OF AGING AND NONAGING OF ALKALI CELLULOSE PREPARED FROM DIFFERENT CELLULOSIC MATERIALS UPON SPECIFIC VISCOSITY OF DILUTE VISCOSES

		Cotton	Cotton Linters	Wood Pulp
No aging	Concentration of cellulose (grams/liter)	28.7	29.0	29.6
	Specific viscosity (η_{sp}/c)	153.95	34.1	14.3
Aging 3 days	Concentration of cellulose (grams/liter)	33.8	32.1	28.0
	Specific viscosity (η_{sp}/c)	21.40	3.90	1.08

per. Since copper has no catalytic effect upon aging, Lottermoser and Wultsch have explained the higher viscosity on the assumption that the copper which was introduced into the viscose with the alkali cellulose favored the tendency of the viscose to coagulate. However, it is difficult to understand why iron should behave differently. Both metals are present in the viscose as sulfides (as indicated by a darkening of the viscose color) and as such would be expected to exert the same effect. The reason for the difference is not yet apparent.

THE NATURE OF THE REGENERATED CELLULOSE

In addition to the aging of the alkali cellulose, the process of xanthation offers an opportunity for the cellulose to become degraded, whereas during the ripening of the viscose the degree of polymerization remains practically unchanged.

To ascertain to what extent each step of the viscose process contributes to the degradation of the cellulose, Heuser and Schuster[187] regenerated cellulose from alkali cellulose during aging (1), from the xanthate during sulfidation (2), and from the viscose during ripening (3), and determined the viscosities of the regenerated cellulose samples in cuprammonium hydroxide. Cotton linters were used for these experiments.

The cellulose was regenerated from the alkali cellulose by washing the samples, taken at intervals, with dilute acetic acid. The data referring to aging have been presented in Fig. 46 (p. 128).

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[187] Heuser and Schuster, *Cellulosechem.*, 7, 40, 52 (1926).

Further degradation takes place during *xanthation*. This may be anticipated from the fact that the essential prerequisites for oxidation, alkali and air oxygen, are still present. But the effect is diminished by the presence of the inorganic by-products, these products consuming oxygen more readily than the cellulose. In addition, from the general behavior of cellulose with substitution reactions, we may possibly infer that the cellulose becomes more resistant to degradation as the degree of xanthation increases.[188] As a result, the cellulose is less degraded during xanthation than during aging.

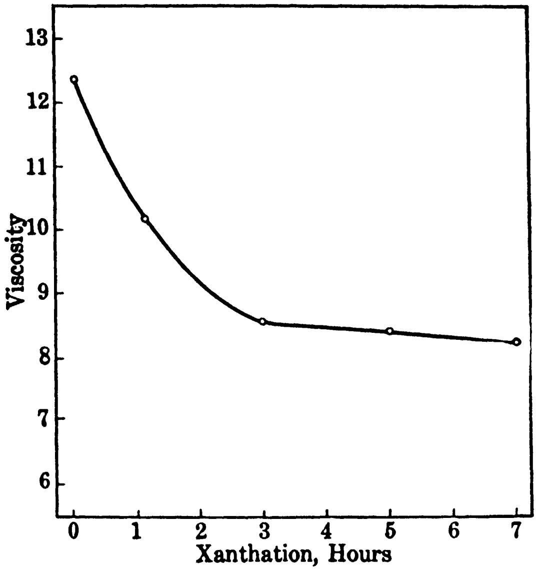

FIG. 75. Degradation of cellulose during xanthation. Heuser and Schuster.

In Fig. 75, the cuprammonium viscosities of cellulose preparations regenerated from xanthate samples (taken at intervals during the process of xanthation) are plotted against time of xanthation. The alkali cellulose had been aged for 73 hours and was taken from the series which had supplied the data for Fig. 46. Regeneration was accomplished by decomposing the xanthate samples with dilute hydrochloric acid.

It is seen that the cuprammonium viscosity of the regenerated cellulose drops rather rapidly at the beginning of the xanthation process but slows down after about 3 hours, probably because of the lack of oxygen and the increasing degree of substitution. After 7

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[188] See also D'Ans and Jäger, *Kunstseide*, **8**, 58 (1926).

hours of xanthation, the crude xanthate was dissolved in 4 per cent sodium hydroxide solution to give a concentration of cellulose of about 8 per cent. From samples taken at intervals, the cellulose was again regenerated with dilute hydrochloric acid. Each time a sample was taken, the ripening degree of the viscose was determined with ammonium chloride solution. The viscosities were again determined in cuprammonium hydroxide solution. The results are presented in Table 44 and Fig. 76. The second set of figures (II) in the table and in curve II in Fig. 76 pertain to viscose originating from alkali

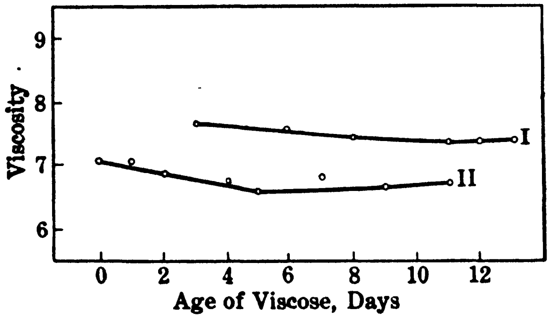

FIG. 76. Viscosity of cellulose regenerated from viscose during ripening. Heuser and Schuster.

TABLE 44

RIPENING DEGREE OF VISCOSE AND VISCOSITY OF CELLULOSE REGENERATED DURING RIPENING

Time of Ripening, Days		Ripening Degree, cc. NH_4Cl sol.		Viscosity of Regenerated Cellulose, Seconds	
I	II	I	II	I	II
3	7 *	54.0	....	7.58	7.04
6	20 *	17.7	Above 50.0	7.50	7.10
7	40 *	11.0	" "	7.33	6.80
8	4	6.5	" "	7.29	6.77
11	5	1.7	37.0	7.24	6.60
12	7	0.6	11.0	7.24	6.80
13	9	Coagulated	1.6	7.28	6.70
..	11	Coagulated	Coagulated	....	6.64

* Hours.

cellulose which had been aged for 3 days. The figures show that the viscosities of both series remained practically unchanged throughout the whole ripening process; this indicates that the cellulose suffered no further degradation during this process.

In Fig. 77, the curves which represent the behavior of the cellulose during aging, xanthation, and ripening are placed beside each other for easier comparison.

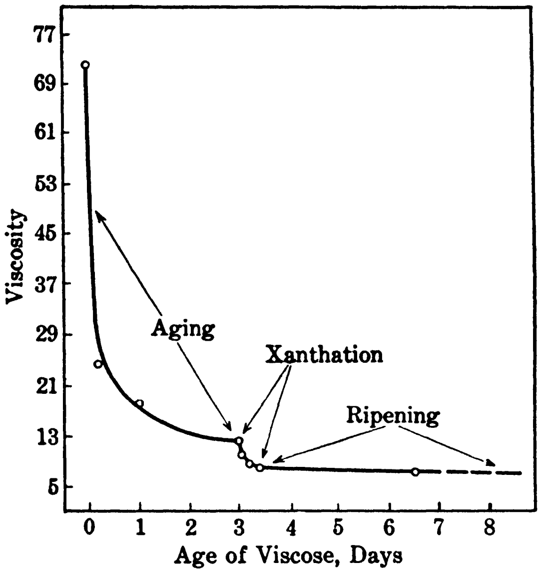

FIG. 77. Degradation of cellulose during the viscose process. Heuser and Schuster.

The observation that the cellulose in viscose is not degraded under normal conditions of ripening, were subsequently confirmed by a number of other investigators, including Rogowin and Schlachover,[189] Lottermoser and Wultsch,[190] Staudinger and Reinecke,[191] and Compton.[192] Lottermoser and Wultsch's results, which were obtained with viscose from wood pulp, are shown in Table 45. This table contains also results of a parallel experiment in which air was introduced into the viscose under violent stirring. All results are expressed in degrees of polymerization, derived from viscosity measurements in cupram-

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[189] Rogowin and Schlachover, *Cellulosechem.*, **14**, 17 (1933).
[190] Lottermoser and Wultsch, *Kolloid-Z.*, **83**, 188 (1938).
[191] Staudinger and Reinecke, *Papier-Fabr.*, **36**, 557 (1938).
[192] Compton, *Ind. Eng. Chem.*, **31**, 1256 (1939).

TABLE 45

DEGREE OF POLYMERIZATION OF REGENERATED CELLULOSE DURING RIPENING OF VISCOSE

Ripening Time, Hours	Degree of Polymerization	
	Normal Viscose	Air Introduced
0	328	328
2	332	326
4	325	330
8	325	330
18	336	323
32	337	333

monium hydroxide at very low cellulose concentration (0.01–0.03 per cent).

It is seen that the degree of polymerization remains practically constant throughout the ripening process. That it does not change, even when air is introduced into the viscose, is explained on the assumption that the dense viscous mass and the relatively low alkali concentration prevent the air from reaching and attacking the cellulose (see below).

Compton's data, expressed in centipoises of specific viscosity (η^{25}_{cp}) and measured at a cellulose concentration of 0.5 per cent at 25°, are listed in Table 46. This table contains also the viscosities of samples

TABLE 46

EFFECT OF DISPERSION OF XANTHATE AND OF RIPENING OF VISCOSE UPON SPECIFIC VISCOSITY OF REGENERATED CELLULOSE IN CUPRAMMONIUM SOLUTION

Dispersion		Ripening	
Time, Hours	η^{25}_{cp}	Time, Days	η^{25}_{cp}
0	5.46	1	4.37
1	4.68	2	4.40
2	4.69	3	4.05
3	4.28	5	4.28
7	4.66	9 (coagulation)	4.00

taken during the dissolving (dispersing) procedure (in aqueous sodium hydroxide solution). It is seen that, during this procedure also, the degree of polymerization of the cellulose remained unchanged.

Table 47 shows Staudinger and Reinecke's results, expressed in degrees of polymerization. These values were derived from specific viscosities in cuprammonium hydroxide solution at sol range cellulose concentrations. The viscose was of commercial make. The table contains also the degree of polymerization of the final product (cellophane). The figures show again that the greatest degradation of the cellulose occurs during aging. A comparison between the figures in the second and third columns shows the attack during xanthation. Again, ripening hardly changes the degree of polymerization and, further, there is no change in the end product.

TABLE 47

DECREASE OF DEGREE OF POLYMERIZATION (D.P.) OF CELLULOSE DURING THE VISCOSE PROCESS

Materials	Alkali Cellulose Before Aging		Alkali Cellulose Aged		Viscose After Dissolving		Viscose After Ripening (Salt Point 1.5)		Cellophane from Viscose at Salt Point 1.5	
D.P.	730	720	480	470	380	370	360	360	360	350

Considering that the wood pulp from which the viscose was prepared probably had a degree of polymerization of between 800–1000—refined wood pulps of high *alpha*-cellulose content even show 1400[193] and more—the degree of polymerization of the cellophane shows that the cellulose has suffered a shortening of its average chain length from one-half to one-fourth its original average value. Similar decreases in the original degrees of polymerization are encountered with viscose rayon.

The question whether the cellulose in viscose is dispersed to individual molecules ("macromolecules" according to Staudinger) or to micelles (or chain bundles) has been the subject of controversial opinions. Whereas Staudinger,[194] Bredée,[195] and others have favored the concept of the existence in viscose of macromolecules, the opinion prevails that the particles do not disperse further than to micelles.[196]

No doubt, the highly hydrophilic xanthate groups increase the hydrophilic

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[193] Staudinger and Reinecke, *Papier-Fabr.*, **36**, 558 (1938).

[194] See Staudinger and Zapf, *J. prakt. Chem.*, **156**, 261 (1940).

[195] Bredée, *Kolloid-Z.*, **94**, 81 (1941).

[196] Lieser, *ibid.*, **94**, 96 (1941); Schramek, *ibid.*, **94**, 92 (1941); Meyer, "Die hochpolymeren Verbindungen, Cellulose, etc.," Akad. Verlags-Ges., Leipzig (1940), p. 285.

properties of the cellulose so that the forces of cohesion are overcome and far-reaching dispersion occurs. However, the chains are usually only partly xanthated, and could thus remain connected through unxanthated groups even in solution. Moreover, the tendency of the chains to associate to aggregates counteracts the dispersion to single molecules.

The degree of dispersion may be expected to increase with increasing degree of substitution, and it appears possible that the higher substituted xanthates which are soluble in organic solvents (particularly the trixanthate, and probably also the chloroacetamide derivatives) would yield solutions in which the chains may be assumed to exist as single molecules, provided the concentration is sufficiently low.

However, attempts to arrive at an idea of the degree of polymerization of cellulose by calculations based on the viscosity of ordinary viscose itself (instead of on that of the regenerated cellulose in cuprammonium hydroxide) [197] are of little use because the interference by the colloidal changes (aggregation) cannot be sufficiently eliminated,[198] even in viscose which has been very considerably diluted.

The viscosity of viscose is rather sensitive to oxygen of the air. This behavior may be demonstrated by allowing viscose to stand in sealed bottles of varying sizes. The effect of the different air spaces above the viscoses in the partly filled bottles is reflected in different viscosities: The more air space, the lower the viscosity and *vice versa*.

Likewise, Lottermoser and Schwarz [199] showed a curve in which the viscosity of a ripening viscose proceeded in a zigzag line (Fig. 78). This particular course was due to the fact that, after each viscosity reading, the air above the viscose in the viscometer was renewed. This caused the viscosity to drop slightly; but, after the air had been consumed, the viscosity rose again. That this drop in viscosity should be due to a degradation of the cellulose by the air oxygen is quite improbable considering that the cellulose was not attacked on ripening, even if air was introduced (see above). In addition, the cellulose in viscose finds itself surrounded by inorganic compounds with reducing properties, and it would seem probable that any air admitted to the system would be consumed by the reducing inorganic compounds. Obviously, the drop in viscosity of the viscose under the influence of air oxygen is due to other causes. It appears possible that the inorganic substances have a different coagulating power in the oxidized than in the unoxidized state.

However, it is doubtful whether this explanation holds also, or only in the case in which oxygen, instead of air, is introduced into the ripening viscose. Under such conditions, Lottermoser and Schwarz found that the viscosity of the viscose became almost as low as that of the caustic soda solution used for dissolving and that it, after having reached its lowest point, continued on a line which ran parallel and close to the abscissa until it rose steeply when coagulation began (Fig. 79).

It would appear that, under such conditions, the greatest part of the drop in

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[197] Staudinger and Daumiller, *Ber.*, **71**, 1995 (1938). See also Staudinger and Reinecke, *loc. cit.*, p. 559; Compton, *loc. cit.*, pp. 1252, 1254; Philippoff and Krüger, *Kolloid-Z.*, **88**, 215 (1939).

[198] Ostwald, *ibid.*, **90**, 370 (1940).

[199] Lottermoser and Schwarz, *Z. angew. Chem.*, **43**, 18 (1930).

viscosity is due to the oxidation of cellulose. In fact, the curves in Figs. 80 and 81 seem to make it doubtful if the effect of the oxygen upon the coagulating power of the by-products predominates over the cellulose attack. Fig. 80 gives results for viscose which was first ripened in the presence of oxygen and then in nitrogen. It is seen that, in the presence of nitrogen, the viscosity increases again. Fig. 81 gives results of viscose which was first ripened in the presence of nitrogen and then in oxygen. As soon as the nitrogen is replaced by oxygen, the viscosity drops sharply. Unfortunately, the degree of polymerization of the regenerated cellulose was not determined. In a later study, Lottermoser

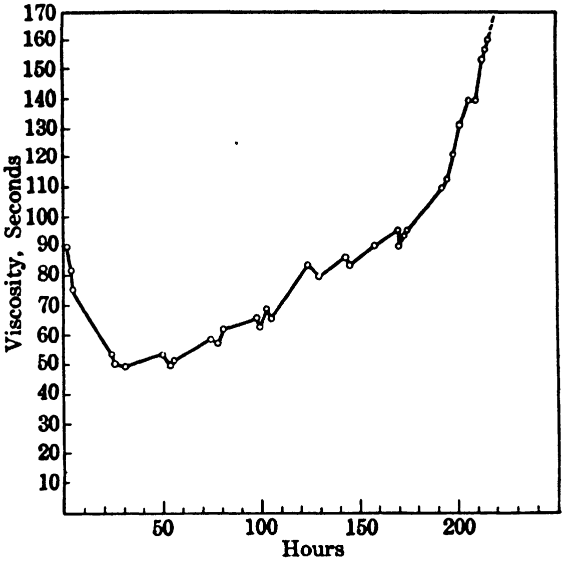

Fig. 78. Viscosity changes of viscose on ripening with renewal of air. Lottermoser and Schwarz.

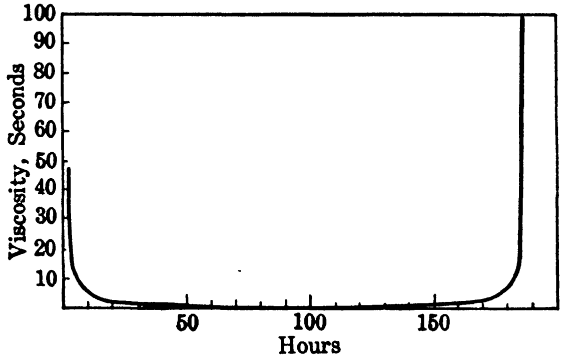

Fig. 79. Viscosity changes of viscose on ripening in oxygen. Lottermoser and Schwarz.

and Schwarz[200] regenerated the cellulose and found that a small part of it was soluble in dilute aqueous alkali; they also revealed the presence of oxycellulose. This result would seem to support the conclusion that the cellulose is attacked if only to a limited extent when oxygen is introduced into the ripening viscose.

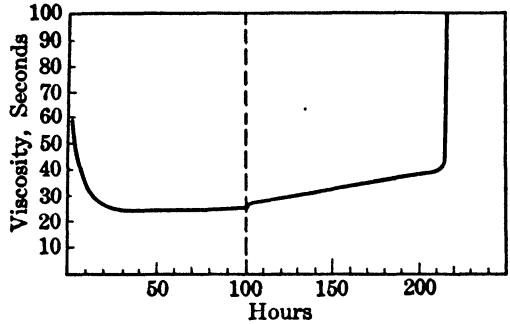

FIG. 80. Viscosity changes of viscose ripened in the presence of oxygen followed by nitrogen. Lottermoser and Schwarz.

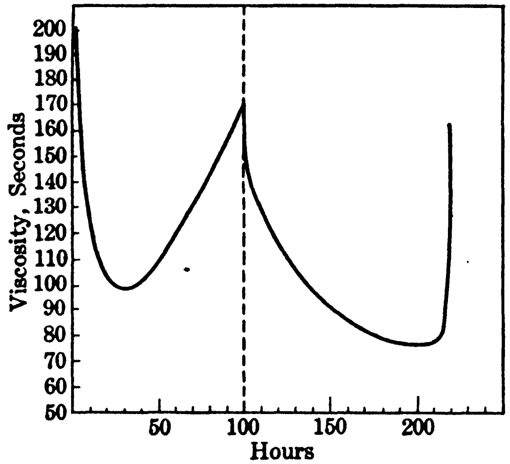

FIG. 81. Viscosity changes of viscose ripened in the presence of nitrogen followed by oxygen. Lottermoser and Schwarz.

As would be expected, the inorganic by-products—in viscose, as well as in the xanthate before dissolving—are completely oxidized under such conditions. The typical orange color disappears, and thiocarbonate, carbon disulfide, and sodium sulfide are converted into thiosulfate, sulfate, sulfite, and carbonate.

Other properties of the regenerated cellulose have been described and discussed previously. These properties are (1) its increased swell-

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[200] Lottermoser and Schwarz, *Kolloid-Beihefte*, **42**, 419 (1935).

ing ability, (2) its increased alkali-solubility,[201] and (3) its greater reactivity compared with the original cellulosic material. These properties designate the cellulose regenerated from viscose as cellulose hydrate, a designation which appears supported by the results of x-ray analysis.

It may be added that Lieser[202] has succeeded in regenerating cellulose in water-soluble form from its xanthate. When the xanthate (which was prepared by allowing carbon disulfide to act upon cellulose dissolved in a quaternary ammonium base) was dialized against water until the xanthate groups and the quaternary ammonium base had been quantitatively removed, a homogeneous colloidal dispersion of the regenerated cellulose in water was obtained. (The cellulose concentration and its degree of polymerization are not mentioned.)

The fact that native cellulose is insoluble in water in spite of its abundance of hydroxyl groups has always been surprising. Obviously, the water-insolubility of cellulose is a result of the strong lateral forces which are operative between individual chain molecules. If these forces are sufficiently overcome, as in the above experiment, the system becomes water-soluble (see also p. 90, regarding alkali-solubility of cellulose regenerated from viscose).

THE ACTION OF CARBON DISULFIDE UPON SODIUM CELLULOSATE

If, in the action of carbon disulfide upon alkali cellulose, sodium cellulosates are formed as intermediates, one should expect that the action of carbon disulfide upon the actual sodium cellulosates would directly lead to the formation of cellulose xanthates.

It will be recalled that the sodium cellulosates may be prepared by allowing sodium metal dissolved in liquid ammonia to react upon dry cellulose (p. 91). By adding carbon disulfide to the suspension of the cellulosate in liquid ammonia, Scherer *et al.*[203] obtained, after about 3 hours' reaction time, a water-soluble product which, indeed, proved to be a cellulose xanthate. Its degree of substitution was slightly below 1 xanthate group per 2 glucose residues. The time could be shortened to about 20 minutes in the presence of sodium halides or of sodium nitrate, which obviously catalyze the reaction.

In the presence of sodium nitrate the sulfur-cellulose ratio had ap-

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[201] Pakshver, Frolov, and Pribylow, *Chem. Abstr.*, **35**, 3434, 3435 (1941), followed the alkali-solubility of cellulose as it passed through the various steps of the viscose process.

[202] Lieser, *Cellulosechem.*, **18**, 121 (1940); *Kolloid-Z.*, **98**, 142 (1942).

[203] Scherer *et al.*, *Bull. Virginia Polytech. Inst.*, **32**, No. 11 (Sept., 1939).

proached roughly that of a cellulose monoxanthate. Lengthening the time of contact to 1 hour increased the degree of substitution to a ratio approaching that required for a cellulose dixanthate. However, with a still longer time, the degree of substitution decreased again and, at the end of 3 hours, the product showed a ratio of sulfur to cellulose corresponding to less than that required for a monoxanthate. Obviously, part of the carbon disulfide is used up in side reactions with the ammonia, resulting in the formation of ammonium thiocarbonates, thiocyanates, and sulfides. Moreover, these salts are acidic in character and as such react, according to Scherer *et al.*, in ammonia in a manner strictly analogous to ordinary acids in water.[204] These observations are interpreted to mean that, after sufficient time has elapsed, the quantity of "acids" has so increased that the xanthate with a higher degree of substitution may suffer partial decomposition and that further substitution in the acid medium is inhibited.

When the reaction was allowed to proceed in the absence of ammonia, higher substituted products were obtained only if a certain amount of water had been added to the carbon disulfide. The amount of water appears to play an important part in the reaction. When the water content of the carbon disulfide was 2.65 per cent, the highest degrees of xanthation were obtained, averaging 3 xanthate groups per glucose unit, whereas, with higher or lower percentages of water, the degree of substitution dropped to that corresponding to a dixanthate or below. It would appear that, in the presence of water, the system approaches conditions as they exist when carbon disulfide is allowed to act upon *alkali cellulose*. In fact, the amount of water used in any of the experiments would have been sufficient to decompose the cellulosate into cellulose and sodium hydroxide and thus produce an aqueous sodium hydroxide solution of sufficient strength to exert the mercerization effect. In these cases, therefore, cellulose was probably present originally in the form of alkali cellulose as under normal conditions of xanthation.

If this interpretation is correct, it is still remarkable that, under these conditions, so high a stage of substitution was reached. It is conceivable that trisodium cellulosate, a compound in which many sodium atoms are evenly distributed through the whole micellar system of the fiber, swells more uniformly and strongly on contact with water than cellulose itself in contact with sodium hydroxide solution. This may explain much of the result. In addition, in the above experiments, carbon disulfide was present in a very large excess, and the time of contact between the reactants was relatively long (24 hours).

CELLULOSE FOR COMMERCIAL VISCOSE MANUFACTURE

Viscose is the most important source for the manufacture of rayon and cellophane. More than 80 per cent of all rayon and practically all the cellophane manufactured today originate from viscose. When Cross and Bevan's inven-

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[204] Scherer, Gotsch, *et al.*, *loc. cit.*, p. 10.

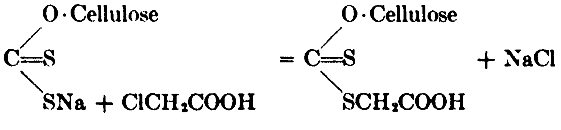
tion was first practiced in Europe, wood pulp served as the cellulosic material from the start, whereas in this country cotton linters were used in the beginning and then in mixtures with the cheaper wood pulp. Today, however, wood pulp is practically the only cellulosic material.

Bleached sulfite pulp is the most suitable raw material. The purity requirements, measured by its *alpha*-cellulose content, have increased in the course of the years. Whereas about 15 years ago an *alpha*-cellulose content of 87–88 per cent was considered satisfactory, the rayon industry has become used to regard about 90 per cent as an average figure. In addition, wood pulp for rayon manufacture should be low in copper number, in ash (particularly lime), and in resin. The most important characteristic is its solution viscosity, because this determines the viscosity of the spinning (and, in the manufacture of cellophane, of the casting) solution. Uniformity of viscosity is most essential. Whereas the usual (i.e., discontinuous) rayon and cellophane manufacturing processes require pulp of medium viscosity, which produces a viscose of a not too high and, hence, easily workable consistency, the more recently developed continuous processes call for pulp of very low viscosity, which needs little or no aging of the alkali cellulose.[205]

CELLULOSE XANTHATE DERIVATIVES AND RELATED COMPOUNDS

Cellulose xanthates have been converted into many derivatives. Most of the information is confined to the patent literature. Only a few combinations, e.g., those obtained by the action of the halides of fatty acid derivatives upon cellulose xanthates, have been investigated from a scientific point of view. The most important representative of these compounds, the diethylchloroacetamide derivative, has been discussed earlier.

Lilienfeld,[206] who has taken out most of the patents on the preparation of cellulose xanthate derivatives, found that monochloroacetic acid reacts with cellulose xanthate. This results in a compound in which the sodium atom is replaced by the acetic acid radical thus:



$$\mathrm{Cellulose{\cdot}O{-}C({=}S){-}SNa} + \mathrm{ClCH_2COOH} = \mathrm{Cellulose{\cdot}O{-}C({=}S){-}SCH_2COOH} + \mathrm{NaCl}$$

This acid, in the form of its sodium salt, is soluble in hot water, in alkali, and in organic bases, and may be precipitated from these solutions with acids or salts.

It is claimed[207] that the action of aliphatic or aromatic amines on this acetic acid derivative of cellulose xanthate yields a thiourethan (thiocarbonic acid

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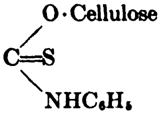
[205] Fischer, *Rayon Textile Monthly*, **19**, 551 (1938).

[206] Lilienfeld in Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 103; Marsh and Wood, "Introduction to the Chemistry of Cellulose," p. 340.

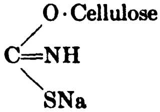
[207] Lilienfeld, *loc. cit.;* Marsh and Wood, *loc. cit.*, p. 303.

ester) of cellulose. Thus, the action of aniline is said to result in the formation of the phenylthiourethan of cellulose,



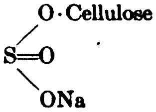
$$C(=S)(O\cdot\text{Cellulose})(NHC_6H_5)$$

Other compounds which are related to the xanthate have been prepared from cellulose. Dubosc[208] describes a cellulose thiocyanate said to be obtainable by the action of thiocyanic acid upon alkali cellulose under pressure. This treatment results in a viscous mass. The reaction product has been given the formula



$$C(=NH)(O\cdot\text{Cellulose})(SNa)$$

Scherer and Brooks[209] obtained a sulfite product by allowing liquid sulfur dioxide to act upon trisodium cellulosate. The sulfur content of this product of 17.91 per cent is in agreement with the formula

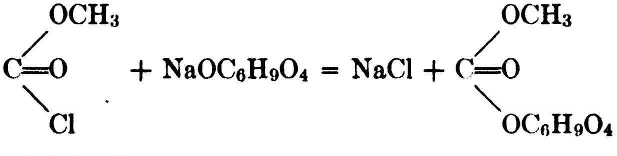


$$S(=O)(O\cdot\text{Cellulose})(ONa)$$

It decomposes in water.

Carbonic Acid Esters of Cellulose

In analogy with the action of alkyl chlorocarbonates upon sodium alcoholate, alkylated carbonic acid esters of cellulose may be obtained by allowing, for example, methyl chlorocarbonate (methyl chloroformate) to act upon alkali cellulose:



$$C(=O)(OCH_3)(Cl) + NaOC_6H_9O_4 = NaCl + C(=O)(OCH_3)(OC_6H_9O_4)$$

Heuser and Schneider[210] obtained such esters by allowing methyl chlorocarbonate to act upon hydrocellulose dissolved in 8 per cent sodium hydroxide solution. Since the ester thus formed is insoluble in alkali, it precipitates from the solution. It may also be isolated by extracting the suspension with chloroform. The degree of substitution

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[208] Dubosc, *Caoutchouc & gutta-percha*, **10**, 6895 (1913); Heuser, *loc. cit.*, p. 94. As for isocyanates of cellulose, see Celltex, *Silk and Rayon*, **15**, 320 (1941).

[209] Scherer and Brooks, *Rayon Textile Monthly*, **23**, 657 (1943).

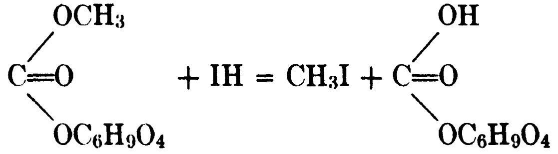
[210] Heuser and Schneider, *Ber.*, **57**, 1389 (1924).

corresponds closely to 2 methyl carbonate groups per glucose residue, $C_6H_8O_3(OCOOCH_3)_2$ (found: 30.35–31.50 per cent CO_2; calculated: 31.60 per cent).

The diester stage is not always obtained, evidently because the ester is relatively unstable to alkali. Complete saponification is accomplished by heating with 10 per cent sodium hydroxide solution at 60–70°. The ester decomposes slightly in cold water and more easily in hot water. It is insoluble in ether, alcohol, acetone, and benzene, but soluble (besides in chloroform and glacial acetic acid) in pyridine, from which it may be reprecipitated with water.

The molecular structure of the ester as represented by the formula above is derived from the following experimental evidence:

1. Hydrogen iodide eliminates the methyl group to form methyl iodide:



$$\overset{\mathrm{OCH_3}}{\underset{\mathrm{OC_6H_9O_4}}{\mathrm{C{=}O}}} + \mathrm{IH} = \mathrm{CH_3I} + \overset{\mathrm{OH}}{\underset{\mathrm{OC_6H_9O_4}}{\mathrm{C{=}O}}}$$

The free acid is unstable and decomposes into carbon dioxide and cellulose.

2. Saponification of the ester results in the formation of methyl alcohol, carbon dioxide and cellulose.

The formation of carbonic acid esters of cellulose may be regarded as another proof of its alcoholic nature.

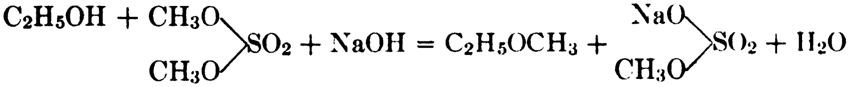
CHAPTER IX

CELLULOSE ETHERS

The introduction of alkyl groups into cellulose may be accomplished by methods which are commonly employed in the preparation of the ethers of aliphatic alcohols and of sugars. The alcoholates or the alkali compounds of the sugars may react with alkyl halides. For example:

$$C_2H_5ONa + CH_3I = NaI + C_2H_5OCH_3$$

or alkyl esters of inorganic acids may be allowed to react with the alcohols and sugars in the presence of alkali. Thus, for example:



$$C_2H_5OH + (CH_3O)_2SO_2 + NaOH = C_2H_5OCH_3 + (NaO)(CH_3O)SO_2 + H_2O$$

Dimethyl sulfate in the presence of alkali was used by Maguenne[1] for the preparation of β-glycosides, and Haworth and his school[2] adopted this technique for the complete methylation of di- and oligosaccharides. Under carefully controlled conditions (low temperature) the aldehydic hydroxyl is methylated first to form the methyl glycoside. Therefore, more rigorous conditions—as required for the methylation of the alcoholic hydroxyls—may be applied without risking decomposition of the saccharide by the alkali. The advantage of this method lies in the fact that the commonly applied primary step of protecting the aldehydic hydroxyl group of the sugar by the action of methylalcoholic hydrogen chloride may be abandoned. Moreover, the latter method could not be applied to di- and oligosaccharides because the glycosidic linkages are cleaved under the influence of the hydrogen chloride. Once the glycosidic hydroxyl is stabilized, other agents for the methylation of alcoholic hydroxyl groups may be applied—thus, for example, Purdie and Irvine's classical method of allowing methyl iodide to act upon the sugars in the presence of silver oxide;[3] or the glycoside may be converted into its alkali compound

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[1] Maguenne, *Bull. soc. chim.*, [3] **33**, 469 (1905).

[2] Haworth, *J. Chem. Soc.*, **107**, 8 (1915); Haworth and Leitch, *ibid.*, **113**, 188 (1918), and many subsequent publications. See also Schlubach and Maurer, *Ber.*, **57**, 1686 (1924).

[3] Purdie and Irvine, *J. Chem. Soc.*, **83**, 1021 (1903); **85**, 1049 (1904).

and in this form be subjected to the action of methyl iodide.[4] A modification of this method consists in allowing sodium metal and methyl iodide dissolved in liquid ammonia to act upon the sugar.[5]

Compared with cellulose esters, the preparation of cellulose ethers is of relatively recent date. Obviously, the renewed success which sugar chemistry had experienced by the introduction of alkylation and subsequent oxidation or hydrolysis as a most suitable means of elucidating the molecular structure of di- and oligosaccharides led to attempts to introduce alkyl groups into polysaccharides, such as starch, inulin, and cellulose.

The first attempt to introduce alkyl groups into cellulose seems to have been made by Suida,[6] who subjected cotton to slight methylation with dimethyl sulfate and aqueous sodium hydroxide with the object of changing the dyeing properties of the fiber. Subsequent publications are confined to the patent literature.[7] The first exhaustive scientific study was made by Denham and Woodhouse.[8] This study and the numerous investigations which were subsequently undertaken by Haworth and his school and others have contributed essentially to the elucidation of the molecular structure of cellulose.

Of the various possible cellulose ethers, the combinations with methyl, ethyl, benzyl and triphenylmethyl groups have been studied more extensively, but by far most of the laboratory work has been on the methylation of cellulose with dimethyl sulfate in the presence of aqueous alkali.

THE METHYLATION OF CELLULOSE WITH DIMETHYL SULFATE IN THE PRESENCE OF AQUEOUS ALKALI

For preparing methylcellulose in the laboratory, the cellulosic material is simultaneously subjected to the action of dimethyl sulfate

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[4] Feudenberg and Hixon, *Ber.*, **56**, 2119 (1923); Levene and Meyer, *J. Biol. Chem.*, **70**, 343 (1926); **74**, 701 (1927).

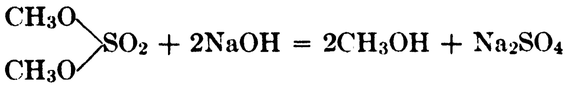
[5] Muskat, *J. Am. Chem. Soc.*, **56**, 693 (1934).

[6] Suida, *Monatsh.*, **26**, 413 (1905); *J. Soc. Chem. Ind.*, **24**, 543 (1905).

[7] Bayer & Co. and Leuchs, German patent 322,586 (1912), pertaining to the use of alkyl halides upon cellulose in the presence of alkali; Lilienfeld, Austrian patent 78,217 (1912), French patent 447,974 (1913); see also Dreyfus, British patent 166,767 (1920); U. S. patent 1,502,379 (1924). In regard to these and numerous subsequent patents the reader may be referred to Worden (First); "Technology of Cellulose Ethers," 5 vols.; The Worden Laboratory and Library, Milburn, N. J. (1930).

[8] Denham and Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913); **105**, 2357 (1914); **119**, 77 (1921).

(boiling point, 188°) and sodium hydroxide solution (18–35 per cent by weight and higher), first at room temperature and later at 50–70° while the mixture is being stirred. The methylating agents are added separately and continuously but at a slow rate in order to keep the reaction in hand. The reaction is exothermic, and the heat developed may cause excessive boiling and foaming. This is due to the formation of methyl alcohol (boiling point, 66°), being the result of a side reaction between dimethyl sulfate and sodium hydroxide, according to the equation:

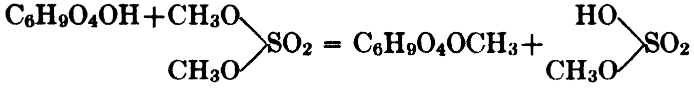


$$\left.\begin{matrix}\mathrm{CH_3O}\\ \mathrm{CH_3O}\end{matrix}\right\rangle \mathrm{SO_2} + \mathrm{2NaOH} = \mathrm{2CH_3OH} + \mathrm{Na_2SO_4}$$

This reaction will occur to a greater extent if the reactivity of the cellulosic material is impeded for one reason or another, particularly since cellulose itself may act as a surface catalyzer for the side reaction. After a time the temperature may be increased gradually to 60–65°. Soon after all the methylation agent has been added, the methylated product, which has retained the fibrous cellulose structure, may be isolated by freeing it of sodium sulfate and excess dimethyl sulfate (and possibly excess sodium hydroxide), by washing with *hot* water (cold water may dissolve the ether partly or entirely; see later).

The occurrence of the side reaction mentioned above is one of the reasons which makes it necessary to use a considerable excess of dimethyl sulfate. At elevated temperature the hydrolysis of dimethyl sulfate[9] acquires considerable proportions, even in water alone. On the other hand, the presence of salts decreases the hydrolysis. In the presence of aqueous alkali, the amount of dimethyl sulfate which is removed during methylation may be considerable.[10]

The reaction between cellulose and dimethyl sulfate may be expressed by the following equation:



$$\mathrm{C_6H_9O_4OH} + \left.\begin{matrix}\mathrm{CH_3O}\\ \mathrm{CH_3O}\end{matrix}\right\rangle \mathrm{SO_2} = \mathrm{C_6H_9O_4OCH_3} + \left.\begin{matrix}\mathrm{HO}\\ \mathrm{CH_3O}\end{matrix}\right\rangle \mathrm{SO_2}$$

The way in which this equation is presented may indicate the preferential reactivity of one of the methyl groups of the methylating agent.[11] Only 1 methyl group is consumed in the methylation of

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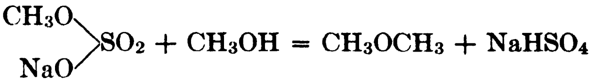
[9] Lewis, Mason, and Morgan, *Ind. Eng. Chem.*, **16**, 811 (1924); see also Heuser and Hiemer, *Cellulosechem.*, **6**, 120 (1925).

[10] Heuser and Hiemer, *Cellulosechem.*, **6**, 160 (1925).

[11] Ullmann and Wenner, *Ber.*, **33**, 2476 (1900).

cellulose;[12] the other may subsequently react with the methyl alcohol to form dimethyl ether and, in the presence of excess alkali, sodium bisulfate; thus:



$$\left.\begin{matrix}CH_3O\\NaO\end{matrix}\right\rangle SO_2 + CH_3OH = CH_3OCH_3 + NaHSO_4$$

The great excess of dimethyl sulfate requires a correspondingly large excess of aqueous sodium hydroxide. The reaction must not be allowed to become acid, because no methylation occurs in the acid medium. To avoid the use of large volumes of liquid, the concentration of the aqueous sodium hydroxide is kept as high as possible. Moreover, it was found that the decomposition of the dimethyl sulfate decreases and the degree of substitution increases with increasing alkali concentration.[13] High alkali concentration also favors the yield and the retention of the fibrous structure.[14]

It remains doubtful whether the alkali has any other function beyond those just descussed. This seems to hold particularly with regard to a possible swelling effect of the alkali. The concentration of the alkali used in the methylation process is far above the range within which maximum swelling is usually observed, i.e., from 12 to 14 per cent at room temperature. At this concentration, the degree of substitution remains below that obtained at higher concentrations. This is well illustrated in Fig. 82. Hess and co-workers explained this observation by the fact that the occurrence of the swelling maximum coincides with the taking up of an optimum quantity of water and that, thus, the presence of water at the place of reaction delays or even inhibits the methylation.[15]

Whether the formation of alkali cellulose or any of its modifications is a prerequisite for the entry of alkyl groups is difficult to prove or disprove. The observation that the degree of substitution increases with the alkali concentration may be merely the result of a corresponding decrease of the rate of decomposition of the dimethyl sulfate. Or it may be assumed that, with increasing alkali concentration, more and more hydroxyl groups are converted into sodium cellulosate groups which subsequently react with the dimethyl sulfate.[16] The reaction

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[12] Lewis, Mason, and Morgan, *Ind. Eng. Chem., loc. cit.*; see also Heuser and Hiemer, *loc. cit.*, p. 120.

[13] Denham and Woodhouse, *loc. cit.*; Hess, Abel, Schön, and Komarewsky, *Cellulosechem.*, **16**, 71 (1935).

[14] Hess, Abel, Schön, and Komarewsky, *loc. cit.*

[15] Hess, Abel, Schön, and Komarewsky, *loc. cit.*

[16] Hess and co-workers, *loc. cit.*; see also Berl and Schupp, *Cellulosechem.*, **10**, 42 (1929); Lorand, *Ind. Eng. Chem.*, **31**, 894 (1939).

would thus be analogous to the formation of cellulose xanthate inasmuch as the equilibrium reaction

$$C_6H_9O_4OH + NaOH \rightleftarrows C_6H_9O_4ONa + H_2O$$

shifts to the right as the concentration of alkali increases and as the cellulosate reacts with the dimethyl sulfate. On the other hand, it must be considered that cellulose loses its capability of combining with alkali after a certain degree of substitution has been reached.[17] Thus, methylated cellulose, the methoxyl content of which corresponds to an average of 2 methoxyl groups per glucose residue, does not combine with additional alkali.[18]

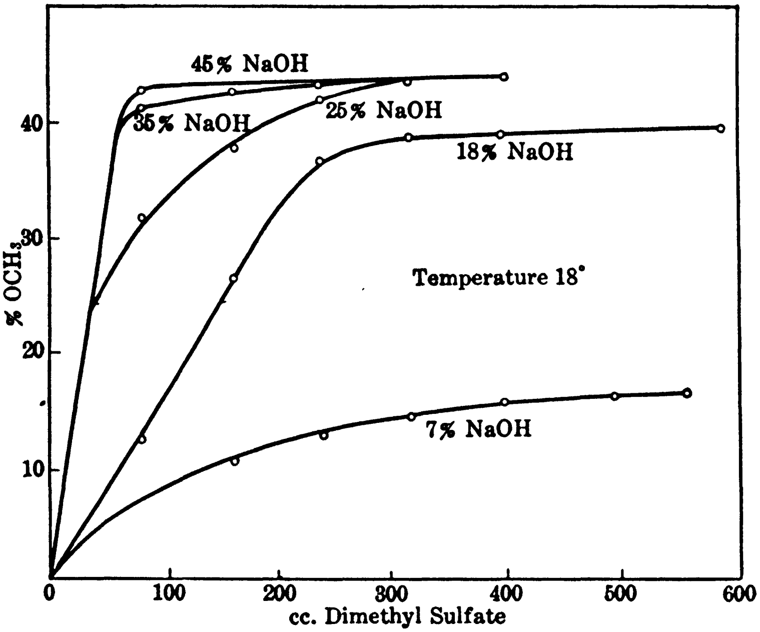

FIG. 82. Methylation of ramie fiber at varying alkali concentrations. Hess and co-workers.

Strong alkali in the presence of air has, as has been seen, a degrading effect upon cellulose, even if the outside air is prevented from entering the system. This effect would, of course, be more pronounced at an elevated temperature. Indications are that an appreciable amount of degradation must be expected. In order to avoid degradation it has

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[17] Heuser and Hiemer, *loc. cit.*

[18] Heuser and Schuster, *Cellulosechem.*, **7**, 29 (1926); Berl and Bitter, *ibid.*, **7**, 140 (1926).

been suggested that methylation be allowed to take place in a hydrogen or nitrogen atmosphere.[19]

Although the rate of substitution increases with rising temperature, the chances of avoiding degradation and of retaining undamaged fibrous structure are greater, of course, if methylation is carried out at room temperature[20] or lower. A high degree of substitution may even be obtained at a temperature of 0° if the alkali concentration is sufficiently high.[21] Other factors, such as stirring and the rate at which the agents, particularly the dimethyl sulfate, are added, may play a part in reaching the desired degree of substitution.

The methoxyl content obtainable under usual conditions in a one-step operation corresponds to 1½ to 2 methoxyl groups per glucose residue (26.42 to 32.6 per cent methoxyl), but sometimes the degree of substitution remains even below the monomethyl ether stage (17.61 per cent methoxyl).

An interesting method of preparing a low-substituted product was described by Hess.[22] When alkali cellulose, after having been dehydrated with 18 per cent sodium hydroxide in methyl alcohol but still containing some methyl alcohol, was dipped into dimethyl sulfate for about 10 minutes, it had taken up 9–11 per cent methoxyl, corresponding to a ratio of 1 methoxyl group to 2 glucose units. Hess is inclined to regard this "half-methylate" as a homogeneous product.

A low-substituted methyl ether, containing 8–16 per cent methoxyl, was also obtained by allowing dimethyl sulfate to act upon copper-alkali cellulose (Normann compound, see p. 155).[23]

Higher degrees of substitution are obtainable only by repeating the usual methylating operation several times. Since the rate of substitution decreases markedly with increasing degree of substitution, the number of operations necessary to reach a high degree of substitution must be increased the more closely the trimethyl stage (45.6 per cent CH_3O) is approached. Thus, Denham and Woodhouse,[24] using fibrous cotton, had to apply 18 to 20 methylations to reach a methoxyl content of 44.6 per cent. Irvine and Hirst,[25] who followed Denham and Woodhouse's method, applied 18 to 20 operations to reach 42–43 per

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[19] Staudinger and Scholz, *Ber.*, **67**, 84 (1934); Staudinger and Reinecke, *Ann.*, **535**, 47 (1938).

[20] Urban, *Cellulosechem.*, **7**, 76 (1926).

[21] Hess, Abel, Schön, and Komarewsky, *loc. cit.*, pp. 75, 76.

[22] Hess, *Ann.*, **506**, 295 (1933).

[23] Traube, Pivonka, and Funk, *Ber.*, **69**, 1483, 1490 (1936).

[24] Denham and Woodhouse, *loc. cit.*

[25] Irvine and Hirst, *J. Chem. Soc.*, **123**, 518, 529 (1923).

cent; Heuser and von Neuenstein,[26] who also employed Denham and Woodhouse's method, obtained 20.69 per cent after 5 methylations; and Berl and Schupp had to repeat the operation 28 times to obtain a methoxyl content of 44.9 per cent.

The rate of methylation expressed in the number of operations required to reach a certain methoxyl content may be seen from Fig. 83, which refers to Egyptian cotton, regenerated from its cuprammonium solution with carbon dioxide.[27] The trend of the curve is typical for the course of cellulose substitution reactions.

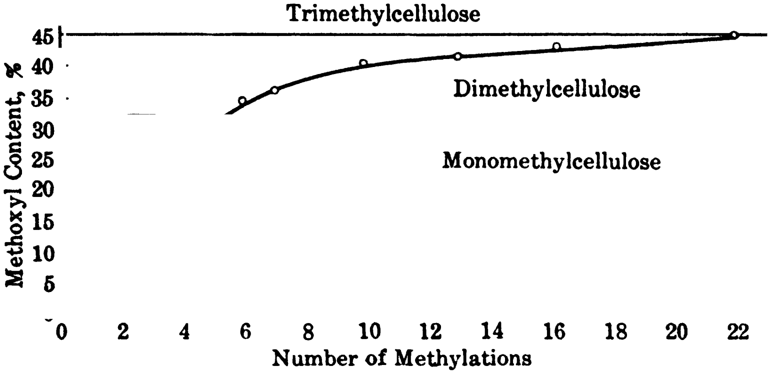

FIG. 83. Rate of methylation of cellulose regenerated from cuprammonium hydroxide solution. Heuser and Hiemer.

Sometimes it has been possible to reach a high degree of substitution even after a few operations. Urban prepared methylcellulose with 44.7 per cent methoxyl after only 2 operations, using raw cotton. Urban's conditions do not reveal any peculiarity which would explain this result. The only deviation from the usual conditions was that potassium instead of sodium hydroxide was used, which, however, was found by others [28] to be less effective than the sodium base.

By methylating fibers while they were under tension, 4 operations sufficed to bring the methoxyl content of ramie fiber to 44.7 per cent. A very slow rate in adding the dimethyl sulfate to the fibers submerged in the sodium hydroxide solution seems to be another essential factor for reaching a high degree of substitution with only a few oper-

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[26] Heuser and von Neuenstein, *Cellulosechem.*, **3**, 93 (1922).

[27] Heuser and Hiemer, *loc. cit.*, p. 105.

[28] Klemenc, *Monatsh.*, **38**, 553 (1918); Lewis, Mason, and Morgan, *loc. cit.*

ations. However, under such conditions, the time required is considerable.[29]

In spite of numerous attempts, it has not been possible to reach the theoretical methoxyl content of trimethylcellulose (45.58 per cent), unless the starting material consisted of distinctly degraded cellulose and possibly unless it suffered additional degradation while it was being methylated. Thus, alkali-soluble hydrocellulose prepared by the action of hydrogen chloride upon viscose rayon (according to the method suggested by Knoevenagel and Busch[30]) and methylated under conditions under which considerable further degradation very probably took place, gave, after only 9 methylations, a methoxyl content of 45.42 per cent.[31] Cellulose A, another alkali-soluble hydrocellulose preparation, gave, after 10 methylations, a methoxyl content of 45.0–45.1 per cent.[32] These results show that the number of methylations required to reach a certain methoxyl content decreases with decreasing degree of polymerization.

Before the possible reasons for the difficulty of reaching the theoretical methoxyl content for trimethylcellulose with cellulosic materials of a relatively high degree of polymerization are discussed, some modifications of the dimethyl sulfate-alkali method which have not already been mentioned previously may be briefly reviewed. All these modifications are attempts to increase the reactivity of the cellulosic material and to secure more intimate contact between the reactants during the reaction.

Haworth, Hirst, and Thomas[33] subjected cellulose, in the form of finely ground filter paper suspended in acetone, to the methylating reagents and obtained a methoxyl content of 45 per cent after only 2 methylations. No doubt, the finely divided form in which the cellulosic material was exposed to the reagents facilitated the reaction. In addition, it must be borne in mind that filter paper represents a cellulosic material of a relatively low degree of polymerization.

Barsha and Hibbert[34] tried to overcome the difficulties encountered in effecting complete methylation by dissolving the partly methylated product (43.32 per cent methoxyl) in chloroform, reprecipitating it into petroleum ether and remethylating the precipitate suspended in acetone. However, their best result [obtained with purified (*alpha*) wood pulp] was 44.63 per cent methoxyl after 2 methylations. This figure was not increased after a third methylation.

A similar idea underlies the technique which was applied by Hess and co-

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[29] Hess, Abel, Schön, and Komarewsky, *loc. cit.*, p. 75.

[30] Knoevenagel and Busch, *Cellulosechem.*, **3**, 42 (1922).

[31] Heuser and Hiemer, *loc. cit.*, pp. 122, 127.

[32] Hess and Weltzien, *Ann.*, **442**, 46 (1925); Hess and Pichlmayr, *ibid.*, **450**, 37 (1926).

[33] Haworth, Hirst, and Thomas, *J. Chem. Soc.*, 821 (1931); see also Jung and Heumann, *Naturwissenschaften*, **27**, 770 (1939).

[34] Barsha and Hibbert, *J. Am. Chem. Soc.*, **58**, 1006 (1936).

workers.[35] By subjecting premethylated ramie (40–42 per cent methoxyl) in finely divided form to several remethylations, an average value of 44.5 per cent methoxyl was obtained.

The Methylation of Acetylated Cellulose

Many attempts have been made to overcome the difficulties encountered in reaching the theoretical trimethyl value by "activating" the hydroxyl groups of the cellulosic material by way of acetylation. The first attempt in this direction was made with partially methylated cellulose (the cellulose was regenerated from viscose), having 32.12 per cent methoxyl.[36] This product was acetylated to yield a preparation corresponding to dimethyl-monoacetyl cellulose[37] and subsequently methylated with dimethyl sulfate and aqueous sodium hydroxide. After 2 methylations, a methoxyl content of 45.42 per cent was obtained, which is very close to the theoretical value (45.58). Likewise, triacetyl cellulose, prepared from purified cotton linters, was methylated to a methoxyl content of 44.98 per cent. This lower value was possibly due to the higher degree of polymerization of the cotton linters in comparison with the regenerated viscose cellulose.

The methylation of acetylated cellulose was subsequently studied by many investigators. To insure a more homogeneous reaction, Haworth, Hirst, and Thomas[38] dissolved a secondary cellulose acetate (prepared from cotton linters) in acetone and subjected the acetone solution to methylation with dimethyl sulfate and aqueous sodium hydroxide. Only one operation was necessary to reach a methoxyl value close to the theoretical 45.6 per cent. Since no precautions had been taken during acetylation and partial hydrolysis, the high degree of substitution was, at least in part, a result of substantial degradation of the cellulosic material which thus occurred before it came into contact with the methylating agents. This view appears to be supported further by the fact that this high degree of substitution has never been reached by subsequent investigators.[39] Haworth and Machemer's[40] best results were not higher than 45.0 per cent; Haworth, Hirst, *et al.*,[41] converted cellulose triacetate dissolved in a mixture of acetone and dioxane into a methylcellulose of 41 per cent methoxyl after one operation. Other investigators, using secondary acetates as the starting material and following Haworth, Hirst, and Thomas' original procedure, obtained the following values: 42.00 per cent (Hess and co-workers[42]),

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[35] Hess, Abel, Schön, and Komarewsky, *loc. cit.*, p. 77.

[36] Heuser and Hiemer, *loc. cit.*, p. 125.

[37] Regarding acetylation of partially alkylated cellulose see also Denham and Woodhouse, *J. Chem. Soc.*, **103**, 1736 (1913); Hess, *Z. angew. Chem.*, **34**, 449 (1921); Heuser and von Neuenstein, *Cellulosechem.*, **3**, 95 (1922); Staudinger and Reinecke, *Ann.*, **535**, 66, 74, 87 (1938).

[38] Haworth, Hirst, and Thomas, *J. Chem. Soc.*, **821** (1931).

[39] Sperka, unpublished work at The Institute of Paper Chemistry (1934), reached 45.6 per cent with an acetone-soluble acetate prepared from *alpha* wood pulp.

[40] Haworth and Machemer, *J. Chem. Soc.*, **2270** (1932).

[41] Haworth, Hirst *et al.*, *J. Chem. Soc.*, **1885** (1939).

[42] Hess, Abel, Schön, and Komarewsky, *loc. cit.*, p. 70.

42.2 per cent (Karrer and Escher[43]), 43–44 per cent (Wolfrom, Sowden, and Lassettre[44]), and 34–41 per cent (Staudinger and Scholz[45]). Staudinger and Scholz took precautions against degradation when the triacetate was converted into the secondary acetate and, moreover, carried out the methylation operations in the nitrogen atmosphere.

A comparison of the various results seems to indicate that, again, a low degree of polymerization favors substitution. Karrer and Escher have demonstrated this relationship with a series of acetylated cellulose preparations of increasing degree of degradation. The results are represented in Table 48. The degree of degradation of the acetates is seen from the copper numbers. The table also gives the number of methylations employed to reach various methoxyl contents.

TABLE 48

INFLUENCE OF DEGRADATION UPON DEGREE OF METHYLATION

Copper No. of acetylcellulose	1.23		2.86				12.61			27.93		
Number of methylations	6	10	2	4	6	8	1	3	5	2	4	8
Methoxyl content, %	40.86	41.25	25.50	38.90	42.00	42.77	43.60	45.23	45.45	41.17	42.83	45.93

Further support of the above conclusion is derived from results listed in Table 49. In this table, the degrees of polymerization of a number of cellulose acetates and that of cotton linters (calculated from specific viscosity measurements in cuprammonium, according to Staudinger's equation) are listed together with the methoxyl contents obtained after a single methylation operation applied to the acetates.[46] It is seen from the data that the methoxyl content of the methylated products increases as the degree of polymerization decreases.

Moreover, the experiments here involved showed that remethylation of the products referred to in Table 49 did not raise the methoxyl

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[43] Karrer and Escher, *Helv. Chim. Acta*, **19**, 1192 (1936).

[44] Wolfrom, Sowden, and Lassettre, *J. Am. Chem. Soc.*, **61**, 1072 (1939).

[45] Staudinger and Scholz, *Ber.*, **67**, 84 (1934).

[46] Johnston, doctoral dissertaton, prepared under the direction of E. Heuser at The Institute of Paper Chemistry, Appleton, Wisconsin, *J. Am. Chem. Soc.*, **63**, 1043, 1044 (1941).

content to the theoretical value; the highest result was 44.8 per cent. In further attempts to reach the theoretical value, two methylcellulose preparations (44.5 and 43.5 per cent CH_3O) were reacetylated and the resulting acetylmethylcelluloses were subjected to remethylation. This procedure resulted in 45.3 and 45.0 per cent methoxyl. The degree of polymerization of these two preparations was extremely low, namely, 30 and 50, respectively.

TABLE 49

DEGREE OF POLYMERIZATION AND METHOXYL CONTENT OF CELLULOSE ACETATES AND COTTON LINTERS

Materials	Degree of Polymerization	Methoxyl Content, %
1. Fibrous secondary acetate (Prepared according to Hess and Ljubitsch *)	. .	18.0
2. Fibrous triacetate (Prepared according to Böhringer and Söhne †)	666	21.0
3. Nonfibrous triacetate (Prepared according to Barnett ‡)	234	32.8
4. Commercial secondary Acetate I	160	44.7
5. Commercial secondary Acetate II	140	44.5
6. Laboratory secondary Acetate I, nonfibrous (Prepared according to Haworth and Machemer §)	141	43.3
7. Laboratory secondary Acetate II, nonfibrous (Prepared according to Haworth and Machemer §)	131	44.65
8. Bleached cotton linters	1500	34.6

* Hess and Ljubitsch, *Ber.*, **61**, 1460 (1928).

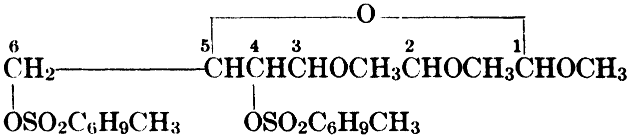
† Böhringer and Söhne, British patent 387,533 (1932); *J. Textile Inst.*, **29**, T189 (1933).

‡ Barnett, *J. Soc. Chem. Ind.*, **40**, 8T (1921).

§ Haworth and Machemer, *loc. cit.*

Karrer and Escher have explained the difficulty in reaching the theoretical value by assuming that either steric or other hindrances prevent some of the hydroxyl groups in cellulose from becoming methylated and that the theoretical value for the triether is eventually reached only as a result of degradation by which additional hydroxyl groups become available. This interpretation seems to imply that the blocked hydroxyl groups withstand the hydrolysis by the sulfuric acid of the acetylation mixture as well as the introduction of acetyl groups. In fact, Karrer and Escher were unable to introduce acetyl groups into methylcellulose containing 42–43 per cent methoxyl. That the hydroxyl groups in the 6-position of the glucose residues are involved in the blocking was deduced from the following experiment:

Methylcellulose containing 42–43 per cent methoxyl was completely hydrolyzed with hydrogen chloride dissolved in methyl alcohol. A mixture of trimethylmethylglucoside and dimethylmethylglucoside was obtained. The glucosides were separated and the dimethylmethylglucoside was subjected to treatment with *p*-toluenesulfonyl chloride. The tosylation resulted in the formation of a methylated tosyl ester which was identified as 2,3-dimethylmethylglucoside-4,6-di-*p*-toluenesulfonic acid ester:



$$\underset{OSO_2C_6H_9CH_3}{\overset{6}{CH_2}}\text{———}\overset{5}{C}H\underset{OSO_2C_6H_9CH_3}{\overset{4}{C}H}\overset{3}{C}HOCH_3\overset{2}{C}HOCH_3\overset{1}{C}HOCH_3 \quad (\text{O bridge } 5\text{—}1)$$

It is seen that 2 tosyl groups have entered the glucoside. One has reacted with a hydroxyl group in the 4-position, this hydroxyl group having been restored as a result of the cleavage of the 4,1-glycosidic linkages of the chain molecules. The fact that the other tosyl group has entered a primary alcoholic group, i.e., the 6-position, is interpreted to show that the hydroxyl groups which in cellulose withstood the introduction of methyl groups were located in the 6-position of the glucose residues. It is thought that some of these hydroxyl groups are involved in linkages to hydroxyl groups of neighboring chains (cross linkages). Karrer and Escher have calculated that approximately in every fourth or fifth glucose residue of the chains, 1 hydroxyl group could be involved in a cross linkage.

Karrer and Escher's explanation of the difficulty of introducing the theoretical quantity of methyl into cellulose would appear quite satisfactory if it were not for the fact that, as has been seen, other investigators have encountered no difficulties in substituting the hydroxyl groups left unmethylated in partially methylated cellulose with acetyl groups.[47] This fact would make it seem improbable that, at least in methyl-acetyl derivatives of cellulose, any hydroxyl groups are left in a blocked condition, and another explanation would have to be found. Mahoney and Purves [48] have discussed the possibility that alkylation

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[47] Heuser and Hiemer, *loc. cit.*; Staudinger and Reinecke, *Ann.*, **555**, 51 (1938); Compton, *J. Am. Chem. Soc.*, **60**, 2823 (1938).

[48] Mahoney and Purves, *J. Am. Chem. Soc.*, **64**, 17 (1942).

of a hydroxyl group in one position hinders alkylation of the adjacent one.

Certain observations seem to indicate that the difficulties may be of a physical rather than a chemical nature.

Johnston has shown that the benefit of allowing methylation to take place on cellulose acetate dissolved in acetone, i.e., in a homogeneous system, is not actually realized. In fact, the strong caustic soda solution does not mix with the acetone solution of the acetate so that little contact is established between the reactants in the early stages of methylation. Moreover, when a certain methoxyl content is reached, the partially methylated product precipitates from the acetone solution. Although this phenomenon results in a more intimate contact between the reactants, further methylation takes place on the precipitate and, hence, continues in a heterogeneous system. In addition, the introduction of methyl groups above a certain limit changes the originally hydrophilic cellulose into a distinctly hydrophobic derivative. It is conceivable that this transition favors the strengthening of the cohesive forces which are active between the individual chain molecules of the micellar system so that it becomes more and more difficult for the reagents to enter such a system.

Methylation of Cellulose in Solution

It would appear that the difficulties of reaching the theoretical trimethyl value could be overcome if it were possible to find a solvent or solvent mixture which, uninfluenced by the increasing degree of substitution, would keep the product of reaction in solution indefinitely. Such a solvent is not easily found because it also must be resistant to methylation.

Earlier attempts to methylate cellulose in solution did not aim at complete methylation. Thus, Berl and Schupp[49] prepared low-substituted methylethers with cellulose (probably cotton linters) which had been dissolved in strong sulfuric acid, regenerated therefrom by precipitation in water, and redissolved in a 15 per cent sodium hydroxide solution, and Bock[50] obtained low-substituted products with cellulose dissolved in a quaternary ammonium base.

Bock's method was thought to be a suitable way of introducing the full amount of methyl required for trimethylcellulose.[51] Dimethyl sulfate was allowed to act upon cellulose (commercial wood pulp) dis-

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[49] Berl and Schupp, *Cellulosechem.*, **10**, 44 (1929).

[50] Bock, *Ind. Eng. Chem.*, **29**, 985 (1937).

[51] Johnston, *loc. cit.*, p. 1048.

solved in 40 per cent trimethylbenzylammonium hydroxide. It was found that low temperature favored the reaction (possibly because of increased swelling). However, even under seemingly most suitable conditions and in spite of the fact that the cellulosic material had a rather low degree of polymerization, the best result was only 43.5 per cent methoxyl. This value was reached after only one operation, but could not be increased by further methylations. Nor could higher values be obtained with cellulose acetate dissolved in the organic base. Obviously, the same phenomena as discussed above are responsible for the failure to reach the theoretical value.

The method of alkylation with alkyl sulfate and sodium hydroxide has only seldom been used for the introduction into cellulose of other than methyl groups.

Hess and Müller[52] obtained *triethylcellulose* from various degraded cellulosic materials such as viscose and cuprammonium rayon and hydrocellulose prepared from viscose rayon. No difficulties were encountered in reaching the triethyl value. After 7 ethylations nonfibrous products with ethoxyl contents of 55.20 and 54.90 per cent were obtained from the rayon materials and 55.27 from the hydrocellulose (theoretically 54.87).

Berl and Schupp[53] encountered more difficulties in introducing ethyl groups into regenerated cellulose, dissolved in 15 per cent sodium hydroxide solution, than with methylation. No reaction and no rise in temperature were observed at room temperature. At 50°, one operation resulted in an ethoxyl content of 29.24 per cent. With increasing amounts of alkylating agents more ethyl could be introduced. The best result obtained in this series, 40.84 per cent ethoxyl, corresponds to the diethyl stage (theoretically 41.26 per cent).

THE ALKYLATION OF CELLULOSE WITH ALKYL HALIDES

Although alkyl halides have been employed in the laboratory relatively less frequently than alkyl sulfates, they are used to a considerable extent in commercial practice. The patent by Bayer and Co. and Leuchs already mentioned (p. 379) has shown the method of preparing methyl, ethyl, propyl, butyl, and other cellulose ethers, apparently for the first time. The cellulosic material is first allowed to stand in strong aqueous sodium hydroxide for 1 to 2 days and then freed from the excess alkali by pressing or centrifuging. The product is dried, either *in vacuo* or by subjecting a suspension in petroleum or petroleum ether to distillation until most of the water has been removed. The almost dry alkali cellulose is now heated with about three parts of alkyl chloride—for example, ethyl chloride—(calculated on the weight

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[52] Hess and Müller, *Ann.*, **455**, 206 (1927).

[53] Berl and Schupp, *loc. cit.*, p. 51.

of the original cellulose) under pressure[54] for 8 hours at 130° while the mass is stirred. Whereas the low-substituted products may be obtained in fibrous form, the higher alkylated ethers have lost most of the original fibrous structure. The reaction product is freed of excess alkyl chloride by distillation and of salts by leaching with hot water. The method as described may also be used in the laboratory, although some modifications of it have been proposed.

The reaction may be expressed by the following equation:

$$C_6H_9O_4ONa + ClC_2H_5 = NaCl + C_6H_9O_4OC_2H_5$$

it being implied that cellulose reacts in the form of its sodium cellulosate, and that the function of the excess alkali is merely that of neutralizing the hydrochloric acid formed in the reaction. However, the alkyl chlorides are partly decomposed by the alkali in side reactions; this results in the formation of the respective alcohols. The latter may enter into further reaction with the unchanged alkyl halides to form the corresponding alkyl ethers, for example:

$$C_2H_5Cl + NaOH = C_2H_5OH + NaCl \quad [1]$$

$$C_2H_5OH + C_2H_5Cl + NaOH = C_2H_5OC_2H_5 + NaCl + H_2O \quad [2]$$

Thus, here also a considerable amount of the alkylating agent may be withdrawn from its actual purpose. Little direct information seems to be available on the rate of these side reactions in competition with the methylation and ethylation of cellulose, but the main conclusions which Lorand[55] has drawn from a study of the action of benzyl chloride and sodium hydroxide upon cellulose (see later) may be extended to the former systems.

With the use of the alkyl halides, the same difficulties of reaching a high degree of substitution are encountered, if not even to a greater extent, as with dimethyl sulfate. On the other hand, less research seems to have been devoted to accomplishing complete alkylation of cellulose with alkyl halides.

No data seem to be available on cellulose ethers prepared with methyl chloride; a few publications refer to the use of ethyl and butyl chlorides, but most of the studies have been carried out in connection with the use of benzyl chloride.

In their preparation of ethyl ethers of cellulose with ethyl chloride

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[54] The alkyl halides have a low boiling point, that of ethyl chloride being 12.5°.

[55] Lorand, *Ind. Eng. Chem.*, **31**, 891 (1939).

and sodium hydroxide, Berl and Schupp[56] followed the direction of the afore-mentioned patent of Bayer and Co. and Leuchs. The reaction was carried out in a sealed glass tube. Medical cotton had acquired an ethoxyl content of 33.99 after one operation and of 54.28 per cent after three more operations. At the most suitable ratio of the ethylating agents to cellulose, the value for triethylcellulose was closely approached (54.76, theoretically 54.87 per cent). But it is very probable that the ether thus obtained was the derivative of considerably degraded cellulose. This may be anticipated from the treatment at 115° for 20 hours. In fact, Berl and Schupp found that the solution viscosity of the reaction products was considerably lower than that of the original cellulosic material and that it dropped with each operation.

Less degraded ethyl ethers seem to have been obtained by Nitikin and Rudneva[57] and by Uschakow and Schneer.[58]

Butyl cellulose has been prepared by allowing butyl bromide to act upon cotton linters in the presence of strong aqueous sodium hydroxide.[59] The chloride was found to be without effect. Apparently, no serious attempts were made to reach the theoretical value required for the tributyl ether. Butoxyl contents, ranging between 2.5 and 3 butoxyl groups per glucose residue, were obtained after two to four operations. Since side reactions between butyl bromide and alkali proceed at an extremely slow rate, even at the relatively high temperature necessary for esterification (100°), the possibility of cellulose becoming degraded by hydrogen bromide remaining unneutralized appears to be minimized.

Allylcellulose, $C_6H_9O_4OCH_2CH{=}CH_2$, also with 2 and 3 allyl groups per glucose residue, has been obtained by the action of allylbromide upon alkali cellulose,[60] preferably in the presence of xylene which exerts a swelling effect upon the partially substituted ether and thus facilitates further substitution.[61] The double bond remains intact and has retained its capacity to combine with halides. Thus, the tetrabromide of cellulose diallyl ether was obtained.[60]

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[56] Berl and Schupp, *loc. cit.*, pp. 44, 53.

[57] Nitikin and Rudneva, *J. Applied Chem. U.S.S.R.*, **6**, 45 (1933); *Chem. Abstr.*, **27**, **5964** **(1933)**.

[58] Uschakow and Schneer, *Plasticheskie Massy*, **1**, 17 (1931); *Chem. Abstr.*, **26**, **3373** **(1932)**.

[59] Nowakowski, *Cellulosechem.*, **13**, 105 (1932); see also Hagedorn and Möller, *ibid.*, **12**, 29 (1931).

[60] Sakurada, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **8**, 114 (1929).

[61] Haller and Heckendorn, *Helv. Chim. Acta*, **24**, 85 (1941).

Etherification with Alkyl Iodides

Alkyl iodides have been used rather seldom for the etherification of cellulose. Obviously, greater difficulties are encountered in introducing an appreciable quantity of alkyl than with alkyl chlorides[62] and the cellulosic material is considerably degraded. An attempt[63] to etherify carefully purified cotton by allowing methyl iodide to act upon the material containing an excess of aqueous sodium hydroxide (alkali cellulose) in a sealed tube at 100° for 16 hours resulted in a product with about 38 per cent methoxyl. However, the very low yield of ether indicates that considerable degradation had taken place. Similar results were obtained with hydrocellulose and methyl iodide in the presence of silver oxide. A somewhat higher alkyl content was obtained with ethyl iodide (corresponding to 2.75 OC_2H_5 groups per glucose residue).[64]

When methyl iodide was allowed to act upon copper-thallium cellulose, methylcellulose preparations were obtained which contained 8–9 per cent methoxyl, corresponding to somewhat less than 1 methoxyl group per 2 glucose residues.[65]

The action of methyl iodide upon sodium cellulosate may serve to complete the substitution of premethylated cellulosic material or to methylate cellulose directly. For example, Freudenberg and Boppel[66] suspended ramie and carded cotton which had been methylated with dimethyl sulfate and aqueous alkali (to a methoxyl content of 43–44 per cent) in sodium-containing liquid ammonia and treated it with methyl iodide. The reaction products showed methoxyl contents of between 44 and 46 per cent. The higher value, which is above that theoretically required for the triether, would indicate that considerable degradation had taken place. This conclusion seems to be in agreement with the very low viscosity the materials showed in solution (chloroform) and which has been explained by the authors on the assumption that the degrading action is exerted by sodium or sodium amide in liquid ammonia as well as by liquid ammonia alone. Whereas the observation on the degrading action of sodium metal in liquid am-

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[62] This experience appears to be in disagreement with that of Nitikin and Orlowa, *J. Applied Chem. U.S.S.R.*, **6**, 1093 (1933), *Chem. Abstr.*, **28**, 3891 (1933), who found that the reactivity of the halides increases in the order Cl $<$ I $<$ Br.

[63] Heuser and von Neuenstein, *Cellulosechem.*, **3**, 92 (1922).

[64] Nitikin and Rudneva, *J. Applied Chem. U.S.S.R.*, **6**, 145 (1933).

[65] Traube, Pivonka, and Funk, *Ber.*, **69**, 1483, 1489 (1936).

[66] Freudenberg and Boppel, *Ber.*, **70**, 1542 (1937); Freudenberg, Plankenhorn, and Boppel, *ibid.*, **71**, 2435, 2506 (1938); *Naturwissenschaften*, **26**, 123 (1938).

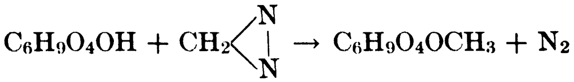
monia could be confirmed, it was found that liquid ammonia alone has no degrading effect upon cellulose.[67]

When ramie fiber, which had not been premethylated, was subjected to the action of sodium and methyliodide in liquid ammonia, the first methylation resulted in 33 per cent methoxyl, and 4 to 5 more methylations were required to raise the methoxyl content to 45.6 per cent.

METHYLATION WITH DIAZOMETHANE

The methylation of cellulose with diazomethane has been investigated several times but it has not been possible to reach the same degree of etherification as with other methods. Schmid [68] observed no reaction at all with cellulose, whereas substantial methylation was obtained with starch, inulin, and lichenin. On the other hand, Geake and Nierenstein [69] obtained products with methoxyl contents of 1.5 to 2.4 per cent from cellulose, the higher value being obtained in the presence of copper metal as catalyst. Lieser [70] obtained a product with only 0.75 per cent methoxyl from cellulose regenerated from viscose, whereas Reeves and Thompson [71] could introduce as much as 19 per cent.

The action of diazomethane obviously consists of an addition of the CH_2 group to a hydroxyl group of the cellulose with liberation of nitrogen, thus:



$$C_6H_9O_4OH + CH_2\left\langle\begin{matrix}N\\|\\N\end{matrix}\right. \rightarrow C_6H_9O_4OCH_3 + N_2$$

It will be recalled that Lieser used diazomethane for replacing the dithiocarbonate group in cellulose xanthate by a methyl group. The product of reaction showed 9.13 per cent methoxyl, the formula $C_6H_{10}O_5C_6H_9O_4OCH_3$ requiring 9.18 per cent (p. 337).

THE ETHERIFICATION OF CELLULOSE WITH ARALKYL HALIDES

The representative of this class of cellulose ethers which has been investigated most completely is *benzyl cellulose*. It seems to have been prepared first by Gomberg and Buchler,[72] who allowed benzyl

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[67] Heuser and Green, unpublished data.

[68] Schmid, *Ber.*, **58**, 1963 (1925).

[69] Geake and Nierenstein, *Ber.*, **58**, 2615 (1925).

[70] Lieser, *Cellulosechem.*, **10**, 162 (1929).

[71] Reeves and Thompson, *Contrib. Boyce Thompson Inst.*, **11**, 55 (1940); **13**, 1 (1943).

[72] Gomberg and Buchler, *J. Am. Chem. Soc.*, **43**, 1904 (1921).

chloride to react upon cellulose in the presence of aqueous sodium hydroxide at a temperature of 90–95° and at atmospheric pressure (the boiling point of benzyl chloride is 179°). The method is based on studies which the authors previously had undertaken with methyl glucoside, sucrose, lactose, inulin, dextrin, and starch, all of which form benzyl ethers more or less readily. However, neither in these cases nor in that of cellulose has an attempt been made to ascertain the best conditoins for most complete benzylation. With cotton, one operation usually resulted in products with less than 1 benzyl radical per 2 glucose residues, but 1.5 benzyl group per 1 glucose residue could be introduced, when filter paper was the starting material. With two operations, the aralkyl content could be raised to a slightly higher value.

The benzyl content of the reaction products was estimated by elementary analysis; indeed, the differences in the carbon contents are sufficiently large to distinguish between the various stages of substitution. The reaction may be expressed by the following equation:

$$C_6H_9O_4OH + ClCH_2C_6H_5 = C_6H_9O_4OCH_2C_6H_5 + HCl \quad .$$

The method applied by Gomberg and Buchler was subsequently modified in various respects.[73] It appears to be advantageous to subject the cellulosic material to two subsequent operations, in the first of which alkali of lower concentration (for example, 17.5 per cent by weight) than in the second (for example, 40–50 per cent) is applied. Also, a somewhat higher temperature than originally suggested is favored (about 100°) because the rate of etherification is increased.

Mienes[74] has compiled the investigations on the benzylation of cellulose until 1934 and has supplemented this compilation with a summary of his own studies. A summary of the work carried out until 1939 was written by Lorand.[75]

Lorand and Georgi[76] have followed the benzylation of cotton linters microscopically under conditions favorable to the preservation

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[73] Lilienfeld, British patent 149,320 (1923); *Chem. Zentr.*, **IV**, 808 (1933); Clément and Rivière, *Z. angew. Chem.*, **40**, 1579 (1927); Niethammer and König, *Cellulosechem.*, **10**, 201 (1929); Nakazima, *J. Soc. Chem. Ind., Japan*, **10**, 21 (1929); Nakazima and Sakurada, *ibid.*, **10**, 24 (1929); Okada, *ibid.*, **12**, 11 (1931); Brandt, doctoral dissertation, Buchdruckerei L. Begach, Berlin (1933); Atsuki and Kagawa, *J. Soc. Chem. Ind., Japan, Supplementary Binding*, **37**, 128 (1934).

[74] Mienes, "Cellulose-Ester und Cellulose-Ether, unter besonderer Berücksichtigung der Benzylcellulose," Chem.-Technischer Verlag Bodenbender, Berlin-Steglitz (1934).

[75] Lorand, *Ind. Eng. Chem.*, **31**, 891 (1939).

[76] Lorand and Georgi, *J. Am. Chem. Soc.*, **59**, 1166 (1937).

of the fibrous structure and have developed a most elucidating picture of the various phenomena which take place within this typically heterogeneous system and which seem to explain the difficulties encountered, not only in the benzylation but also in other etherifications as well as in the esterification of cellulose in fibrous form.

Niethammer and König[77] prepared *p*-chlorobenzyl and 1,2,4-chlorodinitrobenzene ethers of cellulose. The presence of chlorine and nitrogen facilitates the determination of the degree of substitution in such ethers. The former were obtained by allowing *p*-chlorobenzyl chloride to act upon cellulose in the presence of 17.5–30 per cent sodium hydroxide solution at about 105°. The reaction product was freed of unreacted cellulose by extraction with cuprammonium hydroxide solution. The highest degree of substitution obtained with carefully purified cotton corresponded to a chlorine content of 17.30 per cent, which is in agreement with the formula $C_6H_8O_3(OCH_2C_6H_4Cl)_2$, i.e., containing 2 chlorobenzyl groups per glucose residue. It was found that the ortho compound hardly reacted with cellulose, since only traces of chlorine were found in the product.

However, *o*-chlorobenzyl ethers of cellulose were prepared by Ball and Hibbert.[78] These ethers could be separated into fractions of different degrees of substitution with chloroform (12.37 and 15.25 per cent chlorine).

Under similar conditions, dinitrobenzene groups may be introduced into cellulose by allowing 1,2,4-chlorodinitrobenzene, $ClC_6H_3(NO_2)_2$, to act upon alkali cellulose.[79] However, this reaction seems to be confined to the surface of the fiber. The nitrogen content of a compound thus prepared remained below 1 per cent, whereas cellulose monodinitrophenyl ether, $C_6H_9O_4OC_6H_3(NO_2)_2$, requires 8.54 per cent nitrogen. Attempts to increase the degree of substitution led to degradation of the cellulosic constituent.

The Properties of Cellulose Ethers

Compared with cellulose esters, the most outstanding characteristics of cellulose ethers are perhaps the great resistance of the alkyl groups to acids and alkalies[80] and the solubility of the ethers of certain degrees of substitution in dilute alkali and water. In addition, the ethers are more resistant to the action of ultraviolet light[81] and possess relatively lower inflammability.[82]

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[77] Niethammer and König, *Cellulosechem.*, **10**, 201 (1929).

[78] Ball and Hibbert, *Can. J. Research*, **7**, 481 (1932).

[79] Niethammer and König, *loc. cit.*, p. 203; see also p. 304 on the conversion of the ether into a dyed modification.

[80] See for example Berl and Schupp, *Cellulosechem.*, **10**, 47, 59 (1929).

[81] Spitze, Mooradian *et al.*, *J. Am. Chem. Soc.*, **63**, 1576 (1941).

[82] Traill, *J. Soc. Chem. Ind.*, **53**, 77, 337 (1934); Conaway, *Ind. Eng. Chem.*, **30**, 516 (1938); Ott, *ibid.*, **32**, 1641 (1940); Hercules Powder Co., "Ethyl Cellulose," 1940.

Commercially these properties place the cellulose ethers in an advantageous position and, in connection with their compatibility with plasticizers, make them particularly suitable for many uses. Certain types of cellulose ethers are believed to be capable of replacing cellulose xanthate (viscose) for various purposes. On the other hand, the alkylating agents are relatively expensive.

Hygroscopicity and Water-Solubility of Cellulose Ethers

The hygroscopic properties of cellulose ethers are chiefly a function of the nature and size of the ether radical and of the degree of substitution. We thus encounter a state of affairs similar to that with cellulose esters. The hygroscopicity (or the sensitiveness to water) decreases with the increasing number of carbon atoms in the substituted groups from methyl to ethyl, propyl, butyl, etc., as well as with increasing degree of substitution.[83] Whether more importance must be ascribed to the degree of substitution (more exactly, to the ratio of substituted to free hydroxyl groups) than to the nature of the substituent [84] remains to be seen.

The influence of the increasing size of the substituent upon the water-binding capacity of cellulose ethers is shown in Table 50.[84] The decrease of hygroscopicity of ethylcellulose with increasing degree of substitution is shown in Fig. 84.

TABLE 50

	Ethylcellulose	Butylcellulose	Amylcellulose
Degree of substitution (groups per glucose residue)	2.15	2.28	1.91
Moisture absorbed, %	3.00	1.673	0.975

Under the usual conditions of alkylation with alkyl sulfate or alkyl halides, partial water-solubility is observed in the early stages of alkylation.[85] With increasing alkoxyl (methoxyl) content, the water-solubility of the ether increases to a maximum, whereafter it decreases and finally becomes zero. This is shown in Table 51.

Commercial methylcellulose is completely water-soluble within the range of 1.5 to 2.0 methoxyl groups per glucose residue (corresponding to 26.42–32.6 per cent methoxyl), and commercial ethylcellulose with somewhat less than 1.5 groups per glucose unit (corresponding to somewhat less than 35 per cent ethoxyl).[86]

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[83] Dörr, *Cellulosechem.*, **13**, 85 (1932).

[84] Lorand, *Ind. Eng. Chem.*, **30**, 528 (1938).

[85] Heuser and von Neuenstein, *Cellulosechem.*, **3**, 93 (1922).

[86] Lorand, *loc. cit.*; Traill, *loc. cit.*

TABLE 51

METHOXYL CONTENT AND WATER-SOLUBILITY OF CELLULOSE ETHERS

Methoxyl content, %	17.42	24.62	26.06	28.54	31.58	33.23	34.79	38.15	43.91	Prepared from cotton linters *
Water-soluble, %	13.5	15.5	14.0	13.21	11.81	10.04	0.0	0.0	0.0	
Methoxyl content, %	10.66	18.25	22.37	32.55	34.09	36.68	40.80	42.00	44.90	Prepared from cotton regenerated from cuam. solution †
Water-soluble, %	16.32	49.05	64.27	43.80	40.06	21.72	7.14	0.0	0.0	

* Berl and Schupp, *loc. cit.*, p. 43.
† Heuser and Hiemer, *Cellulosechem.*, **6**, 105 (1925).

It is conceivable that, with a degree of substitution below that which causes water-solubility, a range would exist in which the ethers would show merely pronounced hygroscopicity and in which the hygroscopicity would increase with increasing alkoxyl content until a state is reached in which the ethers would again become water-soluble. In fact, the increase in hygroscopicity was demonstrated in methylcellulose: Sheets of carefully methylated sulfite pulp fibers absorbed increasing quantities of moisture as the methoxyl content was raised[87] (Table 52). At methoxyl contents above 13.65 per cent, the fibers swelled to such an extent that they could not be converted into sheets and even became water-soluble to an appreciable extent.

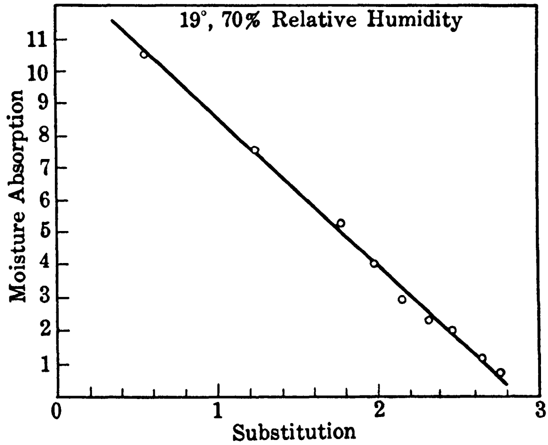

FIG. 84. Effect of substitution on moisture absorption of ethylcellulose. Lorand.

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[87] Jayme and Froundjian, *Cellulosechem.*, **18**, 9 (1940); Froundjian, doctoral dissertation, Darmstadt (1940), p. 73.

TABLE 52

METHOXYL CONTENT AND HYGROSCOPICITY OF METHYL CELLULOSE

Methoxyl content, %	Unmethylated	2.55	3.60	6.16	9.67	13.65
Moisture absorbed, %	7.91	8.20	8.66	8.79	10.32	10.53

The increased hydrophilic properties of slightly methylated pulp fibers were utilized in producing a sheet of paper which showed considerable improvement in physical properties. This was obviously due to the fact that the hydration of the fibers and the subsequent bonding between fiber surfaces was considerably increased (see p. 57).[87]

A comparison of the two sets of data in Table 51 shows that water-solubility is also a function of the degree of polymerization of the cellulosic constituent of the ether, the ethers prepared from regenerated cellulose possessing the greater solubility. This observation is substantiated by the following results:[88] Whereas only 6 per cent of methylated cotton cellulose with 32.6 per cent methoxyl content was water-soluble, methylated hydrocellulose of the same methoxyl content was completely water-soluble. The same behavior was observed with a series of cellulose preparations of increasing degrees of degradation. Likewise, methylcellulose of 42–43 per cent methoxyl content which had been prepared from a largely degraded cellulosic material (cellulose A) was completely soluble in both cold and hot water.[89] Thus, we may conclude that the commercial products are completely water-soluble because, besides having a suitable alkoxyl content, they are derivatives of considerably degraded cellulose.

The interesting fact that the introduction of hydrophobic groups into cellulose results in markedly enhanced hydrophilic properties, instead of causing the opposite effect, may be explained on the assumption that the distances between adjacent micelles as well as between individual chain molecules are increased as the ether groups deposit themselves within the inter- and intramicellar spaces.[90] As a result, cohesive forces, being active between hydroxyl groups of neighboring chains, are broken down, and a greater number of free hydroxyl groups

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[87] Jayme and Froundjian, *Cellulosechem.*, **18**, 9 (1940); Froundjian, doctoral dissertation, Darmstadt (1940), p. 73.

[88] Heuser and von Neuenstein, *loc. cit.*

[89] Heuser and Hiemer, *loc. cit.*

[90] See, for example, Sponsler and Dore, *Colloid Symposium Monographs*, IV, 174 (1926).

becomes accessible for hydration.[91] Hence, maximum water-solubility is reached when the physical effect has produced the maximum number of accessible hydroxyl groups.

It will be recalled that a similar hypothesis was invoked to explain the greater degree of hydration which slightly acetylated cellulose fibers developed on beating (p. 56). On the basis of this hypothesis, one could expect also water-soluble cellulose *esters* to exist, if the optimum balance between substituted and unsubstituted hydroxyl groups were attained.

Water-soluble cellulose acetates have been described by Fordyce.[92] They are obtained by partial hydrolysis of the primary cellulose acetate in the presence of larger quantities of water than usually employed, which results in a relatively low acetyl content. In this way, water-soluble secondary acetates containing less than 19 per cent acetyl were obtained. That the acetates were water-soluble at this relatively high acetyl content is surprising, for it will be recalled that the products described by Bletzinger and others (p. 56) were water-repellent at similar degrees of substitution. This difference might be explained on the assumption that the cellulose constituent in Fordyce's preparations was considerably degraded compared with the other preparations. On the other hand, it is noteworthy that Araki observed water-solubility in the early stages of acetylation.

On the basis of the hypothesis mentioned above one would expect the water-solubility of cellulose ethers to increase with the size of the group introduced. However, the opposite is true. Obviously, the effect caused by the increased distance between neighboring chains here fails to materialize, because the hydrophobic properties of the groups increase considerably with their size (in much the same way as with esters, see p. 44) and may thus obviate the former effect entirely. In fact, Lorand[93] found that the introduction of even a very small quantity of benzyl sufficed to produce a highly water-repellent cellulose ether.

The range of water-solubility is markedly influenced by the uniformity of alkylation.[94] That is to say, the more uniformly the alkoxyl groups are distributed over the system of the aggregated chain molecules, the less alkyl is required to bring about complete water-solubility of the ether. Such a uniform distribution of alkyl groups may be accomplished by etherifying cellulose dissolved in a quater-

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[91] Bock, *Ind. Eng. Chem.*, **29**, 985 (1937); Lorand, *loc. cit.;* Ott, *Ind. Eng. Chem.*, **32**, 1643 (1940).

[92] Fordyce and Eastman Kodak Co., U. S. patent 2,129,052 (1938); see also Araki, *Cellulosechem.*, **18**, 109 (1940).

[93] Lorand, *Ind. Eng. Chem.*, **30**, 528 (1938).

[94] Lorand, *loc. cit.*, p. 528.

nary ammonium base. In this way, Bock[95] prepared completely water-soluble methylcellulose with as little as 0.7 methoxyl group (corresponding to about 12 per cent methoxyl) and an analogous ethylcellulose with not more than 0.6 ethoxyl group per glucose residue (corresponding to about 15 per cent ethoxyl). As has been seen, such quantities of alkyl would, under normal conditions of alkylation, result only in increased hygroscopicity and perhaps partial water-solubility. The effect has been explained on the assumption that a more uniform distribution of alkoxyl groups leads to a more uniform separation of the chain molecules and consequently to a more uniform accessibility of free hydroxyl groups to water. It is probable that the increased water-solubility of these low-substituted ethers was aided by a low degree of degradation of the cellulose constituent, although Bock found that the cellulose regenerated from its solution in the quaternary ammonium base was less degraded than the cellulose in alkali cellulose which had been aged for 20 hours and from which commercial cellulose ethers are usually prepared by the direct method.

More uniform distribution of alkyl groups is also claimed to result when cellulose is subjected to alkylation in the form of its copper-alkali compound. (Normann compound, p. 155).[96] The ethers so prepared were water-soluble when they contained 0.8 to 0.9 methoxyl group per glucose residue (corresponding to 14–16 per cent CH_3O and compared with 22–23 per cent, as usually required for water-solubility). Indications are that the copper-alkali cellulose complex is particularly reactive[97] and that this increased reactivity causes the reaction to take a more homogeneous course.

The lower members of the homologous series of cellulose ethers—methyl- and ethylcellulose—are characterized by their solubility in cold water and their insolubility in hot water; i.e., they precipitate from their cold aqueous solution on heating, but redissolve when the suspension is sufficiently cooled.[98] This interesting phenomenon, which may be reproduced indefinitely, has been explained on the assumption that the ether forms a hydrate with water in the cold which, however, undergoes cleavage on heating;[99] this is analogous to the behavior of

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[95] Bock, *loc. cit.;* see also Compton, *J. Am. Chem. Soc.*, **60**, 2832 (1938).

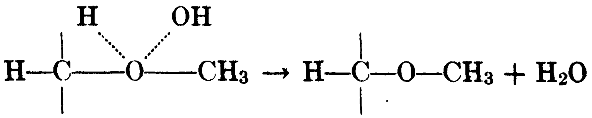
[96] Traube, Pivonka, and Funk, *Ber.*, **69**, 1483, 1489 (1936); see also Compton, *loc. cit.*

[97] Spurlin, *J. Am. Chem. Soc.*, **61**, 2222 (1939).

[98] Patents granted to Lilienfeld and to Bayer & Co. (p. 379); also Denham and Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913).

[99] Heuser and von Neuenstein. *Cellulosechem.*, **3**, 94 (1922).

methylated starch[100] and methylated xylan.[101] Some investigators are inclined to explain the phenomenon on the basis of oxonium hydroxide formation.[102] The cleavage of the oxonium hydroxide at elevated temperature may be expressed thus:



$$\mathrm{H{-}\underset{|}{\overset{|}{C}}{-}\overset{H\ \ \ OH}{O}{-}CH_3 \rightarrow H{-}\underset{|}{\overset{|}{C}}{-}O{-}CH_3 + H_2O}$$

The temperature required for redissolving the precipitate on cooling depends upon the degree of polymerization of the cellulose constituent.

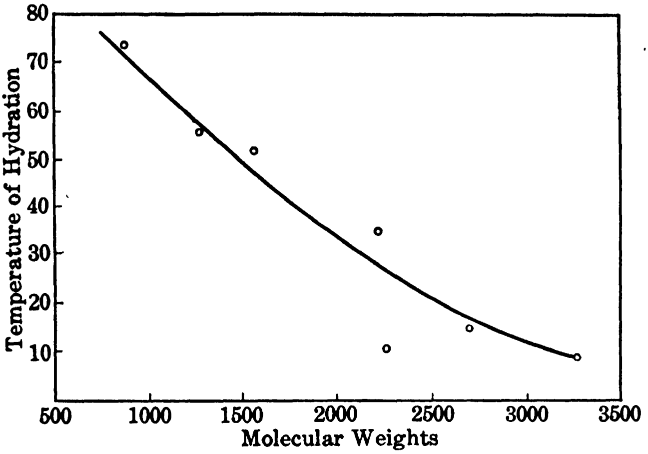


Fig. 85. Temperature of hydration and molecular weights of methylcellulose preparations. Heuser and Hiemer.

On the hypothesis that the ether forms a hydrate with cold water, this temperature was termed "temperature of hydration." As an example, a methyl derivative prepared from cellulose which had been regenerated from its cuprammonium solution required a temperature of 8–12° for solution when the precipitate suspended in boiling water was gradually cooled, whereas for the preparation of a methylated hydrocellulose, the temperature at which the precipitate would redissolve was 50–55°. By plotting the temperatures of hydration against the molecular weights of methylcelluloses prepared from variously degraded celluloses, practically a straight line was obtained as will be seen from

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[100] Karrer, *Helv. Chem. Acta,* **4,** 185 (1921).

[101] Heuser and Ruppel, *Ber.,* **55,** 2084 (1922).

[102] Frey, doctoral dissertation, Zürich (1926); Staudinger and Schweitzer, *Ber.* **33,** 2328 (1930); Staudinger and Reinecke, *Ann.,* **535,** 47 (1938).

Fig. 85.[103] The molecular weights were determined on the aqueous solutions (0°, concentration 0.1–2.0 per cent) by the freezing point method (Raoult-Beckmann). Although the values which were obtained with this method are much lower than those obtained with other more suitable methods (see Chapter XV), they reveal the difference in degree of polymerization of the various preparations quite distinctly and satisfactorily. Therefore, the curve in Fig. 85 may be interpreted to show that the temperature of hydration increases as the molecular weight of the methylcellulose decreases. The temperature of hydration may thus serve as an indication of the degree of polymerization of the cellulose ether.

Alkali-Solubility of Cellulose Ethers

Before the lower members of a homologous series of cellulose ethers prepared under normal conditions of alkylation become water-soluble, a still lower range of substitution is observed at which they are soluble in dilute aqueous alkali. In the light of the hypothesis discussed earlier, alkali-solubility at a low range of substitution may possibly be explained on the well-known fact that cellulose is more easily hydrated if alkali serves as a vehicle for the water molecules. No doubt, the ability of cellulose to swell even in dilute alkali to a greater extent than in water is of essential influence. The concentration of the dissolving alkali usually ranges between 4 and 10 per cent sodium hydroxide but, often, cooling, even to the freezing point of the suspension, is required for complete solution of the low-substituted ether.

Aqueous alkali, particularly at low temperature, thus adds to the effect which is caused primarily by the introduction of a certain amount of alkyl and, hence, this amount may be reduced to a few per cent—that is, a quantity which is too small to cause water-solubility. On the other hand, if the ether becomes water-soluble on the introduction of a larger amount of alkyl, it is also soluble in aqueous alkali.

Ethers containing only 3–4 per cent methoxyl[104] or about 0.5 per cent ethoxyl[105] have been prepared which become soluble in 4–10 per cent sodium hydroxide solution on freezing of the alkaline suspension but which are insoluble in water.

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[103] Heuser and Hiemer, *Cellulosechem.*, **6**, 127, 163 (1925).

[104] Traill, *J. Soc. Chem. Ind.*, **53**, 77, 337 (1934).

[105] Lorand, *loc. cit.*, p. 529.

Solubility of Cellulose Ethers in Organic Solvents

As the alkyl content increases above the water-soluble range, the ethers become more and more hydrophobic and organophilic[106] and the triethers which have lost their water (and alkali) solubility entirely are soluble in a great variety of organic solvents and solvent mixtures.[107] However, the fact that a cellulose ether is soluble in an organic solvent does not always mean that it is insoluble in dilute alkali and in water. This depends upon the degree of polymerization of the cellulose constituent. It was found that such preparations as trimethylcellulose obtained on the alkylation of cellulose A, "dimethyl" hydrocellulose (32 per cent methoxyl content),[108] or the "disorganized" trimethylcellulose preparations described by Hess and co-workers[109] are water-soluble. In these cases, water-solubility is a result of the degradation of the cellulose constituent.

Conversely, highly substituted cellulose ethers may not be soluble in organic solvents because their degree of polymerization is too high, in much the same way as highly substituted esters are insoluble under the same circumstances. Denham[110] has described a methylcellulose with a methoxyl content of 44.6 per cent which had been prepared from cotton and which was entirely insoluble in alcohol, acetone, and chloroform, and Irvine and Hirst[111] found trimethylcellulose—also prepared from cotton—"remarkably insoluble" in organic solvents.

Other Properties of Cellulose Ethers

Other properties which aid in the characterization and classification of cellulose ethers are the softening point and the solution viscosity.

Softening Point. This is an important property for commercial uses; it is influenced by the nature of the ether group, the degree of substitution, and the degree of polymerization. The softening point seems to decrease with the number of carbon atoms in the ether radical.[112] The occurrence of sharp minima in the softening point at a

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[106] Heuser and Hiemer, *Cellulosechem.*, **6**, 106, 156 (1925); Berl and Schupp, *ibid.*, **10**, 43, 44 (1929).

[107] Kauppi and Bass, *Ind. Eng. Chem.*, **30**, 74 (1938); Sponsel, *Kunststoffe*, **28**, 322 (1938).

[108] Heuser and von Neuenstein, *Cellulosechem.*, **3**, 94 (1922).

[109] Abel and Hess, *Cellulosechem.*, **16**, 79 (1935).

[110] Denham, *J. Chem. Soc.*, **119**, 77 (1921).

[111] Irvine and Hirst, *ibid.*, **123**, 521 (1923).

[112] The same relation has been observed with cellulose esters, Sheppard and Newcome, *J. Phys. Chem.*, **39**, 143 (1935).

certain degree of substitution was observed with ethyl- and benzylcellulose.[113] The degree of polymerization influences the softening point quite distinctly. The melting point of methyl ethers of increasingly degraded cellulose preparations was found to decrease, for example, from 350 to 200°.[114] Similar observations were made on ethyl- and benzylcellulose of different degrees of polymerization.[115]

Viscosity. The viscosity of cellulose ethers in organic solvents and the factors which result in changes of this characteristic have been investigated only to a limited extent. The data available reveal a situation which is largely analogous to the behavior of cellulose esters. Thus, the degree of polymerization of the starting cellulosic material is reflected by the viscosity of the ether. If no precautions are taken, each alkylation operation causes a further drop in viscosity of the resulting ether.[116]

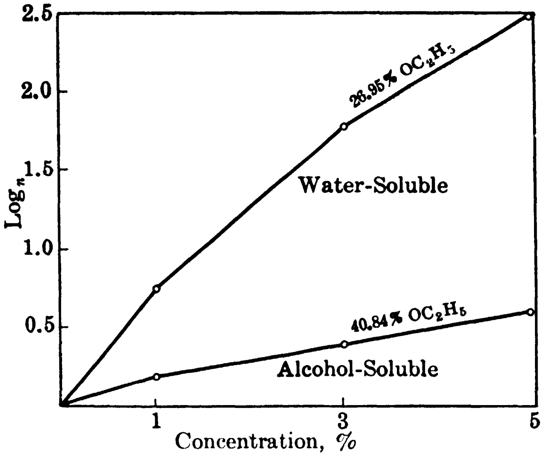

FIG. 86. Relation between log viscosity and cellulose ether concentration. Water-soluble and alcohol-soluble ethylcellulose. Berl and Schupp.

A relatively small increase in the cellulose ether concentration of the solution causes a very considerable increase in viscosity. If the logarithms of the relative viscosities (measured in alcohol or in chloroform) are plotted against the concentration of the solution, an almost straight-line relationship is observed for all degrees of substitution of methyl- and ethylcellulose[117] (Fig. 86).

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[113] Lorand, *Ind. Eng. Chem.*, **30**, 527 (1938).

[114] Heuser and Hiemer, *loc. cit.*, p. 130.

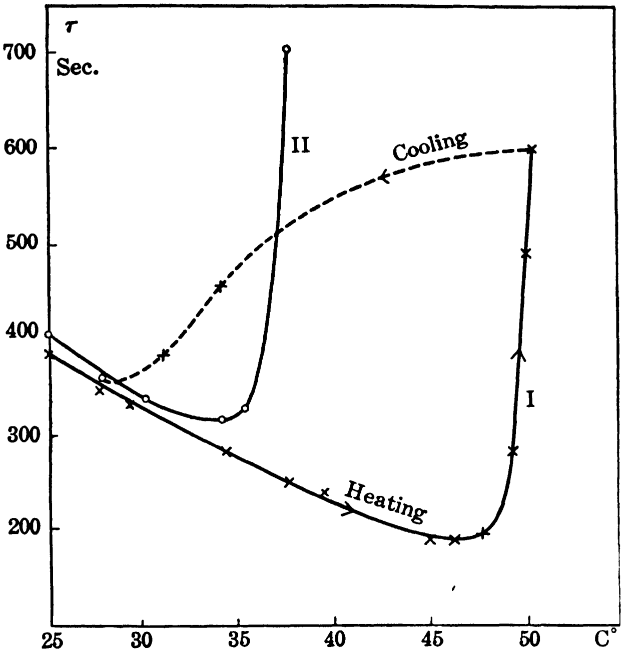
[115] Lorand, *loc. cit.*

[116] Berl and Schupp, *Cellulosechem.*, **10**, 47 (1929).

[117] Berl and Schupp, *loc. cit.*, p. 52 *ff.*

Some solvents seem to form complex compounds with the cellulose ether, resulting in viscosity anomalies. Such behavior has been observed with methylcellulose in *m*-cresol[118] and with ethylcellulose in benzene.[119]

The peculiarity which causes methyl- and ethylcellulose of a certain degree of substitution to be soluble in cold water and insoluble in hot water and to redissolve on cooling the hot suspension has been considered by colloid chemists as a typical system of reversible sol-gel transformation.[120] It was found that the viscosity of a solution of commercial methylcellulose (35.4 per cent methoxyl) in cold water decreased on heating but, when a certain temperature had been reached, increased very rapidly until a gel was formed. On cooling, the viscosity decreased slowly until it reached the value of the original cold solution. The turning point of the curve seems to coincide with the



I. Methylcellulose 1.56 per cent.
II. Methylcellulose 1.52 per cent + 0.1 mole K_2SO_4.

FIG. 87. Viscosity of methylcellulose in water on heating and cooling. Heymann.

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[118] Staudinger and Scholz, *Ber.*, **67**, 88 (1934).

[119] Staudinger and Reinecke, *Ann.*, **535**, 71 (1938).

[120] Heymann, *Trans. Faraday Soc.*, **31**, 846 (1935); see also Boedeker, *Kolloid-Z.*, **94**, 163 (1941).

"temperature of hydration" (see p. 403). This behavior is shown in Fig. 87. The figure also shows that, when the solution is cooled, a very pronounced hysteresis effect occurs; that is, the viscosity at the same temperature is much higher when the solution is cooled than when it is heated.[121]

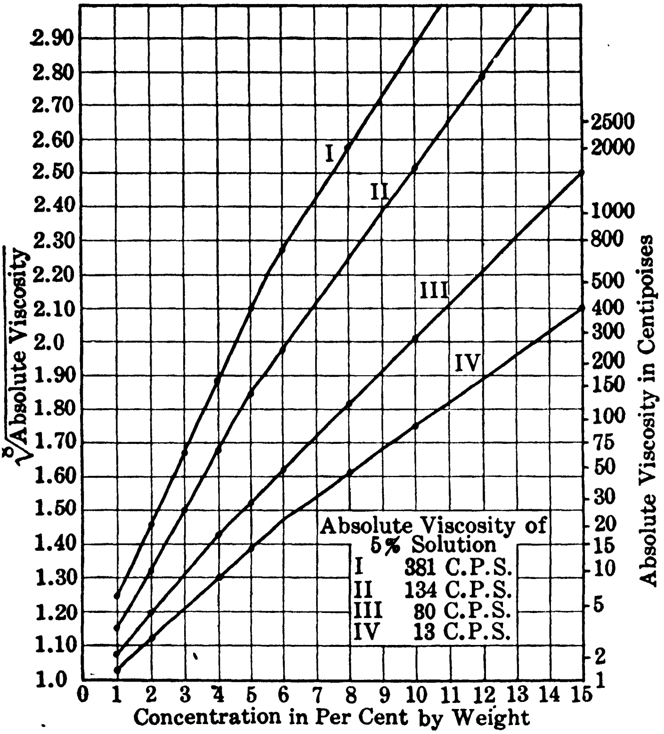

FIG. 88. Viscosity-concentration curves of ethylcellulose in 80–20 toluene-ethanol. Kauppi and Bass.

When kept for a long time at higher temperature, the gel undergoes syneresis. A 1.6 per cent dispersion, for example, which was kept at 80° for 50 days, produced about 20 per cent of its own volume of water, the separated liquid being free of organic material.

Heymann has explained the sol-gel transformation by the dehydration of the methylcellulose particles. This concept appears to be supported by the behavior of the methylcellulose-water system with added electrolytes and by the occurrence of certain other phenomena in regard to which the reader is referred to the original.

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[121] See also Brown and Houghton, *J. Soc. Chem. Ind.*, **60**, 254, 257 (1941). referring to the glycolic-acid ethers of cellulose (see p. 421).

A method of expressing the viscosity concentration-relation of ethylcellulose in simplified graphical form was worked out by Kauppi and Bass.[122] The equation proposed by Philippoff,[123] relating viscosity of a polymer to its concentration, was applied to ethylcellulose solutions. The eighth root of the absolute viscosity was shown to be a linear function of the concentration under conditions of viscosity measurements obtaining in an Ostwald viscometer at concentrations above 5 per cent ethylcellulose (Fig. 88). Moreover, a viscosity-concentration chart was constructed which expresses the viscosity of commercially available ethylcellulose at concentrations from 5–20 per cent by weight as a straight-line relationship. A blending chart serves to obtain intermediate viscosities.

It is believed that the graphical method is applicable to all other cellulose compounds and to solutions of linear polymers in general.

The viscosity of methyl- and ethylcellulose may be lowered by exposing them, either as such or in solution, to the action of ultraviolet light.[124] Provided the air is excluded, the degree of substitution remains unchanged.[125]

The Heterogeneity of Cellulose Ether Preparations

Experimental evidence seems to indicate that ether groups are less uniformly distributed over the chain molecules of the cellulose system than are ester groups, this nonuniform distribution being more pronounced with low- than with high-substituted ethers. Whereas, as has been seen, the fractionation of cellulose esters yields fractions of very nearly the same degree of substitution, it has been possible to separate the lower-substituted ethers into fractions of considerably different alkoxyl content.

The presence of unetherified cellulose in low-substituted ethers has been deduced from the observation that it may be extracted with cuprammonium hydroxide solution. Likewise, this agent is a good solvent for the low-substituted portions of partially etherified cellulose. Again, Denham[126] has shown that the solubility of methylcellulose in cuprammonium hydroxide decreases as the degree of substitution is increased. Moreover, a relationship seems to exist between cupram-

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[122] Kauppi and Bass, *Ind. Eng. Chem.*, **29**, 800 (1937); regarding further data on the viscosity of methyl- and ethylcellulose, see Dow Co. "Ethocel" (1937), and Hercules Powder Co. "Ethyl Cellulose" (1940).

[123] Philippoff, *Cellulosechem.*, **17**, 55 (1936); see also Martin, paper presented before the Cellulose Division of the American Chemical Society, Memphis (April, 1942).

[124] Clément, Rivière, and Beck, *Chimie & industrie*, Special Number, 702 (March, 1932); Steurer, *Z. phys. Chem.*, **B47**, 127 (1940); Spitze, Mooradian, *et al.*, *J. Am. Chem. Soc.*, **63**, 1576 (1941).

[125] I. G. Farbenindustrie and Bincer, German patent 601,478 (1934).

[126] Denham, *J. Chem. Soc.*, **119**, 77 (1921).

monium and water-solubility. Berl and Schupp[127] found that methylcelluloses were insoluble in cuprammonium hydroxide at a methoxyl content at which they became water-insoluble. Therefore, cuprammonium hydroxide solution appears to be a means of extracting not only unetherified cellulose but also low-substituted water-soluble portions. The results of such a procedure reveal the uneven distribution of the alkyl groups.

A similar separation into water-soluble and water-insoluble ethers may be accomplished by extracting the ether with concentrated ammonium hydroxide[128] and, more conveniently, with cold water. When the latter method was applied to methylcellulose preparations, differences were observed in the methoxyl content of the fractions of, for example, 32.6 per cent (water-soluble fraction) and 21.0 per cent (water-insoluble fraction) or 30.4 per cent (water-soluble) and 25.54 per cent (water-insoluble).[129] With increasing methoxyl content, however, separation into fractions of different degrees of substitution becomes less successful; this may be interpreted to mean that etherification proceeds more uniformly as the degree of substitution approaches that of the completely etherified product.[130]

Another method of separating partially substituted cellulose ethers into fractions of varying alkoxyl content consists of fractional precipitation. With saturated sodium sulfate solution as the precipitating agent,[131] a solution of commercial water-soluble methylcellulose (30 per cent methoxyl) could be separated into various fractions, the lowest of which showed 22.6 and the highest 34.6 per cent methoxyl.

As would be expected, the cellulose ethers are also heterogeneous with respect to chain length. The fractions just mentioned showed molecular weights (derived from viscosity data) varying from 5000 to 120,000, the lowest molecular weight fractions showing the highest methoxyl contents. This seems to be in agreement with the observation that the rate of methylation increases with decreasing degree of polymerization (p. 385).

It is thus seen that the cellulose constituent in commercial cellulose ethers is rather degraded. This view is confirmed by results of osmotic pressure measurements carried out on solutions of commercial products, ranging from

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[127] Berl and Schupp, *Cellulosechem.*, **10**, 43, 49 (1929).

[128] Berl and Schupp, *loc. cit.*

[129] Heuser and von Neuenstein, *Cellulosechem.*, **3**, 93 (1922).

[130] Heuser and Hiemer, *Cellulosechem.*, **6**, 121 (1925); see also Abel and Hess, *ibid.*, **16**, 78 (1935); Mahoney and Purves, *J. Am. Chem. Soc.*, **64**, 17, 18 (1942).

[131] Signer and Liechti, *Helv. Chim. Acta*, **21**, 530 (1938).

22.5 to 25.3 per cent methoxyl content.[132] The molecular weights found were 82,000, 79,000, 49,000, and 46,000. It may be mentioned here that methyl- and ethylcellulose are now commercially prepared from bleached sulfite pulp which usually has a lower degree of polymerization than cotton or cotton linters.

That the alkyl groups are more uniformly distributed in cellulose ethers of higher degrees of substitution seems to be shown by data obtained by Okamura [133] with commercial ethylcellulose (49.4 per cent ethoxyl). By adding increasing quantities of water to the solution of the (water-insoluble) ethyl cellulose in glacial acetic acid,[134] a number of fractions was obtained, the ethoxyl content of which varied relatively little, whereas the degree of polymerization was quite different. The results are shown in Table 53.

TABLE 53

ETHOXYL CONTENT AND MOLECULAR WEIGHT OF FRACTIONS OF ETHYL CELLULOSE

	Unfractionated	I	II	III	IV	V
Ethoxyl content, %	49.37	49.24	49.36	49.56	48.67	46.86
Molecular weight *	63,000	47,600	26,600	18,200	15,200	14,300

* Derived from osmotic pressure data.

Hydrolysis as a Means of Determining the Distribution of Substituents in Cellulose Ethers. Further information on the distribution of alkyl groups in cellulose ethers may be obtained by hydrolysis. Under the action of hydrolyzing agents, the ethers are broken down to a mixture of alkylated monomeric sugars which may be separated into the individual components of different degrees of substitution. The usefulness of this technique is based upon two facts: On hydrolysis and, at least in part, in contrast to the behavior of cellulose esters, (1) the substituents are not removed and (2) the substituents do not change their original positions.

On complete hydrolysis of partially methylated cellulose, a mixture of methylated glucoses (possibly with unmethylated glucose) is obtained which subsequently may be separated into mono-, di-, and trisubstituted glucoses (and unsubstituted glucose). The yield of each

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[132] Staudinger and Schulz, *Ber.*, **68**, 2327 (1935); as for values derived from viscosity data of commercial ethylcellulose preparations, see Mahoney and Purves, *J. Am. Chem. Soc.*, **64**, 11, 15 (1942).

[133] Okamura, *Cellulosechem.*, **14**, 135 (1933); see also Staudinger and Reinecke, *Ann.*, **535**, 52 (1938), who used water as a precipitating agent for solutions of commercial methylcellulose in dioxane.

[134] It was assumed that the use of this solvent did not result in acetylation of unsubstituted hydroxyl groups.

of the three or four compounds reflects the proportion in which mono-, di-, and trisubstituted cellulose (and unsubstituted cellulose) chains were present in the original ether.

This technique was first applied by Denham and Woodhouse.[135] On hydrolysis of methylated cellulose with 24–26 per cent methoxyl content (with highly concentrated hydrochloric acid, according to Willstätter and Zechmeister's method), a mixture of trimethyl-, dimethyl-, and monomethylglucose was obtained. Although the yields of the various products and of unmethylated glucose were not determined, the results show that the hydroxyl groups of cellulose reacted in an irregular manner, in some chains only one, in others two, and in still others all three hydroxyl groups being methylated. This conclusion appears to be well confirmed by the results obtained by subsequent investigators. On the hydrolysis of a commercial methylcellulose, containing 24.4 per cent methoxyl, 34.7 per cent monomethyl-, 41.2 per cent dimethyl-, and 9.3 per cent trimethylglucose, besides 14.7 unmethylated glucose, were obtained.[136]

In agreement with the observation that the distribution of methoxyl groups becomes more regular as the degree of substitution increases, hydrolysis of methylcellulose containing 42.5 per cent methoxyl resulted in a mixture of tri- and dimethylglucose, with monomethylated glucose and unmethylated glucose no longer present.[137] An only slightly higher methoxyl content increased the uniformity of distribution quite considerably. Thus, methylcellulose of 43.8 per cent methoxyl yielded on hydrolysis 86 per cent trimethylglucose (quoted in percentage of the theoretical amount and referring to an analytically pure product) and a small amount of dimethylglucose, which corresponded to the margin of deficiency (2.6 per cent) in the methoxyl content of the methylcellulose used.[138] Methylcellulose of a still higher methoxyl content, namely, 45 per cent (obtained from alkali-soluble cellulose *A*), yielded practically only trimethylglucose.[139]

X-ray analysis seems to indicate the presence of trimethylcellulose in preparations with methoxyl contents even much below the range mentioned above. Indeed, it was found that methylated cellulose of as low a methoxyl content as 3 per cent yielded some trimethylglucose,[140] on hydrolysis.

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[135] Denham and Woodhouse, *J. Chem. Soc.*, **105**, 2363 (1934).
[136] Traube, Pivonka, and Funk, *Ber.*, **69**, 1487 (1936).
[137] Karrer and Escher, *Helv. Chim. Acta*, **19**, 1192 (1936).
[138] Irvine and Hirst, *J. Chem. Soc.*, **123**, 521, 528 (1923).
[139] Hess and Weltzien, *Ann.*, **442**, 49 (1925).
[140] Hess, Trogus, Eveking, and Garthe, *Ann.*, **506**, 267, 273 (1933).

However, under certain special conditions, substitution seems to arrest itself at only 1 hydroxyl group. Three such cases are known. On hydrolysis of preparations containing 9–11 per cent methoxyl (obtained by quick methylation, see p. 383), only monomethylglucose and unmethylated glucose were obtained.[141] Likewise, a preparation with 6.16–8.45 per cent methoxyl content (corresponding to 0.35–0.48 methoxyl group per glucose residue), which had been prepared by methylations of copper-thallium cellulose (p. 394), yielded, on hydrolysis, only monomethylglucose and unmethylated glucose. Finally, the monomethylcellulose having 1 methoxyl group per 2 glucose units (9.13 per cent methoxyl), which resulted from the methylation of cellulose xanthate with diazomethane (p. 395), gave, on hydrolysis with sulfuric acid, a mixture of monomethylglucose and unmethylated glucose.[142] Similar results were obtained with methylated cellulose prepared from copper-alkali cellulose (p. 383).

However, with increasing degree of substitution an increasing number of chains becomes disubstituted. The quantities of mono-, di-, and trisubstituted, as well as of unsubstituted, glucose isolated from the mixture of products of hydrolysis are shown in Table 54.[143]

TABLE 54

MONO-, DI-, AND TRISUBSTITUTED GLUCOSE FROM HYDROLYSIS OF METHYLCELLULOSE

CH_3O of Methylated Cellulose, %	Unmethylated Glucose, %	Monosubstituted Glucose, %	Disubstituted Glucose, %	Trisubstituted Glucose, %
13.0	30.2	61.8	8.0	Not Identifiable
14.1	25.6	63.2	11.1	" "
16.0	23.1	62.3	14.6	" "
16.0	23.9	57.3	18.8	" "
34.6 *	Not determined	21.0	52.5	26.3

* By remethylation.

A summary of the data discussed above (except for the first four columns of Table 54) is presented in Table 55.

No doubt, a more complete picture could be obtained by subjecting cellulose to step-wise methylation and by ascertaining the results of hydrolysis after each step.[144] In the same way, an idea could be obtained of the distribution of

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[141] Traube, Pivonka, and Funk, *loc. cit.*, pp. 1483, 1486.

[142] Lieser, *Ann.*, **470**, 104 (1929).

[143] Traube, Pivonka, and Funk, *loc. cit.*

[144] See Hess, Trogus, Eveking, and Garthe, *Ann.*, **506**, 270, 290 (1933), who, however, determined only the amounts of unmethylated glucose corresponding to the amounts of unreacted cellulose.

TABLE 55

SUMMARY OF DATA ON HYDROLYSIS OF METHYLCELLULOSE PREPARATIONS

Investigated by	CH_3O in Methylated Cellulose, %	Monosubstituted Glucose, %	Disubstituted Glucose, %	Trisubstituted Glucose, %	Unsubstituted Glucose, %
Hess, Trogus, Eveking, and Garthe	9–11	50	Absent	Absent	50
Denham and Woodhouse	24–26	Yield not determined	Yield not determined	10	Yield not determined
Traube, Pivonka, and Funk	24.4	34.7	41.2	9.3	14.7
Traube, Pivonka, and Funk *	34.6	21.0	52.5	26.3	Not determined
Karrer and Escher	42.5	Absent	Relatively small amount	Most of the glucose present in this form	Absent
Irvine and Hirst	43.8	Absent	Possibly 14%	86.0	Absent
Hess and Weltzien	45.0	Absent	Probably absent	90.0	Not determined

* By remethylation.

methoxyl groups in fractions of partially methylated cellulose preparations, resulting from the methods of fractionation mentioned earlier in this section.

Instead of hydrolysis, *acetolysis* may be used as a means of breaking down the methylated cellulosic material. As a result, acetylated alkyl glucoses of varying acetyl and alkyl contents are obtained. In these products, the acetyl groups cover the hydroxyl groups which were left free on the partial methylation of cellulose, as well as those which were set free under the hydrolyzing influence of the acetylating mixture. Determination of the positions of the acetyl groups in the products of acetolysis (which may be estimated as in other acetylated alkyl sugars[145]) would permit distinction between the positions of the hydroxyl groups which were the result of the breakdown of the chains and the positions in which hydroxyl groups remained unsubstituted on methylation. (See also p. 389.)

Another method of breaking down the methylated chains may consist in first acetylating the partially methylated cellulose and then subjecting the mixed derivative to methylalcoholysis in the presence of hydrogen chloride. Compton [146] applied this technique to a low-substituted methyl cellulose (12–16 per cent methoxyl, corresponding to 0.7–0.9 CH_3O groups, prepared by dissolving the cellulose in dimethyldibenzylammonium hydroxide and subjecting it in this solution to the action of dimethyl sulfate) and obtained a mixture of 30–35 per cent α- and β-methylglucosides and 65–70 per cent of a mixture of partially methylated and acetylated methylglucosides. The latter were separated by dis-

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[145] See, for example, Micheel and Hess, *Ber.*, **60**, 1903 (1927), regarding the conversion of 2,3,6-trimethylglucose into 2,3,6-trimethyl-1,4-diacetyl-β-glucose; also Hess and Wittelsbach, *Z. Elektrochem.*, **26**, 232, 244, 250 (1920); *Ber.*, **54**, 3232 (1921); Hess, *Ann.*, **506**, 295 (1933).

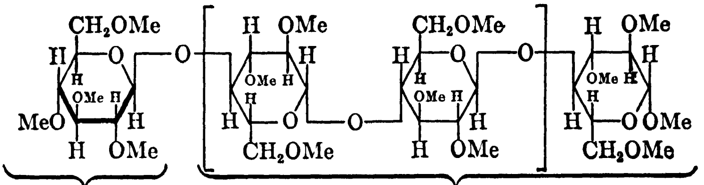
[146] Compton, *J. Am. Chem. Soc.*, **60**, 2823 (1938).

tillation in the high vacuum into dimethyldiacetylmethylglucoside, 2-methyltriacetyl-α-methylglucoside, and tetraacetyl-β-methylglucoside.

If acetolysis is not carried to completion, cellotriose and cellobiose (in their acetylated and alkylated form) are obtained. Thus, acetolysis of trimethylcellulose at 15° was found to yield 18 per cent heptamethyl-β-methylcellobioside, and 15 per cent decamethyl-β-methylcellotrioside[147] (besides 15 per cent tetramethylmethylglucoside).

Cleavage of ethylcellulose (2.5 OC_2H_5 groups per glucose unit) with ethyl bromide and hydrogen bromide resulted in the formation of bromodiacetyldiethylglucose.[148]

The Formation of Tetramethylglucose. On the assumption that cellulose represents an association of open chains, one of the terminating units of each chain would lend itself to the formation of a tetramethylglucose unit. Hence, on hydrolysis, a certain small amount of tetramethylglucose may be expected. With fully methylated cellulose, the only other main product of hydrolysis would be trimethylglucose as indicated in the formula



Hydrolysis gives tetramethylglucopyranose.

Hydrolysis gives 2,3,6-trimethylglucose and MeOH.

It should be recalled that, on the action of dimethyl sulfate and alkali upon cellulose, the potential reducing groups also become methylated (glucoside formation); this is the reason that methylcellulose, even if originating from considerably degraded cellulose, possesses no reducing power.[149] The fact that even partially methylated cellulose lacks reducing power seems to indicate that glucosidification of the free reducing groups occurs simultaneously with the methylation of the alcoholic hydroxyl groups. However, under the influence of hydrolyzing acids the glucosidically combined methoxyl groups are cleaved off, whereas the alcoholic methoxyl groups remain.

Although Denham and Woodhouse[150] believed to have had indications of the presence of a "trace" of tetramethylglucose among the products of hydrolysis of their partially methylated cellulose (24–26 per cent methoxyl), later investigators have searched for this com-

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[147] Haworth, Hirst and Thomas, *J. Chem. Soc.*, 824 (1931).

[148] Hess, *Ann.*, **506**, 295 (1933).

[149] Heuser and von Neuenstein, *Cellulosechem.*, **3**, 94 (1922); see also Zemplén, *Ber.*, **58**, 2566 (1925).

[150] Denham and Woodhouse, *J. Chem. Soc.*, **105**, 2359 (1914).

pound in vain.[151] However, Haworth and Machemer[152] established the existence of tetramethylglucose among the products of hydrolysis of highly methylated cellulose (45 per cent methoxyl content) without doubt, and their result was confirmed by other investigators of the Haworth school.[153] On the other hand, Hess and co-workers showed that the formation of tetramethylglucose observed by Haworth and co-workers was a result of the high degree of degradation of the cellulose constituent of their methylcellulose.[154] Indeed, Hess and co-workers found that cellulose, such as unbleached ramie fiber, carded cotton, and the like, which is hardly degraded at all, yielded considerably less tetramethylglucose,[155] whereas the quantities obtained from cellulose regenerated from viscose and from a solution of cellulose in concentrated sulfuric acid were considerably higher.[156] Moreover it could be demonstrated that the quantities of tetramethylglucose which were obtained from the practically undegraded cellulosic materials owed their formation to degradation during methylation. When this latter source of degradation was eliminated (by allowing methylation to proceed in a nitrogen atmosphere), no tetramethylglucose was found.[157]

Hess and co-workers have interpreted their results to mean that either the chains of untreated (i.e., practically undegraded) native cellulose are so long that even the most perfect method[158] does not permit the detection of the correspondingly very small number of tetramethylglucose units in the product of hydrolysis, or that the chain molecules in cellulose are not terminated but are arranged in some type of a ring structure. Hess and co-workers are inclined to accept the latter possibility as the more probable explanation.[159]

The observation that no tetramethylglucose is obtained from prac-

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[151] Hess and Weltzien, *Ann.*, **442**, 49 (1925); Freudenberg and Braun, *ibid.*, **460**, 289 (1928).

[152] Haworth and Machemer, *J. Chem. Soc.*, 2270 (1932); Haworth and Hirst, *Trans. Faraday Soc.*, **29**, 14 (1933).

[153] Averil and Peat, *J. Chem. Soc.*, 1244 (1938); Hirst and Young, *ibid.*, 1247 (1938); Hirst, *J. Textile Inst.*, **27**, 159P (1936).

[154] Hess and Neumann, *Ber.*, **70**, 710 (1937).

[155] Hess and Neumann, *loc. cit.*, p. 728.

[156] Hess, Grigorescu, Steurer, and Frahm, *Ber.*, **73**, 505 (1940); Hess and Jung, *ibid.*, **73**, 980 (1940).

[157] Hess and Neumann, *loc. cit.*; Leckzyck, *ibid.*, **71**, 829 (1938).

[158] Neumann and Hess, *Ber.*, **70**, 721 (1937); Hess and Grigorescu, *Ber.*, **73**, 499 (1940); see also Neumann, *ibid.*, **70**, 734 (1937).

[159] See also Meyer, *Ber.*, **70**, 274 (1937).

tically undegraded cotton, if methylation is allowed to take place in a nitrogen atmosphere, was recently confirmed by Haworth and his school.[160] However, this result was in contrast to that derived from viscosity and osmotic pressure measurements, which indicated that, in spite of the use of nitrogen, degradation had occurred during methylation. When methylation was allowed to take place in the air, tetramethylglucose was obtained.[161] For an explanation of this discrepancy see p. 581.

The Positions Occupied by the Alkoxyl Groups in Cellulose Ethers. The location of the methoxyl groups in trimethylcellulose in the 2-, 3-, and 6-positions of the glucose residues which had been made probable by Denham and Woodhouse was more firmly established by Haworth and Leitch[162] and confirmed by Irvine and Hirst.[163] Likewise, it was found that the three ethoxyl groups in triethylcellulose occupy the 2-, 3-, and 6-positions.[164]

The results obtained by Karrer and Escher,[165] discussed earlier in this chapter (p. 389), have shown that methylcellulose of a methoxyl content corresponding to the dimethylcellulose stage, contained the 2 methoxyl groups in the 2- and 3-positions. It will be recalled that, on hydrolysis with subsequent tosylation, 2,3-dimethyl-4,6-ditosylglucose was obtained.

The position of the methoxyl group in monomethylglucose resulting from hydrolysis of low-substituted cellulose seems to vary with the nature of the starting cellulosic material and the method of methylation. Thus, the small amount of monomethylglucose obtained on methylation of cellulose xanthate and subsequent hydrolysis contained the methoxyl groups in the 2-position (p. 395). On the other hand, the mixture obtained on hydrolysis of a methylcellulose with 9–11 per cent methoxyl content was found to contain a monomethylglucose with the methoxyl in the 2-position as well as one with the methoxyl either in the 3- or the 6-position.[166] Hydrolysis of a preparation which had been obtained by partial methylation with sodium metal

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[160] Haworth, Hirst, Owen, Peat, and Averill, *J. Chem. Soc.*, 1885 (1939); Haworth, Montonna and Peat, *ibid.*, 1899 (1939).

[161] Haworth, *J. Soc. Chem. Ind.*, **58**, 917 (1939).

[162] Haworth and Leitch, *J. Chem. Soc.*, **113**, 193 (1918).

[163] Irvine and Hirst, *J. Chem. Soc.*, **121**, 1213 (1922); **123**, 518, 529 (1923).

[164] Hess, Wittelsbach, and Messmer, *Z. angew. Chem.*, **34**, 449 (1921); Hess and Salzmann, *Ann.*, **445**, 111 (1925); Hess and Müller, *Ann.*, **466**, 94 (1928); see also **455**, 205 (1927); and Mahoney and Purves, *J. Am. Chem. Soc.*, **64**, 14 (1942).

[165] Karrer and Escher, *Helv. Chim. Acta*, **19**, 1192 (1936).

[166] Hess, Trogus, Eveking, and Garthe, *Ann.*, **506**, 278, 279 (1933).

and methyl iodide in liquid ammonia yielded a considerable proportion of 2-methylglucose.[167]

The statement that the hydrolysis of methylcellulose prepared from copper alkali cellulose resulted in monomethylglucose with the methoxyl in the 3-position exclusively[168] has later been corrected to the extent that 2-monomethylglucose was also formed.[169] Again, the only methylated sugar which resulted from the hydrolysis of methylcellulose with 5–9 per cent methoxyl (prepared by the action of anhydrous methyl sulfate upon potassium hydroxide cellulose) was 2-methylglucose.[170]

Summing up the data available, it would appear that in low-substituted methylcellulose the methoxyl groups are chiefly located in the 2- and 3-positions and that the 2-position is preferred. It is surprising that, in no instance, did methylation preferentially occur in the 6-position, since this hydroxyl group has been shown to be the most reactive group in disaccharides—for example, in cellobiose[171] and in α- and β-glucosides.[172] This deviation in behavior seems to indicate that, in cellulose, the hydroxyl groups in the 6-position are, at least in part, shielded in some manner and become accessible only after alkylation has advanced to a certain stage. It is possible that these hydroxyl groups are involved in cross linkages between individual chain molecules, as has been postulated by Karrer (p. 389),[173] and that such linkages are broken only in the later stages of alkylation.

Such hindrances seem to be less operative when alkylation is allowed to take place with cellulose dissolved in a quaternary ammonium base, i.e., in a homogeneous system. Mahoney and Purves obtained data which seem to indicate that, in this case, the reactivity of the primary hydroxyl groups was approximately twice as great as the average of the two secondary ones.

To differentiate between unsubstituted groups in the 6- and those in the 2- and 3-positions in partially alkylated cellulose, Mahoney and Purves[174] applied the same principle to a commercial ethylcellu-

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[167] Schorigin and Makrowa-Semljanskaja, *Ber.*, **69**, 1713 (1936).

[168] Traube, Pivonka, and Funk, *Ber.*, **69**, 1483 (1936); Pivonka, *ibid.*, **69**, 1965 (1936); Spurlin, *J. Am. Chem. Soc.*, **61**, 2222 (1939).

[169] Heddle and Percival, *J. Chem. Soc.*, 249 (1939).

[170] Heddle and Percival, *J. Chem. Soc.*, 1690 (1938).

[171] Percival and Ritchie, *J. Chem. Soc.*, 1765 (1936).

[172] Heddle and Percival, *loc. cit.*

[173] See also Heddle and Percival, *J. Chem. Soc.*, 249 (1939); Cox, *Annual Reports*, **34**, 189 (1937); Mahoney and Purves, *J. Am. Chem. Soc.*, **64**, 18 (1942).

[174] Mahoney and Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942).

lose that Cramer and Purves[175] had applied to secondary cellulose acetates (p. 260)—i.e., tosylation with subsequent iodination. The ethylcellulose investigated had 2.48 ethoxyl groups and 0.52 unsubstituted hydroxyl group per glucose residue. It was found that 29 per cent of the unsubstituted hydroxyl groups were in the 2-position, 47 per cent in the 3-, and 24 per cent in the 6-position.

The distribution of unsubstituted hydroxyl groups in a number of other cellulose ethers is given in Table 56. In this table[176] are listed

TABLE 56

DISTRIBUTION OF UNSUBSTITUTED HYDROXYL GROUPS IN CELLULOSE ETHERS

Alkoxyl, %	Degree of Substitution (Groups per $C_6H_{10}O_5$)	D.P. (Viscosity Method)	Solubility at 0°	Unsubstituted Groups, Total per $C_6H_{10}O_5$	In the 2- and 3-Positions	In the Primary Position
48.5	2.48	120	Organic solvents	0.52	0.40	0.12
30.5	1.85	150	Water	1.15	0.66	0.49
10.7	0.588	210	Caustic soda	2.41	1.67	0.74
14.7	0.583	300	Water	2.42	1.71	0.71
27.6	1.20	425	Water	1.80	1.16	0.64
17.5	0.707	...	Caustic soda	2.29	1.59	0.70

also the average chain length (D.P.) and the solubility of the ethers in organic solvents, in water, and in caustic soda solution. The data in the first line are those of the ethylcellulose mentioned above.

METHYLENE ETHERS (ACETALS) OF CELLULOSE

Methylene ethers (acetals) of cellulose may be obtained by allowing formaldehyde or aliphatic methylene ethers or methylal to react upon alkali cellulose.

The reaction of formaldehyde with cellulose has its parallel in the action of this aldehyde upon *d*-glucose, which leads to methyleneglucose (Tollens), the mechanism being that of acetal formation. Since acetals are rather sensitive to water, a dehydrating medium must be used. By heating cellulose at 100° with acetic anhydride and the propyl or isopropyl acetal of formaldehyde (formal)—a combination

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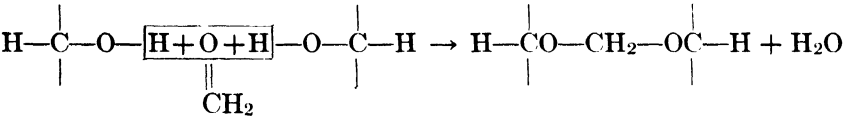
[175] Cramer and Purves, *ibid.*, **61**, 3458 (1939).

[176] Mahoney and Purves, *J. Am. Chem. Soc.*, **64**, 16 (1942).

which liberates formaldehyde easily—approximately 8 per cent of methylene radical may be introduced; this indicates that 1 methylene group is in combination with 2 hydroxyl groups per one $C_6H_{10}O_5$ unit.[177] Under the influence of the acetic anhydride, partial acetylation takes place, but the respective hydroxyls may be regenerated with dilute alkali, and an acetyl-free methylene ether of cellulose is obtained.

With dichlorodimethyl sulfate, $(ClCH_2O)_2SO_2$, or similar esters which contain the —CH_2O group, it is possible to increase the methylene content considerably (17.2 per cent CH_2O),[178] whereas by the action of methylal $[CH_2(OCH_3)_2]$, a product containing about 7 per cent CH_2O is obtained.[179]

Since, for steric reasons, it is rather improbable that "methylenation" takes place on —CHOH groups of glucose residues of one and the same chain[180] (for example, on those in the 2- and 3-positions) lying in different planes, it appears more likely that two hydroxyls of *neighboring* chains join in this reaction, possibly according to the following scheme:



$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}O{-}}\underset{\underset{\mathrm{CH_2}}{\|}}{\boxed{\mathrm{H+O+H}}}\mathrm{{-}O{-}\overset{|}{\underset{|}{C}}{-}H} \rightarrow \mathrm{H{-}\overset{|}{\underset{|}{C}}O{-}CH_2{-}O\overset{|}{\underset{|}{C}}{-}H} + \mathrm{H_2O}$$

This concept of the reaction may explain the fact that only a small amount of methylene radical in cellulose suffices considerably to reduce or entirely to eliminate its ability to swell in water. As a result, the fibrous methylene ethers may be so brittle that they may be pulverized. Likewise, with increasing methylene content, the ethers become more and more insoluble in cuprammonium solution, do not react with alkalies to form alkali cellulose, and fail to undergo the xanthate reaction.

Cellulose methylene ethers which swell in water are said to be obtained by treating cellulose with strong sulfuric acid in the presence of formaldehyde.[181] Possibly, the ability of the formaldehyde to reduce the swelling of the fiber is counteracted by the swelling effect exerted by the strong acid.

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[177] Schenk, *Helv. Chim. Acta,* **14,** 527 (1931); **15,** 1088 (1932).

[178] Wood, *J. Soc. Chem. Ind.,* **50,** 411T (1931).

[179] Schorigin and Rymaschewskaja, *Cellulosechem.,* **14,** 81 (1933).

[180] Meunier and Gyot, *Compt. rend.,* **188,** 506 (1929).

[181] Foulds and Barrett, British patent 200,881 (1923); Spietel and Schenk, *Bull. Soc. Ind. Mulhouse,* **50,** 109 (1934).

The reaction between cellulose and formaldehyde in the presence of organic and inorganic acids has been utilized as a means of improving the water resistance and strength properties of textile fibers and fabrics. The process, a modification of which is termed "Sthenosage,"[182] has been patented by Eschalier[183] but was of no lasting success.

Again, it has been claimed that an aqueous formaldehyde solution exerts a swelling effect upon cellulose fibers when both are beaten together for a certain length of time.[184]

The various, apparently contradictory, results await an explanation.

GLYCOLIC ACID ETHER OF CELLULOSE

Cellulose derivatives of this type are obtained by the action of monochloroacetic acid upon alkali cellulose[185] (see p. 284). Obviously, this reaction is analogous to the formation of ethylglycolic acid from monochloroacetic acid and sodium ethylate and may therefore be expressed by the following equation:

$$C_6H_9O_4ONa + ClCH_2COOH = NaCl + C_6H_9O_4OCH_2COOH$$

The reaction product is thus an ether acid and, hence, on drying, may form a lactone (with the participation of an unetherified hydroxyl group of the chain). That we are actually dealing with the cellulose ether of glycolic acid is seen from the fact that, on the action of phosphorus triiodide and water, glycolic acid ($CH_2OHCOOH$) is liberated. A small amount of acetic acid is also formed, which may be a result of the reduction of part of the glycolic acid.[186]

The glycolic acid ethers of cellulose lend themselves to salt formation with alkalies, as well as copper, lead, and zinc. The sodium salt is soluble in water.[187]

Since, as the formula shows, one hydrogen atom of a methyl group is replaced by a carboxyl group, Brown and Houghton[188] prefer the term "carboxymethylcellulose" rather than "celluloseglycolic acid" by which the derivative is more popularly known.

Sodium glycolates are finding more and more commercial uses.[189]

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[182] Karplus, German patent 382,086 (1923).

[183] Eschalier, French patent 347,724 (1906).

[184] Musser and Engel, *Paper Trade J.*, **115**, No. 8, 33 (1942).

[185] Jansen, German patent 332,203 (1921); see also Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 114.

[186] Chowdbury, *Biochem. Z.*, **148**, 85 (1924).

[187] Sakurada, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **8**, 96 (1929).

[188] Brown and Houghton, *J. Soc. Chem. Ind.*, **60**, 254 (1941).

[189] Höppler, *Chem. Ztg.*, **66**, 132 (1942).

The action of the homologues of chloroacetic acid results in the formation of similar compounds. Thus, chloropropionic acid yields the cellulose ether of lactic acid.[190]

In contrast to monochloroacetic acid, the action of its acid chloride on cellulose in the presence of pyridine seems to result in the formation of an ester:

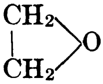
$$C_6H_9O_4OH + ClCOCH_2Cl = C_6H_9O_4OCOCH_2Cl + HCl$$

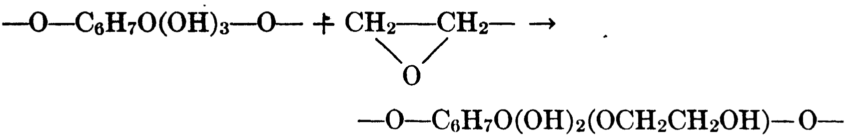
The monochloroacetate thus formed reacts with water to yield a glycolic acid *ester* of cellulose.[191]

$$C_6H_9O_4OCOCH_2Cl + H_2O = C_6H_9O_4OCOCH_2OH + HCl$$

Hydroxyalkyl Ethers of Cellulose

The possibilities of converting cellulose into ethers of interesting properties seems to be almost unlimited. Hydroxyl ethers were first mentioned in 1923.[192]

Ethylene oxide,  $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>O$, reacts with alkali cellulose to form "glycolcellulose" or hydroxyethylcellulose, a product of possible commercial value. It is soluble in water and acetic acid, but insoluble in acetone, alcohol, and ether. Since the simpler monosubstituted glycol ethers are soluble in water, it may be assumed that in hydroxyethylcellulose the ethylene oxide radical is present with a free hydroxyl group, —OCH_2CH_2OH. The reaction apparently is that of addition and may be formulated thus:



$$—O—C_6H_7O(OH)_3—O— + \underset{\diagdown\ O\ \diagup}{CH_2——CH_2}— \rightarrow$$

$$—O—C_6H_7O(OH)_2(OCH_2CH_2OH)—O—$$

Acetylation of the product formed leads to a triacetate in which 2 acetyls occupy the 2 free hydroxyl groups of the glucose residues and the third acetyl has entered the hydroxyethylene radical. It may be formulated thus:[193]

$$C_6H_7O_2(OCOCH_3)_2(OCH_2CH_2OCOCH_3)$$

Schorger and Shoemaker[194] studied the various factors which influence the rate and completeness of the reaction and developed a number of promising

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[190] Chowdbury, *Biochem. Z.*, **148**, 85 (1924).

[191] Barnett, *J. Soc. Chem. Ind.*, **40**, 253 (1921).

[192] Hubert, *J. Soc. Chem. Ind.*, **42**, 348 (1923).

[193] Schorigin and Rymaschewskaja, *Ber.*, **66**, 1014 (1933).

[194] Schorger and Shoemaker, *Ind. Eng. Chem.*, **29**, 114 (1937).

commercial applications, the principal aim having been to produce ethers which were soluble in dilute alkali. The ethers were found to be completely soluble in 5–6 per cent sodium hydroxide solution on freezing of the suspension. Under these conditions, water separates out in the form of ice crystals. As a result, the growth of the crystals within the fiber disrupts its structure so that it is peptized in the presence of sodium hydroxide. Under the microscope during thawing, the fibrils of the cellulose fibers may be seen unwinding and dispersing.

Hydroxyalkyl ethers of cellulose may also be prepared by allowing halogen hydrins of polyalcohols, such as, for example, glycol chlorohydrin to act upon alkali cellulose[195]:

$$C_6H_9O_4ONa + ClCH_2CH_2OH = NaCl + C_6H_9O_4OCH_2CH_2OH$$

Likewise, the action of glycerol α-monochlorohydrin upon alkali cellulose results in the formation of dihydroxypropyl cellulose ethers.[196]

The primary hydroxyl group of the alkoxy radical in the hydroxyalkyl ethers (see formulas above) enables them to take up additional ester and ether groups. The acetyl derivative of only slightly hydroxyethylated cellulose was found to be acetone-soluble.[197]

Methyl- and ethylcellulose, as well as some of the hydroxyalkyl ethers are prepared commercially and have found a considerable number of uses.[198] The water-soluble ethers are used in the preparation of adhesives, and of various types of emulsions and as thickening agents; the alkali-soluble products are used as sizing and coating agents in the textile[199] and in the paper[200] industry, and the higher substituted ethers are of interest in the plastics,[201] lacquer, and film industries.[202]

TRIPHENYLCARBINYL ETHER OF CELLULOSE

The reaction resulting in the formation of triphenylcarbinyl ethers of cellulose is apparently analogous to the action of triphenylchloromethane upon alcohols and upon certain sugars, such as α-methylglucoside, *d*-glucose, and *d*-galactose, and may therefore be formulated thus:

$$C_6H_9O_4ONa + ClC(C_6H_5)_3 \rightarrow C_6H_9O_4OC(C_6H_5)_3 + NaCl$$

Only 1 triphenylmethyl group seems to enter per glucose residue, when

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[195] Lilienfeld, U. S. patent 1,722,929 (1929).

[196] Schorger and Shoemaker, *loc. cit.*, p. 115.

[197] Schorger and Shoemaker, *loc. cit.*, p. 117.

[198] Conaway, *Ind. Eng. Chem.*, **30**, 516 (1938).

[199] Clark, *Cotton* (*Atlanta*) (July, Sept., 1938); Gorlik, *Textile World* (March, 1940).

[200] Upright and Peterson, *Paper Trade J.*, **110**, No. 18, 31 (1940).

[201] Kline and Malmberg, *Ind. Eng. Chem.*, **30**, 542 (1938).

[202] See also Lawrie, Reynolds, and Ward, *J. Soc. Dyers Colourists*, **56**, 6 (1940).

cellulose is heated with triphenylchloromethane in pyridine.[203] The ether, which dissolves in pyridine, and in chloroform and bromoform to viscous colloidal solutions, is very sensitive to acids (e.g., hydrochloric) and suffers cleavage to cellulose and triphenylmethyl chloride (or carbinol), respectively. The cellulose is said to have undergone scarcely any degradation during etherification. This, however, appears rather improbable.

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[203] Helferich and Koester, *Ber.*, **57**, 587 (1924); Helferich, Moog, and Jünger, *Ber.*, **58**, 872 (1925); see also Hearon, Hiatt, and Fordyce, American Chemical Society meeting, Detroit, April, 1943.

CHAPTER X

THE OXIDATION OF CELLULOSE

An inspection of the molecular structure of cellulose reveals at once that the hydroxyl groups may be attacked by oxidizing agents and converted into aldehyde and further into carboxyl groups. Provided the chains are open, the oxidant may also convert terminating reducing and hydroxyl groups and, finally, glycosidic linkages may be attacked which will give rise to the cleavage of longer into shorter chains.

It appears fairly safe to assume also that the secondary valence forces between individual chains, as well as primary valence cross linkages (if such actually exist in cellulose), are broken down under the influence of the oxidizing agent.

The facts that 1 of the 3 free hydroxyl groups in each glucose residue is of primary and 2 are of secondary nature, and that a third secondary hydroxyl group exists in one of the terminating units are likely to give rise to preferential attack.

Thus it is obvious that the oxidation of cellulose represents a rather complex phenomenon. Moreover, this complexity is enhanced by the peculiarities of the physical structure of cellulose which, in general, causes oxidation, like other cellulose reactions, to take a heterogeneous course. Indications are that most oxidizing agents attack the fiber in a topochemical fashion, that is, gradually advancing from layer to layer. However, unlike substitution reactions which practically come to a standstill when all available hydroxyl groups have reacted, oxidation may continue, and it will cease only when the entire organic matter has been converted into the final products of oxidation, carbon dioxide, and water. As a result, we may expect the primary products of oxidation, as they are formed on the surface layers of the fiber, to suffer further attack, unless they are removed from the areas of local reaction by mechanical agitation or extraction. Whereas in the earlier stages undisturbed oxidation may result in the breaking down of chain molecules on the surface of the fiber to products of lower molecular weight (even to those of monomeric character and further to carbon dioxide and water), deeper layers may be attacked less and still deeper portions may remain entirely unattacked, unless the oxidizing agent is given time to penetrate all layers to a sufficient degree.

This being the usual course of the oxidation reaction, most "oxycelluloses," as the reaction product was termed by its discoverer, Witz,[1] represent mixtures of products of varying degrees of oxidation and polymerization. When a sufficient number of chain molecules has been broken, the fiber has become friable and brittle and may easily be disintegrated into powder.

However, with some oxidizing agents, and depending upon the medium—i.e., whether acid, alkaline, or neutral—the oxidation of cellulose is confined to certain positions of the hydroxyl groups and seems to proceed partly or entirely without cleavage of glycosidic linkages. In addition, under such conditions the reaction seems to take a more homogeneous course, even if carried out with cellulose in fibrous form. On the other hand, a reaction which proceeds in heterogeneous fashion with cellulose in fibrous form may be made to take a more homogeneous course, if carried out with cellulose in solution. Thus far, only a few examples of oxycelluloses of these types are known. These are as follows.

1. The oxidation of cellulose dissolved in cuprammonium hydroxide with potassium permanganate leads to the formation of glucuronic acid units. These units appear to be still linked together in polymeric fashion until the product of reaction is converted into its cinchonine derivative.[2] The yield of about 10 per cent (on the weight of cellulose) in which this product of oxidation is obtained seems to indicate that, under the conditions mentioned, the reaction is, at least to a considerable extent, confined to the oxidation of primary alcohol groups to carboxyl groups. The chains which have been so oxidized would then represent polyglucuronic acid chains.

That glycosidic linkages may remain unattacked under certain conditions is quite within the realm of possibility. Whereas, under the influence of nitric acid, cellobiose suffers oxidation and cleavage, resulting in the formation of the dibasic saccharic acid (besides oxalic acid), the glycosidic linkage remains unattacked when bromine is the oxidizing agent, the result being cellobionic acid.

2. Under the action of periodic acid upon fibrous cellulose, only the hydroxyl groups in the 2- and 3-positions are oxidized, and diketone (dialdehyde) groupings are formed.[3] Glycosidic linkages seem to be broken down only to a limited extent, and the substantial yield in

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[1] Witz, *Bull. Rouen,* **10,** 447 (1882); **11,** 2210 (1883).

[2] Kalb and Falkenhausen, *Ber.,* **60,** 2514 (1927).

[3] Jackson and Hudson, *J. Am. Chem. Soc.,* **59,** 2049 (1937); **60,** 989 (1938).

which the product of oxidation is obtained seems to indicate that side reactions also take place only to a limited extent.

3. The two examples have recently been augmented by a third one of equal, if not even greater, scientific interest.[4] Nitrogen dioxide, allowed to act on dry cellulose at room temperature, preferentially converts primary hydroxyl groups into carboxyl groups and is said to leave glycosidic linkages unaffected.[5] Although the oxycellulose thus obtained possesses an apparently undamaged fibrous structure, it dissolves completely in 2 per cent sodium hydroxide solution. Cellulose in which all primary hydroxyl groups have been thus oxidized may be regarded, therefore, as an aggregate of polyanhydroglucuronic acid chains and, if only partially oxidized, as an aggregate of polyanhydroglucose and polyanhydroglucuronic acid chains.

It is noteworthy that older investigators, like Tollens [6] and Vignon,[7] imagined oxycellulose to be a combination of anhydroglucose and anhydroglucuronic acid chains, without, however, having been able to give satisfactory experimental proof for this concept.

OXYCELLULOSE REACTIONS

Most oxycelluloses have certain reactions in common, namely, those which indicate the presence of carbonyl groups, of carboxyl groups and of shortened chain molecules.

Reactions Indicative of the Presence of Carbonyl Groups

1. Most oxycelluloses possess pronounced *reducing power.* This property may be observed by their behavior with Fehling solution [8] or with hypoiodite solution,[9] as well as with silver nitrate solution either in the presence of thiosulfate and alkali [10] or in the presence of ammonia.[11] Any of these solutions may be used for determining the

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[4] Yackel and Kenyon, *J. Am. Chem. Soc.*, **64**, 121 (1942); Unruh and Kenyon, *ibid.*, **64**, 127 (1942).

[5] The degree of polymerization has not yet been determined.

[6] von Faber and Tollens, *Ber.*, **32**, 2600 (1899).

[7] Vignon, *Bull. soc. chim.*, [3] **21**, 599 (1899).

[8] Schwalbe, *Ber.*, **40**, 1347 (1907); Clibbens and Geake, *J. Textile Inst.*, **15**, T27 (1924); Knecht and Thompson, *J. Soc. Dyers Colourists*, **36**, 255 (1920). See also Dorée, "The Methods of Cellulose Chemistry," p. 31.

[9] Willstätter and Schudel, *Ber.*, **51**, 780 (1918).

[10] Harrison, *J. Soc. Dyers Colourists*, **28**, 359 (1912).

[11] Goetze, *Mell'and Textilber.*, **8**, 624 (1927); Haller, *Helv. Chim. Acta*, **14**, 578 (1931).

reducing power of oxycellulose quantitatively (see also p. 429). Table 57 contains some examples. The reducing power of the oxycellulose preparations is expressed as copper number.

TABLE 57 *

REDUCING POWER OF OXYCELLULOSES

Observer	Cellulosic Material	Oxidizing Agent	Copper Number
Schwalbe and Becker †	Cotton	Hypochlorite	11.0
Schwalbe and Becker †	Cotton	Permanganate	8.0
Schwalbe §	Filter paper	Bleach powder	7.9; 7.6
Schwalbe §	Cotton	Hydrogen peroxide	5.8
Dorée **	Cotton	Ozone	14.96; 16.9
Hibbert and Hassan ‡	Cotton	Chromic acid	24–27
Oertel §§	Cotton	Electrolysis	39.5

* From Dorée, "The Methods of Cellulose Chemistry," p. 125.

† Schwalbe and Becker, *Ber.*, **54**, 545 (1921); *Z. angew. Chem.*, **31**, 50 (1918); *Zellstoff u. Papier*, **1**, 4, 100, 135 (1921).

§ Schwalbe, *Ber.*, **40**, 1347, 4523 (1907).

** Dorée, *J. Soc. Dyers Colourists*, **29**, 205 (1913).

‡ Hibbert and Hassan, *J. Soc. Chem. Ind.*, **46**, 409T (1927).

§§ Oertel, *Z. angew. Chem.*, **26**, 246 (1913); doctoral dissertation, Hanover (1912).

2. The reducing power of oxycellulose may be demonstrated in several other ways, for example, by substituting this preparation for hydrosulfite in the process of reducing the alkaline suspension of a vat dye to its leuco base. Thus, oxycellulose may be used in the reduction of indigo,[12] indanthrene,[12] flavanthrene,[13] etc.

3. Another way of demonstrating the presence of carbonyl groups in oxycellulose is to allow it to react with phenylhydrazine under certain conditions.[14] Although this test does not seem to be very reliable as a quantitative measurement,[15] it is very useful for identifying oxycellulose in fabrics.[16]

4. The presence in oxycellulose of aldehyde groups is revealed by the pronounced golden yellow coloration which the product shows when boiled for a short time with dilute caustic soda solution. On longer boiling, the color is taken up by the solution.

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[12] Knecht and Thompson, *loc. cit.*, p. 251. Ermen, *J. Soc. Dyers Colourists*, **28**, 132 (1912); Haller, *loc. cit.*

[13] Scholl, *Ber.*, **44**, 1312 (1911).

[14] Nastukoff, *Bull. Mulhouse*, **62**, 493 (1892); Knecht, *Melliand Textilber.*, **6**, 507 (1925); see also Heuser, "Lehrbuch des Cellulosechemie," 3rd ed., p. 124.

[15] Dorée, "The Methods of Cellulose Chemistry," p. 125.

[16] Müller, *Helv. Chim. Acta*, **22**, 208, 217, 376 (1939).

5. A recent suggestion for the estimation of carbonyl groups in certain oxycellulose types is based upon the reaction of such groups with hydroxylamine hydrochloride.[17] Aqueous solutions of this agent are known to form oximes with many simple aldehydes and ketones:

$$RC{=}O + H_2NOH \cdot HCl \rightarrow RC{=}NOH + H_2O + HCl$$

The hydrochloric acid liberated may be titrated, using bromphenol blue in alcohol as an indicator, and is a measure of the carbonyl content of the oxycellulose. The accuracy of this estimation is 5 per cent.

Reactions Indicating the Presence of Carboxyl Groups

1. The acidity of oxycellulose may be measured by *titrating* an aqueous suspension with alkali in the presence of an indicator. Schwalbe and Becker[18] found that the acidity (expressed in percentage of COOH, calculated on the weight of the sample) of various oxycellulose preparations ranged from 0.30 to 1.32 per cent, whereas the titration of unoxidized cellulose as well as of hydrocellulose yielded much lower values (0.03 and 0.04 per cent COOH, respectively). These differences thus permit the differentiation between oxy- and hydrocellulose and unmodified cellulose.

Instead of titrating the carboxyl groups directly, Lüdtke[19] has suggested the addition of an excess of calcium acetate solution to the aqueous suspension and titration of the acetic acid (which is liberated by the carboxyl groups of the oxycellulose to the extent of an equivalent quantity) with very dilute sodium hydroxide solution, using phenolphthalein as indicator. As an example, Lüdtke[20] found an "acid number" (expressed in cubic centimeters of $N/100$ acid produced by 1 gram of the sample) of 2.45 for cotton which had been bleached by successive treatments with 0.1 per cent chlorine water and 0.5 per cent ammonia.

Lüdtke's method was modified in different ways by subsequent investigators—by Heymann and Rabinow[21] and by Yackel and Kenyon.[22] The latter found

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[17] Gladding and Purves, *Paper Trade J.*, **116**, No. 14, 26 (1943).

[18] Schwalbe and Becker, *Ber.*, **54**, 545 (1921); see also Karrer and Lieser, *Cellulosechem.*, **7**, 1 (1926); Heuser and Stöckigt, *ibid.*, **3**, 61 (1922); Dorée, "The Methods of Cellulose Chemistry," p. 122.

[19] Lüdtke, *Biochem. Z.*, **268**, 372 (1934); *Papier-Fabr.*, **32**, 509, 528 (1934); *Angew. Chem.*, **48**, 650 (1935).

[20] Lüdtke, *Biochem. Z.*, **285**, 78, 82 (1936).

[21] Heymann and Rabinow, *Trans. Faraday Soc.*, **38**, 209 (1942); see also *J. Phys. Chem.*, **45**, 1152 (1941), and Rabinow and Heymann, *ibid.*, **45**, 1167 (1941).

[22] Yackel and Kenyon, *J. Am. Chem. Soc.*, **64**, 121 (1942).

values ranging from 6.6 to 18.6 per cent of COOH for nitrogen dioxide oxycelluloses, depending upon the length or severity of the treatment.

The acidic groups in oxycellulose (and cellulose) may also be estimated by conductometric titration. A comparison of the results of this method with those obtained with the calcium acetate method was made by Heymann and Rabinow.[23]

Lüdtke has also proposed and used another method for the estimation of carboxyl groups in cellulose and oxidized cellulose. A mixture of potassium iodate and potassium iodide reacts with a mineral acid (e.g., hydrochloric) in the following way:

$$KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O$$

With an organic instead of a mineral acid, an equilibrium is reached, depending upon the hydrogen-ion concentration. On the assumption that, in this reaction, the carboxyl groups in cellulose represent the organic acid, the iodine liberated is equivalent to the carboxyl groups present. The iodine is titrated with thiosulfate solution. The advantage of this method is seen in the absence of absorption and other interfering colloidal phenomena which are present in the use of alkali. It was found that acid numbers thus determined for various cellulosic materials were of the same order of magnitude as those produced by the calcium acetate method. The method has only seldom been used, and Lüdtke himself seems to prefer the calcium acetate method.

The first attempt to determine the acidic groups in cellulose by conductometric titration was made by Schmidt and co-workers.[24] The method has recently been improved by Neale and Stringfellow[25] and by Heymann and Rabinow.[26]

According to Neale, the values for the carboxyl content of cellulose and oxycellulose preparations obtained with Schwalbe and Becker's direct titration method, with Lüdtke's calcium acetate method, and with Schmidt's conductometric method are not very exact, the end point of the titrations being quite indefinite.[27] Neale gave sodium chloride preference over calcium acetate[28] and explained the effect of the electrolytes in the solution as follows: Whereas the carboxyl groups in cellulose and oxycellulose are ionized within the cellulose phase, the hydrogen ions are unable to escape into the external water, since the anions form part of the cellulose structure. Theoretical deliberations lead to the expectation that the constraint on the movement of the hydrogen ions would be overcome by the addition of a neutral electrolyte. If the Donnan membrane equilibrium is applicable in the presence of

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[23] Heymann and Rabinow, *Trans. Faraday Soc.*, **38**, 209 (1942).

[24] Schmidt and co-workers, *Ber.*, **60**, 503 (1927); **67**, 2037 (1934).

[25] Neale and Stringfellow, *Trans. Faraday Soc.*, **33**, 881 (1937).

[26] Heymann and Rabinow, *Trans. Faraday Soc.*, **38**, 209 (1942).

[27] Neale, *Nature*, **135**, 583 (1935).

[28] Lüdtke used neutral salt solutions before selecting calcium acetate—a salt which easily undergoes hydrolytic dissociation, Lüdtke, *Biochem. Z.*, **268**, 375 (1934).

excess of sodium chloride, the concentration of sodium ion and, therefore, that of hydrogen ion in the external solution should become equal to the respective concentration within the fiber.

Thus, in the presence of an excess of sodium chloride solution, more exact values for the presence of carboxyl groups in cellulose and oxycellulose should, according to Neale, be obtained. On the basis of these considerations Neale and Stringfellow[29] have suggested a method in which the mobilization of the hydrogen ions in the presence of sodium chloride is utilized. A number of oxycellulose preparations were investigated. Some of the results, together with that obtained with unoxidized cotton, are shown in Table 58. The carboxyl content is expressed in milliequivalents of COOH per 100 grams of cellulosic material.

TABLE 58

CARBOXYL CONTENT OF OXYCELLULOSE

(According to the Method of Neale and Stringfellow)

Materials	Standard Cotton Cloth	Oxycellulose (BrO)	Oxycellulose* (BrO)	Oxycellulose (Oxygen + NaOH)	Oxycellulose ($KMnO_4$, Na_2CO_3)
Carboxyl content	0.2	1.9	8.2	2.2	11.2

* From mercerized cotton.

Neale and Stringfellow's method was also applied by Nabar, Scholefield, and Turner[30] to oxycelluloses prepared with alkali hypochlorite solution.

Oxycellulose of sufficiently high carboxyl content, such as that prepared with nitrogen dioxide, may be dissolved in pyridine and directly titrated with dilute aqueous sodium hydroxide solution and phenolphthalein or it may be dissolved in a mixture of pyridine and dilute aqueous sodium hydroxide solution and the excess alkali titrated to the phenolphthalein end point with dilute aqueous sulfuric acid.[31]

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[29] Neale and Stringfellow, *Trans. Faraday Soc.*, **33**, 881 (1937); see also Hanson, Neale, and Stringfellow, *ibid.*, **31**, 1738 (1935); Brissaud, *Mém. poudres*, **28**, 43 (1938).

[30] Nabar, Scholefield, and Turner, *J. Soc. Dyers Colourists*, **53**, 5 (1937)

[31] Yackel and Kenyon, *loc. cit.*

Since the carboxyl groups may be present in the form of end groups, as well as in the glucose residues within the chains, it is reasonable to assume that on titration both types of carboxyl groups are determined together.

The reducing groups in the terminating units of the chains may have undergone oxidation before the cellulose is isolated from the plants, and it is probable that these carboxyl groups are in part combined with cations. The same may be true with respect to the other carboxyl groups—for example, as a result of the washing of the oxycellulose preparation with hard tap water. To obtain a correct value, it is necessary, therefore, to free the cellulose and oxycellulose preparations from all cations before an attempt is made to ascertain the total acidity by any of the titration methods.[32] The cations may be removed by treating the cellulosic material with mineral acid (for example, hydrochloric) and subsequently removing the acid and salts by careful and thorough washing with distilled water. Removal of cations may also be accomplished by electrodialysis (p. 586).

On the assumption that all carboxyl groups in cellulose are combined with cations, its acid-binding capacity becomes a means of estimating its acidity. Sookne and Harris [33] estimated the acidity of raw and purified cotton by thoroughly soaking the fibers in an excess of hydrochloric acid and by titrating the unconsumed portion of the acid with sodium hydroxide solution.

Another source of error may originate from the presence of pectic material in cellulose, which, as has been seen, is present to an appreciable extent in raw cotton. Hence, in cellulosic materials and in oxycelluloses prepared therefrom, from which the pectin has not been removed, carboxyl groups attached to the pectin are titrated together with the other types of carboxyl groups.[34]

2. The carboxyl end groups in cellulose may be regarded as belonging to gluconic acid units and, as such, as being more stable than the carboxyl groups belonging to glucuronic acid units. The latter undergo decarboxylation under the action of dilute hydrochloric acid. The carbon dioxide liberated from oxycellulose under the action of hydrochloric acid may be used as a measure of the degree of oxidation of hydroxyl groups in the 6-position.

Since the quantity of carbon dioxide liberated from oxycellulose is

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[32] Schmidt, *Ber.*, **67**, 2037 (1934).

[33] Sookne and Harris, *J. Research Natl. Bur. Standards*, **25**, 47 (1940); *J. Textile Research*, **10**, 405 (1940).

[34] Heuser and Stöckigt, *Cellulosechem.*, **3**, 62, 65 (1922); see also Sookne and Harris, *loc. cit.*

essentially greater than from cellulose[35] and from hydrocellulose, another method is available for the differentiation between cellulose and oxycellulose and between oxycellulose and hydrocellulose.[36] Some data taken from the work of Heuser and Stöckigt are shown in Table 59. The figures represent the percentage of COOH calculated on the dry weight of the cellulosic materials.

TABLE 59

CARBON DIOXIDE LIBERATED FROM OXYCELLULOSES

	Oxycellulose Prepared with					Cotton	Hydrocellulose
	H_2O_2	$KMnO_4$	CrO_3	$KClO_3$	HNO_3		
COOH %	0.29	0.65 1.04	1.32	0.66	0.97 0.83	0.026	0.04

The small amount of carbon dioxide liberated from the original cellulose may be due to slight oxidation during the purification of the cotton sample, to small pectin residues,[37] or to the decomposition of the glucose formed during the hydrolysis of the cellulose under the action of the boiling hydrochloric acid.[38] It was found that pure *d*-glucose, treated under the same conditions as the other preparations, liberated 0.04 per cent carbon dioxide. On the other hand, this amount is too small to influence the very considerable difference between oxidized and unoxidized cellulose.

Later investigators, however, found that *d*-glucose subjected to boiling with 10–12 per cent hydrochloric acid for 4 or more hours (under conditions which are usually employed for the determination of the uronic acid content of carbohydrates) yielded greater quantities of carbon dioxide than mentioned above. Thus Campbell, Hirst, and Young[39] found 0.4 per cent, Norman[40] 0.19 per cent,

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[35] Vignon, *Bull. soc. chim.*, [3] **19**, 811 (1898).

[36] Heuser and Stöckigt, *Cellulosechem.*, **3**, 61 (1922); see also Hibbert and Parsons, *J. Soc. Chem. Ind.*, **44**, 479T (1925); Nanji, Paton, and Ling, *J. Soc. Chem. Ind.*, **44**, 253T (1925).

[37] Carded cotton was purified by boiling with sodium hydroxide solution, bleached according to Schwalbe and Robinoff [Robinoff, doctoral dissertation, Darmstadt (1912), p. 19], and subsequently boiled with water in the autoclave for 1 hour at 2 atmospheres in order to lower the pectin content of the sample.

[38] The samples (about 2 grams) were boiled in a flask with reflux condenser with 100 cc. of 12 per cent hydrochloric acid for 3½–4 hours, while the carbon dioxide was sucked through a number of purification devices and neutralized with an excess of barium hydroxide solution.

[39] Campbell, Hirst, and Young, *Nature*, **142**, 192 (1938).

[40] Norman, *Nature*, **143**, 284 (1939).

and Whistler, Martin, and Harris[41] 0.38 per cent. The differences can probably be explained by the difference in experimental conditions, such as the concentration of the hydrochloric acid, the time of distillation, the size of the distillation apparatus in relation to the weight of the sample, the absorbing device, etc.

On the other hand, the values more recently obtained for cotton cellulose carefully freed of pectin—0.052 per cent[41] and 0.04–0.05 per cent[42]—are within the range found by Heuser and Stöckigt (0.026 per cent).

The higher figures found for esparto cellulose[40] (0.16 per cent) and for cotton cellulose[39] (0.17 per cent) can probably be explained by the use of incompletely purified cellulosic materials.

In view of the possibility of obtaining faulty results, a correction for cellulose should be made when the carbon dioxide values for oxycelluloses are determined. It would appear possible that the data for such a correction could be obtained by using the method worked out by Whistler, Martin, and Harris for the exact determination of uronic acid carbon dioxide in pectin-containing cellulosic materials. This method is based upon earlier observations of Norman.

Norman directed attention to the fact that the rate of carbon dioxide evolution from materials containing uronic acid groupings, such as pectin, is high at the beginning and that the evolution ceases after some time, whereas with glucose and carbohydrates containing no uronic acid groupings the rate is low in the beginning but the evolution continues at an approximately constant rate. Thus, the presence of uronic acid groupings may be inferred from a curve representing the rate of carbon dioxide evolution, a high initial rate indicating the presence of uronic acid groupings.

The principle of the method of Whistler, Martin, and Harris is illustrated in Fig. 89 which shows the difference in the rate of carbon dioxide evolution from galacturonic acid, glucose, and a known mixture of both. It is seen that the total amount of carbon dioxide evolved by the mixture at any time, as shown by curve *C*, is equal to the sum of the amounts evolved by each of the components in the same time, as shown by curves *A* and *B*. Conversely, it follows that the amount of carbon dioxide evolved from uronic acid groupings in this or similar mixtures may be readily estimated from the differences between the ordinates of the parallel portions of the curves *B* and *C*. The average of these differences is 20.5 mg. of carbon dioxide, whereas the theory requires 20.75 mg.

The application of the method to the determination of the uronic acid content of pectin-containing cotton (freed of wax by extraction with alcohol and with diethyl ether) is illustrated in Fig. 90. It is seen that the curve for pectin-freed cotton[43] is similar in shape to that of glucose (Fig. 89), indicating that purified cotton is free from a measurable amount of uronic acids. The amount of carbon dioxide originating from the uronic acid groups in the pectin-containing (dewaxed) cotton is obtained by taking the average distance between the parallel positions of the curves, which gives a value of 2.4 mg. of carbon dioxide per gram of cotton.

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[41] Whistler, Martin, and Harris, *J. Research Natl. Bur. Standards,* **24,** 13 (1940).

[42] Nickerson and Leape, *Ind. Eng. Chem.,* **33,** 83 (1941).

[43] By boiling the sample for 7½ hours in a 1 per cent solution of sodium hydroxide according to the method recommended for the preparation of standard cotton cellulose.

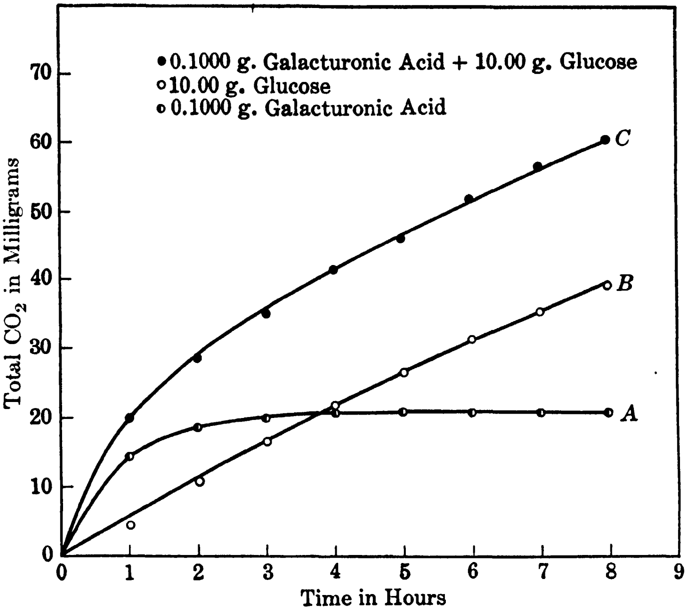


FIG. 89. Rate of evolution of carbon dioxide from various carbohydrates. Whistler, Martin, and Harris.

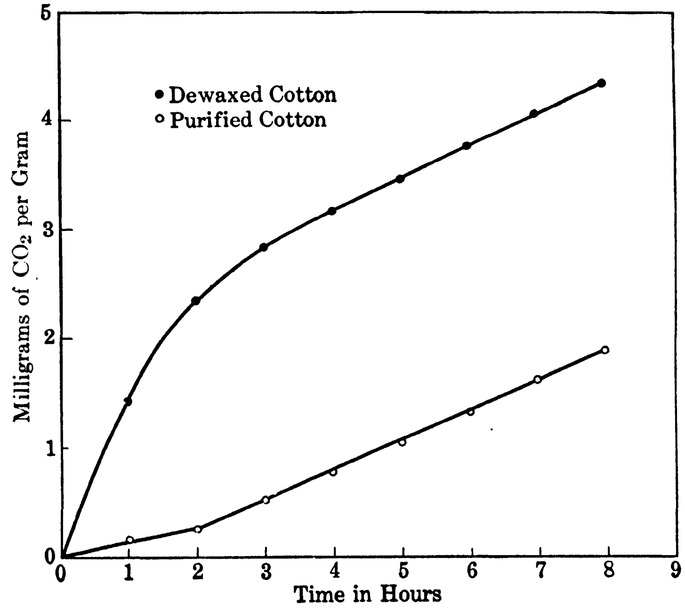


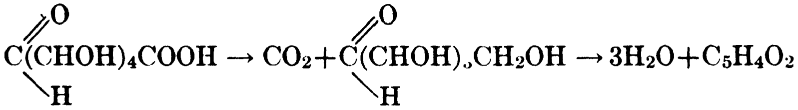
FIG. 90. Rate of evolution of carbon dioxide from pectin-containing (dewaxed) and from pectin-freed cotton. Whistler, Martin, and Harris.

No doubt, similar curves could be obtained from cellulose (freed of pectin and other uronic acid sources) and from oxycellulose prepared therefrom. In this way, that portion of the carbon dioxide which is responsible for the carboxyl groups produced by oxidation could be more accurately estimated.

A correction for cellulose (glucose) would, of course, not be necessary when the carboxyl content is extremely high, as in nitrogen dioxide oxycelluloses. The highest value reported by Unruh and Kenyon was 25.5 per cent COOH.

The nature of the reaction which leads to the liberation of carbon dioxide from glucose is not yet clearly understood.[44] That the potential reducing group is involved seems to follow from the observation that mannitol gives no carbon dioxide at all. Since on boiling with hydrochloric acid part of the glucose is converted with loss of water into hydroxymethylfurfural,[45] and since the latter may decompose further to yield levulinic and formic acids,[46] some of these reactions or a combination of them may lead to decarboxylation and thus be responsible for the liberation of carbon dioxide from glucose.

3. Simultaneously with the liberation of carbon dioxide a certain quantity of *furfural* is obtained.[47] Since, again, this quantity is in general greater than that obtainable from unoxidized cellulose, it may be regarded as being characteristic of oxycellulose. The simultaneous liberation of carbon dioxide and furfural is significant because it supports the assumption that oxycellulose contains glucuronic acid units. As has been shown by Tollens and Lefèvre,[48] glucuronic acid, on boiling with hydrochloric acid, liberates carbon dioxide to form xylose as an intermediate. With the loss of 3 molecules of water, the latter is converted into furfural:



$$\overset{\displaystyle /\!\!/^{O}}{C}\underset{\displaystyle \diagdown_{H}}{}(CHOH)_4COOH \rightarrow CO_2+\overset{\displaystyle /\!\!/^{O}}{C}\underset{\displaystyle \diagdown_{H}}{}(CHOH)_3CH_2OH \rightarrow 3H_2O+C_5H_4O_2$$

It should be borne in mind that the yield of furfural thus obtained from glucuronic (and from other uronic) acids is not quantitative—in some cases it remains far behind the theoretical—whereas the yield of carbon dioxide is almost quantitative.[49]

Attention has been directed to the observation that the yield of fur-

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[44] Nickerson, *Ind. Eng. Chem., Anal. Ed.*, **13**, 423 (1941).

[45] van Ekenstein and Blanksma, *Ber.*, **43**, 2355 (1910); Heuser and Eisenring, *Cellulosechem.*, **4**, 20 (1923); Heuser and Schott, *ibid.*, **4**, 85 (1923).

[46] Pummerer and Gump, *Ber.*, **56**, 999 (1923).

[47] Cross, Bevan, and Beadle, *Ber.*, **26**, 2527 (1893).

[48] Tollens and Lefèvre, *Ber.*, **40**, 4519 (1916).

[49] Nanji, Paton, and Ling, *J. Soc. Chem. Ind.*, **44**, 253T (1925).

fural is greater if the oxidizing agents used for the preparation of oxycellulose can also exert a hydrolyzing effect upon cellulose and that it is smaller with those agents which may be expected to exert an oxidizing effect only.[50] The difference is demonstrated in Table 60. The oxycelluloses were prepared by various investigators.

TABLE 60

FURFURAL FROM OXYCELLULOSE

No.	Oxycellulose Prepared with	Furfural, %
1	Bleach powder	1.09
2	Potassium permanganate	1.09; 1.90
3	Bromine	1.40; 1.85
4	60 per cent nitric acid	2.30
5	Second treatment of preparation 4	3.20
6	Potassium chlorate and hydrochloric acid	2.11
7	Chromic acid	3.50
8	Chromic acid	4.10
9	Chromic acid (double the amount for preparation 8)	6.30
10	Chromic acid (three times the amount for preparation 8)	8.20
11	Nitrogen dioxide	8.8–9.8

The generally higher yield of furfural obtained on the oxidation with simultaneously hydrolyzing oxidants (Nos. 4–10 in the table) has been explained on the assumption that oxidation is preceded by hydrolysis of glycosidic linkages.[51] It is likely that the free reducing groups, as they are restored by hydrolysis, are particularly sensitive to oxidation.

The quantity of furfural obtainable from unoxidized cotton cellulose is usually not more than 1 per cent, and it is mostly below this figure. It originates from the pectin, because it becomes practically zero after the pectin has been extracted. In cellulose from wood, straw, esparto, etc., the furfural liberated by the action of mineral acid originates from the presence in these cellulosic materials of varying amounts of pentosans.

The furfural obtained from oxidized cellulose is contaminated with varying amounts of ω-hydroxymethylfurfural[52] which results from the conversion of glucose units under the influence of the boiling hydrochloric acid and which is an intermediate in the formation of levulinic acid under these conditions (see above). If furfural is to be estimated by condensing it with phloroglucinol to furfural phloroglucide, a correction has to be made for ω-hydrooxymethylfurfural.

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[50] Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., pp. 132, 133; for more data on carbon dioxide and furfural from oxycellulose preparations, see Hibbert and Parsons, *J. Soc. Chem. Ind.*, **44**, 483T (1925).

[51] Heuser, "Textbook of Cellulosechemistry," p. 98.

[52] Heuser and Stöckigt, *loc. cit.*

4. Certain oxycelluloses possess a pronounced *affinity for basic dyes*,[53] obviously because of the presence in such preparations of a sufficient number of carboxyl groups. The amount of basic dye taken up may serve as a means of ascertaining the degree of oxidation to the acidic stage.[54] One of the most frequently used basic dyes is methylene blue. Oxycelluloses, containing an appreciable amount of carboxyl groups, dye considerably more deeply and resist the removal of the dye from the fiber by washing to a greater extent than does unoxidized cellulose. Methylene blue may be used for following the process of oxidation (see later).

That the methylene blue absorption of oxycelluloses is a function of their carboxyl groups has been confirmed by Yackel and Kenyon[55] with nitrogen dioxide oxycelluloses. These oxycelluloses readily absorb basic dyes which are present in aqueous solution as salts of weak acids. Preparations of a moderate degree of oxidation quickly and completely remove the color from a dilute aqueous solution of rosaniline acetate, the basic dye forming a salt with carboxyl groups of the oxycellulose and liberating acetic acid. The dye may be displaced by treatment of the dyed material with dilute aqueous mineral acid.

Carboxyl groups may also be identified and possibly estimated by treating the cellulose preparation with the pseudobase of crystal violet.[56] After sufficient contact with the cellulose sample this colorless base acquires an intensively purple color, and the dye thus formed is fixed upon the fiber. This reaction is obviously due to salt formation between the pseudobase and carboxyl groups present in the cellulose preparation. Alcoholic hydroxyl groups, as in glucose or sucrose, do not react with the dye base.

A similar reaction involving the carboxyl groups in cellulose has been observed by Krüger and Oberlies.[57] It was found that cellulosic materials which were first freed of their cations by treatment with dilute hydrochloric acid and then exposed to the vapors of dimethylaniline for several days had become more or less deeply blue. Spectrographic analysis showed that the dyestuff thus formed was identical with crystal violet. Although the mechanism of the reaction is not yet fully understood, it would appear possible to establish a quantitative relation between the dye quantity produced and the carboxyl content of the cellulosic material under investigation.

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[53] Witz, *Bull. Soc. Ind. Mulhouse*, **43**, 334 (1883).

[54] Thies, *Leipz. Färber-Ztg.*, **24**, 525 (1913); Knecht, *J. Soc. Dyers Colourists*, **37**, 76 (1921); Ristenpart, *Cellulosechem.*, **5**, 8 (1924); Ristenpart and Petzold, *Leipz. Monatschr. Textil-Ind.*, **40**, 307 (1925); Ristenpart, *Melliand Textilber.*, **6**, 803 (1925); Dorée, "The Methods of Cellulose Chemistry," p. 21; Thomas, *J. Soc. Chem. Ind.*, **55**, 79T (1933); Krüger, *Klepzig's Textil-Z.*, **44**, 647 (1941).

[55] Yackel and Kenyon, *J. Am. Chem. Soc.*, **64**, 121 (1942); see also Weber, *J. prakt. Chem.*, **158**, 33 (1941).

[56] Rebek, *Kolloid-Z.*, **92**, 217 (1940).

[57] Krüger and Oberlies, *Ber.*, **74**, 663 (1941).

Reactions Indicative of the Cleavage of Glycosidic Linkages

If the oxidizing agent effects both oxidation and hydrolysis, part of the increased reducing power of oxycellulose will be due to the restoration of free reducing groups, i.e., to the cleavage of glycosidic linkages. On the other hand, it is conceivable that, under certain conditions, oxygen may add to the glycosidic linkages. As will be seen later, such a reaction may result in the cleavage of glycosidic linkages but without free reducing groups being restored. Moreover, ketonic and diketonic groupings, primarily formed on oxidation, could be further oxidized or hydrolyzed and thus give rise to decomposition into fragments which exhibit no reducing power.

On the assumption that all three types of reactions take place, the increased reducing power of oxycellulose would supply no measure of the full extent to which cleavage has occurred. This may, however, be ascertained by determining the degree of polymerization.

The few data available from the older literature show that the oxycelluloses investigated possessed a lower viscosity than the original cellulosic materials from which they were prepared.[58] More recent data show the relation between the degree of polymerization and the intensity of the oxidative treatment.[59] Various oxycellulose preparations were obtained by treating cellulose regenerated from its cuprammonium hydroxide solution with different oxidizing agents. These oxycelluloses were subjected to viscosity measurements in cuprammonium hydroxide. From the latter, the molecular weight and the degree of polymerization were calculated. It was found that, under the action of calcium hypochlorite solution (containing 2.6 grams of chlorine per liter) at 20°, the degree of polymerization of the starting material had decreased from 2340 (molecular weight, 380,000) to 735 (molecular weight, 119,000) after 1 hour; to 490 (79,500) after 5 hours, and to 89 (14,400) after 25 hours. Raw cotton of a degree of polymerization of 2640 (428,000) after treatment with calcium hypochlorite solutions of the same concentrations, at the same temperature and for the same lengths of time as before showed the following values: 1575 (255,000), 982 (159,000), and 510 (82,000). Chlorine water and neutral potassium permanganate solution produced similar reductions, whereas acid hydrogen peroxide and particularly chlorine dioxide solution caused

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[58] See for example Oertel, doctoral dissertation, Hanover (1912), p. 23; Hibbert and Parsons, *J. Soc. Chem. Ind.*, **44**, 484T (1925).

[59] Staudinger and Jurisch, *Papier-Fabr.*, **35**, 459, 462 (1937).

considerably less reduction.[60] Fig. 91 shows the reduction produced by the various oxidizing agents on regenerated cellulose, expressed as percentage reduction of the original degree of polymerization with time of treatment.

Oxycelluloses are soluble in dilute alkali to a greater extent than the original cellulosic materials. This may be interpreted as another

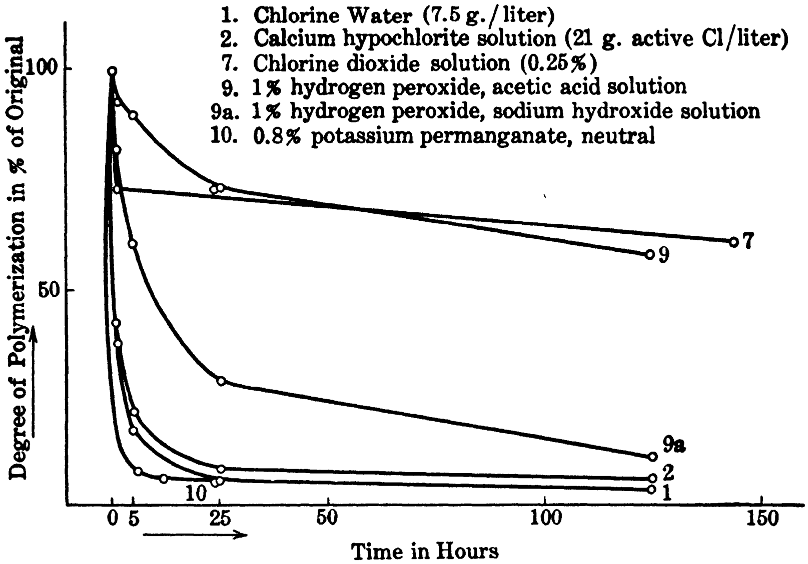

FIG. 91. Reduction of degree of polymerization of regenerated cellulose by various oxidizing agents. Staudinger and Jurisch.

indication that the average chain length in oxycelluloses is smaller than that of the original materials.[61] However, it may also be the result of the presence of carboxyl groups. It will be recalled that oxycellulose prepared by the action of nitrogen dioxide is completely soluble in dilute caustic soda solution without showing signs of decreased average chain length.

The increase in alkali-solubility of various oxycelluloses with increasing degree of degradation, produced by increased oxygen consumption and expressed as the copper number, is shown in Table 61.

The increase in alkali-solubility with the copper number is in agreement with the observation that the cuprammonium viscosity dropped

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[60] See particularly Staudinger, Dreher, and Jurisch, *Ber.*, **70**, 2506 (1937).

[61] Heuser and Niethammer, *Cellulosechem.*, **6**, 13 (1925).

TABLE 61

OXYGEN CONSUMPTION, COPPER NUMBER, AND ALKALI-SOLUBILITY OF VARIOUS OXYCELLULOSES *

Oxidant	Atoms of Oxygen per $C_6H_{10}O_5$	Copper Number	Solubility in 10% NaOH, %
$KMnO_4$	0.33	4.6	24
"	1.00	7.1	17
"	2.00	7.8	28
$Mg(MnO_4)_2$	0.33	5.3	21
"	1.00	7.7	35
"	2.00	8.9	42
$Ba(MnO_4)_2$	0.33	5.7	29
"	1.00	8.6	35
"	2.00	9.9	..
CrO_3	0.33	13.6	35
"	1.00	18.4	49
"	2.00	19.3	55

* Birtwell, Clibbens, and Geake, *J. Textile Inst.*, **19**, T349 (1928).

simultaneously, although no straight-line relationship was found with the higher oxidized samples.

Straight-line relationships between copper number, alkali-solubility, and viscosity were found by Davidson[62] for oxycelluloses prepared with various oxidizing agents, oxycelluloses of very low viscosity being completely soluble in dilute alkali.

The solubility of oxycellulose has frequently been associated exclusively with the presence of carboxyl groups.[63] It would appear, however, that the relatively very small number to which such groups are confined in most oxycelluloses could hardly account for such behavior alone. Table 62 shows the solubility of various oxycellulose preparations in comparison with their carboxyl content (determined as carbon dioxide liberated by boiling in 12 per cent hydrochloric acid).[64] No doubt, in such oxycellulose preparations, the pronounced alkali-solubility is chiefly caused by a decrease in degree of polymerization.

An oxycellulose in which the presence of carboxyl groups takes a greater part in causing alkali-solubility than in the preparations shown in Table 62 is evidently represented by the product which Kalb and Falkenhausen[65] obtained by oxidizing cellulose dissolved in cupram-

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[62] Davidson, *J. Textile Inst.*, **25**, T174 (1934).

[63] See for example Pringsheim, *Cellulosechem.*, **2**, 57 (1921).

[64] Hess and Katona, *Ann.*, **455**, 221 (1927).

[65] Kalb and Falkenhausen, *Ber.*, **60**, 2514 (1927).

TABLE 62

CARBOXYL CONTENT AND ALKALI-SOLUBILITY OF VARIOUS OXYCELLULOSES

Oxycellulose Prepared with	Bromine	Permanganate	Nitric Acid	Chromic Acid	Original Cellulose (Linters)
COOH, %	1.2	0.9	0.67	1.06	0.43; 0.22
Solubility in 2 *N* NaOH, %	26.8	33.8	22.7	40.5	....

monium (containing a small amount of sodium hydroxide) with potassium permanganate solution and which, as will be recalled, contained an appreciable number of glucuronic acid chains. The product thus obtained was completely soluble in dilute alkali. Moreover, this point was reached with as little oxygen as 0.003 atom per $C_6H_{10}O_5$ unit with filter paper, and with 0.2 atom with cotton. With quantities above 0.5 atom of oxygen, the products of oxidation even became water-soluble. The fact that so much less oxygen was required for producing these effects than in the experiments reported by Hibbert and Parsons is, no doubt, in part a result of the greater accessibility of the dissolved cellulose chains to the oxidizing agent. However, it is very probable that the alkali- and water-solubility of Kalb and Falkenhausen's product were also a result of degradation.

The sole influence of the presence of carboxyl groups upon the alkali-solubility of oxycellulose can best be seen from results which Yackel and Kenyon[66] obtained with nitrogen dioxide oxycellulose preparations of varying degrees of oxidation. As has been seen, it is very probable that these preparations were practically undegraded. Whereas preparations containing less than 13 per cent carboxyl formed only gelatinous swollen masses when in contact with sodium hydroxide solution (and other bases), those containing 13 per cent and more carboxyl dissolved quickly and completely in 2 per cent sodium hydroxide solution. This result seems to indicate that, provided the chain molecules are not shortened, the carboxyl content has to be appreciable to cause alkali-solubility.

Nitrogen dioxide oxycellulose with sufficiently high carboxyl content is also soluble in dilute ammonia, aqueous sodium carbonate, and aqueous pyridine, as well as in aqueous solutions of quaternary ammonium hydroxides. It may be precipitated from these solutions by pouring them into ethyl alcohol or other

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[66] Yackel and Kenyon, *J. Am. Chem. Soc.*, 64, 121 (1942).

water-miscible nonsolvents. In all cases, the oxycellulose forms a water-soluble salt with the base.

Insoluble salts are formed with polyvalent cations. Yackel and Kenyon have explained the insolubility of these salts on the assumption that the cation forms a cross linkage between oxidized chain molecules which results in a three-dimensional structure. Such a structure may possibly be compared with the arrangement which results from the hypothesis that adjacent chain molecules also in native cellulose are connected through primary valence cross linkages (p. 584).

The solubility of oxycelluloses in *strong* aqueous alkali generally follows the rules which have been established for the behavior of unmodified cellulose. That is to say, the solubility of oxycellulose at any temperature shows a maximum at a certain alkali concentration[67] and, as the temperature is lowered, the maximum solubility is greatly increased and occurs at a lower alkali concentration.[68] Likewise, if oxycellulose is first treated with a more concentrated sodium hydroxide solution (such as 10 *N*) and the solution is subsequently diluted by adding water to the mixture, a much larger quantity may then be brought into solution,[69] obviously because of the enhanced swelling so produced.

Davidson[70] studied the effect of different bases upon the solubility of oxycellulose and found that the solvent power of lithium hydroxide and of tetramethylammonium hydroxide was qualitatively similar to that of sodium hydroxide solution. However, the maximum solubilities with the three bases were found to differ, the order of increasing solvent power being $LiOH < NaOH < N(CH_3)_4OH$ at 15°, and $N(CH_3)_4OH < LiOH < NaOH$ at −5°. Potassium hydroxide was found to have less solvent power and to differ also in being less affected by temperature.

The addition of certain alkali metal sulfates reduces the solvent power of sodium hydroxide solution. This fact may be of practical importance in view of the loss in weight expected to occur on the mercerization of oxycellulose-containing textiles which thus may be reduced by the presence in the treating liquor of sodium sulfate or similar salts. On the other hand, salts (such as sodium zincate and sodium beryllate) increase the solubility of oxycellulose in sodium hydroxide solutions considerably.[71]

The solubility of oxycelluloses in other organic bases (for example, trimethylbenzyl- and dimethyldibenzylammonium hydroxide) was studied by Brownsett and Davidson[72] and that in cuprammonium and in cupriethylenediamine solutions was studied by Jolley.[73]

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[67] Birtwell, Clibbens, and Geake, *J. Textile Inst.*, **19**, T349 (1928); Davidson, *ibid.*, **25**, T174 (1934).

[68] Davidson, *loc. cit.*

[69] Birtwell, Clibbens, and Geake, *loc. cit.*

[70] Davidson, *J. Textile Inst.*, **27**, T112 (1936).

[71] Davidson, *J. Textile Inst.*, **28**, T27 (1937).

[72] Brownsett and Clibbens, *J. Textile Inst.*, **32**, T32 (1941).

[73] Jolley, *J. Textile Inst.*, **30**, T4, T22 (1939).

The removal of low-molecular-weight products by alkaline extraction deprives oxycellulose of a great deal of its reducing power; part of it is found to be associated with the filtrate from the extraction of the oxycellulose.[74] However, most of the reducing groups seem to be destroyed by the action of the alkali.[75]

FRACTIONATION OF OXYCELLULOSE

In an attempt to free crude oxycellulose of its low-molecular-weight products by extraction with alkali,[76] dilute solutions, preferably in the form of sodium bicarbonate or barium hydroxide [77] and at room temperature, should be used to avoid the simultaneous solution of longer-chain material. However, even under such conditions of extraction, sharp separation cannot be expected. The presence of somewhat longer-chain material in the solution is indicated by precipitation on acidification. The degree of polymerization of the precipitated material is probably somewhat lower than that of *beta*-cellulose, which corresponds to approximately 100 glucose units.

The extracted oxycellulose may be further fractionated into portions of varying degrees of polymerization, either by subjecting it to extractions with alkalies of varying concentrations or by converting it into a (partially substituted) derivative—for example, its acetate or methyl ether—either of which may then be fractionated from its solution in an organic solvent by precipitation with water or other nonsolvents (Godman, Haworth, and Peat).

The Soluble Products of Oxidation

The nature of the water- and alkali-soluble products of degradation resulting from the oxidation of cellulose with various oxidizing agents has been given relatively little attention. Since the heterogeneous type of oxycellulose loses its peculiar properties when these products are removed, they must be regarded as the actual products of oxidation. However, being fragments of short and very short chains and, in addition, having been further oxidized, they have lost their cellulosic nature entirely. Hence, they are of little help in an attempt to throw light upon the primary reaction between the oxidizing agent and

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[74] Birtwell, Clibbens, and Geake, *loc. cit.,* p. T349.

[75] Godman, Haworth, and Peat, *J. Chem. Soc.,* 1908 (1939).

[76] Bay, doctoral dissertation, Giessen (1913); Heuser, "Textbook of Cellulose Chemistry," p. 113.

[77] Schwalbe and Becker, *J. prakt. Chem.,* 100, 19 (1920).

the original chain molecules. Nevertheless, it is interesting to review briefly the pertinent investigations.

von Faber and Tollens[78] isolated saccharic acid from the filtrate of an oxycellulose preparation which had been obtained by the action of bromine and aqueous calcium carbonate upon cotton cellulose. This acid may also be obtained from glucose and maltose, as well as from other disaccharides. Its formation has been observed also from the action of hot concentrated nitric acid on cellulose.[79]

In the filtrate of an oxycellulose preparation which had been obtained by the action of nitric acid on cotton cellulose von Faber and Tollens isolated tartaric acid and a dibasic acid with 5 carbon atoms which, according to Hess,[80] might have been hydroxyglutaric acid.

Isosaccharinic acid was obtained[81] by boiling bromine oxycellulose, nitric acid oxycellulose, and Vignon's oxycellulose[82] (obtained by the action of potassium chlorate and hydrochloric acid on cotton) with calcium hydroxide solution. *Cellulose*, treated under the same conditions, does not yield this acid.[83] However, since it may be obtained from cellobiose[84] and, in small amounts, also from *d*-glucose,[85] it is probable that it owes its formation to the production of glucose as the primary product in the formation of these oxycelluloses. Lactose also yields isosaccharinic acid,[86] the glucosidically combined glucose component being the source of its formation.

The mother liquor of isosaccharinic acid yielded dihydroxybutyric acid. Hess,[87] however, doubts whether this acid has been identified with certainty and whether its formation can be explained on the assumption that it is a product of decomposition of isosaccharinic acid.[88] Since dihydroxybutyric acid has been frequently observed on the action of alkali upon aldohexoses,[89] it is more likely that it results from the action of the calcium hydroxide upon glucose as the primary product of hydrolytic oxidation.

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[78] von Faber and Tollens, *Ber.*, **32**, 2589, 2594 (1899).

[79] Häussermann, *Z. angew. Chem.*, **23**, 1763 (1910); Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 152.

[80] Hess, "Chemie der Cellulose," p. 522.

[81] von Faber and Tollens, *loc. cit.*, p. 2595.

[82] Vignon, *Bull. soc. chim.*, [3] **19**, 790 (1898).

[83] Schwalbe, *J. prakt. Chem.*, **100**, 19 (1920).

[84] Hintikka, cited in Pringsheim, "Die Polysaccharide," Springer, Berlin (1931), 3rd ed., p. 88.

[85] Hess, "Chemie der Cellulose," p. 523, footnote 5.

[86] Pringsheim, *Cellulosechem.*, **2**, 61 (1921); *Z. angew. Chem.*, **35**, 348 (1922).

[87] Hess, *loc. cit.*, p. 524.

[88] Heuser, "Textbook of Cellulosechemistry," p. 95.

[89] Nef, *Ann.*, **357**, 301 (1907); Meisenheimer, *Ber.*, **41**, 1009 (1908); Kiliani, *Ber.*, **44**, 109 (1911).

From the aqueous barium hydroxide extract of acid permanganate oxycellulose, Godman, Haworth, and Peat[90] isolated formic and acetic acids, as well as lactic, dihydroxybutyric, and a mixture of saccharinic acids. It will be recalled that these products (including dihydroxybutyric acid) may also be obtained by the action of alkali upon mono- and disaccharides.[91] Uronic acid units (which are destroyed under the influence of alkali) were identified in the solution which resulted from the hydrolysis of acid permanganate oxycellulose with 72 per cent sulfuric acid in the cold. A barium salt appeared to have the composition of that of an aldobionic acid.

The glucuronic acid which Kalb and Falkenhausen[92] obtained on the oxidation of cotton in cuprammonium hydroxide solution was qualitatively identified by Tollens' naphthoresorcinol test and isolated as the cinchonine salt, according to the method of Neuberg.

Saccharinic acids were also found in the waste liquor resulting from the preparation of soda pulp. Conversion into trihydroxyadipic acid[93] identified *m*-saccharinic acid.

THE METHODS OF OXYCELLULOSE PREPARATION

Although almost any oxidizing agent may be used to convert cellulose into oxycellulose, only relatively few have been employed for preparative purposes. The selection is chiefly governed by practical considerations. The methods for the preparation of oxycellulose may be divided into those which employ purely oxidizing agents and those which simultaneously involve hydrolysis. A hydrolytic effect may also be caused by acids which form during the reaction.

Methods Using Purely Oxidizing Agents

Ozone[94] has only little effect on dry cellulose, but wetted cellulose is considerably attacked. In fact, if ozone or ozonized oxygen is brought

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[90] Godman, Haworth, and Peat, *loc. cit.*, p. 1909.

[91] See for example Plunkett and Evans, *J. Am. Chem. Soc.*, **60**, 2897 (1938); Upson, Noyce, and Albert, *ibid.*, **61**, 779 (1939).

[92] Kalb and Falkenhausen, *Ber.*, **60**, 2514 (1927).

[93] Klason, *Tek. Tid.* (1893), p. 33; *Arkiv Kemi Mineral. Geol.*, **4**, 17 (1910); Klason and Segerfeldt, *ibid.*, **4**, 1 (1911); Hägglund, *Cellulosechem.*, **5**, 81 (1924); see also Cirves, *Paper Trade J.*, **91**, No. 19, 55 (1930).

[94] Cunningham and Dorée, *J. Chem. Soc.*, **101**, 497 (1912); Dorée, *ibid.*, **103**, 1347 (1913); Dorée and Healey, *J. Soc. Dyers Colourists*, **49**, 290 (1933); *J. Textile Inst.*, **29**, T27 (1938).

into contact with wetted cellulose for a few hours at room temperature, the copper number of the treated cellulose increases considerably. It is interesting to note that there seems to exist a critical moisture content of cellulose at which the effect of ozone is most pronounced. In the experiment referred to, this maximum attack occurred when the moisture content of the cellulosic material had reached 45–50 per cent. From this point onward, the activity of the ozone slowed down to about two-thirds of its maximum value, and then remained approximately constant with increasing water content. The copper number rose from 0.56 to 4.35 for cotton and from 0.82 to 6.90 for mercerized cotton. The change of the copper number with increasing water content under the influence of ozone is shown in Fig. 92. This figure also gives the curve for mercerized cellulose, and the greater reactivity of the cellulose in its hydrate form is quite noticeable.

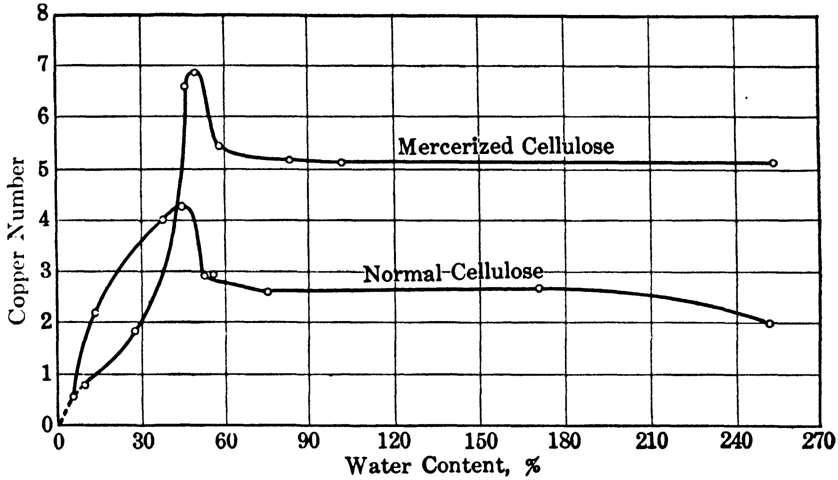

FIG. 92. The action of ozone upon cellulose and mercerized cellulose. Influence of water content upon copper number. Dorée and Healey.

The occurrence of the maximum at a certain moisture content of the cellulose has been explained by the distinction which is made between water of hydration and water mechanically held within the intermicellar spaces of the fiber. It is assumed that the water of hydration (moisture contents up to 50 per cent) accelerates the oxidation because it activates the hydroxyl groups of the cellulose, and the oxidizing agent is chiefly gaseous ozone. The mechanically held water (above 50 per cent), however, dissolves the ozone, and the oxidizing agent, now a solution of ozonized oxygen in water, is less active.

Cellulose is not attacked by oxygen. Girard [95] observed that cotton was not oxidized when it was kept in an oxygen atmosphere in a sealed glass tube for several months. The bleaching effect ascribed to oxygen [96] is probably due to the formation of ozone and its action upon noncellulosic substances.

The claim that ozone,[97] as well as ammonium persulfate in the presence of sulfuric acid,[98] acts first to form a cellulose peroxide needs further experimental substantiation (see also p. 480).

Hydrogen peroxide may be used for the preparation of oxycellulose under various conditions of concentration, temperature, etc.[99] Hydrogen peroxide is also used as a textile and wood pulp bleaching agent.[100]

Concentrated hydrogen peroxide is highly efficient, particularly if applied in the presence of a catalyst, such as metal salts. A drop of perhydrol in combination with a crystal of ferric chloride ignites filter paper; sometimes slight heating is required to initiate the reaction. Metal oxides act as oxygen conveyors. It is known that cellulosic materials are attacked by rust. If the rust spots are removed (for example, by means of oxalic acid), the corresponding portions of the cellulose, particularly after alkaline washing, are found to be brittle; this is a result of the formation of oxycellulose.[101] Hydrogen peroxide of 60 per cent dissolves cellulose.[102]

The action of air oxygen in the presence of strong sodium hydroxide solution upon cellulose (the aging of alkali cellulose, p. 126) may be used for the preparation of oxycellulose.[103] A higher degree of oxidation is achieved than by aging in air if oxygen as such or in the form of hydrogen peroxide is added to alkali cellulose.

Potassium permanganate [104] has been frequently used for the preparation of oxycellulose. If applied in neutral solution, the reaction is

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[95] Girard, *Ann. chimie phys.*, [5] **24**, 337 (1881), cited by Schwalbe, "Chemie der Cellulose," 1st ed., p. 6.

[96] Hochberger, "Die Bleiche des Zellstoffs," in Heuser and Opfermann, "Technik und Praxis der Papierfabrikation," Vol. III, Part 2, pp. 311, 328.

[97] Cunningham and Dorée, *loc. cit.*

[98] Dietz, *Chem.-Ztg.*, **31**, 833, 844, 857 (1907); *J. prakt. Chem.*, **78**, 343 (1908).

[99] Bumcke and Wolffenstein, *Ber.*, **32**, 2493 (1899); Haller, *Textile Forsch.*, **1**, 79 (1920).

[100] Smolens, *Am. Dyestuff Reptr.*, **28**, 495 (1939); Reichert *et al.*, U. S. patents 2,199,376 (1940) and 2,290,601 (1942).

[101] Schwalbe, "Chemie der Cellulose," 1st ed., p. 134; Kauffmann, *Chem.-Ztg.*, **50**, 101 (1926).

[102] Bamberger and Nussbaum, *Monatsh.*, **40**, 411 (1920).

[103] Ost, *Z. angew. Chem.*, **24**, 1895 (1911); Oertel, doctoral dissertation, Hanover (1912), p. 9; Davidson, *J. Textile Inst.*, **23**, T95 (1932).

[104] Nastukoff, *Ber.*, **33**, 2237 (1900); Clifford and Fargher, *J. Textile Inst.*, **13**, T189 (1922); Hibbert and Parsons, *loc. cit.;* Hess and Katona, *loc. cit.*

relatively mild. However, in alkaline medium, permanganate is an efficient oxidant. Its use in the presence of sulfuric acid has been suggested as a more efficient method of controlling the reaction than allowing it to proceed in the neutral or alkaline medium.[105] Under the conditions as suggested, cellulose is probably not much attacked by the sulfuric acid.

Nitrogen dioxide oxycellulose[106] may be prepared by allowing the gaseous agent[107] to act upon dried cellulose at room temperature (21°) or slightly less for a certain length of time. The time governs the degree of oxidation. Completely alkali-soluble oxycellulose, having a carboxyl content of 13–14 per cent, was obtained after about 64 hours. Part of the nitrogen dioxide is converted into nitric oxide.

To avoid degradation of the cellulose, it is obviously important to work with absolutely dry materials, for even very small amounts of moisture give rise to the formation of nitric and nitrous acid which, during the long time of treatment, would attack glycosidic linkages.

In Yackel and Kenyon's experiments, the nitrogen dioxide was dried over phosphorus pentoxide, and the cellulose (long-fibered cotton and cotton linters) was dehydrated by benzene or over phosphorus pentoxide. The moisture contents after these treatments were 1.2 and approximately 0.1 per cent, respectively. The degree of polymerization of the oxycellulose preparations was not determined, and the high copper numbers which were obtained by the determination with Fehling solution have been explained by the assumption that they arise from reducing groups *formed* during the test rather than from free reducing groups present in the oxycelluloses: The uronic acid chains hydrolyze with ease under the influence of the alkali of the hot Fehling solution, thus producing the aldehyde groups which are determined by the copper number test.

The action of periodic acid upon cellulose may also be regarded as that of a purely oxidizing agent (see also pp. 426 and 468).

Methods Using Agents which Exert Oxidizing and Hydrolyzing Effects

The halides (chlorine and bromine) are strongly oxidizing agents for cellulose and the inorganic acids formed in this reaction exert a hydro-

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[105] Knecht and Thompson, *J. Soc. Dyers Colourists,* **36,** 251 (1920); Hibbert and Parsons, *loc. cit.;* Godman, Haworth, and Peat, *loc. cit.*

[106] Yackel and Kenyon, *J. Am. Chem. Soc.,* **64,** 121 (1942); Unruh and Kenyon, *ibid.,* **64,** 127 (1942).

[107] "Nitrogen dioxide" refers to the equilibrium mixture of nitrogen dioxide and nitrogen tetroxide.

lyzing effect upon cellulose, depending upon concentration, temperature, and time of exposure. It is noteworthy that the halides exert no effect upon cellulose in the absence of water. For the preparation of oxycellulose, chlorine may be applied as chlorine water or in its gaseous form.[108] Sunlight and elevated temperature further the reaction.

Cellulose in wood or other lignified material or in the form of unbleached wood pulp, raw cotton, and the like, is less affected by chlorine. Obviously, the noncellulosic substances, being more readily attacked than cellulose, exert a protecting influence. This fact explains why chlorine, in gaseous form or dissolved in water, may be used as a bleaching agent for wood pulp without unduly attacking the cellulose.

Chlorine, allowed to act upon wood, converts the lignin constituent into chlorolignin by substituting chlorine for hydrogen. Part of the lignin is also oxidized. Both reactions result in the formation of hydrochloric acid.[109]

The protecting influence of the lignin makes it possible to use chlorine as a means of isolating cellulose from wood and other lignified material without destroying the cellulose, either as an analytical method (Cross and Bevan[110]) or for commercial purposes (Pomilio process[111]). The "Cross and Bevan" cellulose, if obtained from wood or straw, still contains a small percentage of pentosans,[112] as well as of noncellulosic hexosans.[113] These have to be determined in order to obtain the value for cellulose alone. Under certain conditions, practically all the noncellulosic carbohydrates may be retained together with the cellulose ("holocellulose").[114]

Likewise if, instead of chlorine, chlorine dioxide (ClO_2) is used for the isolation of cellulose, practically all noncellulosic carbohydrates are retained. Chlorine dioxide carefully employed attacks cellulose to a lesser extent than chlorine (p. 439). The preparation obtained has been termed "skeleton substance."[115]

Bromine has been used more often than chlorine for the preparation of oxycellulose. In the presence of aqueous calcium carbonate, the hydrolyzing effect of the hydrogen bromide is diminished.[116]

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[108] Beutel and Kutzelnigg, *Monatsh.*, **66**, 249 (1935).

[109] Cross and Bevan, "Cellulose," Longmans and Green, London (1903); Heuser and Sieber, *Z. angew. Chem.*, **26**, 801 (1913).

[110] Dorée, "Methods of Cellulose Chemistry," p. 331; a modification was suggested by Heuser and Cassens, *Papier-Fabr.*, Special Number, **20**, 80 (1922); *Paper Trade J.*, **75**, No. 9, 47 (1922).

[111] Pomilio, *Ind. Eng. Chem.*, **31**, 657 (1939).

[112] Heuser and Haug, *Z. angew. Chem.*, **31**, 99 (1918).

[113] Heuser and Dammel, *Cellulosechem.*, **5**, 45 (1924).

[114] Ritter and Kurth, *Ind. Eng. Chem.*, **25**, 1250 (1933); van Beckum and Ritter, *Paper Trade J.*, **108**, No. 7, 27 (1939); **109**, No. 22, 107 (1939); Hajny and Ritter, *ibid.*, **113**, No. 13, 83 (1941).

[115] Schmidt and co-workers, *Ber.*, **54**, 1860, 3241 (1921); *Cellulosechem.*, **13**, 129 (1932).

[116] von Faber and Tollens, *Ber.*, **32**, 2592 (1899); Hess and Katona, *loc. cit.*

Other bleaching agents, such as sodium[117] or calcium hypochlorite,[118] may be used for converting cellulose into oxycellulose. If the hydrolyzing influence of the acid formed in these reactions is to be eliminated, care must be taken to maintain alkalinity.

Cellulose suspended in aqueous potassium chloride and subjected to the electric current is oxidized by the electrolytically formed potassium hypochlorite.[119] The process, given sufficient time, leads to highly oxidized cellulose, a large portion of it being dissolved in the alkaline hypochlorite solution without being recoverable on acidification of the solution. It was found that the copper number of the insoluble portion was extremely high, reaching almost 40. The soluble reaction products have not yet been identified.

The use of nitric[120] and chromic[121] acids may be expected to include pronounced hydrolyzing effects.

Chloric acid (liberated from potassium chlorate with hydrochloric or sulfuric acid) was used by older investigators[122] for the preparation of oxycellulose.

Chloric acid in concentrated form reacts violently with cellulose.[123] This may be demonstrated by inserting a piece of filter paper into a mixture consisting of a small amount of potassium chlorate and a drop of concentrated sulfuric acid. Violent ignition is observed, and the paper is destroyed entirely. Great care ought to be taken in mixing the agents and in inserting the paper. The reaction is still more violent with oxycellulose. This may be demonstrated by carefully adding a drop of concentrated sulfuric acid to a mixture of powdery oxycellulose and potassium chlorate.

Perchloric acid has a similar effect. Filter paper on which a drop of perchloric acid has been placed ignites on heating, sometimes with explosion-like vehemence. Under less severe conditions, oxycellulose and oxalic acid are formed.

The Formation of Oxycellulose under Exactly Controlled Conditions

In the first part of this chapter, we dealt with properties and reactions of oxycellulose preparations as they result from the more or less

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[117] Schwalbe, *Z. angew. Chem.*, **20**, 2171 (1907).

[118] Nastukoff, *Ber.*, **33**, 2237 (1900); **34**, 720 (1901); Bay, doctoral dissertation, Giessen (1913), p. 44. See also Craik, *Chemistry & Industry*, **43**, 171T (1924).

[119] Oertel, *loc. cit.*

[120] von Faber and Tollens, *loc. cit.*; Hess and Katona, *loc. cit.*

[121] Cross and Bevan, *Ber.*, **26**, 2520 (1893); Hibbert and Parsons, *loc. cit.*; Hibbert and Hassan, *J. Soc. Chem. Ind.*, **46**, T407 (1927); Hess and Katona, *loc. cit.*

[122] Vignon, *Bull. soc. chim.*, **19**, 790 (1898); Murmurow, Sack, and Tollens, *Ber.*, **34**, 1428 (1901).

[123] Schwalbe, "Chemie der Cellulose," p. 137.

uncontrolled action of various oxidizing agents upon cellulose. Owing to the severe conditions applied in these investigations, cellulose loses its fibrous structure and, with it, its most important commercial property, its physical strength.

In the following section, an account is given of work which applies only to relatively mildly oxidized cellulose, as it may be formed in various commercial processes and whereby the fibrous structure is not destroyed but only affected to a limited extent. Under such conditions, it has been possible to follow the process of oxidation more satisfactorily than by allowing cellulose to be transformed into a structureless conversion product.

As a result of such carefully controlled investigations, much new light has been thrown upon the factors which essentially govern the effect of oxidation, as well as upon the mechanisms which are possibly involved in this complex reaction. Moreover, from these investigations much benefit has been derived for the understanding of the nature of the various commercial processes in which the formation of oxycellulose is a most undesirable feature.

The Effect of the Nature of the Oxidizing Agent

The method employed by Birtwell, Clibbens, and Ridge[124] in studies of this type consisted in shaking a certain quantity of carefully bleached cotton, either loose or in the form of cloth, with definite volumes of solutions containing various oxidizing agents until the whole of the oxidizing agent was consumed. Each oxidizing agent was employed at five different concentrations, and the complete consumption of the oxidizing agents, irrespective of their nature, corresponded to oxygen consumptions of 0.032, 0.064, 0.096, 0.16, and 0.32 per cent, calculated on the weight of the air-dry cotton. The extent to which oxidation was carried in these experiments may be seen from the fact that normal cotton bleaching results in the consumption of 0.01–0.02 per cent oxygen calculated on the weight of the material.

The oxidizing agents used were chlorine water, acid permanganate, anl alkaline hypobromite, and the effect of oxidation was followed by determining the copper number, the methylene blue absorption, the loss in weight on subsequent alkali boiling, and the viscosity of the oxidized material.

The changes brought about in copper number and in methylene blue absorption by the three oxidizing agents are shown in Fig. 93 and

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[124] Birtwell, Clibbens, and Ridge, *J. Textile Inst.*, **16**, T13 (1925).

Fig. 94. Fig. 93 shows that the rate of increase in copper number with progressive oxidation varies widely with the nature of the oxidizing agent employed, the chlorine series being characterized by high and rapidly increasing copper numbers, whereas the hypobromite series shows low and very slowly rising copper numbers. The permanganate series exhibits a behavior intermediate between the two extremes. Fig. 94 shows that the opposite relations obtain with respect to the methylene blue absorptions, those of the chlorine series being low and rising very slowly, those of the hypobromite series being high and increasing rapidly, with the permanganate series again occupying an intermediate position.

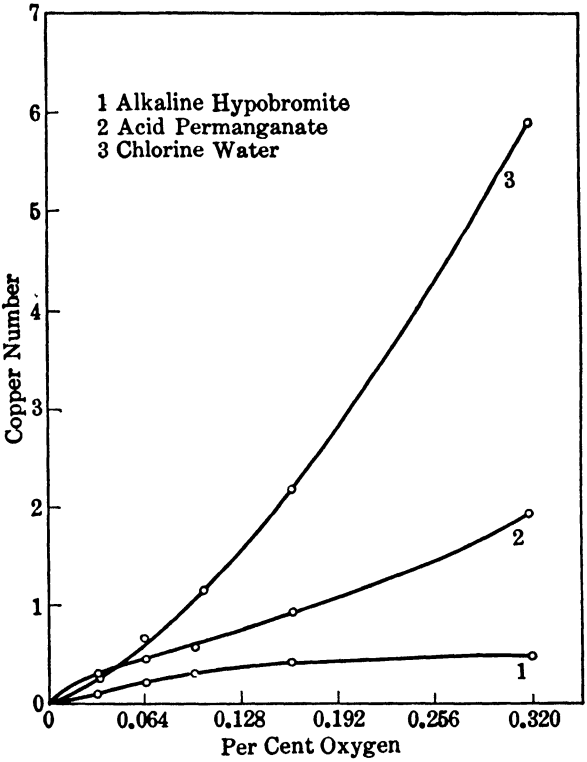

FIG. 93. Change of copper number with oxygen consumption. Birtwell, Clibbens, and Ridge.

The results of these experiments clearly demonstrate that the effect of oxidation is essentially a function of the nature of the oxidizing agent.

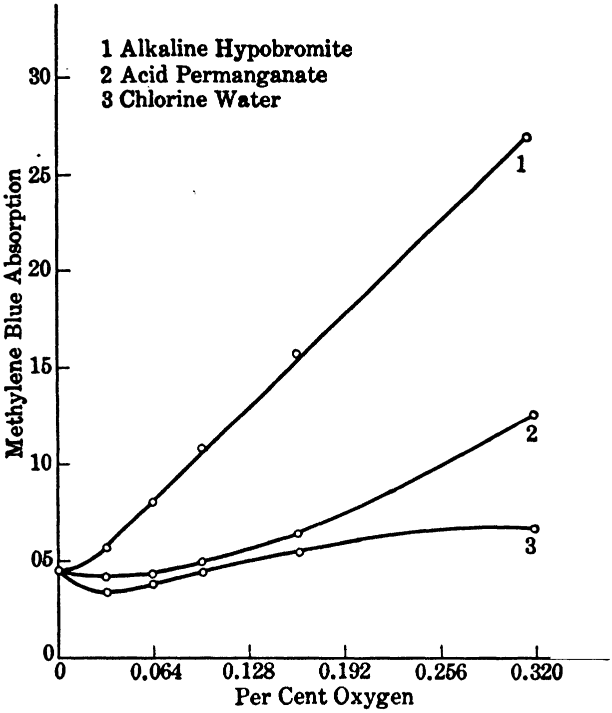

FIG. 94. Change of methylene blue absorption with oxygen consumption. Birtwell, Clibbens, and Ridge.

The Effect of the Medium of the Oxidizing Agent

The nature of the medium in which oxidation is allowed to proceed is of equally essential influence, for the same range of properties obtained by the use of different oxidizing agents may be secured by employing the same oxidizing agent at various hydrogen-ion concentrations.

With sodium hypochlorite as an oxidizing agent, the consumption of oxygen was kept constant over the whole series of experiments but the hydrogen-ion concentration was varied from 1 to 15. When the copper number and the methylene blue absorption values were plotted against hydrogen-ion concentration, the two curves shown in Fig. 95 were obtained.

It is seen that, beginning with the extreme alkaline side, the methylene blue absorption rises with decreasing alkalinity and reaches a maximum on the alkaline side of the neutral point (*p*H 11 to 9). It then falls continuously through the neutral point (*p*H 7) and continues to decrease on the acid side but at an increasingly slower rate. The behavior of the copper number is the reverse of this.

The peculiar form of the two curves shows very clearly that a maximum copper number is accompanied by a minimum methylene blue absorption and *vice versa*. As a result of this influence of the hydrogen-ion concentration, the hypochlorite oxycellulose of minimum copper number and maximum methylene blue absorption approaches closely in properties the hypobromite oxycellulose with the same oxygen consumption, whereas the hypochlorite oxycellulose of maximum copper number but minimum methylene blue absorption closely resembles the corresponding chlorine water oxycellulose.

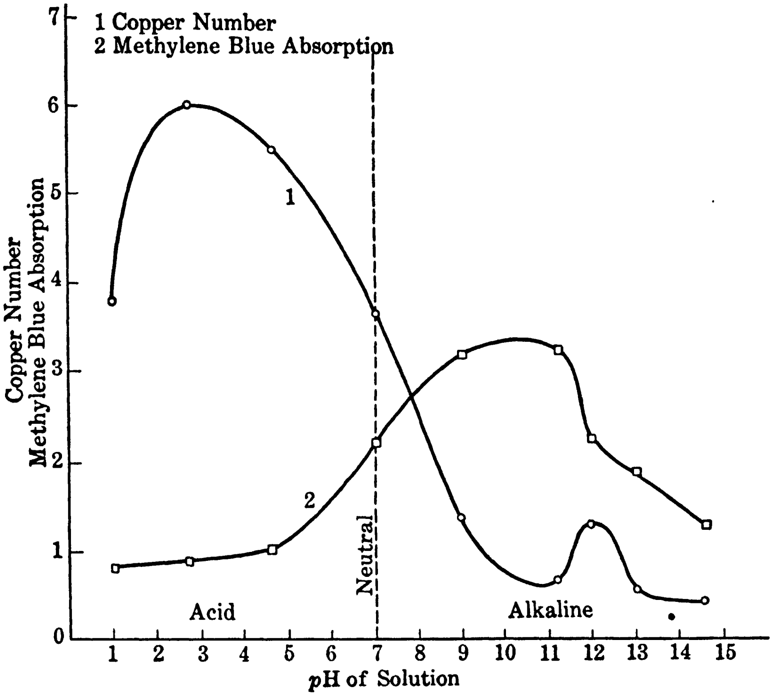

FIG. 95. Change of copper number and methylene blue absorption with hydrogen-ion concentration. Birtwell, Clibbens, and Ridge.

Since the alkalinity of the ash of cellulose markedly influences the methylene blue absorption (the latter increasing with increasing ash alkalinity[125]), care

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[125] Birtwell, Clibbens, and Ridge, *J. Textile Inst.*, **14**, T297 (1923); on the influence of the presence of inorganic salts upon methylene blue absorption see also Krüger, *Klepzig's Textil-Z.*, **44**, 647 (1941).

must be taken to secure samples of minimum ash alkalinity by means of thorough acid washing. The ash alkalinity of material so treated has been termed "residual ash alkalinity" for convenience. Those oxycelluloses which exhibit a high methylene blue absorption also possess a high residual ash alkalinity and show increasing methylene blue absorption with increasing residual ash alkalinity. Intensified treatment with acid, such as boiling with $N/10$ hydrochloric acid for 1 hour, reduces both the ash alkalinity and the methylene blue absorption value considerably. Since such a severe acid treatment is known to exert a substantial hydrolytic action upon cellulose, it cannot be considered as definitely proved that the decrease in methylene blue absorption is due solely to the diminished ash alkalinity. The acid-boiled material regains a high absorption and ash alkalinity on subsequent steeping in dilute alkali followed by normal (standard) cold acid washing (see Table 63).

TABLE 63

METHYLENE BLUE ABSORPTION AND ASH ALKALINITY OF OXYCELLULOSE

	Methylene Blue Absorption *	Ash Alkalinity †
A. Normally acid washed	5.8	5.4
B. Boiled with $N/10$ HCl, 1 hour	2.4	0.51
C. As in *B*, then steeped in $N/10$ NaOH and normally acid washed	4.8	4.55

* Results are recorded in millimoles of methylene blue per 100 grams of dry material and correspond to an end concentration of approximately 0.2 millimole of methylene blue per liter.

† Results are expressed in milliequivalents per 100 grams of dry material.

The Rate of Oxidation

If the time required for consuming the available chlorine from a hypochlorite solution of a given concentration is taken as a measure of the rate of oxidation, the influence of the hydrogen-ion concentration upon this rate may be investigated.

The rate of oxidation (half-time of complete consumption of available chlorine) as influenced by the hydrogen-ion concentration is shown in Fig. 96.[126]

The point on the extreme right represents the behavior of the most alkaline hypochlorite solution ($N/10$ in free sodium hydroxide), and the time required for complete consumption of the available chlorine (i.e., for overbleaching) is relatively long; that is, the rate of oxidation is very slow. With decreasing alkalinity of the hypochlorite solution, the rate of oxidation increases rapidly, as indicated by the fall of the time curve between *p*H 13 and 11. At *p*H 11 the rate increases;

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[126] Clibbens and Ridge, *J. Textile Inst.*, **18**, T136 (1927).

the increase is more marked at pH 9, and it reaches an accentuated maximum (shortest time for exhaustion of the hypochlorite solution) at the neutral point. The same maximum rate of oxidation is reached from the other (acid) side of the neutral point. Thus, the most rapid oxidation occurs in neutral solution, the reaction in a slightly acid as well as in a slightly alkaline solution being less rapid. This pronounced effect of the neutral solution (which is about ten times that of a solution at pH 9 or 4.6) is not caused by an action of the buffer salts used for adjusting the alkalinity and acidity, but is solely the result of the hydrogen-ion concentration.

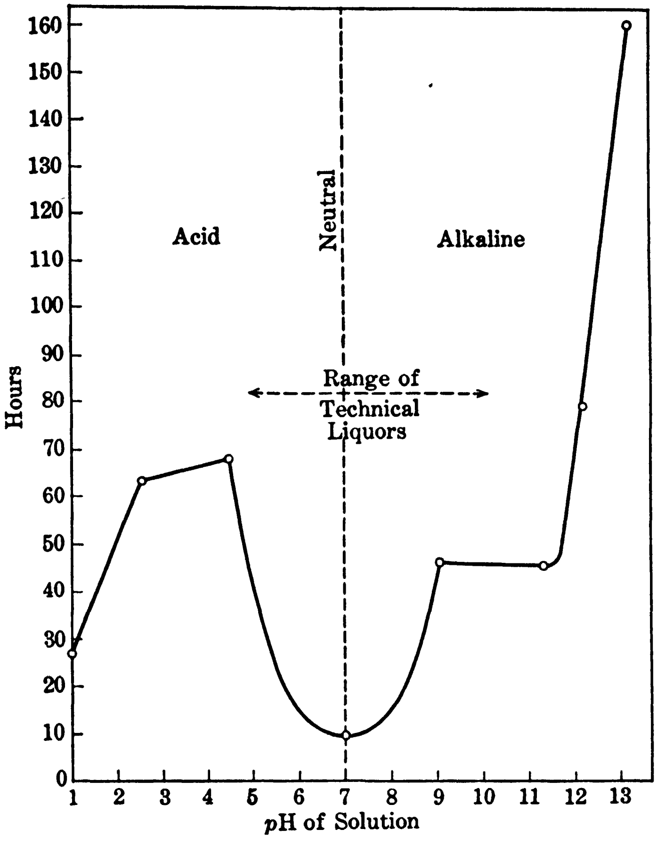

FIG. 96. Rate of oxidation as influenced by hydrogen-ion concentration. Clibbens and Ridge.

The interesting observation that the rate of oxidation is fastest near the neutral point has frequently been confirmed by other investigators, in both textile and wood pulp bleaching.[127] It is easy to understand that this fast rate of chlorine consumption involves the possibility of the cellulosic material being attacked far more than is desirable, and for this reason the neutral range is avoided in practical textile and pulp bleaching.

The effect of the hydrogen-ion concentration upon the rate of oxidation is, as could be anticipated, reflected in the copper number of the cellulose so oxidized. The copper number increases at an extremely low rate with alkaline bleach liquors at hydrogen-ion concentrations corresponding to *p*H 13 and 11; it is only slightly changed even after 50 hours of treatment. But as the solutions become less alkaline (*p*H 9 and 8), the rate of increase in copper number rises rapidly and becomes very high in the neutral solution until it again falls at *p*H 4.6. Likewise, the methylene blue absorption is most pronounced in the neutral solutions compared with the effect exerted in slightly acid or alkaline liquors.

The rapid action of *neutral* hypochlorite solutions is explained by the relatively high concentrations of the effective oxidizing agents, i.e., hypochlorous acid and hypochlorite ion, which exist simultaneously in such solutions.[128]

If the concentration of the alkali in the hypochlorite solution is increased to values corresponding to 3 *N* or 4 *N*, an interesting, *a priori* unexpected, effect is noticed.[129] The rate of oxidation becomes very high. This is due to the mercerizing action of the strong alkali, the mercerized cotton being attacked much more rapidly than the unmercerized material.

The results of investigations pertaining to the rate of oxidation under the influence of *other oxidizing agents* may be summarized as follows: Under the same conditions of alkalinity, the rate of oxidation by hypobromite solution is considerably more rapid than by hypochlorite solutions; this shows that the activities of the two oxidizing agents are of a different order. On the other hand, a pure potassium dichromate solution is without significant effect upon bleached cotton but, in the presence of *N*/10 sulfuric acid, a rapid rise of the copper number occurs with the time of treatment. This effect becomes still more pronounced with the use of *N*/5 sulfuric acid. Under the same conditions, sulfuric acids of these concentrations have practically no

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[127] Hochberger in Heuser and Opfermann, "Die Bleiche des Zellstoffs," Vol. II, O. Elsner Verlags-Ges., Berlin (1936), p. 92, with other literature quoted; see also Elöd and Vogel, *Melliand Textilber.*, **18**, 64 (1937); Crain, *Paper Trade J.*, **63**, No. 24, 37 (1936); Hisey and Koon, *ibid.*, **103**, No. 6, 36 (1936); Weber and Huseman, *J. prakt. Chem.*, **161**, 24 (1942).

[128] Förster and Jorre, *J. prakt. Chem.*, **59**, 53 (1899); **63**, 147 (1901).

[129] Clibbens and Ridge, *loc. cit.*, p. T141.

effect upon cellulose of the type used in these experiments. Since the copper number increases very nearly proportionally to the time of treatment, the method appears useful for the preparation of oxycellulose of a desired copper number.[130]

The substitution of oxalic for sulfuric acid in the dichromate combination supplies an interesting example of oxycellulose formation in which the reaction between cellulose and the oxidizing agent is greatly accelerated by the simultaneous oxidation of a third substance. If dichromate in the presence of oxalic acid is allowed to act upon bleached cotton, both substances, cellulose and oxalic acid, are oxidized, and the oxidation of the cellulose, measured by the increase of the copper number with increasing dichromatic concentration of the oxidizing solution, takes place roughly 100 times more rapidly than with sulfuric acid. Since the relation between the copper number and the volume of the dichromate solution employed is strictly linear, an oxycellulose of very high reducing properties may be conveniently prepared.[131]

Another example [132] which shows the acceleration of the oxidation of cellulose by a third substance (which itself is also oxidized) is afforded by treating cotton which has absorbed a reduced vat dye with hypochlorite solution. The dye is converted into its oxidized form with great rapidity and, within this short time, the cellulose is also oxidized to an extent which is attained with undyed cotton only after treatment with hypochlorite solution for several hours.[133]

Likewise, cotton into which a very small quantity of basic chromium carbonate has been incorporated is oxidized by sodium hypochlorite solution at a much faster rate than when chromium is absent. It is probable that the effect is due to the presence of trivalent chromium, for any conditions which affect the rate of oxidation of trivalent to hexavalent chromium by the hypochlorite solutions were found also to effect the rate of the cellulose oxidation.[134]

On the other hand, it is interesting to note that certain dyestuffs are capable of protecting cellulose against oxidative attack.[135]

The action of alkaline permanganate [136] resembles that of alkaline hypobromite. Experiments with graded permanganate solutions have shown that the activity of this oxidizing agent is smallest in solutions at *p*H 9. Produced with solutions on the acid side of *p*H 9, the oxycelluloses were characterized by high copper number and, on the alkaline side, by high methylene blue absorption. The great activity of

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[130] Clibbens and Ridge, *loc. cit.*, pp. T141–T147.

[131] Clibbens and Ridge, *loc. cit.*

[132] Turner, Nabar, and Scholefield, *J. Soc. Dyers Colourists,* **51,** 5 (1935); Nabar, Scholefield, and Turner, *ibid.*, **53,** 5 (1937).

[133] Davidson, *J. Soc. Dyers Colourists,* **56,** 59 (1940).

[134] Clibbens and Ridge, *loc. cit.*, p. T148.

[135] Knecht and Egan, *J. Soc. Dyers Colourists,* **39,** 67 (1923).

[136] Dorée and Healey, in Dorée, "The Methods of Cellulose Chemistry," p. 142; *J. Soc. Dyers Colourists,* **49,** 290 (1933); see also Knecht and Thompson, *ibid.*, **38,** 132 (1932).

permanganate buffered to pH 11.2 with sodium carbonate and the slow action in the acid medium are remarkable. It was found that 0.5 atom of permanganate oxygen per $C_6H_{10}O_5$ unit was consumed by cotton in 1 N sodium hydroxide solution in 25 minutes, whereas in 1 N sulfuric acid solutions 10 hours were required.

The Various Types of Oxycellulose and Their Properties

The results which have been presented in the foregoing sections indicate that we may distinguish between two types of oxycelluloses.[137] Those characterized by high copper number and low methylene blue absorption may be termed *oxycelluloses of the reducing type* (1) and those possessing a high methylene blue absorption with comparatively low copper number, *oxycelluloses of the nonreducing or acidic type* (2). However, in most cases, the properties overlap each other. Exceptions are evidently Jackson and Hudson's periodate oxycellulose and Yackel and Kenyon's nitrogen dioxide oxycellulose.

It is noteworthy that the differentiation of the two types of oxycelluloses is essentially the same as that which Witz had suggested in 1883 and Nastukoff in 1900, a fact which—as Birtwell, Clibbens, and Ridge have pointed out—has been overlooked by most subsequent investigators.

Thus, celluloses of the reducing type are generally obtained by oxidation in an acid or neutral medium, whereas oxidation in an alkaline medium results in oxycelluloses of the nonreducing type. The two types may be distinguished by the reactions which have been discussed in an earlier section.

In addition, some other tests may be employed. The following are suitable for the identification of the reducing type: Cross and Bevans' Turnbull's blue test,[138] Haller's gold purple reaction,[139] and, particularly, Witz' and Nastukoff's phenylhydrazine test.[140] The usefulness of these tests has been recently reviewed by Müller.[141] It was found that the presence in cotton fabrics and yarns of oxycellulose resulting from the action of calcium hypochlorite solution may be revealed more distinctly by replacing phenylhydrazine with arylhydrazines,

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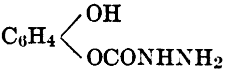
[137] Birtwell, Clibbens, and Ridge, *J. Textile Inst.*, **16**, T47 (1925).

[138] Schwalbe, "Chemie der Cellulose," 1st ed., p. 251; Thomas, *J. Soc. Chem. Ind.*, **52**, 79T (1933).

[139] Haller, *Helv. Chim. Acta*, **14**, 578 (1931); *Melliand Textilber.*, **12**, 257, 517 (1931).

[140] Witz, *Soc. Ind. Rouen*, **10**, 448 (1882); Nastjukoff, *Ber.*, **33**, 2237 (1900).

[141] Müller, *Helv. Chim. Acta*, **22**, 208, 217, 376 (1939). For still other tests see Freiberger, *Melliand Textilber.*, **11**, 127 (1930), and Forster, Kaji, and Venkataraman, *J. Soc. Chem. Ind.*, **57**, T130 (1938).

such as hydrazinonaphtholsulfonic acid. The compound thus formed is made visible by allowing the treated oxycellulose to react with diazo compounds; this results in the formation of an intensively colored dye. Likewise, the reaction of the pyrocatechol ester of hydrazinocarboxylic acid,  $C_6H_4\langle{}^{OH}_{OCONHNH_2}$ (which is a specific for the identification of aldehyde in contrast to keto groups), may be utilized. When the treated oxycellulose is coupled with diazo compounds, an intensively colored dye is formed.

Oxycelluloses of the nonreducing (acidic) type, which are characterized by pronounced absorptivity for basic dyes, exhibit diminished affinity for direct dyes.[142] When the absorption of a direct dye (Sky Blue FF) by alkaline hypobromite oxycellulose was plotted against the carboxyl content of the oxycellulose (determined by the titration method of Neale and Stringfellow[143]) the curve obtained (Fig. 97) showed that the absorption of the dye decreased as the carboxyl content increased.[144]

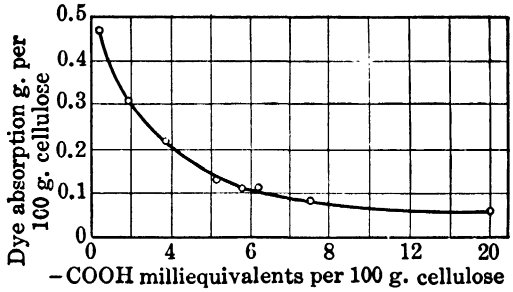


FIG. 97. Direct-dye absorption and carboxyl content of oxycellulose. Absorption of sky blue FF by various oxycelluloses at 90° and pH 6.2 from a solution containing 0.05 g. dye per l. and 5.0 g. sodium chloride per l. Neale and Stringfellow.

The reducing and the nonreducing types of oxycellulose may be distinguished also by their behavior with *boiling dilute sodium hydroxide solution.*[145] The abnormal loss in weight which occurs on this treatment is chiefly a property of the reducing type. The percentage loss

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[142] Birtwell, Clibbens, and Ridge, *loc. cit.*, p. T48; see also Knecht, *J. Soc. Dyers Colourists,* **37,** 76 (1921).

[143] See the discussion of this method on p. 430.

[144] Neale and Stringfellow, *J. Soc. Dyers Colourists,* **56,** 17 (1940); see also Hanson, Neale, and Stringfellow, *Trans. Faraday Soc.*, **31,** 1719 (1935); Neale, *J. Soc. Dyers Colourists,* **52,** 252 (1936), and Boulton and Morton, *ibid.*, **56,** 151 (1940).

[145] Birtwell, Clibbens, and Ridge, *loc. cit.*, pp. T15, T25, T45.

on boiling with dilute alkali and the copper number of such oxycelluloses follow approximately a straight line—the higher the copper number of the oxycellulose, the higher the loss in weight. In contrast, the nonreducing oxycelluloses are more stable to alkaline boiling; also, their ability to absorb methylene blue is increased rather than diminished.[146]

As mentioned earlier in this chapter, the copper number is diminished by boiling with alkali and, if this treatment is sufficiently prolonged, the boiled material cannot be distinguished from unmodified cellulose by the copper number test.

The Viscosity of Oxycelluloses and Its Relation to Various Properties

The direct relation which exists between the consumption of oxygen and the viscosity of oxycelluloses is somewhat disturbed in the early stages of oxidation because part of the oxygen is consumed for the bleaching of impurities left in the cellulose preparations. These disturbances disappear, however, when the oxygen attacks the cellulose more thoroughly, and the fall in viscosity then follows the consumption of oxygen rather closely. Under such conditions, the relation is independent of the nature of the oxidizing agent and, consequently, of the type of oxycellulose produced.[147]

Similar conclusions may be drawn from a comparison of the fall in viscosity and the fall in *tensile strength* of textile materials containing increasing quantities of oxycellulose. In general, the relation between viscosity and tensile strength follows a straight line.[148] Viscosity measurements thus represent a valuable method for detecting tendering effects in cotton and other textiles resulting from the formation of oxycellulose on bleaching. Such strength-decreasing effects are, of course, also to be expected from the presence of hydrocellulose (see later).

A similar relation exists between physical properties and viscosities of paper-making cellulosic materials.[149] When an attempt is made to establish this relation with cellulose fibers in the form of a sheet of pulp or paper, it should be borne in mind that the physical properties of the sheet depend not only upon the strength of the single fibers but also to a great extent upon the manner in which the fibers are arranged in the sheet and the resulting entanglement and bonding between them. An undisturbed relationship between viscosity and physical strength properties can therefore be expected only if the strength test

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[146] Clibbens, Geake, and Ridge, *J. Textile Inst.*, **18**, T277 (1927).

[147] Birtwell, Clibbens, and Ridge, *J. Textile Inst.*, **16**, T16, T40, T46 (1925).

[148] Farrow and Neale, *J. Textile Inst.*, **15**, T157 (1924); Clibbens and Ridge, *ibid.*, **19**, T389 (1928); Ridge and Bowden, *ibid.*, **23**, T319 (1932).

[149] Staudinger, Sorkin, and Franz, *Melliand Textilber.*, **18**, 681 (1937); Staudinger and Sorkin, *Ber.*, **70**, 1565 (1937).

is applied to single fibers. This limitation, no doubt, also holds to a varying extent with cellulose fibers in the form of fabrics, yarns, etc.

The relation which exists between viscosity (degree of polymerization) *and alkali-solubility* of cellulose has been confirmed with oxycellulose-containing materials and oxycelluloses prepared under strictly standardized conditions. Thus, the solubility increases rather regularly as the viscosity decreases.[150] However, it was found that the relation between the alkali-solubility of oxycelluloses (in a 2.5 N sodium hydroxide solution at $-5°$) and the viscosity in cuprammonium hydroxide solution is not the same for all types of oxycelluloses.[151] Whereas samples prepared by the action of alkaline hypobromite or alkaline hypochlorite or dichromate in the presence of sulfuric or oxalic acid showed approximately the same viscosity-solubility relationship as hydrocelluloses, neutral hypochlorite and acid hypochlorite oxycelluloses were considerably more soluble than hydrocelluloses of the same viscosity. This difference may possibly be explained, at least in part, by a difference in chain length distribution in the two types of modified cellulose.

The Effect of Alkali Treatments upon Viscosity and Related Properties

The viscosity of certain oxycellulose preparations or oxycellulose-containing materials suffers a more or less pronounced reduction on boiling with a dilute alkali—for example, with 1 per cent sodium hydroxide solution for 6 hours. The oxycelluloses differ in this respect from hydrocelluloses and from normally bleached cotton which are but slightly affected in viscosity by the same treatment.[152] This effect is particularly pronounced with oxycelluloses of the reducing type, i.e., those prepared in an acid medium, whereas those prepared in an alkaline medium are hardly affected. As an explanation it has been suggested,[153] that, in general, the oxidation of cellulose does not lead directly to the rupture of glycosidic linkages (except of those which may break under the influence of the acid medium) but merely renders them extremely susceptible to hydrolysis by alkali. By analogy, it is assumed that the attack of hydroxyl groups adjacent to glycosidic linkages is accompanied by a weakening of the latter. However, oxy-

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[150] Birtwell, Clibbens, and Geake, *J. Textile Inst.*, **19**, T360 (1928).

[151] Davidson, *J. Textile Inst.*, **25**, T174 (1934).

[152] Birtwell, Clibbens, and Ridge, *J. Textile Inst.*, **16**, T44 (1925); Clibbens, Geake, and Ridge, *ibid.*, **18**, T277 (1927); Ridge and Bowden, *ibid.*, **23**, T321 (1932).

[153] Davidson, *J. Textile Inst.*, **25**, T174 (1934); *ibid.*, **27**, P163 (1936).

celluloses which are prepared in an alkaline medium would contain no such sensitive linkages because these are broken by the alkali present in the oxidizing mixture. Oxycelluloses of this type may be expected to behave similarly to hydrocelluloses which likewise contain no alkali-sensitive linkages. Thus, whereas the types of oxycelluloses differ widely with the type of oxidation involved and the extent to which the oxidation has been carried, they are reduced to about the same viscosity level by boiling with dilute alkali. Consequently, the viscosity-alkali solubility relation established for the boiled materials of very different types may be expressed by a single curve which is almost coincident with the curve for (unboiled) hydrocellulose. The effect of cold sodium hydroxide solution (0.1 *N* for 24 hours at 20°) is very similar,[154] and so is that exerted by a number of organic bases.[155]

Boiling with dilute alkali also affects the tensile strength of oxycelluloses and, to a much greater extent, that of oxycelluloses of the highly reducing type.[156] This has been demonstrated with potassium dichromate oxycellulose. The rapid increase of the reducing power is accompanied by a very slow reduction in tensile strength, which seems to indicate that only slight cleavage of chain molecules has occurred. However, on boiling the dichromate oxycellulose in dilute alkali, a further but considerable decrease of tensile strength is produced. The glycosidic linkages in oxycelluloses of this type are so sensitive that the drop in tensile strength may be observed even after treatment with cold alkali, soap solutions, or water (Davidson). Such treatments, as well as boiling with dilute alkali, do not have an appreciable effect upon unmodified cellulose, as will be recalled; likewise, they have but little effect upon hydrocellulose.

If the weakened glycosidic linkages are so easily broken by the action of bases, it is to be expected that they will be affected also when an oxycellulose of this type is dissolved in cuprammonium hydroxide, which is a strong base. In fact, it was found that the cuprammonium viscosity of the highly reducing dichromate oxycellulose was abnormally low considering that its tensile strength had suffered only little. Hence, it would seem that, in such cases, the cuprammonium viscosity does not express the (average) chain length of the oxycellulose as it results from the acid dichromate treatment but a chain length which has subsequently been shortened under the influence of the cuprammonium base. If, however, the oxycellulose were subjected to alkaline treatment before it is dissolved in cuprammonium, little or no further change of the viscosity should occur on solution.

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[154] Brownsett and Davidson, *J. Textile Inst.*, **32**, T25 (1941).

[155] Brownsett and Davidson, *loc. cit.*, p. T57.

[156] Clibbens and Ridge, *J. Textile Inst.*, **19**, T389 (1928).

The Relation Between Cuprammonium and Nitrate Viscosity

To obtain evidence to test the above hypothesis, it was thought[157] that a true measure of the actual average chain length of oxycellulose would be available for all cases, if its viscosity could be determined without the use of an alkaline medium. The method adopted for this purpose was to nitrate the oxycellulose under conditions under which cellulose is not degraded and to determine the viscosity of the solution of the oxycellulose nitrate in acetone. Under the action of the nitration acid the alkali-sensitive glucosidic linkages should be retained.

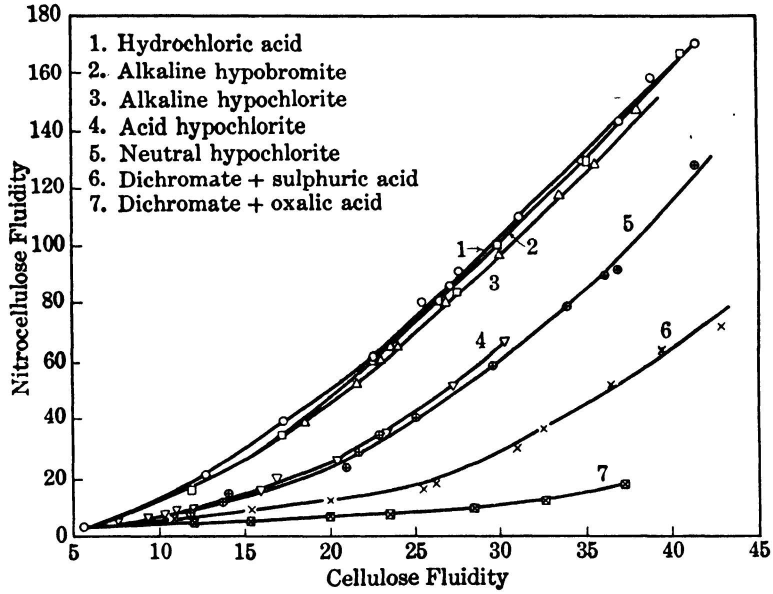

FIG. 98. Relation between cuprammonium and nitrate fluidities of modified cotton. Davidson.

The experiment has largely confirmed the hypothesis: Oxycelluloses of the reducing type were found to display the same nitrate viscosity as, but a considerably lower cuprammonium viscosity than, hydrocellulose. Likewise, it was found that the nitrate viscosity of those oxycelluloses which had been subjected to treatment with alkali was lower than that of oxycellulose not so treated, whereas the nitrate viscosity of hydrocellulose which had been subjected to the same alkaline treatment remained unaffected. In further agreement with

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[157] Davidson, *J. Textile Inst.*, **29**, T195 (1938).

the hypothesis, the relation between cuprammonium viscosity and nitrate viscosity differed widely for the different kinds of oxycellulose, the cuprammonium viscosity corresponding to a given nitrate viscosity being much lower for the reducing types of oxycellulose than for hydrocellulose, whereas the nonreducing types gave almost the same relation as hydrocellulose. This is demonstrated in Fig. 98, in which viscosities are expressed in reciprocal values, i.e., in fluidities ("cellulose fluidity" meaning cuprammonium fluidity of the modified celluloses).

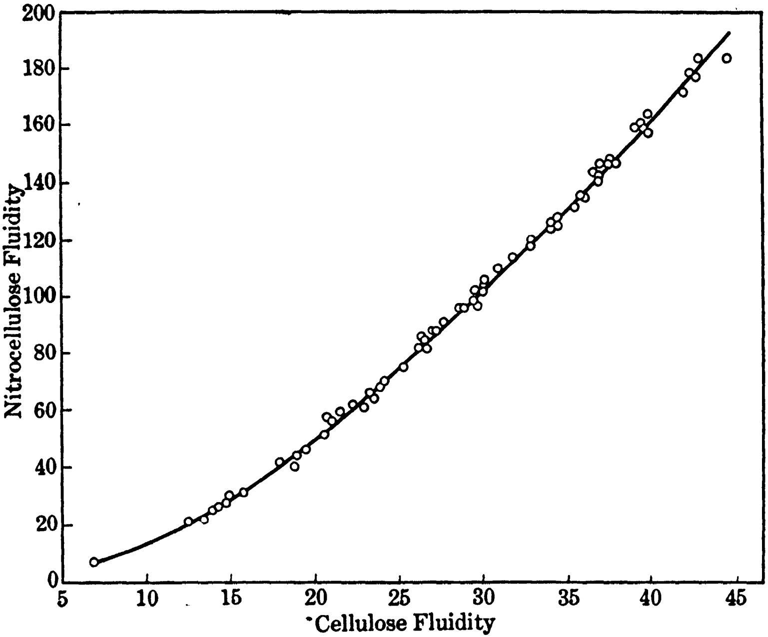

FIG. 99. Relation between cuprammonium and nitrate fluidities of modified cotton exposed to boiling with dilute alkali. Davidson.

Fig. 99 demonstrates that the relation between the two types of viscosities was the same for all types of modified cotton, irrespective of the method of modification, provided that the materials had been boiled in dilute sodium hydroxide solution prior to nitration.

If the nitrate viscosity is a measure of the average chain length as it exists in the oxidized fiber prior to alkaline treatment, and if the tensile strength is a function of the chain length, the relation between nitrate viscosity and tensile strength ought to be the same for all types of modified cellulose. Indeed, a much closer approach to a general relation between the two properties, applicable to all methods of modification, was observed when the nitrate viscosities rather than the cuprammonium viscosities were used in an attempt to establish this relation.

Since the effect of cuprammonium hydroxide solution upon alkali-sensitive glycosidic linkages in oxycellulose of the reducing type is, apparently in some cases, not quite so profound as that of aqueous alkalies,[158] Davidson believes that the most generally satisfactory method of using viscosity measurements as an indication of the extent of damage is to carry them out after the material has been boiled with dilute sodium hydroxide solution. After this treatment, it appears immaterial whether the cuprammonium or the nitrate viscosity method is used. For practical purposes, the cuprammonium method is preferable because it is simpler.[159]

MECHANISMS INVOLVED IN THE OXIDATION OF CELLULOSE

Experimental evidence seems to indicate that most oxidizing agents attack the primary alcohol groups (in the 6-position) of the glucose residues, converting them into aldehyde and further into carboxyl groups. These conversions may be followed and recognized as two consecutive reactions if the oxygen consumption of the cellulose is kept at a low level.[160] With more oxygen being admitted—and particularly under suitable *p*H conditions—the second reaction becomes predominant, resulting in the formation of glucuronic acid units.

Whereas in most cases only a relatively small quantity of the cellulose is converted into such units, *nitrogen dioxide* converts most, if not all, of the primary hydroxyl groups into carboxyl groups (p. 427). That no other hydroxyl groups are oxidized is seen from (1) the fact that, in the presence of an excess of oxidant, the production of carboxyl groups practically ceased when the carboxyl content approached the theoretical value for polyanhydroglucuronic acid, from (2) the high acetyl content of an acetate prepared from the nitrogen dioxide oxycellulose, and from (3) the fair agreement between the carboxyl content values resulting from the titration methods and those resulting from the decarboxylation method. If other than primary hydroxyl groups had been oxidized, the acetyl content should have been lower and the titration values should have been considerably higher than the decarboxylation values. Further proof of these conclusions may be expected from the results of hydrolysis of the nitrogen dioxide oxycellulose.

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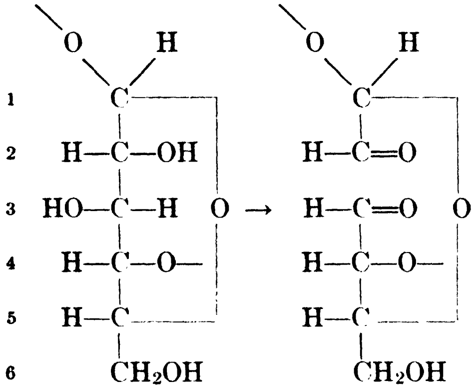
[158] Davidson, *loc. cit.*; Brownsett and Davidson, *loc. cit.*, p. T28.

[159] See, however, Berl, *Ind. Eng. Chem., Anal. Ed.*, **13**, 322 (1941).

[160] Kalb and Falkenhausen, *Ber.*, **60**, 2514 (1927); Birtwell, Clibbens, Geake, and Ridge, *J. Textile Inst.*, **21**, T97 (1930).

In contrast to nitrogen dioxide and other oxidizing agents, *periodic acid* preferentially oxidizes the two secondary hydroxyl groups, i.e., those in the 2- and 3-positions of the glucose residue which thus, are converted into 2 carbonyl groups (p. 426). As a result dialdehyde (diketone) units are formed. The reaction is illustrated by the two formulas:



Evidence that the product of periodic acid oxidation of cellulose possesses the indicated structural units is seen from the fact that complete hydrolysis with hydrochloric acid yields glyoxal and *d*-erythrose. Thus, periodic acid breaks the carbon chain of the glucose residues between carbon atoms 2 and 3. The low yields of glyoxal and *d*-erythrose (about 20 per cent of the theoretical) is regarded as due, at least in part, to some destruction of material, which evidently occurs during hydrolysis, and to incomplete oxidation of the cellulosic material. Other types of units may also be formed in minor quantities.[161] Besides, recondensation of glyoxal and erythrose in the acid medium appears probable.[162]

In agreement with the dialdehyde structure shown above, the oxidized cellulose possesses high reducing power and reacts immediately with phenylhydrazine. There is little indication of the presence of carboxyl groups in the early stages of oxidation, and oxycellulose thus prepared may be classified as belonging to the highly reducing type.

However, on prolonged oxidation, carboxyl groups are formed, and its formation continues after the oxidation to the dialdehyde stage has come to an end.[163] The solubility of the oxidized cellulose in aqueous sodium hydroxide solution

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[161] Jackson and Hudson, *J. Am. Chem. Soc.*, **59**, 2049 (1937); **60**, 989 (1938).

[162] Mitchell and Purves, *ibid.*, **64**, 589 (1942); Grangaard, Gladding, and Purves, *Paper Trade J.*, **115**, No. 7, 41 (1942).

[163] Goldfinger, Mark, and Siggia, *Ind. Eng. Chem.*, **35**, 1083 (1943).

showed a linear increase with increasing degree of oxidation but not more than 40 per cent was soluble in 17.5 per cent caustic soda solution at 20°. From the trend of the rate of oxidation and the relatively low solubility of the oxidized cellulose, Goldfinger, Mark, and Siggia conclude that first the glucose units on the internal surface are oxidized, first to dialdehyde groupings, and as the availability of unoxidized glucose units decreases, the aldehyde groups are oxidized to carboxyl groups. Further penetration of the oxidizing agent and oxidation of glucose units in the interior of the fiber is detectable only after completion of the oxidation at the readily available surface. In the light of this interpretation it would appear that the alkali-solubility data indicate depth of oxidation rather than alkali-resistance and solubility to be a function of the degree of polymerization.[164]

The presence in periodic acid oxycellulose (of a limited degree of oxidation) of units of the structure indicated would let us expect that it would be particularly sensitive to alkali but stable to acids. On this basis, the assumption may be made that oxidation with periodic acid leads to cleavage of glycosidic linkages only when the product is subjected to treatment with alkali, or, although possibly to a lesser extent, with cuprammonium hydroxide solution.

The work of Davidson[165] has given convincing proof of this assumption and has thus supplied an excellent confirmation of his hypothesis on the existence of alkali-sensitive glycosidic linkages in oxycelluloses of the highly reducing type.

In following the restricted action of periodic acid upon cellulose[166] in its early stages (during which alkali-sensitivity could be expected to be most strikingly displayed), Davidson observed a rapid decrease in the cuprammonium viscosity but only a very small decrease in the nitrate viscosity of the oxidized samples. Indeed, the nitrate viscosities of the oxycelluloses were only slightly lower than those of the original cellulose. At the same time, the oxidized fiber retained considerable tensile strength. However, after treatment with cold dilute alkali, the nitrate viscosity and the tensile strength were considerably lower. Even such mild agents as very dilute borax solution or even boiling water resulted in a steadily falling nitrate viscosity. Moreover, after alkali boiling, the periodic acid oxycelluloses showed the same relation between cuprammonium viscosity and nitrate viscosity as hydrocellulose and alkali-boiled oxycelluloses of other types.

Davidson's results were confirmed by Harris and co-workers.[167]

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[164] Any influence of the presence of carboxyl groups upon alkali-solubility would depend upon the quantity produced (see p. 442).

[165] Davidson, *J. Textile Inst.*, **29**, T195 (1938); *ibid.*, **32**, T25 (1941).

[166] The oxygen consumption was limited to 1.0 atom per 100 glucose residues.

[167] Rutherford, Minor, Martin, and Harris, *J. Research Natl. Bur. Standards*, **29**, 131 (1942).

Indeed, the alkali-sensitivity of the periodic acid oxycellulose appears to be proportional to its content of aldehyde groups. It is most interesting that the alkali-instability practically disappeared upon the conversion of the aldehyde groups into carboxyl groups. This result suggests that the sensitivity to alkali does not depend solely on the rupture of the glucose ring between carbon atoms 2 and 3 but is related to the specific instability of the dialdehyde formed during the oxidation (see also Goldfinger, Mark, and Siggia, above).

Davidson believes that the mechanism which is involved in the action of periodic acid upon cellulose is probably also operative in the formation of other alkali-sensitive oxycelluloses of the highly reducing type. Of the two kinds of primary oxidation, the one in which rupture of the pyranose ring occurs would appear to affect the ease of hydrolysis of neighboring glycosidic linkages (attached to carbon atoms 1 and 4) more readily than that in which conversion of a side group (the primary alcohol group in the 6-position) occurs. Nevertheless, the behavior of Yackel and Kenyon's nitrogen dioxide oxycellulose seems to indicate that carboxyl groups in the 6-position, at least if present in sufficient number, also have a certain weakening influence upon the glycosidic linkages. It will be recalled that these linkages in this type of oxycellulose are broken down to a considerable extent under the influence of hot Fehling solution; this results in the formation of numerous reducing groups. A similar result was observed when the oxycellulose was boiled in water.

Similar hypotheses to explain the difference between cuprammonium and nitrate viscosity of oxycelluloses prepared in an acid medium as suggested by Davidson have been advanced by Staudinger and co-workers.[168] They confirmed Davidson's observation that chromic acid oxycellulose dissolved in cuprammonium hydroxide reveals a lower degree of polymerization than the nitrate prepared therefrom and dissolved in acetone. Moreover, they found that chromic acid oxycellulose, regenerated from its solution in cuprammonium hydroxide, possessed very nearly the same degree of polymerization as the original oxycellulose (in cuprammonium), and that practically no change occurred when the regenerated oxycellulose was converted into the nitrate. The results obtained with four chromic acid oxycellulose preparations of increasing degree of oxidation are summarized in Table 64.

The difference between the degree of polymerization of the oxycelluloses in cuprammonium hydroxide and that of their nitrates in acetone is explained on the assumption that, in oxycellulose, the glucose residues are united not only by glycosidic but also by "ester linkages" and that these ester linkages break down under the influence of cuprammonium hydroxide and alkali, whereas they are stable to acids and thus are retained during the process of nitration. The difference in degree of polymerization thus disappears, if oxycellulose, regener-

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[168] Staudinger and Sohn, *Ber.*, **72**, 1712 (1939); *J. prakt. Chem.*, **155**, 184 (1940).

TABLE 64

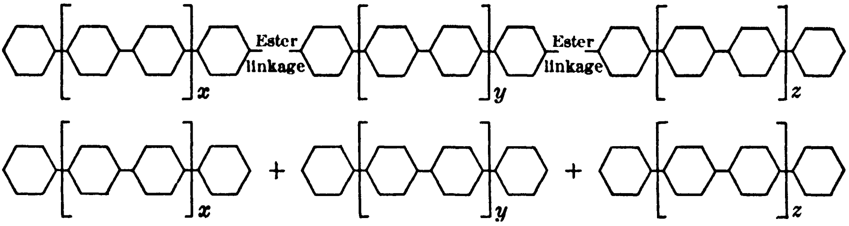
VISCOSITIES OF OXYCELLULOSES IN CUPRAMMONIUM HYDROXIDE AND OF THEIR NITRATES IN ACETONE

Chromic Acid Oxycellulose, D.P. Cuam.*	Oxycellulose Nitrate, D.P. Acetone	Regenerated Oxycellulose, D.P. Cuam.	Regenerated Oxycellulose Nitrate, D.P. Acetone
460	1530	400	430
360	1700	290	310
260	1400	240	255
185	740	170	195

* Degree of polymerization calculated from viscosities in cuprammonium hydroxide.

ated from its solution in cuprammonium, is converted into the nitrate (third and fourth columns of Table 64).

Staudinger has illustrated the occurrence of ester linkages (in addition to glycosidic linkages) and the hydrolysis of the ester linkages thus:



According to Staudinger and Sohn,[169] ester linkages may be formed in various ways. One of these possibilities consists of the oxidation of the hydroxyl groups in the 2- and 3-positions to diketone groupings and subsequent oxidation of these groupings to carbonic acid ester groupings. The latter would be easily saponified by alkali.

Oxycelluloses of the type indicated above have been given the name "ester oxycelluloses."

The difference between the "cuprammonium degree of polymerization" and the "nitrate degree of polymerization" is expressed as the "chain length difference" (*Kettenlängendifferenz*) and equals

$$\frac{\text{D.P. Nitrate} - \text{D.P. Cellulose (Cuam.)}}{\text{D.P. Cellulose (Cuam.)}} \times 100$$

When the chain length difference was determined for a large number of pulps from different sources, it was found that this difference varied within wide limits, but disappeared when the pulps were dissolved in cuprammonium hydroxide and regenerated therefrom. Likewise, the chain length difference became much less pronounced after the pulps had been subjected to a short treatment

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[169] See particularly Staudinger and Sohn, *J. prakt. Chem.*, **155**, 186 (1940).

with dilute alkali. For the same reason, alkali-refined pulps ("*alpha*-pulps") showed a smaller chain length difference.[170]

To detect chain length differences in oxycelluloses, viscosity determinations may be made with their *acetates* instead of their nitrates.[171] An "ester oxycellulose" of a degree of polymerization of 340, subjected to the action of acetic anhydride and pyridine, according to the method of Hess and Ljubitsch, yielded an acetate which was insoluble in organic solvents.[172] If, however, the oxycellulose had been subjected to a swelling treatment with 90 per cent phosphoric acid, the acetate was soluble in *m*-cresol. Viscosity measurements showed that the degree of polymerization of the oxycellulose acetates was considerably higher than that of the original oxycelluloses in cuprammonium hydroxide (Table 65). Moreover, it was found that the cuprammonium viscosity of the oxycelluloses was not affected by the swelling procedure (column 3) and that the degree of polymerization of the oxycelluloses regenerated from their acetates by alkali (column 5) was about the same as that of the original oxycelluloses (column 2).

TABLE 65

DEGREE OF POLYMERIZATION OF OXYCELLULOSES AND OXYCELLULOSE ACETATES AND INFLUENCE OF TREATMENT WITH PHOSPHORIC ACID

Type of Cellulose	D.P. Oxycellulose—Cuam.	D.P. Oxycellulose After Swelling in H_3PO_4—Cuam.	D.P. Oxycellulose Acetate—*m*-Cresol	D.P. Oxycellulose Regenerated from Acetate—Cuam.
Cotton	340	310	460	270
Cotton	950	950	1150	900
Ramie	400	410	640	350

The Mechanism Involved in the Aging of Alkali Cellulose

The aging of alkali cellulose, i.e., the oxidation of cellulose by air or oxygen in the presence of strong alkali (p. 126), could be expected to lead to oxycellulose of the nonreducing type. Indeed, the formation of oxycellulose on aging has been compared with that resulting from the action of potassium hypobromite in the presence of alkali, the same mechanism being postulated in both cases.[173]

When an *adjusted* amount of oxygen is admitted to alkali cellulose and the oxygen absorption values, determined at intervals, are plotted against the time of aging, a curve is obtained which shows that the rate of oxygen absorption increases for some time and then becomes

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[170] Staudinger and Sohn, *loc. cit.*, pp. 198, 213 (1940); *Cellulosechem.*, **18**, 25 (1940).

[171] Staudinger and Sohn, *loc. cit.*, p. 198.

[172] A surprising result, considering the fact that cellulose acetates of such low degree of polymerization are usually soluble in organic solvents.

[173] Davidson, *J. Textile Inst.*, **23**, T95 (1932).

practically constant. This has been explained by the hypothesis that, under these conditions, oxidation consists of two consecutive reactions. Further support of this hypothesis was derived from the following experiment. Alkali cellulose was allowed to absorb oxygen for 8 hours at 40°, when the initial increase in the rate of absorption had ceased and the rate had been constant for about 4 hours. After the sample had been evacuated, it was again exposed to oxygen and the experiment repeated. Here (except for a slight disturbance near the beginning, i.e., until thermal equilibrium had been attained) the rate of absorption was constant from the start, and equal to the maximum rate reached in the first run. The results are shown in Fig. 100. The oxygen absorption is expressed in decrease of volume of gas in the apparatus in which the sample of cotton alkali cellulose was being exposed. Davidson has interpreted these curves as follows.

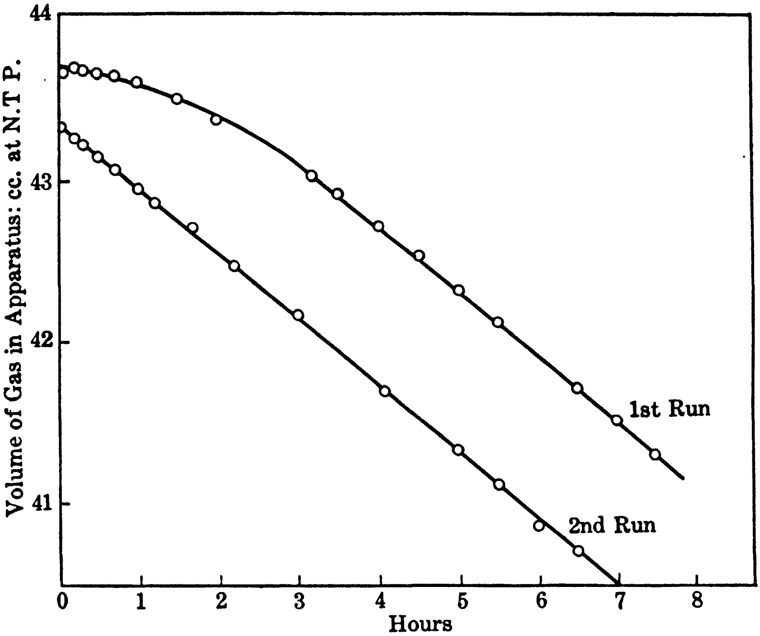

FIG. 100. Rate of oxygen absorption by alkali cellulose. Davidson.

The first reaction proceeds at a constant rate. However, the product of this reaction is in turn oxidized and, as the product increases in amount, the rate of absorption of oxygen in this second reaction will increase. When the reaction has been in progress for some time, a stage will be reached in which the product of the first reaction is oxidized as fast as it is formed; its amount will then remain constant and, hence, its rate of oxidation will also remain constant. In order that an increase in the rate of oxidation may occur, the velocity constant of the second reaction must be great compared with that of the first reaction, since the active mass of the intermediate product must be small compared with that of the cellulose. This interpretation proved to be in good agreement with the results of the mathematical treatment of the reactions.

The hypothesis was further tested by following the changes of the copper number and the methylene blue absorption over the period of oxidation; it was found that the copper number rose rapidly at first, but the rate of increase with increasing oxygen consumption gradually fell, whereas the methylene blue absorption increased continuously with the absorption of oxygen.[174] The change of the copper number with increasing absorption of oxygen is shown in Fig. 101 (representing alkali celluloses from six cotton samples, unpurified and purified in various ways).

The relations between copper number and methylene blue absorption and oxygen consumption are quite similar to those obtaining when cellulose is oxidized by alkaline hypobromite. As with the mechanism which has been proposed for this reaction,[175] it is suggested that the first of the two consecutive reactions involved in the oxidation of cellulose during aging leads to the formation of a product of aldehydic character, whereas the oxidation of this product in the second reaction causes it to lose its reducing power and to acquire acidic properties.

In the light of Davidson's hypothesis on the absence of alkali-sensitive linkages in the acidic oxycellulose type, it may be assumed that it is the hydroxyl groups in the 6-position that are oxidized to aldehyde and further to carboxyl groups rather than those in the 2- and 3-positions.

It is an interesting fact that the absorption of oxygen depends upon the concentration of the sodium hydroxide solution which is used for preparing the alkali cellulose and, thus, upon the alkali concentration which prevails within the pressed-out material. The oxygen absorption increases with increasing alkali concentration and reaches a maximum at a certain concentration. Whereas Weltzien and zum

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[174] Davidson, *loc. cit.*, pp. T129, 132.

[175] Birtwell, Clibbens, Geake and Ridge, *J. Textile Inst.*, **21**, T85 (1930); see also Kalb and Falkenhausen, *Ber.*, **60**, 2514 (1927), pertaining to the oxidation of cellulose with permanganate in the alkaline medium.

Tobel[176] observed the maximum at an alkali concentration of about 24 grams of NaOH in 100 grams of the solution, Davidson's[177] results show that the maximum was not reached until the alkali concentration of the mercerizing liquor was as high as 10 *N* (40 per cent). The temperature during the oxygen absorption was 60° in both investigations.[178] Davidson's results are shown in Fig. 102.

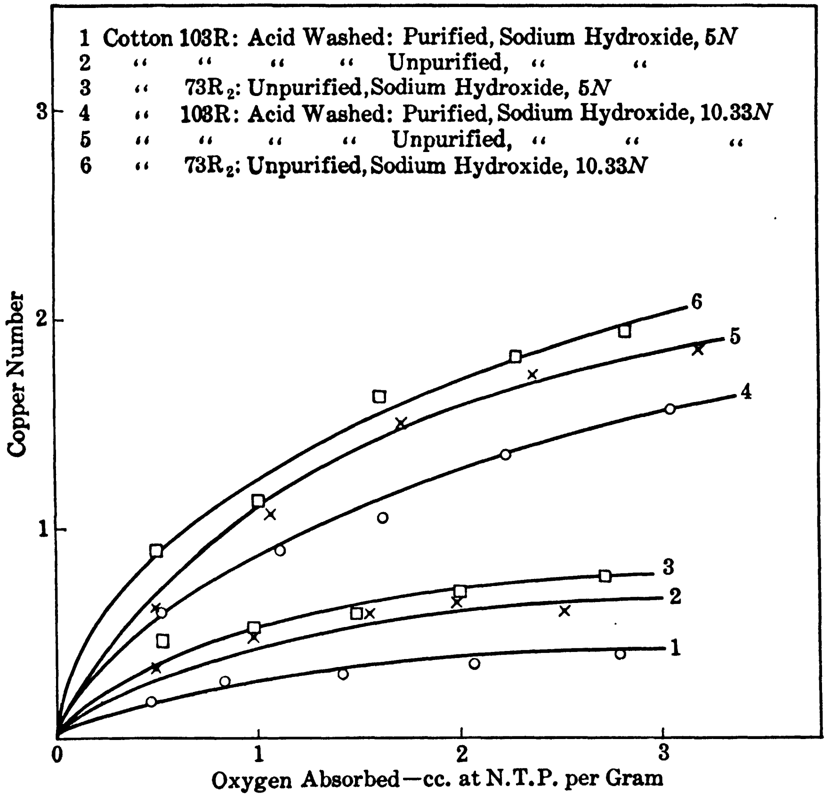

FIG. 101. Oxygen absorption and copper number of alkali cellulose prepared from various cotton samples. Davidson.

Davidson has explained the relationship between oxygen absorption and alkali concentration in the following way: The increase in oxygen absorption with increasing alkali concentration is due to the increase in reactivity of the cellulose that takes place at the onset of swelling

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[176] Weltzien and zum Tobel, *Ber.*, **60**, 2024 (1927); *Seide*, **32**, 371 (1927).

[177] Davidson, *J. Textile Inst.*, **23**, T95, T110 (1932).

[178] Davidson is inclined to explain the difference from the results of Weltzien and zum Tobel by the inadequacy of their experimental technique.

(about 3 *N*) and to the progressive increase in the concentration of the sodium hydroxide in the alkali cellulose. Meanwhile, the solubility and the rate of diffusion of the oxygen probably decrease gradually as the alkali concentration increases and, at a concentration above 10 *N*, these phenomena become predominant and so produce a diminution of the rate of oxidation.

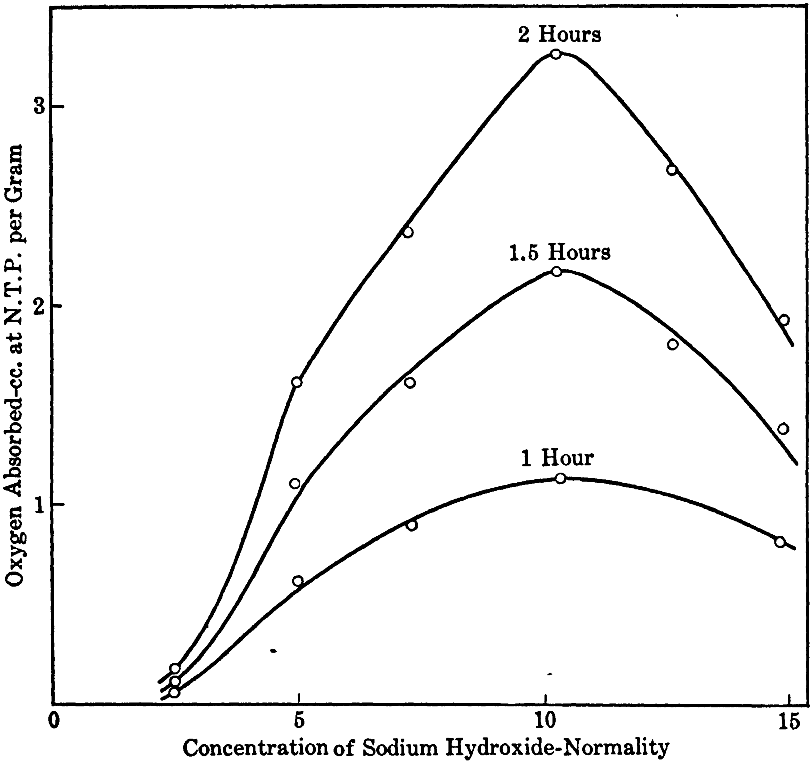

FIG. 102. Oxygen absorption of alkali celluloses and alkali concentration of mercerizing liquor. Davidson.

Plausible as the hypothesis to explain the mechanism of the aging process may be, it would appear that the two consecutive reactions are not the only ones involved, for they do not explain the fall in viscosity of the alkali cellulose on aging, i.e., the cleavage of the cellulose chain molecules into smaller fragments (p. 128).

To account for this important change, the assumption may be made[179] that oxygen is added to the hydrogen atom linked with the

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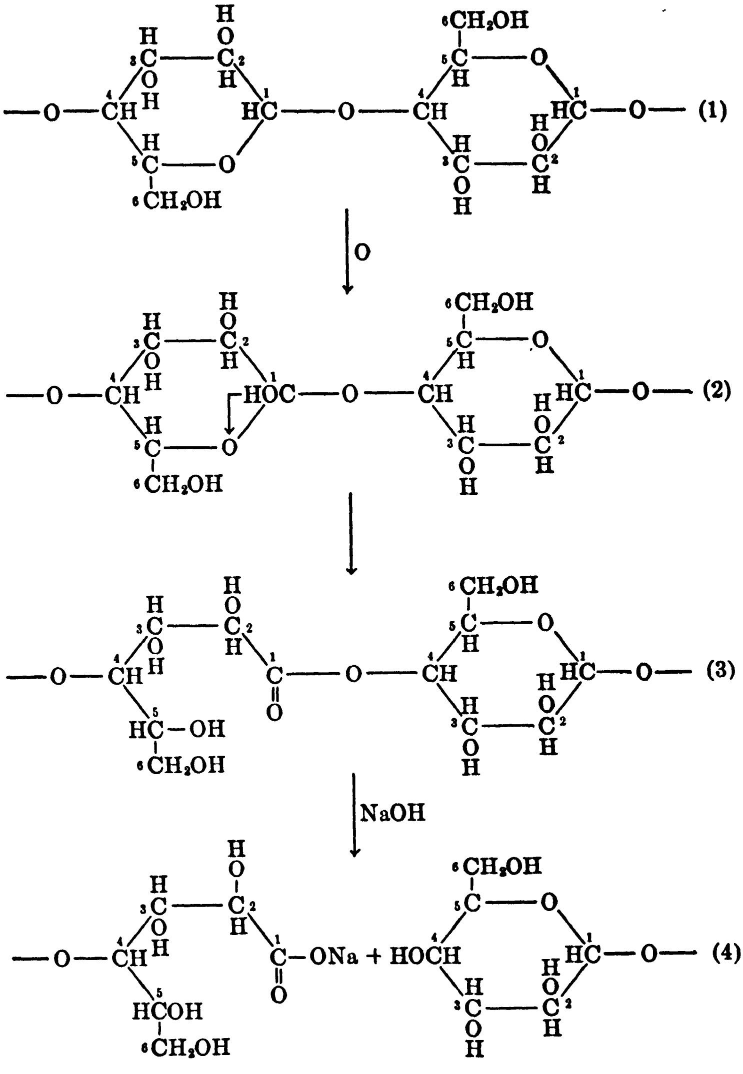
[179] Haskins and Heuser (1938), unpublished data; see also Weber and Huseman, *J. prakt. Chem.*, **161**, 20 (1942).



carbon atom in the 1-position of the glycosidic linkages (see formulas 1, 2, 3 and 4). As a result, the ring structure of the glucose residues may be assumed to open and the hydrogen atom in the 1-position to migrate to carbon atom 5. Thus, an acid grouping is formed at carbon atom 1, this grouping being combined with the neighboring glucose residue through an ester linkage. Under the influence of the alkali, the ester is hydrolyzed; this results in the cleavage of the ester linkage with the formation of two shortened chains, one having a gluconic acid unit (sodium salt) as its terminating unit, whereas in the other the hydroxyl group in the 4-position is restored.

According to this hypothesis, the reduction of the average chain length produced by alkaline hydrolysis would depend upon the number of ester groups per chain, and this in turn on the amount of oxygen consumed. It will be recalled that any desired viscosity may be produced by adjusting the amount of oxygen admitted to the alkali cellulose (p. 132).

Since the viscosity decrease is observed to occur from the start, it must be assumed that both reactions—the formation of ester linkages and alkaline hydrolysis—occur simultaneously.

It remains to be seen whether this hypothesis can be supported by further experimental evidence.

It is significant that very little oxygen is required to bring about a considerable fall in viscosity.[180] The quantity of oxygen present in alkali cellulose aged under normal conditions is considerably smaller than the smallest amount which Davidson applied in his studies. The profound effect of such small amounts of oxygen seems to suggest that oxygen and, for that matter, other oxidizing agents attack the cellulose chains at points near the center rather than at the ends, for in the latter case much more oxygen would be required to reduce the chain, for example, to half of its original length. Moreover, the attack from the ends would result in a considerable loss of cellulose. Actually, however, the loss is very small.

Staudinger and Jurisch[181] determined the quantity of oxygen necessary to reduce the degree of polymerization of cotton linters cellulose from 1000 to about 500 by comparing its specific viscosity (in phosphoric acid solution[182]) before and after oxidation with adjusted volumes of very dilute aqueous potassium permanganate solution. The quantity of oxygen required was small and was found to vary within narrow limits for a great number of different cellulosic materials. In most cases, 2 to 4 atoms of oxygen per 1 mole of cellulose were required. On the assumption that 4 atoms of oxygen suffice to reduce the degree of polymerization to half its original value, 1 mg. of oxygen is required per 7.5 grams of cellulose.

Since the aging process takes place only in the presence of *strong* alkali, the question arises whether its sole function is to exert the

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[180] Hibbert and Parsons, *loc. cit.;* Weltzien and zum Tobel, *Ber.,* **60,** 2024 (1927); Waentig, *Papier-Fabr.,* **26,** 64 (1928); Scheller, *Melliand Textilber.,* **16,** 787 (1935).

[181] Staudinger and Jurisch, *Ber.,* **71,** 2283 (1938).

[182] Cellulose dissolved in this acid is much less sensitive to oxygen than that dissolved in cuprammonium hydroxide.

known physical effects. The probability that the alkali takes an active part, different from its saponifying effect upon hypothetical ester linkages, in the chemical reaction should not be entirely discarded. It is quite possible that the strong alkali produces some sort of enolization of cellulose in a manner analogous to that known to occur in the simple sugars.[183] Although such an enolization is difficult to visualize in the light of the fact that the aldehyde groups are stabilized in the cellulose molecule, some such shifting of bonds could conceivably occur, particularly if the amylene oxide ring is assumed to open up. If such a shift did occur, it seems probable that the strong alkali would cause the shift to go successively from the 1,2- to the 2,3- and the 3,4-positions of the glucose residue, where it would have to stop because of the glycosidic linkage (with the next glucose residue). The action of an oxidizing agent should be greater at this point, and rupture of the glycosidic linkage (4,1) could occur. This would result in a shortened chain and, after acid hydrolysis, in the formation of certain molecules containing 3 or less carbon atoms.

Still another explanation for the marked effect of strong alkali lies in the possibility that the aging takes place through the intermediate formation of ozone by the action of air on a large surface. This would also require the presence of strong alkali.

The Mechanism Involved in the Oxidation of Cellulose with Ozone

Oxycellulose which has been prepared by the action of ozone on cotton (p. 446) may be classified as belonging to the reducing type. It possesses a relatively high copper number but a low methylene blue absorption value. Dorée and Healey [184] have suggested that the first step involved in the mechanism is the oxidation of —CH_2OH groups to —CHO groups and that this will alter the polarity of the carbon atom to which the primary alcohol group is attached and consequently disturb the electrical balance of the glucose ring system, leading to the cleavage of the chain by the water present.[185] The next step may consist of the formation of keto groups, if one or both of the CHOH groups (resulting from the cleavage of glycosidic linkages) were oxidized at the moment of formation. The formation of keto groups would account for the persistence of the reducing property of the ozone

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[183] Evans, *Chem. Revs.*, **6**, 281 (1929).

[184] Dorée and Healey, *J. Textile Inst.*, **29**, T27 (1938).

[185] Although no data are presented, the authors state that the viscosity of the ozone oxycellulose drops and that this drop occurs before the rise of the copper number becomes noticeable.

oxycellulose on continued oxidation. The keto groups may be assumed to be only slowly oxidized to carboxyl groups. This would in part explain the low methylene blue absorption value of the ozone oxycellulose. Its limited acidity is further explained on the assumption that carboxyl groups which, no doubt, are formed on further oxidation of the aldehyde groups in the six positions (see above) are decarboxylated. Indeed, it was found that considerable quantities of carbon dioxide were evolved during the reaction.

To elucidate the mechanism involved in the ozonization of cellulose further, Dorée and Healey subjected fibrous cellulose triacetate to the action of ozone. It was found that the acetyl content did not change and thus afforded some protection against ozonization: the copper number rose only very slowly in the beginning. But after 24 hours, it had reached a value similar to that of the ozone-treated cellulose. The production of acid groups (which would be responsible for methylene blue absorption) appeared, however, to have been prevented completely by acetylation. The fact that there is some reaction between cellulose acetate and ozone suggests that a further mechanism, different from that suggested for the ozonization of unacetylated cellulose, is involved whereby the ring system is broken at the glycosidic linkages. This may result from peroxide formation which might occur either at the amylene oxide ring oxygen atom or at the oxygen atoms of the glycosidic linkages. The decomposition of such a peroxide could result in the formation of a keto group in the 1-, 4-, or 5-position of the anhydroglucose ring.

In this connection the results which Dorée and Healey obtained on the oxidation of cellulose triacetate with alkaline and acid potassium permanganate are of interest. It was found that the action of permanganate at a pH of 11.2 was almost entirely prevented by acetylation. Permanganate at a pH of 1.0, however, increased the copper number to a certain extent, but caused only a slight increase in methylene blue absorption. This copper number increase might be explained by the fact that the acetate had lost 2.3 per cent acetyl, i.e., by oxidation of restored hydroxyl groups to aldehyde groups.

However, the inability of the *alkaline* oxidant to produce any reducing groups in the acetate appears surprising. The possibility exists that keto groups, which might have been formed by the mechanism suggested for the ozonization reaction, were destroyed under the action of the alkali.

The similarity between the molecular structure of *starch* with that of cellulose would let us expect that the oxidation of starch involves possibilities similar to those which have been discussed on the preceding pages. Indeed, the different types of oxidation which starch seems to undergo according to Farley and Hixon[186] find their parallels in the oxidation of cellulose.

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[186] Farley and Hixon, *Ind. Eng. Chem.*, **34**, 677 (1942); see also Felton, Farley, and Hixon, *Cereal Chem.*, **15**, 678 (1938).

THE ACTION OF ULTRAVIOLET LIGHT UPON CELLULOSE

The action of ultraviolet light upon cellulose is usually regarded as leading to the formation of oxycellulose. However, oxidation can take place only if oxygen is present in some form. Since a reaction occurs also with most careful exclusion of oxygen, the changes which cellulose undergoes when exposed to ultraviolet light under such conditions are most probably the result of a photochemical reaction.

It has long been known that cotton and other cellulosic fibers, as well as pulp and paper, become tender and brittle under the action of light and that the wavelength range of the ultraviolet (below about 350 mμ) is most detrimental to cellulosic materials.[187] The photochemical reaction is preceded by the absorption of the ultraviolet light by the cellulose. In other words, if no light is absorbed no reaction takes place. The ultraviolet absorption spectrum of cellulose, at least of cellulose of a high degree of polymerization, is not known, possibly because of experimental difficulties. Some data obtained with Cellophane,[188] with hydrocellulose dissolved in dilute sodium hydroxide solution,[189] and with methylcellulose[190] seem to indicate that the absorption is appreciable at the higher level of the ultraviolet range.

Numerous investigations pertain to the physical and chemical changes which cellulosic materials suffer under the action of ultraviolet light. In most of these investigations, the source of ultraviolet light was the mercury quartz lamp in its various modifications. The results of these investigations may be summarized as follows.

The most obvious effects of ultraviolet light on cellulose are the loss of strength and the change in color which occur when fibrous materials are exposed to sunlight. Scharwin and Pakschwer[191] report that samples of cloth sealed in glass in an oxygen atmosphere and irradiated for 30 hours with a quartz mercury arc lamp showed a considerable loss of strength. Exposure of cotton fabric to sunlight for 5 weeks was found by Barr and Hadfield to result in an appreciable loss in tensile strength. Turner exposed linen threads in sealed quartz tubes with a

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[187] Schwalbe, "Chemie der Cellulose," 1st ed., p. 5; Turner, *J. Soc. Dyers Colourists,* **36,** 165 (1920); Ditz, *Z. angew. Chem.,* **40,** 1478 (1927); Kauffmann, *Melliand Textilber.,* **7,** 617 (1926); Barr and Hadfield, *J. Textile Inst.,* **18,** T490 (1927); Hirschkind, Pye, and Thompson, *Paper Trade J.,* **105,** No. 18, 118 (Oct. 28, 1937); Oguri and co-workers, *J. Soc. Chem. Ind., Japan, Supplementary Binding,* **37,** 201, 620 (1934); **38,** 392 (1935); **39,** 35, 143, 286 (1936); **40,** 300, 356 (1937); **41,** 3 (1938); Richter, *Ind. Eng. Chem.,* **27,** 432 (1935); Launer and Wilson, *J. Research Natl. Bur. Standards,* **30,** 55 (1943).

[188] Oguri, *loc. cit.;* Hodgman, *Phys. Rev.,* **31,** 1114 (1928).

[189] Marchlewski and Skulmowski, *Biochem. Z.,* **276,** 453 (1935).

[190] Steurer, *Z. physik. Chem.,* **B47,** 127 (1940).

[191] Scharwin and Pakschwer, *Angew. Chem.,* **40,** 1008 (1927).

similar result. Cotton hairs, yarn, and cloth were irradiated under a variety of conditions by Cunliffe and Farrow,[192] who found that hairs lost strength at a constant rate until 40 per cent of the original value was lost; then the rate fell off slowly. Yarn and cloth lost strength at a slower rate, the bleached being more rapidly affected than the unbleached material. An extensive study of light between 330 and 750 mμ upon paper was made by Launer and Wilson.[193]

Henk,[194] in contrast to other observers, claimed that short action of ultraviolet light results in an increase in strength due to polymerization. The copper number and the alkali-solubility were found to be decreased.

The chemical changes which occur when cellulose is irradiated by ultraviolet light have been studied by use of common tests. Exposure to sunlight caused a decrease in cuprammonium viscosity, an increase in copper number and silver number, and little change in the methylene blue absorption (Barr and Hadfield). The copper number was increased, but the methylene blue absorption was little affected when cotton was exposed to irradiation from a quartz mercury arc (Cunliffe and Farrow). When rag pulps and *alpha*-pulp were exposed to the light of a carbon arc "Fade-Ometer," Foote,[195] in all cases, observed a decrease in viscosity and *alpha*-cellulose content, an increase in copper number and 1 per cent alkali-solubility, and no change in pentosan content. An increase in copper number was also observed by Mason and Rosevear,[196] when ramie was exposed to the light of a quartz mercury vapor lamp and when a variety of cellulosic materials was exposed to irradiation from the same source (Oguri).

Montana[197] found that light of wavelength below 290 mμ caused a considerable drop in viscosity of cellulose in cuprammonium hydroxide solution, and Löbering[198] followed the fall in viscosity of cellulose dissolved in phosphoric and in sulfuric acids.

The formation of carbon dioxide was noted by Scharwin and Pakschwer, Barr and Hadfield, and Henk. Carbon monoxide and an aldehydic odor were also reported by Barr and Hadfield, and Henk observed the formation of water. No loss in weight could be detected by Kauffmann.

The divergent results which have been reported on the influence of the surrounding atmosphere upon the exposed cellulosic material are very probably due to experimental deficiencies. Because of the difficulty encountered in removing all oxygen from the system, it cannot be decided with certainty whether the changes are due to the action of the ultraviolet light as such or to small amounts of oxygen, possibly activated in the presence of ultraviolet light. Nevertheless, indications derived from the investigations summarized above make it seem probable that ultraviolet light as such exerts an effect upon cellulose and

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[192] Cunliffe and Farrow, *J. Textile Inst.*, **19**, T169 (1928).

[193] Launer and Wilson, *loc. cit.*

[194] Henk, *Melliand Textilber.*, **19**, 730 (1938).

[195] Foote, unpublished data from master's thesis, The Institute of Paper Chemistry (1932); see also Lewis, *Paper Trade J.*, **95**, No. 21, 29 (Nov. 24, 1932).

[196] Mason and Rosevear, *J. Am. Chem. Soc.*, **61**, 2995 (1939).

[197] Montana, *Holz Roh- u. Werkstoff*, **1**, 438 (1937–1938).

[198] Löbering, *Z. Elektrochem.*, **44**, 746 (1938).

that this effect is enhanced considerably in the presence of oxygen. Since oxygen in the absence of ultraviolet light is without effect upon cellulose and since oxygen is converted into ozone [199] under the action of ultraviolet light of a certain wavelength range, the effect of oxygen in the presence of ultraviolet light might conceivably be due to ozone.

Other factors which have been studied for their influence upon the effect are moisture and the presence of substances which might act as catalysts. Whereas the presence or absence of moisture does not seem to be essential, a number of substances certainly exert a catalytic effect. In contrast, others have a protective influence. Whereas ferric hydroxide accelerated the action of ultraviolet light upon cellulose (Barr and Hadfield), chromic oxide (chromium green) exerted a pronounced protecting influence, prolonging the life of fabrics so treated as much as five or six times, and a mixture of chromic oxide and peroxide was as good as chromic oxide alone (Cunliffe and Farrow, Turner). Likewise, dyestuffs may act as catalysts or as protectors.[200] Certain dyes present in small amounts seem to be capable of transferring the absorbed radiant energy to fibers and thus causing deterioration.[201]

Mason and Rosevear [202] made the interesting observation that when ramie was exposed to *polarized* ultraviolet light, vibrating crosswise to the fiber, the increase in copper number was 25 per cent greater than when the light vibrated lengthwise to the fiber. Thus, the effect was greatest when the light vibrated in the direction in which the aggregate of cellulose chain molecules is most deformable.

Studies on the action of ultraviolet light on cellulose have been resumed recently for the purpose of deciding definitely, if possible, whether ultraviolet light acts by itself or only in combination with oxygen.[203] Rigid precautions were taken to remove all air oxygen from the system. Only traces of oxygen, about 0.002 per cent by volume, remained in the nitrogen used after purification by passing it through a copper gauze furnace. It was calculated that this quantity of oxygen amounted to only 0.024 millimole or 1.8×10^{-4} per cent on the weight of the cellulose sample.

To prepare oxycellulose of the same copper number as was shown by the exposed sample after 96 hours (0.70 against 0.28 in the unexposed cellulose), 0.05 per cent oxygen would be required, assuming oxidation was carried out under conditions which would give the greatest increase in copper number for a given

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[199] Briner and Perrottet, *Helv. Chim. Acta,* **23,** 1480 (1940); Ellis, Wells, and Heyroth, "The Chemical Action of Ultraviolet Rays," rev. and enl. ed., Reinhold Pub. Co., New York (1941), pp. 431–436.

[200] See the compilation by Henk, *loc. cit.*

[201] Scholefield and Turner, *J. Textile Inst.,* **24,** P130 (1933); see also Launer and Wilson, *loc. cit.*

[202] Mason and Rosevear, *loc. cit.*

[203] Stillings, doctoral dissertation, prepared under the direction of E. Heuser, The Institute of Paper Chemistry, Appleton, Wisconsin (1941).

oxygen consumption. This is 280 times the amount of oxygen which was actually present in the nitrogen-filled exposure chamber.

The cellulose sample (finely ground cotton linters, D.P. 1,400) was freed of air by evacuation, heating, and flushing with nitrogen a large number of times. In spite of these precautions, a very small quantity of oxygen could doubtless have been retained by the cellulose. However, if this amount of oxygen had been responsible for the changes observed, the rate of reaction could be expected to be at a maximum at the beginning and to fall to zero as the oxygen is consumed. Actually, no such effect was observed. The changes continued over the whole range of exposure studied.

The changes which were observed on the irradiation of the carefully dried cellulose samples in nitrogen consisted chiefly of an increase in copper number and in alkali-solubility (decrease in *alpha*-cellulose content), a decrease in the degree of polymerization (calculated from viscosity measurements in cuprammonium hydroxide), and an increase in the evolution of carbon monoxide and carbon dioxide. Table 66 shows the magnitude of these changes. The lower section of the table

TABLE 66

CHANGES OF COPPER NUMBER, ALPHA-CELLULOSE AND URONIC ACID CONTENT, AND EVOLUTION OF GASES FROM COTTON CELLULOSE ON IRRADIATION WITH ULTRAVIOLET LIGHT

Length of Exposure, Hours	Copper Number	*Alpha*-Cellulose, %	Degree of Polymerization	Gases Evolved	
				CO_2	CO
				Millimoles	
24 *	0.42	95.1	1070	0.08	0.08
96 †	0.65	92.6	870	0.24	0.39
96 *	0.70	91.4	840	0.34	0.44
Unexposed	0.28	96.8	1400	....	....
N_2 + 10% O ‡	0.58	92.2	950	0.18	0.17
N_2 + 20% O_2 ‡	0.78	90.0	870	0.22	0.22
100% O_2 ‡	1.49	82.9	740	0.39	0.37

* Purified nitrogen continuously passed through apparatus.

† Exposure chamber filled with purified nitrogen and sealed off.

‡ Length of exposure was 24 hours.

shows the results which were obtained when certain proportions of oxygen were admixed to the nitrogen and when irradiation was allowed to take place in oxygen only.

We shall first discuss the results obtained in nitrogen. Whereas the increase in copper number and the evolution of gases were relatively small, the drop in *alpha*-cellulose content and in the degree of polymerization were considerable. The two latter values confirm the relationship encountered on previous occasions, i.e., that the alkali-solubility increases with decreasing degree of polymerization (see the discussions on pp. 127 and 463).

The question arises as to how the evolution of the gases, the drop in viscosity, and the increase in copper number are to be explained if no oxidation takes place.

The formation of carbon monoxide and carbon dioxide apparently did not result from the cleavage of glycosidic linkages of the cellulose chains for, if this were so, cellobiose should produce much greater quantities of these gases because of the much higher proportion of such groups in this simple sugar. Actually, the rates of carbon monoxide and carbon dioxide formation which were determined during the irradiation of cellobiose (and of β-*d*-glucose) in the nitrogen atmosphere, were only about one-third as great as that from cellulose. Likewise, the fact that the exposure of glucose and cellobiose resulted in no measurable decrease in reducing power seems to indicate that the reducing groups in cellulose were not appreciably affected.

It is improbable that the alcoholic hydroxyl groups of cellulose were attacked, for no hydrogen evolution was observed, as could be expected from the action of ultraviolet light upon primary and secondary alcoholic groups with the corresponding formation of aldehyde and ketone groups.[204]

Some indication that the evolution of carbon monoxide and carbon dioxide may be indirectly linked to the cleavage of the chain molecules was obtained by comparing the average number of chain scissions per molecule(s) of the cellulose (calculated from the viscosity data by means of Sakurada and Okamura's equation [205]) with the evolution of the gases, expressed as millimoles per millimole of cellulose. (Based upon an average chain length of 1400 glucose units or a molecular weight of 227,000 of the cellulosic material employed, one millimole of cellulose is 227 grams.) The results are shown in Table 67.

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[204] Farkas and Hirschberg, *J. Am. Chem. Soc.*, **59**, 2450 (1937).

[205] Sakurada and Okamura, *Z. physik. Chem.*, **A187**, 289 (1940).

TABLE 67

RELATION BETWEEN EVOLUTION OF CARBON MONOXIDE AND CARBON DIOXIDE AND CLEAVAGE OF GLYCOSIDIC LINKAGES

D.P.	s	CO Millimoles	CO_2 Millimoles
1070	0.87	0.47	0.35
970	1.22	0.88	0.70
960	1.26	1.29	1.23
860	1.70	2.28	1.40
860	1.70	2.57	1.99
950	1.30	0.99	1.05
870	1.65	1.29	1.29
740	2.31	2.16	2.28
1230	0.40	0.64	0.94

It may be seen, on the whole, that there is a fairly close agreement between the number of chain scissions and the carbon monoxide and carbon dioxide values observed, one molecule of each gas being produced for each glycosidic linkage cleaved. The existence of this relationship may be considered an indication that the evolution of gases is associated with the reaction which subsequently leads to chain cleavage.

Since, on the other hand, no agreement existed between the number of chain scissions and the reducing power, the increase in the number of reducing groups under the action of ultraviolet light must, at least in part, be due to some other reaction not ultimately resulting in a cleavage of glycosidic linkages.

It is of interest that under the action of ultraviolet light, cellobiose yielded no more carbon monoxide and carbon dioxide than glucose exposed under the same conditions. This result, in connection with the observation that the reducing power of cellobiose did not change, seems to indicate that the glycosidic linkage in cellobiose is stable to ultraviolet light. This divergence from the behavior of cellulose is difficult to explain; it is possibly a result of the fact that the glycosidic linkages in cellulose are not exactly equivalent to that in cellobiose, owing to differences in the surrounding groups.

The resistance of the disaccharide linkage in cellobiose to ultraviolet light was also observed by Steurer.[206] In an atmosphere which was most carefully freed of oxygen, similar results were observed with fully methylated cellobiose, although a considerable quantity of methyl was removed.

Methylcellulose (40–42 per cent methoxyl), however, showed a considerable drop in viscosity after irradiation, the methoxyl content remaining unchanged. The degree of polymerization calculated from the viscosity was checked against that derived from end-group assay (tetramethylglucose method), but the latter was considerably higher than the former. The results are shown in Table 68.

Steurer has interpreted this difference between the results of end-group assay

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[206] Steurer, *Z. physik. Chem.*, 47B, 139 (1940); Steurer and Mertens, *Ber.*, 74, 790 (1941).

TABLE 68

Degrees of Polymerization (D.P.) Derived from End-Group Determination and from Viscosity Data of Irradiated Methylcellulose

	End-Group Content, %	D.P. from End-Group Content	Decrease, %	D.P. from Viscosity Data *	Decrease, %
Original	0.0308	3250	45	762	75
Irradiated	0.0558	1790		190	

* Another methylcellulose sample—of a degree of polymerization of 750—had dropped to as low a value as 28, after 8 hours of exposure at 32°.

and viscosity measurements to indicate the presence in cellulose (and methylcellulose) of cross linkages and to show that these are broken under the action of ultraviolet light at a faster rate than the glycosidic linkages (see also p. 584). It remains to be seen whether this explanation can be supported by further experimental evidence. The enormous difference in degree of polymerization from the viscosity data and from the end-group assay in the original cellulose is quite unusual.

The data presented in the lower section of Table 66 show that the effect of irradiation in an atmosphere of nitrogen to which 10 and 20 per cent oxygen had been admixed was more pronounced than in nitrogen alone and that it was considerably greater when oxygen only was employed. That it is the combination of oxygen and irradiation which causes this effect is seen from the fact that oxygen without irradiation has no effect upon cellulose. This result may possibly mean that the elementary oxygen is converted into a more active form under irradiation. However, no ozone could be detected when the potassium iodine starch test was applied to the gases leaving the exposure chamber. Usually ozone formation occurs on irradiation with light of wavelengths below 200 mμ,[207] whereas the lower limit applied by Stillings was about 230 mμ. If ozone had been formed in appreciable quantities, the reducing power of the cellulose should have been much higher, in accordance with results obtained by Dorée and Dyer,[208] who observed a copper number of 8 on a cotton fabric sample which had been exposed to ultraviolet light in air for several days.

It would thus appear as if irradiation prepares the ground, so to speak, upon which the oxygen is able to attack the cellulose. In other words, it would appear that irradiation is capable of weakening glyco-

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[207] Ellis, Wells, and Hayroth, *loc. cit.*

[208] Dorée and Dyer, *J. Soc. Dyers Colourists,* **33,** 17 (1917); Dorée, "The Methods of Cellulose Chemistry," p. 121.

sidic linkages to an extent that they may be broken down under the action of oxygen.

This view seems to be supported by the most interesting observation that cellulose which had been irradiated in nitrogen continued to become degraded when removed from the exposure chamber and placed into air but ceased to become degraded when the air was replaced by (purified) nitrogen. For example, the degree of polymerization of about 1200 (which a sample had acquired after a 96-hour irradiation in nitrogen) dropped to 850 after 85 days of storage in air, when it remained practically constant for 35 more days.

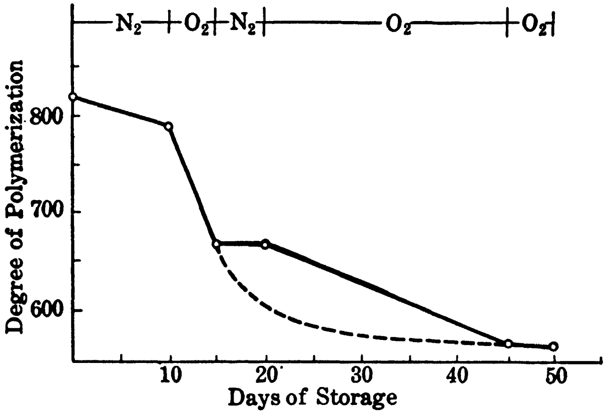

FIG. 103. Changes of the degree of polymerization of cellulose exposed to ultraviolet light and subsequently stored in nitrogen and in oxygen. van Nostrand.

Stillings' results were confirmed by van Nostrand.[209] In addition, it was found that the effect was considerably increased, when the irradiated sample was stored in oxygen instead of in air. and that the degradation may be arrested and started and re-arrested and started again, depending upon the choice of the surrounding atmosphere. A sample which had acquired a degree of polymerization of 823 after 96 hours of irradiation (original value 1250) was alternately stored in nitrogen and in oxygen. The changes in degree of polymerization are shown in Fig. 103. These changes were accompanied by corresponding changes in copper number, *alpha*-cellulose content, and total (titratable) acidity, i.e., the copper number and acidity increased and the *alpha*-cellulose content decreased during storage in oxygen, but the values remained constant in nitrogen.

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[209] van Nostrand, doctoral dissertation, prepared under the direction of E. Heuser, The Institute of Paper Chemistry, Appleton, Wisconsin (1943).

It is also seen that the effect of oxygen comes to a standstill, for there is no further drop in degree of polymerization after about 45 days of storage.

As has been mentioned above, the effect of irradiation is considerably enhanced if oxygen is allowed to be present during this reaction. However, to exhaust the action of the oxygen upon the modified glycosidic linkages during irradiation, the time of contact with the oxygen must be sufficiently long; otherwise, even a sample which has been irradiated in oxygen will be further degraded when stored in oxygen. Thus, the degree of polymerization of a sample which had been irradiated in oxygen for 96 hours and which was 450 had dropped to 320 after storage in oxygen for 40 days. However, no further drop occurred during an extension of this period to 50 days. Thus, the secondary reaction came to a standstill, and probably after a considerably shorter time than after 40 days (see dotted line, Fig. 103).

These results may be interpreted to mean that the secondary reaction is a direct function of irradiation. In other words, the post-exposure effect occurs only as long as there are weakened glycosidic linkages available. When all those produced by irradiation are ruptured by oxidation, the cellulose undergoes no further change.

The susceptibility of ultraviolet-exposed cellulose to oxygen would seem to permit the assumption that the traces of oxygen left in the irradiation system suffice to bring about the rupture of modified glycosidic linkages and are possibly solely responsible for the stated effects of irradiation in purified nitrogen. Although this issue can be decided only by studying the effect of irradiation in the absolute absence of oxygen, it does seem to be rather improbable. It would appear that all that can be concluded thus far is that in irradiation by ultraviolet light we are dealing with two phenomena: the one is the direct breakdown of glycosidic linkages under the action of ultraviolet light, the other, the weakening of glycosidic linkages, both being photochemical reactions which occur simultaneously. To these two phenomena is added a third, which is the rupture of weakened glycosidic linkages in a subsequent reaction. Such a rupture takes place when the cellulose which had been irradiated in nitrogen is subsequently exposed to oxygen, i.e., by oxidation. It also takes place when oxygen is present during irradiation, its extent depending upon the time and the amount of oxygen present.

No doubt, the susceptibility of ultraviolet-irradiated cellulose to oxygen (air) has an important bearing upon the stability of textiles and paper to light. Fabrics and documents may be expected to be subject to decay more readily if such materials are exposed—and if it is only occasionally—to light comprising wavelengths of the ultraviolet range. This brings again to mind the importance of protecting valuable documents against the influence of direct light.

It may be added that Launer and Wilson[210] have observed an increase in titratable acidity of paper which had been irradiated in air by light of wavelengths above 350 and below 750, i.e., light which may be compared with the daylight operative in libraries and offices. No doubt, the acid formed, even if it is organic and therefore weak, may exert a certain harmful effect in the course of a longer time. However, it would appear that the extent of this effect remains below that which is the result of the direct photochemical breakdown of the chain molecules.

THE FUSION OF CELLULOSE WITH ALKALI AND THE ACTION OF AQUEOUS ALKALI UPON CELLULOSE AT HIGH TEMPERATURES AND PRESSURES

Before closing the chapter on the oxidation of cellulose, two other processes of oxidation may be briefly reviewed.

The Fusion of Cellulose with Alkali

On the fusion with solid sodium hydroxide, cellulose yields essentially oxalic acid. This reaction has been known for a long time (Gay-Lussac, 1856)[211] and has served as the main process for the commercial manufacture of this acid from sawdust and other wood waste[212] until its synthetic preparation from sodium and other formates was developed. Fused with potassium hydroxide at 270–280°, cotton yielded 90–92 per cent oxalic acid, besides small amounts of acetic and formic acids and considerable amounts of hydrogen.[213]

The formation of formic acid in connection with large quantities of hydrogen seems to suggest that formic acid (or formates) is the intermediate which, under suitable conditions, decomposes to yield hydrogen and oxalic acid, $2HCOONa \rightarrow (COONa)_2 + H_2$. In fact, at a lower temperature—150–170°—more formic and less oxalic acid are formed than at the temperature most suitable for obtaining a high yield of oxalic acid.

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[210] Launer and Wilson, *J. Research Natl. Bur. Standards*, **30**, 55 (1943).

[211] Hilbert, *Chem. & Met. Eng.*, **22**, 838 (1920).

[212] Sthorger, "The Chemistry of Cellulose and Wood," McGraw-Hill Book Co., New York (1926), p. 366; Hawley and Wise, "Chemistry of Wood," Chem. Catalog Co., New York (1926), p. 266.

[213] Hedenström, *Chem.-Ztg.*, **34**, 613 (1910).

Since oxalic acid appears as the end product of the alkaline oxidation of many organic substances, it is probable that the fusion of cellulose with alkali is a process of oxidation.[214] However, the oxygen required is obviously not supplied by the air but rather by the water and the alkali. This conclusion appears to be supported by the fact that the same yield of oxalic acid was obtained when the reaction was carried out in a hydrogen atmosphere, i.e., in the absence of air oxygen.[215] On the other hand, it was found[216] that air introduced into the melting mass increased the yield.

The Treatment of Cellulose with Alkali at High Temperature and Pressure

The process of oxidation is also involved when cellulose is subjected to the action of strong aqueous alkali under pressure and at a high temperature. Under such conditions, cotton may be dissolved to the extent of 92 per cent in 40 per cent sodium hydroxide solution at a pressure of 5 atmospheres.[217] With less concentrated alkali, more severe conditions are required. Thus, a 15 per cent sodium hydroxide solution required a pressure of 10–11 atmospheres (corresponding to 180° C.) to dissolve cotton to the extent of 96 per cent after 6 to 7 hours, whereas somewhat milder conditions sufficed to dissolve wood pulp almost completely in aqueous alkali of the same concentration and with about the same time of treatment.[218]

Such conditions lead to the degradation of cellulose in much the same way as observed with simple sugars and di- and oligosaccharides.[219] Hence, it is probable that, by the action of alkali upon cellulose, oligo-, di-, and monosaccharides are the primary products of the reaction. The secondary products consist chiefly of aliphatic acids, such as acetic and, particularly, lactic acid. Filter paper heated in 5 *N* caustic soda solution to a temperature of 250° in a high-pressure autoclave yielded 18 per cent lactic acid (calculated on dry cellulose), in addition to great quantities of carbon dioxide and some

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[214] Fry and Otto, *J. Am. Chem. Soc.*, **50**, 1138 (1928).

[215] Heuser and Herrmann, *Cellulosechem.*, **5**, 1 (1924).

[216] Othmer, Garner, *et al.*, *Ind. Eng. Chem.*, **34**, 262, 268, 274 (1942).

[217] Tauss, *Dinglers Polytech. J.*, **273**, 276 (1898); see also Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 38.

[218] Heuser, *Paper Trade J.*, **89**, No. 26, 67 (1929).

[219] Evans *et al.*, *J. Am. Chem. Soc.*, **53**, 4384 (1931); **54**, 698 (1932); Plunkett and Evans, *ibid.*, **60**, 2897 (1938); see also Spengler and Pfannenstiel, *Angew. Chem.*, **48**, 475 (1935); Evans, *Chem. Reviews*, **31**, 549 (1942).

acetic and formic acids, the latter products resulting probably from the decomposition of part of the lactic acid.[220] Similar reaction products, only in lower yields, were obtained under milder conditions.[221] With gaseous oxygen and aqueous sodium carbonate at 200° a greater quantity of volatile fatty acids was formed, particularly acetic acid (27.7 per cent calculated on cellulose), besides some oxalic (about 5 per cent), fumaric and succinic (together 0.7 per cent), and formic acids (0.05 per cent).[222]

If the solution of cellulose obtained on heating under pressure and at high temperature is subsequently subjected to destructive distillation, numerous decomposition products are obtained, chiefly acetone, ethyl alcohol, acetic acid, and oily condensation products of acetone and its homologues. In the presence of lime, the yield of acetone is increased, probably because of the formation of calcium acetate. The formation of these products is accompanied by a marked evolution of gases, particularly hydrogen.[223]

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[220] Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle,* **5,** 332, Gebr. Borntraeger, Berlin (1920); **6,** 115 (1923).

[221] Heuser, *Paper Trade J., loc. cit.*

[222] Fischer and Tropsch, *Ges. Abhandl. Kenntnis Kohle,* **7,** 192 (1925).

[223] Rinman process, see Heuser, *loc. cit.; Papier-Fabr.,* **21,** 325 (1923); Johansson, *Ing. Vetenskaps Akad. Handlingar,* **61,** Stockholm (1927); Odén and Lindberg, *Ind. Eng. Chem.,* **19,** 132 (1927).

CHAPTER XI

THE DECOMPOSITION OF CELLULOSE BY ACIDS

Under the action of strong mineral acids, such as sulfuric or hydrochloric, cellulose swells, dissolves, and undergoes hydrolysis, the end product of which is glucose. In contrast, dilute mineral and even concentrated organic acids do not dissolve cellulose; fibrous structure is maintained but it is considerably weakened. If the treatment is sufficiently severe, the fibers, like oxycellulose, may easily be rubbed to a powder between the fingers. The product of reaction has been called *hydrocellulose.*

HYDROCELLULOSE

As with other treatments, cellulose reacts with dilute acids relatively slowly and irregularly. Degradation starts on the surface of the fiber and may lead to low molecular fragments and even to glucose within a relatively short time. Deeper layers, on the other hand, may be attacked to a lesser degree and, in consequence, interruption of the process of degradation after a certain time yields a variety of degradation products ranging from almost untouched chains to the monomeric glucose.

The term hydrocellulose was coined by Girard[1] in 1876 and was suggested by the observation that the analysis of the reaction product seemed to indicate one molecule of water in chemical combination with each $C_6H_{10}O_5$ unit. This interpretation of the analytical result was later found to be erroneous. The higher hydrogen and oxygen content which hydrocellulose may show on analysis may be explained either by the fact that we are dealing with a mixture of $C_6H_{10}O_5$ and $C_6H_{12}O_6$, $C_{12}H_{22}O_{11}$, and higher units,[2] or simply by an increased hygroscopicity which makes it more difficult to remove the water completely on drying than from unmodified cellulose.[3]

The destructive effect of acids upon cellulosic materials is being utilized in

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[1] Girard, *Compt. rend.*, **81**, 1105 (1875); *Ann. chim. phys.*, [5] **9**, 116 (1876); see also Kolb, *Bull. Mulhouse*, **38**, 922 (1868); Stern, *J. Chem. Soc.*, **85**, 336 (1904); Schwalbe, *Z. angew. Chem.*, **20**, 2167 (1907); **22**, 156 (1909).

[2] Netthöfel, doctoral dissertation, Berlin (1914).

[3] Ost, *Ann.*, **398**, 315, 319 (1913).

the regeneration of wool from mixed wool and cotton fabrics or in the removal of plant material from raw wool ("carbonization").[4]

For some time, hydrocellulose was regarded as the first homogeneous product of the hydrolysis of cellulose.[5] In the light of the now accepted physical and molecular structure of cellulose, this concept is no longer justified, and hydrocellulose can be viewed only as an aggregate of shortened-chain molecules mixed with those products of degradation which have altogether lost their cellulosic character, such as oligosaccharides, cellobiose, and glucose, and which may be removed from the "crude" hydrocellulose by extraction with water or dilute aqueous alkali.

Reactions of Hydrocellulose

Since the only conceivable chemical change which cellulose undergoes by the action of acids consists of the cleavage of glycosidic linkages (and possibly of cross linkages between individual chains if such exist) the reactions shown by hydrocellulose are those which indicate an increase in aldehyde and hydroxyl end groups and a shortening of the chain molecules. The increase in aldehyde groups may be recognized by the increased reducing power, the absorption of phenylhydrazine, and the yellow coloration which occurs when hydrocellulose is heated with dilute alkali. The increase in hydroxyl groups is indicated by an increased degree of substitution on esterification, etc. The shortening of the chains is derived from the decrease in viscosity and the increase in alkali-solubility.

The copper number of hydrocellulose preparations varies within a wide range, depending upon the conditions employed during their preparation. The reader may refer to the early researches of Ost and of Schwalbe and co-workers[6] and to a review by Clifford.[7]

Since the reactions which hydrocellulose undergoes are also characteristic of oxycellulose of the *reducing* type, it is difficult to distinguish between these two types of modified celluloses. On the other

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[4] See Weidenhammer, Prisley, and Ryberg, *Am. Dyestuff Reptr.*, **30**, P348 (1941).

[5] Girard, *loc. cit.*; Knoevenagel and Busch, *Cellulosechem.*, **3**, 50 (1922); see also Heuser and Stöckigt, *Cellulosechem.*, **3**, 61 (1922); Heuser and Jayme, *Ber.*, **56**, 1242 (1922).

[6] Ost, *Ann.*, **398**, 320 (1913); Schwalbe, *Ber.*, **40**, 1347, 4523 (1907); *Z. angew. Chem.*, **20**, 2170 (1907); **23**, 924 (1910); Schwalbe, "Chemie der Cellulose," 1st ed., p. 211; see also Büttner and Neumann, *Z. angew. Chem.*, **21**, 2609 (1908); Kollmann, *Papier-Fabr.*, **8**, 863, 890 (1910).

[7] Clifford, *J. Textile Inst.*, **14**, T69 (1923).

hand, hydrocellulose may be distinguished from the *nonreducing* oxycelluloses by its lower carboxyl content (p. 433) and its lower methylene blue absorption (see also p. 506).[8]

If higher values for methylene blue absorption are encountered, they are probably due to the pronounced tendency of hydrocelluloses to retain acids.[9] Indeed, it is almost impossible to remove the last residues; even boiling with alkali is not always successful. Wood[10] has recommended the extraction of the preparation with alcohol. Traces of acids in hydrocellulose may be recognized by a yellow-to-brown discoloration when the preparation is dried at 100°.

Other reactions which may be useful in distinguishing hydro- and oxycellulose have been summarized by Dorée.[11]

That cellulose is rather sensitive to dilute aqueous mineral acids is shown by the fact that its viscosity drops rather sharply even on relatively mild treatments. Hydrocellulose may thus be distinguished from cellulose in those cases in which its fibrous structure appears to be unharmed on a cursory inspection.

The shortening of the chain molecules under the influence of hydrolyzing agents may also be recognized by end-group determinations.[12] Hydrocellulose prepared by the action of hydrochloric acid, having a copper number of 3.3, was subjected to methylation with subsequent hydrolysis and isolation of the tetramethylglucose thus formed. The yield was 1.62 per cent, corresponding to a chain length of 70 glucose units (see also in Chapter XV).

This value was somewhat higher than that calculated from the specific viscosity of the methylated hydrocellulose in *m*-cresol, which indicated an average of 54 units. Both values show that far-reaching degradation has taken place. It is therefore surprising that the copper number of the hydrocellulose was not higher than 3.3.

The average chain length of hydrocellulose is closely related to its alkali-solubility. Thus, hydrocellulose may be partly[13] or completely soluble[14] in dilute aqueous alkali. The extent of solubility depends also on the alkali concentration and the temperature.

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[8] Briggs, *J. Soc. Chem. Ind.*, **35**, 80 (1916).

[9] Birtwell, Clibbens, and Geake, *J. Textile Inst.*, **17**, T145 (1926).

[10] Wood, *J. Textile Inst.*, **17**, P101 (1926).

[11] Dorée, "The Methods of Cellulose Chemistry," p. 175; see also Thomas, *J. Soc. Chem. Ind.*, **55**, 79T (1933).

[12] Carrington, Haworth, Hirst, and Stacey, *J. Chem. Soc.*, 1901 (1939).

[13] Schwalbe, *Z. angew. Chem.*, **22**, 155 (1909).

[14] Hess, "Chemie der Cellulose," p. 393; Knoevenagel and Busch, *loc. cit.;* Heuser and von Neuenstein, *Cellulosechem.*, **3**, 92 (1922); Heuser and Eisenring, *ibid.*, **4**, 13 (1923); Hess, *Z. angew. Chem.*, **37**, 993 (1924); Heuser and Hiemer, *Cellulosechem.*, **6**, 109, 111 (1925).

Methods of Preparing Hydrocellulose

Hydrocellulose may be prepared in various ways[15]—for example, by impregnating the cellulosic material with dilute sulfuric or hydrochloric acid and subsequently heating the impregnated fibers to 80–100° for 1 or more hours.[16] Gaseous hydrogen chloride may also be used. The latter process produces hydrocellulose completely soluble in alkali.[17]

Organic acids under sufficiently severe conditions are quite efficient in forming hydrocellulose. Oxalic,[18] formic,[19] and acetic acids[20] have been used.

Likewise, aqueous solutions of acid salts (such as sodium bisulfate) and those neutral salts which are dissociated easily in water (such as magnesium chloride, aluminum sulfate, and others) attack cellulose and form hydrocellulose, particularly if employed at an elevated temperature.[21]

On pulping wood with sulfite liquor (containing calcium bisulfite and sulfurous acid), a part of the cellulose and the noncellulosic carbohydrates is hydrolyzed, and the spent liquor contains a certain quantity of glucose in addition to xylose, mannose, and galactose. The glucose content of the waste sulfite liquor is the source of "sulfite alcohol," which in European pulp mills is produced by fermentation of the neutralized waste liquor with yeast.[22] Glucose may be manufactured directly by subjecting wood waste to the action of dilute mineral acids at 100° and above, and the aqueous glucose solution may be fermented with yeast to yield ethyl alcohol.[23] Under these conditions, most of the pentosans in the wood are converted into furfural which may be separated

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[15] Heuser, "Lehrbuch der Cellulosechemie," 1927, p. 168; Dorée, "The Methods of Cellulose Chemistry," p. 144.

[16] Girard, *loc. cit.*; Schwalbe, *loc. cit.*; see also Jentgen, *Z. angew. Chem.*, **23**, 1541 (1910).

[17] Knoevenagel and Busch, *Cellulosechem.*, **3**, 42 (1922); Heuser and von Neuenstein, *ibid.*, **3**, 89 (1927); Heuser and Eisenring, *ibid.*, **4**, 13, 25 (1923).

[18] Simonson, *Z. angew. Chem.*, **11**, 220 (1898); Heuser and Eisenring, *loc. cit.*

[19] Girard, *Ann. chim. phys.*, **24**, 337 (1881); Heuser and Schott, *Cellulosechem.*, **6**, 10 (1925); Staudinger and Dreher, *Ber.*, **69**, 1733 (1936); Staudinger and Sorkin, *Ber.*, **70**, 1565 (1937).

[20] Girard, *loc. cit.*; Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 171; Staudinger and Sorkin, *loc. cit.*

[21] Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 162.

[22] Hägglund, "Die Sulphitablange und ihre Verarbeitung auf Alkohol," Vieweg & John, Braunschweig, 2nd ed. (1921).

[23] Körner, doctoral dissertation, Dresden (1907); Neumann, doctoral dissertation, Dresden (1910); Heuser, *Cellulosechem.*, **1**, 41 (1920); Pringsheim, *ibid.*, **3**, 77 (1922).

from the aqueous alcohol by fractional distillation (Heuser). Furfural, an excellent solvent, is now being manufactured in this country in ever-increasing quantities.

The Fractionation of Hydrocellulose

Crude hydrocellulose may be separated essentially into two portions: low-molecular-weight fragments which represent, as a rule, not more than a few per cent of the total, and a fibrous residue which comprises the less attacked and unattacked chains. Such a separation may be brought about by various means; for example, by boiling with water [24] or with Fehling solution, either in accordance with Schwalbe's method for the determination of the copper number [25] or by a modification of this method suggested by Weltzien and Nakamura [26] or by boiling with aqueous sodium hydroxide or carbonate [27] or with aqueous calcium hydroxide.[28]

All these treatments result in a considerable decrease of the *reducing power* of hydrocellulose; this may be interpreted to mean that the products of low molecular weight—oligosaccharides, cellobiose, and glucose—are removed. Indeed, glucose has been identified in the aqueous extract,[29] and indications are that the extract also contained oligosaccharides.[30]

The formation of isosaccharic and dihydroxybutyric acid on boiling of hydrocellulose with lime,[31] as well as the formation of hydroxymethylfurfural on boil-

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[24] Hauser and Herzfeld, *Chem.-Ztg.*, **39**, 689 (1915); Netthöfel, doctoral dissertation, Berlin (1914); Harrison, *J. Soc. Dyers Colourists*, **28**, 224 (1912).

[25] Netthöfel, *loc. cit.;* Heuser and Niethammer, *Cellulosechem.*, **6**, 17 (1925); Heuser and Hiemer, *ibid.*, **6**, 116 (1925).

[26] Weltzien and Nakamura, *Ann.*, **440**, 290 (1924); Heuser and Hiemer, *Z. Elektrochem.*, **32**, 49 (1926).

[27] Birtwell, Clibbens, and Geake, *J. Textile Inst.*, **17**, T160 (1925); Hess and Katona, *Ann.*, **455**, 221 (1927).

[28] Schwalbe and Becker, *J. prakt. Chem.*, **100**, 19 (1919); Haworth, Peat, and Wilson, *J. Chem. Soc.*, 1904 (1939).

[29] Hauser and Herzfeld, *loc. cit.;* see also Stern, *J. Chem. Soc.*, **85**, 336 (1904).

[30] Hess, Weltzien, and Messmer, *Ann.*, **435**, 128 (1923); **442**, 46 (1925); **443**, 71 (1925); **444**, 301 (1925); Hess and co-workers regarded the products as representing isocellobiose and other isomers of cellobiose. The existence of isocellobiose or other isomers of cellobiose could not be confirmed, however. In other cases in which their occurrence has been claimed, they were identified as a mixture of cellobiose with oligosaccharides (see for example Freudenberg, "Tannin, Cellulose, Lignin," Springer, Berlin (1933), p. 99).

[31] Murmurow, Sack, and Tollens, *Ber.*, **34**, 1431, 1433 (1901); Schwalbe and Becker, *J. prakt. Chem.*, **100**, 19 (1919).

ing with hydrochloric acid,[32] as in the case of oxycellulose are, no doubt, the result of secondary reactions.

Hydrocellulose freed of the low-molecular-weight products must still be regarded as having a shorter average chain length than the original cellulose. Hence, and in spite of the absence of the products of far-reaching degradation, we would expect the reducing power of the purified hydrocellulose to be distinctly greater than that of the original cellulose. In general, however, this is not so, because more or less of the reducing groups are oxidized to carboxyl groups under the influence of the air oxygen in the presence of the alkali or other alkaline agents which may be used for the purification of the crude hydrocellulose. This view, expressed earlier by Bumcke and Wolffenstein,[33] appears supported by an observation of Birtwell, Clibbens, and Geake,[34] according to which the methylene blue absorption of a hydrocellulose preparation increased on boiling with aqueous alkali.

Oxidation of aldehyde groups may, of course, also occur when an attempt is made to determine the reducing power of the purified hydrocellulose, because, again, alkaline agents are used. Such an oxidation seems to occur to a greater extent when the Weltzien and Nakamura modification (suitable only for completely alkali-soluble hydrocellulose) is used than when Schwalbe's original method is used.

The fact that the copper number of hydrocellulose may be reduced to an even lower value than that shown by the original cellulose seems to suggest that treatment with alkali, with Fehling solution (and possibly with other bases and oxidants) would be a means of reducing or eliminating also the copper number of unmodified cellulose. Cellulose thus treated should give rise to a smaller quantity of carbon dioxide on boiling with dilute hydrochloric acid and would thus represent a type of oxycellulose in which carboxyl groups are possibly confined chiefly to end groups (see also p. 506).

In general, data on the *heterogeneity* of hydrocellulose and its change with the intensity of the hydrolyzing treatment are scarce. Some attempts in this direction were made by Davidson[35] by subjecting a hydrocellulose preparation to successive extractions with an aqueous alkali of varying concentrations and temperatures. The fibrous residue was freed thoroughly of alkali after each successive extraction. The dissolved material was regenerated from the various alkaline extracts by precipitation with acid and the viscosities of the

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[32] Heuser and Stöckigt, *Cellulosechem.*, **3**, 61 (1922).

[33] Bumcke and Wolffenstein, *Ber.*, **32**, 2501 (1899); see also Wise, *Trans. Electrochem. Soc.*, **73**, 86 (1938).

[34] Birtwell, Clibbens and Geake, *J. Textile Inst.*, **17**, T145 (1926).

[35] Davidson, *J. Textile Inst.*, **25**, T174, T176, T188 (1934).

various fractions in cuprammonium hydroxide determined. After each extraction, the weight and the moisture content of the insoluble fraction and the weight of that part which was used as the starting material for the next extraction were determined. From these data, the percentage of the original material in each of the four fractions was calculated. The results, expressed as "fluidity," are shown in Table 69.

TABLE 69

FRACTIONATION OF HYDROCELLULOSE WITH DILUTE AQUEOUS ALKALI

	Percentage of Original Hydrocellulose	Fluidity (2% Solution)
Original hydrocellulose	100	6.2
First fraction	19	16.6
Second fraction	19	10.8
Third fraction	29	6.2
Fourth fraction	33	3.6
Insoluble portion after 2 fractionations, i.e., third and fourth fractions	62	4.4
Mixture of fractions in the proportions in which they occur in original material	100	6.7

As the data show, the four fractions differed very definitely in fluidity, the most soluble portion having a value considerably higher and the least soluble portion a fluidity lower than that of the original hydrocellulose. As would be expected, the short-chain material (high fluidity) was dissolved more easily than that of longer (average) chain length. By a suitable choice of alkali concentration and temperature during extraction, the number of fractions may be increased and thus a more complete separation into fractions of different chain lengths achieved.

It is conceivable that the chain length distribution of hydrocellulose would become more uniform with an increasing number of cleavages of glycosidic linkages. This conclusion seems to be borne out by results which were obtained by the fractionation of acetylated and methylated highly degraded hydrocellulose preparations dissolved in organic solvents.[36] Table 70 shows the degree of polydispersity expressed in apparent molecular weight and apparent chain length (degree of polymerization, derived from specific viscosity determinations and calculated by using Staudinger's equation). It is seen that the degree of polymerization of the various fractions does not vary very much and, indeed, the average is very low. To check the data derived

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[36] Carrington, Haworth, Hirst, and Stacey, *J. Chem. Soc.*, 1901 (1939).

from viscosity measurements, the main fraction of the methylated hydrocellulose (45 per cent CH_3O) was subjected to end-group assay. The tetramethylglucose method gave a value of 70 and the iodine method a value of 95 glucose units. All three methods thus gave values of the same order, i.e., between 50 and 100.

TABLE 70

MOLECULAR WEIGHT AND CHAIN LENGTH OF FRACTIONS OF ACETYLATED AND METHYLATED HYDROCELLULOSE

Fractions of Acetylated Hydrocellulose	Acetyl Content, %	Apparent Molecular Weight	Apparent Chain Length
I	39.1	22,300	77
II	44.0	18,000	63
III	43.5	19,500	68
Methylated Hydrocellulose	Methoxyl Content		
I	42.5	8,800	44
II	43.5	12,200	59
III	45.0	10,000	54

It is noteworthy that a separation of hydrocellulose into fractions of different chain lengths may be accomplished merely by mechanical means (Haworth and co-workers). A hydrochloric acid hydrocellulose preparation having a copper number of 2.6 was mechanically separated into a powder and a fibrous residue. Whereas the original hydrocellulose had an average chain length of 120 and the fibrous portion of 200 glucose units (end-group assay, tetramethylglucose method), the powder showed only 70 (iodine method). Likewise, the copper numbers varied, the powder showing the higher figure (5.4), as compared with 1.7 for the fibrous portion. The copper number of the cotton linters from which the hydrocellulose had been prepared was 0.23.

The difference in the degree of polymerization of the two fractions is also reflected in their alkali-solubility. It was found that aqueous alkali of 0.25 *N* concentration dissolved 40 per cent of the powder and only 12 per cent of the fibrous fraction. With 2.5 *N* alkali the figures were 60 and 20 per cent, respectively. Thus it would seem that the solubility of hydrocellulose in alkali is inversely proportional to the average chain length.

The possibility of separating hydrocellulose into fractions of different chain lengths by purely mechanical means seems to indicate that chain length is more closely related to fiber length than was hitherto believed. It is probable that a more systematic investigation would reveal this relationship more exactly and show it to exist also in unmodified cellulose. In this connection, it appears of interest that it has been possible to separate aqueous suspensions of commercial wood pulps by mechanical means into long-fibered and short-fibered ("flour") portions, of which the flour fractions had a considerably higher copper number, a lower viscosity, and a lower *alpha*-cellulose content than the long-fibered fractions.

The Formation of Hydrocellulose under Exactly Controlled Conditions

In view of the importance of hydrocellulose formation during various commercial processes, particularly in textile processing, the attack of cellulosic materials in the form of fabrics, yarns, etc., by acids has been studied under conditions which approach those prevailing in industrial practice. As in oxycellulose, the conditions were carefully controlled and the attack limited, in contrast to the previously discussed investigations which refer to hydrocellulose preparations in which the cellulose was broken down far beyond the state encountered in commercial practice.

The damage done to cotton in commercial processing by the action of dilute mineral acids is reflected in a fall in viscosity and a rise in copper number. Both changes indicate a loss in physical strength properties (tensile strength).

It was found that the viscosity-strength relationship[37] is represented by a single smooth curve in spite of greatly varying conditions under which the "tendering," i.e., the formation of hydrocellulose, occurred. Likewise, the copper number-strength relationship follows a smooth curve, irrespective of the conditions of hydrocellulose formation. The copper number as a measure of tendering is most sensitive in the later stages of acid attack where the loss in strength (expressed as breaking load in percentage of the untreated material) amounts to between 50 and 100 per cent, whereas the viscosity is most sensitive as a measure of strength changes in the early stages of acid attack which correspond to the first 20 per cent loss in breaking load. Moreover, a given copper number always corresponds to the same viscosity, irrespective of the conditions of acid treatment. This relation may be expressed with reasonable accuracy over the most important range of acid attack by a simple equation.

According to Staudinger and Sorkin,[38] cellulose fibers become distinctly brittle when their degree of polymerization has been lowered to 300–400; at this point,

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[37] Birtwell, Clibbens, and Geake, *J. Textile Inst.*, **17**, T145 (1926); see also Farrow and Neale, *ibid.*, **15**, T157 (1924).

[38] Staudinger and Sorkin, *Ber.*, **70**, 1570 (1937).

they may be disintegrated to shorter fibers by mechanical agitation. Cotton suffered no essential loss in strength when degraded to a degree of polymerization of 700–800. A rapid change, however, was observed when the degree of polymerization fell to below 600. Staudinger believes that the loss in strength depends to a greater extent upon the number of "gaps" (*Lücken*) assumed to exist between the ends of the "thread molecules" than upon average chain length. The shorter the thread molecules, the greater is the number of the gaps. The number of gaps (*Knickbruchfestigkeit*) is thus inversely proportional to the degree of polymerization.[39]

The Rate of Hydrocellulose Formation. According to Birtwell, Clibbens, and Geake, the copper number may be taken as a true measure of the extent of cellulose degradation.[40] They showed that, under conditions of an acid-steeping procedure, the increase in copper number with increasing time of treatment was governed by the rule that the copper number is increased by 50 per cent when the time of treatment is doubled. Thus, if a certain acid treatment of cotton for 1 hour results in a copper number of 1.0, it produces a copper number of 1.5 in 2 hours.

The expression of this rule in the form of a simple equation enables one to calculate a velocity constant which measures quantitatively the rate of attack by any definite acid solution at a definite temperature. The mean temperature coefficient of hydrocellulose formation over the range of 20–100° was found to be 2.3; this means that the copper number resulting from a given acid treatment was increased 2.3-fold by a 10° rise in temperature.

Staudinger and Sorkin chose the specific viscosity in cuprammonium hydroxide to measure the rate of cellulose attack. Cotton (obtained from raw cotton by treatment with 2 per cent sodium hydroxide solution and subsequent extraction with alcohol, followed by ether) was subjected to the action of various dilute aqueous acids and salts for various lengths of time. The degradation, expressed as specific viscosity over concentration in grams, η_{sp}/c_g, and converted into the degree of polymerization (D.P.), is shown in Table 71. The data refer to treatment with N hydrochloric acid at 53°.

In Fig. 104, the logarithms of the degree of polymerization are plotted against the time (in hours) for hydrochloric acid as well as for other hydrolyzing agents. It is seen that the reaction is much more rapid in the beginning and that it slows down considerably as

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[39] Franz and Henning, *Melliand Textilber.*, **17**, 121 (1926); see also Staudinger and Feuerstein, *Ann.*, **526**, 72 (1936); Staudinger, *Melliand Textilber* **18**, 53 (1937).

[40] Birtwell, Clibbens, and Geake, *loc. cit.*, p. T161.

TABLE 71

VISCOSITY AND DEGREE OF POLYMERIZATION OF HYDROCELLULOSE PREPARED WITH HYDROCHLORIC ACID

Time, Hours	0	1	6	24	120	1226
η_{sp}/c_g	133 143	64.5 63.0	35.4 36.5	21.5 21.9	13.3 14.6	12.3 12.4
Degree of polymerization	1640 1770	800 780	437 450	266 270	164 181	151 153
Average D.P.	1710	790	445	270	175	150

the time is lengthened. It appears that the rate of degradation comes to a standstill even with strong mineral acids and salts.

The rate of hydrolysis of cellulose with dilute acids may also be determined by a method which is based upon the observation that the normally slow evolution of carbon dioxide from glucose in acid solutions (p. 433) may be increased at will by the use of a suitable catalyst, e.g., ferric chloride. The accelerated evolution rate is di-

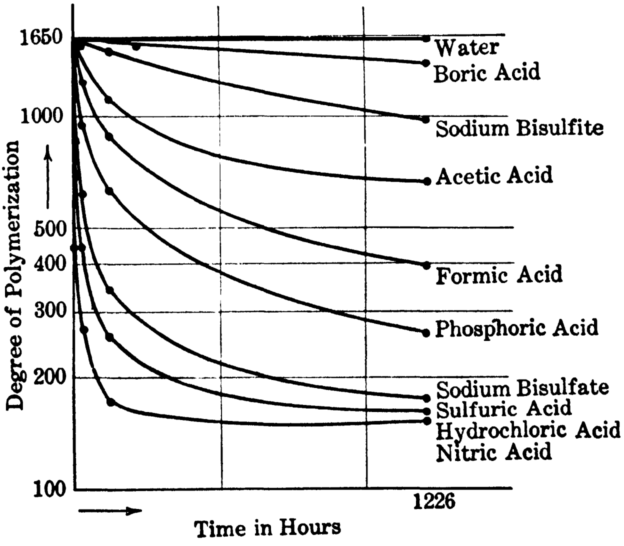

FIG. 104. Change of degree of polymerization of cotton under the influence of various hydrolyzing agents with time. Staudinger and Sorkin.

rectly proportional to the free glucose in the system.[41] In other words, glucose set free by hydrolysis may be estimated continuously.

The results of the application of this method to three different carbohydrate materials are shown in Fig. 105. From the quantities of carbon dioxide, the apparent glucose contents of the solution and the percentages of cellulose broken down per time unit may be calculated.

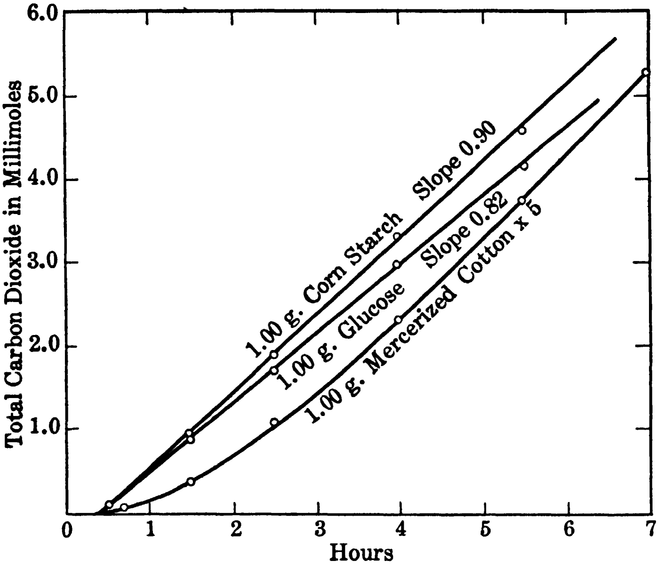

FIG. 105. Evolution of carbon dioxide from various carbohydrate materials under the influence of hydrochloric acid and ferric chloride. Nickerson.

The application of the method to cotton and mercerized cotton[42] seems to confirm the view that, physically, cellulose consists of two structural components, one of which (the amorphous fraction) undergoes scission easily during the hydrolytic treatment, and a more acid-resistant residue, which probably represents the crystalline portion of the structural system. Mercerization, as has been seen, increases the amount of the more accessible amorphous portion. As a result, the rate of hydrolysis is faster with mercerized than with unmercerized cellulose (p. 115).[43]

An attempt was made to calculate the percentage of crystalline and amorphous portions in a given cellulosic material by extrapolation of curves in which time

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[41] Nickerson, *Ind. Eng. Chem., Anal. Ed.*, **13**, 423 (1941).

[42] Nickerson, *Ind. Eng. Chem.*, **34**, 85 (1942).

[43] See also Ant-Wuorinen, *Pappers- Trävarutid. Finland*, **21**, 298, 329 (1939); *Papier-Fabr.*, **37**, Abstracts, p. 98 (1939).

was plotted against percentage cellulose hydrolyzed.[44] Although the values obtained for a variety of cellulosic materials must be regarded as tentative, they may indicate the relative order of magnitude of noncrystalline material present. Indeed, the results would seem to be in agreement with those derived from other considerations. Thus, unmercerized cotton and high grade cotton linters had the smallest content of amorphous material (5 and 6 per cent, respectively), whereas wood pulp, mercerized cotton, and viscose rayon showed the higher values (10, 11, and 12 per cent, respectively).

Moreover, a relation seems to exist between moisture affinity of cellulosic materials and their rate of hydrolysis. Such a relation could be expected from the following consideration: If cellulose contains crystallized and amorphous or expanded regions, a differential moisture affinity might be expected. Amorphous regions would have relatively high moisture affinity and, by virtue of their exposed character, would be highly susceptible to hydrolytic attack. In fact, it was observed that moisture affinity and rate of hydrolysis are roughly parallel.[45] This relation is further substantiated by the striking similarity which was found to exist between the rate of hydrolysis curve and the moisture-regain curve of cotton linters samples.

Simultaneous evaluation of the hydrolysis and moisture-regain data suggests that the crystallites of cellulosic materials have different moisture permeabilities. For example, the crystallites of viscose rayon appear to be completely permeable and their adsorbing power depends upon their size. The crystallites of mercerized cotton are considerably less permeable than those of viscose rayon, whereas the crystallites of unmercerized cotton are more or less completely impervious, i.e., moisture is probably adsorbed only on the outside surfaces of the cotton crystallites.

The Alkali-Solubility of Cellulose Modified by Acid Attack. Various results obtained by the treatment of hydrocellulose with aqueous alkali have been mentioned when the behavior of oxycellulose was discussed (p. 463), as well as at the beginning of the present chapter (p. 497). Additional results, obtained with cotton modified by acid attack under exactly controlled conditions, may be summarized as follows.

The alkali-solubility of cellulose modified by acid attack may be ascertained by boiling the material in 1 per cent sodium hydroxide solution for 4 hours.[46] Acid-treated cotton samples subjected to this test showed a linear relation between their copper number and their alkali-solubility (or loss in weight). In all cases, the copper number was greatly diminished by alkali boiling and would evidently have reached zero after sufficiently prolonged treatment. The viscosity, however, was only slightly affected.[47] Unless the loss in weight be-

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[44] Nickerson, *Ind. Eng. Chem.*, **34**, 1480 (1942).

[45] Nickerson, *Ind. Eng. Chem.*, **33**, 1022 (1941).

[46] Birtwell, Clibbens, and Geake, *loc. cit.*, p. T160.

[47] See also Davidson, *J. Textile Inst.*, **25**, T183 (1934)

came considerable, the tensile strength (breaking load) of single fibers changed very little on alkaline boiling. It will be recalled that oxycellulose of the reducing type, i.e., prepared in an acid or neutral medium, differed greatly from hydrocellulose in this respect; i.e., it suffered a considerable loss under such conditions. When the hydrocellulose was boiled in an alkaline copper solution, for example, of the type used by Braidy [48] for the copper number test,[49] the behavior was similar to that observed with alkali.

The different behavior with aqueous alkali furnishes a means of differentiation between hydrocelluloses and oxycelluloses of the reducing type. It is noteworthy that hydrocelluloses may be distinguished from the nonreducing oxycelluloses only if the former have not been treated with alkali for, under these conditions, the aldehyde groups are eliminated. If these are converted into carboxyl groups, both types of modified cellulose may liberate different quantities of carbon dioxide when subjected to the decarboxylation method.

As with oxycellulose, maximum solubility is observed if hydrocellulose is treated with cold sodium hydroxide solution of increasing concentration. Likewise, the alkali-solubility of hydrocellulose is considerably increased if it is first treated with a concentrated alkali solution and if the alkali is subsequently diluted with water. On such treatment, the alkali-solubility of a given hydrocellulose material may be increased about five times.[50]

Hydrocellulose also behaves similarly to oxycellulose if treated with cold sodium hydroxide solutions at temperatures below normal.[51] The solubility greatly increases as the temperature is lowered and, under these conditions, lower alkali concentration suffices to produce maximum solubility. Hydrocellulose preparations which have lost their fibrous structure entirely are completely soluble in alkali at −5° (2.5 N alkali).

Solubility maxima are also observed with the use of other bases, such as lithium and potassium hydroxide, as well as tetramethylammonium hydroxide. Likewise, the influence of temperature upon the position of the maximum and upon the concentration of the base required to produce the maximum are noticed. Potassium hydroxide possesses less solvent power than the other bases,

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[48] Braidy, *Rev. gén. mat. color.*, **25**, 35 (1921); Dorée, "The Methods of Cellulose Chemistry," p. 38.

[49] Clibbens, Geake, and Ridge, *J. Textile Inst.*, **18**, T277 (1927); Clibbens and Ridge, *ibid.*, **19**, T390 (1928); Birtwell, Clibbens, and Geake, *ibid.*, **19**, T349 (1928).

[50] Birtwell, Clibbens, and Geake, *J. Textile Inst.*, **19**, T349 (1928).

[51] Davidson, *J. Textile Inst.*, **25**, T174 (1934).

and the presence of metal sulfates in the dissolving alkali decreases the solubility.[52]

The Viscosity of Hydrocelluloses in Cuprammonium Hydroxide Compared with that of Their Nitrates and Acetates in Organic Solvents. Hydrocellulose may be converted into esters and ethers by the usual methods. Provided the hydrocellulose preparations have not been dried, they usually exhibit a greater reactivity, no doubt due to the presence of shorter chain molecules but, if the fibrous structure is lost, the greater activity is probably due to the fact that a greater surface is exposed to the reagents.

It was found that the nitrates of hydrocellulose possessed a higher degree of polymerization than the original hydrocelluloses. The difference was revealed when, as with oxycellulose (p. 465), the viscosity of the hydrocellulose nitrate in acetone was compared with that of the original hydrocellulose dissolved in cuprammonium hydroxide.[53] Pertinent data are shown in Table 72. To explain this difference Staudinger and Sohn have resorted to a hypothesis which differs essentially from that which was invoked for explaining the higher degree of polymerization of oxycellulose nitrate compared with that of the original oxycellulose. It will be recalled (p. 470) that this difference was explained by the hypothesis that ester linkages (which, in addition to glycosidic linkages, are thought to be present in oxycellulose) are stable to the nitration acid but unstable to alkali and cuprammonium hydroxide. In the preparation of hydrocellulose, however, no ester linkages are formed, and the assumption is made that, under the influence of the nitration acid, the end groups of the shortened chains undergo condensation (semiacetal formation between the aldehyde end group of one chain and the hydroxyl end group of another) to longer chains. As a result, the hydrocellulose nitrate would show a higher degree of polymerization than the original hydrocellulose.

TABLE 72

DEGREE OF POLYMERIZATION OF HYDROCELLULOSES IN CUPRAMMONIUM HYDROXIDE AND OF HYDROCELLULOSE NITRATES IN ACETONE

Materials	D.P. in Cuam.	D.P. of Nitrate in Acetone
Purified cotton	2800	3100
Hydrocellulose: 0.5% H_2SO_4, 10 minutes at 100°	910	1350
Hydrocellulose: 0.5% HCl, 10 minutes at 100°	620	930

In contrast to the behavior of oxycellulose acetates which were found to display a higher degree of polymerization in acetone than the original oxycellulose in cuprammonium hydroxide (p. 472), the acetates of hydrocellulose prepara-

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[52] Davidson, *J. Textile Inst.*, **27**, T112 (1936); see also Brownsett and Davidson, *ibid.*, **32**, T25, T51 (1941).

[53] Staudinger and Sohn, *Cellulosechem.*, **13**, 28 (1940); *J. prakt. Chem.*, **155**, 198 (1940).

tions were found to possess practically *the same* degree of polymerization as the original hydrocelluloses. For an explanation, the assumption is made that the pretreatment of hydrocellulose with phosphoric acid (which is also required here for solubilizing the otherwise insoluble acetate and for making viscosity measurements possible)[54] leads to a disarrangement of the orientation of the chains and that, as a result, the condensation of the chain fragments is inhibited. Thus, the average chain length of the hydrocellulose acetate would remain the same as in the original hydrocellulose.[55]

The data on which this hypothesis is based are shown in Table 73. This table also lists data on the degree of polymerization of the hydrocelluloses pretreated with 89 per cent phosphoric acid, i.e., before their conversion into acetates. The effect of this pretreatment appears to be confined to swelling, practically no degradation taking place. The last column shows the degree of polymerization of the hydrocelluloses regenerated from the acetates under careful conditions. It is seen that also regeneration took place practically without degradation.

TABLE 73

DEGREE OF POLYMERIZATION OF HYDROCELLULOSES IN CUPRAMMONIUM HYDROXIDE AND OF HYDROCELLULOSE ACETATES IN *m*-CRESOL

Materials	D.P. of Hydrocelluloses before and after Treatment with H_3PO_4, in Cuam.		D.P. of Acetates from H_3PO_4-treated Hydrocelluloses, in *m*-Cresol	D.P. of Regenerated Hydrocelluloses
Cotton degraded with dilute H_2SO_4	910	800	840	800
Cotton degraded with dilute HCl I	1000	920	800	800
Cotton degraded with dilute HCl II	720	680	650	640

According to Staudinger, hydrocelluloses[56] may thus be distinguished from oxycelluloses by their behavior with phosphoric acid, with subsequent determination of the degree of polymerization of the phosphoric acid-treated products and of the acetates prepared therefrom. Whereas the oxycellulose acetates show a higher degree of polymerization than the original (phosphoric acid-treated) oxycelluloses, the values are the same for the hydrocellulose preparations. Any disorientation of the chain molecules (which must be expected to take place under the action of phosphoric acid also in oxycelluloses) has no effect because they are not subject to condensation.

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[54] See footnote 172 on p. 472.

[55] Staudinger and Sohn, *J. prakt. Chem.*, **155**, 205 (1940).

[56] The hypothesis is confined to hydrocelluloses of a moderate degree of degradation.

It remains to be seen whether these various hypotheses can be supported by further experimental evidence.

Microscopical Observations

The process of hydrocellulose formation has frequently been observed under the microscope. That the attack of the fiber starts on the surface is seen from pictures presented by Netthöfel,[57] particularly from a comparison of the microscopical views of crude hydrocellulose fibers with those from which the low molecular substances have been removed by boiling with Fehling solution. Layers of cellulosic material appear to be removed from the surface, leaving a skeleton of apparently unchanged cellulose. However, on longer treatment and particularly under conditions in which the hydrolyzing agent thoroughly penetrates the whole fibrous mass, the reaction seems to take place through the entire structural system. This conclusion is supported by the photomicrographs of hydrocellulose fibers which were treated with 10 per cent sodium hydroxide solution for 24 hours at room temperature and subsequently washed with water.[58] It is seen from Fig. 106 that the removal of the alkali-soluble portions left a cellulose skeleton in which the spiral structure of the original cotton fiber may still be recognized. Hydrolysis thus seems to proceed in a manner which is directed by the microscopical and the submicroscopical structure of the fiber. This view (which may be deduced also from pictures presented by Davidson [59]) is in agreement with those of Frey-Wyssling and I. W. Bailey (pp. 251 and 252).

FIG. 106. Microscopical appearance of hydrolyzed cotton fibers. Hess and Trogus.

In connection with the formation of hydrocellulose, there arises the question of explaining the fact that cellulose fibers in which a certain number of glycosidic linkages have been broken still remain fibers and do not break down to fiber fragments. As has been seen, the average chain length of cellulose in fabrics may be reduced considerably by

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[57] Netthöfel, doctoral dissertation, Berlin (1914).

[58] Hess, "Chemie der Cellulose," p. 443.

[59] Davidson, *J. Textile Inst.*, **25**, T189, T193 (1934).

hydrolytic as well as by oxidative attack without such fabrics losing their fibrous structure. Likewise, the original average chain length of cellulose in wood may be reduced considerably by the pulping action, depending upon the conditions of temperature, time, etc., but the resulting pulp, even if of a very low viscosity, still represents fibers of considerable physical strength properties. Evidently, this is because the anastomosing structure of the fibers has not been seriously disturbed and the cohesive forces between chains and chain bundles in the lateral direction are still operative. It is only when more and more chains are broken that the network of the fiber is seriously disrupted and that, consequently, the cohesive forces are so weakened that hydrocellulose of this type loses its fibrous structure under the slightest mechanical stress.

DECOMPOSITION WITH STRONG MINERAL ACIDS

Cellulose, before being dissolved, swells considerably in strong mineral acid and is assumed to form addition compounds with the acids.[60] According to af Ekenstam, addition compound formation is a prerequisite for the solution of cellulose in the strong acids. It is further postulated that certain quantities of water must take part in the combinations (hydrate formation) to insure quick and complete solubility. Obviously, no attempt has as yet been made to confirm af Ekenstam's conclusions. It is noteworthy that Champetier's results seem to indicate that cellulose dissolved in concentrated phosphoric acid forms an addition compound without the participation of water.[61]

Amyloid and Similar Preparations

On dilution with water shortly after dissolving and with thorough cooling, the greater part of the cellulose may be regenerated in the form of white flakes which show the behavior and the x-ray diagram of mercerized cellulose. In the older literature,[62] the preparation thus obtained is often termed *amyloid,* because it gives the same blue coloration with iodine in the presence of traces of sulfuric acid as starch

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[60] af Ekenstam, "Über die Celluloselösungen in Mineralsäuren," Blom's Boktryckeri, Lund (1936); see also *Ber.*, **69**, 549, 553 (1936).

[61] Champetier, *Compt. rend.*, **196**, 930 (1933); see also Lieser, *Cellulosechem.*, **18**, 122 (1940).

[62] Flechsig, *Z. physiol. Chem.*, **7**, 523 (1883); Schulz, doctoral dissertation, Darmstadt (1910); Schwalbe and Schulz, *Ber.*, **43**, 913 (1910).

("amylum"), a reaction which, although known for more than a century, is not yet fully understood.[63] The reducing power of the preparation is small.

Similar preparations have been designated *Guignet cellulose* or *colloïdal cellulose*.[64] Guignet cellulose, when freed of electrolytes, dissolves in water to give a colloidal solution of considerable stability. The cellulose may be regenerated therefrom by the addition of electrolytes, acids, alcohol, etc.

The initial resistance of cellulose to a breakdown under the action of strong mineral acids is greater in phosphoric than in other mineral acids. af Ekenstam [65] has utilized this behavior in a method of separating cellulose into portions of varying chain length by fractional solution.

Preparations of shorter average chain length are obtained by applying more severe conditions. Thus, cotton may be mixed with a certain amount of 54 per cent phosphoric acid and the paste so obtained allowed to stand for some time. On heating and employing mechanical agitation, the cellulose goes into solution. It may be regenerated therefrom with ice water. The product is completely soluble in 8 per cent sodium hydroxide solution, provided it has not been dried. The copper number of a product thus prepared was 2.9 (Schwalbe method).[66]

Another product was obtained by regeneration of cellulose from its solution in highly concentrated hydrochloric acid (concentrated hydrochloric acid is brought up to 46.5 per cent by saturating it with hydrogen chloride at −5°).[67] Cellulose dissolves in such a strong acid within a very short time but may be almost completely regenerated shortly after dissolving. The regenerated product (in the moist state) was soluble in 8 per cent sodium hydroxide solution at room temperature and in 5 per cent at 0°. On dilution of the sodium hydroxide solution, the modified cellulose precipitated. It also precipitated on heating the undiluted solution but redissolved on cooling. This behavior seems to indicate that the modified cellulose formed an addition compound with the alkali which is stable in the cold but splits on heating, or that the alkali compound formed a hydrate which undergoes the same changes.

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[63] Bergmann, *Ber.*, **57**, 753, 961 (1924); Rowe, doctoral dissertation, The Institute of Paper Chemistry, Appleton, Wis., 1940, under the direction of J. Graff.

[64] Guignet, *Compt. rend.*, **108**, 1258 (1889); Schwalbe and Lange, *Z. angew. Chem.*, **39**, 606 (1926).

[65] af Ekenstam, *Svensk Papperstidn.*, **45**, 81 (1942).

[66] Karrer and Lieser, *Cellulosechem.*, **7**, 1 (1926).

[67] Lieser, *Cellulosechem.*, **7**, 85 (1926).

Cellodextrins

On long standing in concentrated mineral acids, cellulose is more and more seriously attacked, and water is no longer capable of precipitating any appreciable amount of the dissolved material. However, with alcohol, a precipitate known as *cellulose dextrin* or *cellodextrin* is obtained which is characterized by its high reducing power and which has played a great part in the attempts to isolate homogeneous intermediates in the course of the hydrolysis of cellulose. It is probable that the cellodextrins are precipitated in the form of their sulfuric acid esters. On boiling with alcohol, the free cellodextrins are obtained.[68]

On restricted acetolysis of cellulose, the cellodextrins are obtained in the form of their acetates, from which the free cellodextrins may be obtained by saponification with alkali.[69] Likewise, the action of acetyl chloride, under conditions which attack cellulose beyond the acetylation stage, results in the formation of cellodextrin acetates. The free cellodextrins may be regenerated by saponification with methyl alcoholic potassium hydroxide.[70]

It was early recognized that the cellodextrins, as obtained by precipitation with alcohol, consist essentially of two components, one of which, although considerably degraded, still possesses cellulose characteristics, whereas the other contains far-reaching degradation products. Among these, cellobiose has been found. It may be isolated by the same methods by which it is obtained directly from cellulose (see later).

Later investigations have made it seem very probable that the noncellulosic portion of the cellodextrins contains, besides cellobiose, a number of oligosaccharides,[71] possibly of an average degree of polymerization of 30.[72] Likewise, certain biose anhydrides, which at one time were claimed to have been isolated from the acetolysis of cellulose [73] or by the restricted action of hydrogen bromide in glacial acetic

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[68] Hönig and Schubert, *Monatsh.*, **7**, 455 (1886); Mühlmeister, doctoral dissertation, Hanover (1913), pp. 14, 28; see also Ost, *Z. angew. Chem.*, **25**, 1996 (1912).

[69] Madsen, doctoral dissertation, Hanover (1917), p. 44; Hess and Weltzien, *Ann.*, **435**, 46, 58 (1923).

[70] Hess, Weltzien, and Singer, *Ann.*, **443**, 100 (1925).

[71] Meyer and Mark, *Ber.*, **61**, 2432 (1928); Freudenberg, *ibid.*, **62**, 383 (1929); Bergmann and Machemer, *ibid.*, **63**, 316 (1930); Staudinger, "Die hochmolekularen organischen Verbindungen," p. 460.

[72] Freudenberg, Bruch, and Rau, *Ber.*, **62**, 3078 (1929); Freudenberg, Kuhn, *et al.*, *ibid.*, **63**, 1527 (1930).

[73] Hess, *Ber.*, **54**, 2867 (1921); Hess and Friese, *Ann.*, **450**, 40 (1926).

acid upon cellulose triacetate,[74] were later recognized as a mixture of oligosaccharides.[75]

Oligosaccharides

The isolation of oligosaccharides [76] is best accomplished by acetolysis or hydrolysis of cellulose preceded by methylation or by methylation after acetolysis. The products are more stable in the form of their methyl derivatives and thus may be more easily separated. Since on acetolysis the hydroxyl groups steadily increase in number (because of the progressive opening of glycosidic linkages) and are simultaneously acetylated, the determination of the increase in acetyl content provides a general means of pursuing the process of degradation.

Although Tollens' chain formula for cellulose (1895) suggested to early research workers the possibility of restricted degradation to longer fragments than cellobiose, attempts to isolate such fragments were unsuccessful for some time. The existence of a trisaccharide (*procellulose*) in the solution obtained by the acetolysis of cellulose was considered probable by Bertrand and Benoit [77] and confirmed by Ost,[78] who isolated the trisaccharide in crystalline form and termed it *cellotriose*. Ost's results were confirmed by Irvine and Robertson.[79] Earlier, Willstätter and Zechmeister [80] had obtained cellobiose by hydrolyzing cellulose in wood with fuming hydrochloric acid (43–44 per cent), and later Zechmeister and Tóth [81] isolated cellotetraose and cellopentaose from the hydrolysate.

Cellopentaose is the highest member thus far isolated from the mixture of oligosaccharides. It crystallizes in very fine but homogeneous needles; its molecular weight corresponds to the formula $C_{30}H_{52}O_{26}$, requiring a value of 828. Although it has not yet been possible to obtain crystalline derivatives of this pentasaccharide, derivatives of

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[74] Bergmann and Knehe, *Ann.*, **445**, 1 (1925).

[75] Freudenberg, Kuhn, *et al.*, *loc. cit.*

[76] The term *oligosaccharides* was suggested by Helferich, Bohn, and Winkler, *Ber.*, **63**, 989 (1930) for compounds consisting of n molecules of a monosaccharide with loss of $n-1$ molecules of water. Thus, the disaccharides, e.g., cellobiose, are included in this term, although they are usually dealt with under the separate term *disaccharides*.

[77] Bertrand and Benoit, *Compt. rend.*, **176**, 1583 (1923); **171**, 85 (1924); *Bull. soc. chim.*, **33**, 1451 (1923); **35**, 58 (1924).

[78] Ost, *Z. angew. Chem.*, **39**, 1117 (1926).

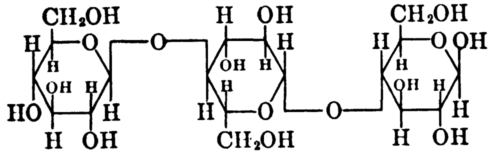
[79] Irvine and Robertson, *J. Chem. Soc.*, **128**, 1488 (1926).

[80] Willstätter and Zechmeister, *Ber.*, **46**, 2403 (1913); *ibid.*, **62**, 722 (1929).

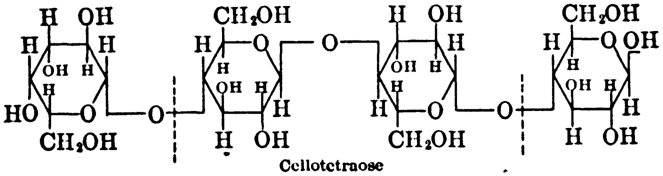
[81] Zechmeister and Tóth, *Ber.*, **64**, 857 (1931); Zechmeister, Mark, and Tóth, *ibid.*, **66**, 269 (1933); Zechmeister and Tóth, *ibid.*, **68**, 2134 (1935); Freudenberg, *Ann.*, **494**, 41 (1932); Staudinger and Leupold, *Ber.*, **67**, 479 (1934); Hess and Dziengel, *Ber.*, **68**, 1596 (1935).

cellotetraose and cellotriose, namely, acetates, methyl ethers, and osazones, have been isolated in crystalline form.[82]

Upon acetolysis, cellotriose yields cellobiose octoacetate; [83] it is thus a cellobiosido-glucose. The structure of cellotriose as cellobiosido-glucose and that of cellotetraose as cellotriosido-glucose is supported by the work of Haworth, Hirst, and Thomas.[84] On the cleavage of the completely methylated cellotrioside (resulting from the acetolysis of trimethylcellulose at low temperature) with aqueous hydrochloric acid, they obtained tetramethylglucose and 2,3,6-trimethylglucose in a ratio of 1 : 2. Another fraction of the products of acetolysis (designated as cellodextrin) underwent cleavage with hydrochloric acid to tetramethylmethylglucoside and heptamethyl-β-methylcellobioside. The results of these cleavage reactions furnish evidence for the structural formulas of cellotriose and cellatetraose. They are represented as follows:



Cellotriose



Cellotetraose

The vertical broken lines in the cellotetraose formula indicate the places of hydrolysis. The two structures thus represent fragments of the cellulose chain formula.

Cellotriose has been synthesized in the form of its fully methylated methylglucoside, decamethyl-β-methylcellotrioside, from 2,3,6-trimethyl-β-methylglucoside and the chlorohydrin of heptamethylcellobiose,[85] which gives definite proof of the molecular structure of cellotriose.

It is interesting that, as could be expected, the reducing power of the oligosaccharides decreases as the number of glucose residues in-

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[82] Freudenberg and Friedrich, *Naturwissenschaften,* **17,** 959 (1929); **18,** 1114 (1930); *Ber.,* **63,** 1963 (1930); Freudenberg, Friedrich, and Bumann, *Ann.,* **494,** 41 (1932); Hess and Dziengel, *Ber.,* **68,** 1594 (1935).

[83] Zechmeister and Tóth, *loc. cit.*

[84] Haworth, Hirst, and Thomas, *J. Chem. Soc.,* 824 (1931).

[85] Freudenberg and Nagai, *Ann.,* **494,** 63 (1932).

creases. Likewise, the physical properties of the oligosaccharides, such as solubility, melting and boiling points, optical rotation, etc., approach those of cellulose as the number of glucose residues increases. The oligosaccharides of about 30 glucose residues show colloidal properties, and these become more pronounced as the chain molecule becomes longer and as more and more of such molecules associate themselves to chain bundles.

This behavior of the oligosaccharides, that is, the increase in colloidal character with the growth of the chain, seems to be analogous to that of Emil Fischer's polypeptides. It was found that the tetrapeptide of *p*-hydroxybenzoic acid and the higher homologues are amorphous, and that the colloidal properties of the polypeptides of a molecular weight of 1000 approach those of the natural proteins.[86]

The condensed formulas of the oligosaccharides may be written in a way which permits recognition of the fact that the two terminating units differ from the rest, thus:

Cellobiose	$C_6H_{11}O_6C_6H_{11}O_5$
Cellotriose	$C_6H_{11}O_6C_6H_{10}O_5C_6H_{11}O_5$
Cellotetraose	$C_6H_{11}O_6[C_6H_{10}O_5]_2C_6H_{11}O_5$
Cellopentaose	$C_6H_{11}O_6[C_6H_{10}O_5]_3C_6H_{11}O_5$

The same oligosaccharides which are obtained from plant cellulose were isolated from the products of hydrolysis of the animal cellulose which is produced by *Phallusia mammillaris*.[87]

Cellobiose

There seems to be general agreement on the interpretation of Franchimont's important experiment[88] in which acetic anhydride and sulfuric acid were allowed to act upon cellulose in the form of Swedish filter paper, namely, that the crystalline substance which he obtained and which he regarded to be an acetylated "triglucose" was actually the octoacetate of cellobiose. Although Skraup,[89] who repeated Franchimont's experiment twenty years later, did not, at the time, recognize the crystallized substance as a disaccharide, Skraup and König[90] es-

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[86] Emil Fischer, *Sitzber. kgl. preuss. Akad. Wiss.*, Berlin (1916), p. 990; quoted from Freudenberg, "Tannin, Cellulose, Lignin," p. 91.

[87] Abderhalden and Zemplén, *Z. physiol. Chem.*, **72**, 58 (1911); Zechmeister and Tóth, *ibid.*, **215**, 267 (1933).

[88] Franchimont, *Ber.*, **12**, 1941 (1879).

[89] Skraup, *Ber.*, **32**, 2413 (1899).

[90] Skraup and König, *Ber.*, **34**, 1115 (1901); *Monatsh.*, **22**, 1011 (1901).

tablished the biosic character of the substance without doubt. It was termed "cellose" and recognized as the "simplest polysaccharide from cellulose, as maltose is the simplest polysaccharide from starch." Later, the term *cellobiose* was given preference.[91]

The support which the discovery of a disaccharide among the products of cellulose degradation lent to the chain formula concept was fully recognized by Skraup and his followers. In this connection the yield was important. Whereas originally not more than 16 to 19 per cent of the cellulose was obtained, Ost and co-workers[92] found up to 37 per cent, Madsen[93] increased it to 43 per cent, Freudenberg[94] found 35–37 per cent, and Hess and Friese[95] 50–51 per cent, the highest yield thus far obtained.

On the assumption that cellulose represents a chain of glucose or cellobiose residues the law of probability would let us expect that, on hydrolysis, a portion considerably less than 100 per cent would be preserved in the form of cellobiose. It has been calculated[96] that a polysaccharide chain of 100 glucose units on hydrolysis may yield, under the most favorable conditions, 32 per cent in the form of a biose. If, however, the biose formed on hydrolysis were entirely preserved, the yield would be 67 per cent. In the case of cellulose, only a portion of the cellobiose formed during hydrolysis crystallizes from its solution, so that the possible yield could be expected to be above 32 and below 67 per cent. The difference between the highest yield actually obtained (50–51 per cent) and the calculated yield (67 per cent) is accounted for by the fact that during acetolysis certain amounts of cellobiose are destroyed.[97]

The agreement between the calculation and the experimental findings may be valued as a strong support for the hypothesis that cellobiose is preformed in cellulose and as a strong argument against an early assumption of Hess, namely, that cellobiose owes its formation to a condensation of glucose anhydride molecules under the action of acetic anhydride and sulfuric acid[98] (see also Franchimont).

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[91] Skraup and König, *Monatsh.*, **22**, 1011 (1901), footnote 1.

[92] Ost, *Ann.*, **398**, 323 (1913).

[93] Madsen, doctoral dissertation, Hanover (1917), pp. 16, 35, 50, 51.

[94] Freudenberg, *Ber.*, **54**, 771 (1921).

[95] Hess and Friese, *Ann.*, **456**, 39 (1927); see also the compilation of results obtained by the various investigators in Hess, "Die Chemie der Cellulose," p. 500, and Spencer, *Cellulosechem.*, **10**, 61 (1929).

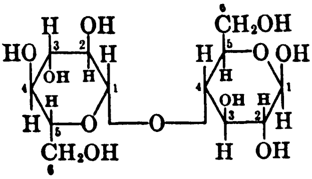
[96] Freudenberg, *Ber.*, **54**, 767 (1921); "Tannin, Cellulose, Lignin," p. 94.

[97] Karrer and Widmer, *Helv. Chim. Acta*, **4**, 174 (1921); Freudenberg, *loc. cit.*

[98] Hess, Weltzien, and Singer, *Ann.*, **443**, 90 (1925).

The molecular structure of cellobiose which has been the object of extensive studies for a considerable number of years[99] was definitely established by Haworth and his school.[100] By employing the previously well-established technique of methylation and subsequent hydrolysis of the methylated product, it was found that octamethylcellobiose was cleaved into 2,3,6-trimethylglucose and 2,3,4,6-tetramethylglucose. The hydrolysis of octamethylcellobionic acid to 2,3,5,-6-tetramethylgluconic acid and 2,3,4,6-tetramethylglucose showed that the glycosidically combined glucose residue was attached to the carbon atom in the 4-position of the other unit. The two glucose residues in cellobiose are thus combined by a 1,4-linkage.[101]

The cellobiose structure was confirmed by the results of an entirely different procedure. Applying Wohl's[102] technique of gradual scission of sugars by conversion into their nitriles and subsequent saponification of the latter, Zemplén[103] converted octaacetylcellobiose into glucoarabinose and the latter into glucoerythrose. The fact that glucoerythrose is no longer capable of forming an osazone indicates that it is the carbon atom next to the aldehyde group in the erythrose residue which is linked to the glucose unit. Because glucoerythrose resulted from cellobiose without any change of the configuration of the disaccharide, the same carbon atom must be involved in the linkage in cellobiose, which is that in the 4-position.



The molecular structure of cellobiose is further supported by the synthesis of cellobiose from acetobromoglucose and levoglucosan, subsequent careful hydrolysis of the 1,6-oxygen linkage of the levoglu-

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[99] See, for example, the historical review in Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 190; Hess, "Die Chemie der Cellulose," p. 503; Haworth, "The Constitution of Sugars," Arnold and Company, London (1929); Haworth, "Die Konstitution der Kohlenhydrate" (Liesegang's Forschungsberichte), Steinkopf, Dresden and Leipzig (1932).

[100] Charlton, Haworth, and Peat, *J. Chem. Soc.*, **129**, 89 (1926); Hirst, *ibid.*, **129**, 350 (1926); Haworth, Long, and Plant, *ibid.*, 2809 (1927).

[101] See also Bergmann and Schotte, *Ber.*, **54**, 1570 (1921), on cellobial, $C_{12}H_{20}O_9$, the deshydroxy derivative of cellobiose.

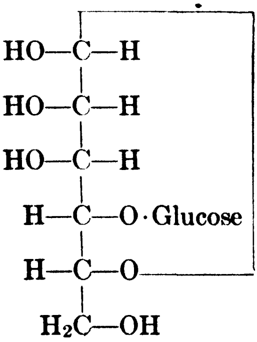
[102] Wohl, *Ber.*, **26**, 730 (1893); **30**, 3101 (1897); **32**, 3666 (1899).

[103] Zemplén, *Ber.*, **59**, 1254 (1926).

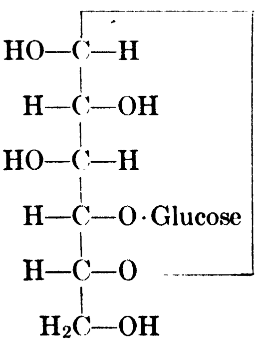
cosan unit, and reacetylation. The yield of cellobiose, however, is small (about 2 per cent, based upon the acetobromoglucose).[104] Cellobiose acetate has also been synthesized, although only in minute amounts, from 2,3,6-triacetyl-β-methylglucoside and acetobromoglucose,[105] and methylcellobiose from 2,3,6-trimethyl-β-methylglucoside and 2,3,4,6-tetramethylglucose.[106]

The most recent synthesis of cellobiose by Hudson and co-workers[107] makes use of 2,3-isopropylidene-*d*-mannosan$<1,5>\beta<1,6>$ for the synthesis of disaccharides which are linked through carbon atom 4 of *d*-mannose. Epicellobiose octaacetate was obtained by the action of an acid acetylating mixture on the condensation product of 2,3-isopropylidene-*d*-mannosan$<1,5>\beta<1,6>$ with acetobromoglucose and converted to the known cellobial hexaacetate by customary procedures. The latter product, upon oxidation with perbenzoic acid, yielded cellobiose hexaacetate, and the hexaacetate, upon acetylation, gave a crystalline mixture of α- and β-cellobiose octaacetates in 63 per cent yield. Crystalline cellobiose was obtained in quantitative yield by deacetylation of the octaacetate mixture. The over-all yield of cellobiose from epicellobiose octaacetate was 35 per cent. The formulas of epicellobiose and cellobiose (written in the older customary manner) are shown below.

According to Hudson and co-workers, the method of synthesis of epicellobiose and cellobiose is applicable in principle to the synthesis of similarly constituted compound sugars of longer chain length, and



EPICELLOBIOSE



CELLOBIOSE

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[104] Freudenberg and Nagai, *Naturwissenschaften*, **20**, 578 (1932); *Ber.*, **66**, 27 (1933).

[105] Heferich and Bredereck, *Ber.*, **64**, 2411 (1931).

[106] Freudenberg, Andersen, Go, Friederich, and Richtmyer, *Ber.*, **63**, 1961 (1930); Zemplén, *Ber.*, **63**, 1820 (1930).

[107] Haskins, Hann, and Hudson, *J. Am. Chem. Soc.*, **64**, 1289 (1942).

an approach by this method to the laboratory synthesis of cellulose is visualized.

That the cellobiose which results from the hydrolysis or acetolysis of cellulose belongs to the β-series of disaccharides is established by its behavior with emulsin. This enzyme is a specific for methylglucosides having the β-configuration. Cellobiose undergoes cleavage into glucose, whereas maltose is not attacked.[108] Maltose, however, undergoes cleavage to glucose by the enzyme maltase, which is a specific for the α-configuration. Likewise, the two disaccharides may be distinguished by their different behavior with yeast. Maltose is fermented but cellobiose is not. Since the two glucose residues in maltose are also united by the 1,4-linkage, the only difference between cellobiose and maltose is the different configuration.

It is interesting to note that emulsin is also capable of *synthesizing* cellobiose. The latter is formed by the action of emulsion upon glucose.[109]

As has been seen (p. 36), cellobiose may also be obtained by allowing the amylases contained in the saps of the sugar maple tree or the birch tree to act upon starch.

The existence of *isocellobiose*, which for some time was thought to be formed simultaneously with cellobiose on the acetolysis of cellulose[110] (although its existence had been doubted from time to time[111]) has not been confirmed. It is now recognized as a mixture of cellobiose with oligosaccharides.[112] The establishment of this fact is of importance, inasmuch as the existence of an isomer of cellobiose among the products of cellulose degradation would favor the assumption that in cellulose different linkages alternate.

Glucose

The end product of the hydrolysis of cellulose is glucose. That this sugar is the only product of the complete degradation of cellulose was

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[108] Fischer and Zemplén, *Ann.*, **365**, 1 (1909); **372**, 254 (1910); Bertrand and Holderer, *Compt. rend.*, **149**, 1385 (1909); **150**, 230 (1910); Fischer, *Ber.*, **47**, 1983 (1914); Haworth and Hirst, *J. Chem. Soc.*, **119**, 196 (1921); Hudson, *J. Am. Chem. Soc.*, **38**, 1566 (1916).

[109] Bourquelot and Bridel, *Compt. rend.*, **168**, 1016 (1919).

[110] Ost and Prosiegel, *Z. angew. Chem.*, **33**, 100 (1920); Ost and Koth, *Cellulosechem.*, **3**, 25 (1922); Ost, *Z. angew. Chem.*, **39**, 1117 (1926); see also Weltzien and Singer, *Ann.*, **443**, 71 (1925).

[111] Bertrand and Benoit, *Compt. rend.*, **177**, 85 (1923).

[112] Meyer and Mark, *Ber.*, **61**, 2432 (1928).

recognized more than 120 years ago. Braconnot[113] subjected various cellulosic materials (including linen and hemp) to the action of 91 per cent sulfuric acid, diluted the solution after some time with water, and finally heated the diluted solution to boiling. He thus recognized that the hydrolysis of cellulose with sulfuric acid must be carried out in these two steps. Later, Flechsig[114] found that this procedure is necessary for obtaining the highest glucose yield and that the use of strong acid alone is not successful, because cellulose tends to become carbonized (see also af Ekenstam, p. 510).

Tschumanow[115] succeeded in converting cellulose into colloidal carbon by allowing concentrated sulfuric acid to act upon it for a long period of time. Likewise, sucrose may be converted into colloidal carbon by treatment with concentrated sulfuric acid.[116] The process of carbonization may be visualized as dehydration, thus: $C_6H_{10}O_5 = 6C + 5H_2O$.

Most of the older investigators were satisfied with determining the yield of glucose without isolating it in a crystallized and purified form, either by ascertaining the reducing power of the solution, by subjecting the neutralized solution to alcohol fermentation with yeast, or by determining the optical rotation. The yields thus determined (with some exceptions) varied from 90 to 98 per cent[117] of the theory, which requires 111.1 per cent on the basis of the equation

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$$

Monier-Williams[118] isolated the glucose, formed on hydrolysis of cotton with sulfuric acid, in crystallized and pure form and obtained a yield of 90.7 per cent of the theoretical, whereas Heuser and Aiyar,[119] applying Monier-Williams' method, obtained very nearly 96 per cent from both cotton and sulfite wood pulp.

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[113] Braconnot, *Ann. chim.*, [2] **12**, 172 (1819); **25**, 81 (1827).

[114] Flechsig, *Z. physiol. Chem.*, **7**, 524 (1882); Ost and Wilkening, *Chem.-Ztg.*, **34**, 461 (1910); Ost, *Ber.*, **46**, 2995 (1913); Mühlmeister, doctoral dissertation, Hanover (1913); Schwalbe and Schulz, *Ber.*, **43**, 915 (1910); see also Pummerer and Gump, *Ber.*, **56**, 999 (1923).

[115] Tschumanow, *Kolloid-Z.*, **14**, 321 (1914).

[116] Sabatani, *Kolloid-Z.*, **14**, 29 (1914).

[117] See the compilation of results in Hess, "Chemie der Cellulose," pp. 476 and 478.

[118] Monier-Williams, *J. Chem. Soc.*, **119**, 804 (1921).

[119] Heuser and Aiyar, *Z. angew. Chem.*, **37**, 27 (1924); see also Heuser and Boedeker, *ibid.*, **34**, 461 (1921); Heuser and Dammel, *Cellulosechem.*, **5**, 52 (1924); Kiesel and Semiganowsky, *Ber.*, **60**, 333 (1927); Lüdtke, *Ann.*, **456**, 222 (1927).

Irvine and co-workers[120] found very similar yields by isolating the glucose in the form of its methylglucoside. On the action of methyl alcoholic hydrochloric acid upon cellulose triacetate, a yield of 95 per cent of the theoretical was thus obtained. The results were confirmed by Heuser and Aiyar with cotton and with sulfite wood pulp.[119]

The almost identical yield of glucose obtainable from cotton and other cellulosic materials freed of accompanying noncellulosic substances, as well as the identity of other characteristics of the preparations, was interpreted to support the hypothesis that all celluloses, regardless of the source from which they are isolated, possess the same molecular structure.[121] This hypothesis was further supported by the fact that the yield of cellobiose from wood pulp was of the same magnitude as that from cotton.[122] In the light of present-day knowledge, the hypothesis of the identity of celluloses, irrespective of their source of isolation, may have to be revised, because it appears possible that in certain types of cellulose, e.g., in wood, cellulose chains are chemically combined with chains of noncellulosic carbohydrates, such as xylan, or their uronic acid derivatives.

The hydrolysis of cellulose with sulfuric acid dissolved in liquid sulfur dioxide was studied by Scherer and Brooks.[123]

The theoretical yield of glucose has never been obtained because part of the glucose is destroyed and part undergoes reversion. Ost and Wilkening found that 5 per cent of the cellulose is converted into organic acids, among them levulinic and formic acids.[124] The formation of these acids is probably preceded by the formation of ω-hydroxyfurfural,[125] which is obtained by the action of acids upon glucose[126] and upon cellulose.[127] (For reversion see p. 523.)

Acetolysis of cellulose yields a mixture of cellobioseoctaacetate and

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[120] Irvine and Soutar, *J. Chem. Soc.*, **119**, 1489 (1920); Irvine and Hirst, *ibid.*, **121**, 1585 (1922).

[121] Heuser and Haug, *Z. angew. Chem.*, **31**, 99, 103, 166, 172 (1918); Heuser and Boedeker, *loc. cit.*; *Paper Trade J.*, **74**, No. 5, 47 (1922).

[122] Wise and Russel, *J. Chem. Soc.*, **121**, 285 (1922); *Ind. Eng. Chem.*, **15**, 711, 815 (1923); see also Harlow and Wise, *Am. J. Botany*, **25**, 217, 760 (1938).

[123] Scherer and Brooks, *Rayon Textile Monthly*, **23**, 718 (1942).

[124] Ost and Wilkening, *loc. cit.*; see also Cross, Bevan, and Smith, *Ber.*, **28**, 1943 (1893); Stern, *J. Chem. Soc.*, **67**, 74 (1895); Simonson, *Z. angew. Chem.*, **11**, 194, 219 (1898); Pummerer and Gump, *loc. cit.*; Neumann, doctoral dissertation, Dresden (1910); Ost and Brodtkorb, *Chem.-Ztg.*, **35**, 1125 (1911); *Z. angew. Chem.*, **25**, 750 (1912).

[125] Pummerer and Gump, *loc. cit.*; Pummerer, Guijot, and Birkhofer, *Ber.*, **68**, 480 (1935); Blanksma, *Helv. Chim. Acta*, **10**, 67 (1927).

[126] van Ekenstein and Blanksma, *Ber.*, **43**, 2355 (1910); Middentrop, doctoral dissertation, Leyden (1917).

[127] Heuser and Eisenring, *Cellulosechem.*, **4**, 20 (1923); Heuser and Schott, *ibid.*, **4**, 85 (1923); **6**, 10 (1925). The product is not an isomer of hydroxymethylfurfural as first thought. See Hess, "Chemie der Cellulose," p. 490, footnote 1.

glucosepentaacetate, the proportions varying with the conditions used. More severe conditions result in a higher yield of glucosepentaacetate.[128]

The Formation of Glucose by the Hydrolysis of Cellulose with Concentrated Hydrochloric Acid. Whereas most of the investigations on the hydrolysis of cellulose were carried out with concentrated sulfuric acid, also concentrated hydrochloric acid was early recognized as a means of converting cellulose into glucose. Béchamp[129] found that fuming hydrochloric acid (38 per cent) partially dissolves cellulose; the sugar formed was later recognized as glucose. Flechsig[130] obtained a yield of 49 per cent. Later investigators[131] reported smaller yields. By using highly concentrated hydrochloric acid (41–44 per cent), Willstätter and Zechmeister[132] succeeded in dissolving cotton completely in less than 1 minute.

The action of highly concentrated hydrochloric acid furnishes a means of removing the cellulose and the noncellulosic carbohydrates from wood. The lignin is left as a residue and may thus be quantitatively estimated. The method may be applied also to other lignified plant material[133] and to unbleached wood and other pulps.[134]

The hydrolysis of cellulose with highly concentrated hydrochloric acid is, however, not completed before 20–24 hours or longer. The yield of glucose from cotton, i.e., 95–96 per cent of the theoretical, corresponds to that obtainable by sulfolysis. This yield was estimated by determining the optical rotation and the reducing power of the diluted solution.[132] As with sulfuric acid, the yield remains below the theoretical for reasons stated above.

Willstätter and Zechmeister's procedure has been modified by various investigators.[135] By dividing the process into various steps (similar to those which were found to be desirable with sulfuric acid) Wohl and Krull[136] could raise the yield of glucose to 97 per cent of the

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[128] Ost, *Z. angew. Chem.*, **25**, 1996 (1912); *Chem.-Ztg.*, **36**, 1999 (1912); *Ann.*, **398**, 313 (1913); Webber, Staud, and Gray, *J. Am. Chem. Soc.*, **52**, 1542 (1930).

[129] Béchamp, *Ann. Chim.*, [3] **48**, 458 (1856).

[130] Flechsig, *Z. physiol. Chem.*, **7**, 525 (1882).

[131] Wohl and Blumrich, *Z. angew. Chem.*, **34**, 18 (1921).

[132] Willstätter and Zechmeister, *Ber.*, **46**, 2403 (1913).

[133] Heuser, *Papier-Fabr.*, **17**, 564 (1919); Dorée, "The Methods of Cellulose Chemistry," p. 347.

[134] Schwalbe, *Papier-Fabr.*, **23**, 174 (1925).

[135] Kauko, *Naturwissenschaften*, **9**, 237 (1921); Sherrard and Froehlke, *J. Am Chem. Soc.*, **45**, 1729 (1923).

[136] Wohl and Krull, *Cellulosechem.*, **2**, 1 (1921).

theoretical (determined by the reducing power of the solution). Instead of hydrochloric acid, hydrobromic and hydrofluoric acids of sufficiently high concentration may be used.[137]

Willstätter and Zechmeister's method of saccharification with highly concentrated hydrochloric acid has been utilized for the commercial manufacture of glucose (and of alcohol) from wood waste. The advantages of this method lie in the higher yield compared with the yields of methods which use dilute mineral acids (see p. 496) and in the fact that the process may be carried out without elevated temperature and pressure.[138]

The problem of saccharification of wood waste has occupied many investigators in many countries, and particularly Germany, for more than 100 years, whereas the interest in this country has been only of a temporary nature.[139] In Germany, the Willstätter and Zechmeister process seems to compete at the present with the Scholler-Tornesch process,[140] in which dilute sulfuric acid is used in a percolator system.

The formation of sugar on the hydrolysis of wood waste and its presence in sulfite waste liquor furnish the basis also for the manufacture of yeast. Under conditions of violent aeration during fermentation, the production of yeast becomes predominant, and but little alcohol is formed.[141]

The influence of the morphological structure of the fiber upon the kinetics of the decomposition of cellulose with hydrochloric acid and the microscopical and submicroscopical changes which the structure undergoes under mechanical agitation in the presence of hydrochloric acid has been studied by Ulmann and Hess.[142]

Degradation of Cellulose and Polymerization (Reversion) of Reaction Products under the Influence of Hydrogen Halides. Schlubach and co-workers[143] observed that, under the action of dry, gaseous 100

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[137] Willstätter and Zechmeister, *loc. cit.*, p. 2406.

[138] Bergius, *Z. angew. Chem.*, **39**, 1205 (1926); Ormandy, *J. Soc. Chem. Ind.*, **45**, 267T (1926); Hägglund, *Papier-Fabr.*, **25**, 52 (1927); Bergius, *Ind. Eng. Chem.*, **29**, 247 (1937).

[139] Ruttan, *J. Soc. Chem. Ind.*, **28**, 1290 (1909); Kressmann, "The Manufacture of Ethyl Alcohol from Wood Waste," *U. S. Dept. Agr. Bull.*, 983, Government Printing Office, Washington, D. C. (1922).

[140] Scholler, *Holz Roh- u. Werkstoff*, **1**, 574 (1938); *Chem.-Ztg.*, **63**, 737, 752 (1939). Regarding saccharification of wood waste see also the following references: Sherrard and Gauger, *Ind. Eng. Chem.*, **15**, 63 (1923); Sherrard and Blanco, *ibid.*, **15**, 611 (1923); Sherrard and Closs, *ibid.*, **17**, 847 (1925); Holmberg and Runius, *Svensk Kem. Tid.*, **37**, 189 (1925); Hoch and Bohunek, *Holz Roh- u. Werkstoff*, **1**, 574 (1938); Bergström, *Svensk Papperstidn.*, **43**, 207 (1940); Brownlie, *Chemistry and Industry*, **59**, 671 (1940); Campbell, *ibid.*, **60**, 47 (1941).

[141] Fink, *Angew. Chem.*, **51**, 475 (1938); Lechner, *Holz Roh- u. Werkstoff*, **1**, 603 (1938); Trendelenburg, "Das Holz als Rohstoff," Lehmann's Verlag, Munich (1939), p. 375.

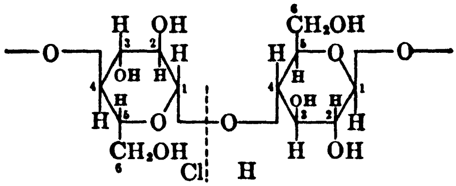
[142] Ulmann and Hess, *Ber.*, **74**, 119, 136, 1465 (1941).

[143] Schlubach, Elmer, and Prochownick, *Z. angew. Chem.*, **45**, 245 (1932); Schlubach and Prochownick, *ibid.*, **47**, 132 (1934).

per cent hydrogen chloride under pressure and at a temperature between 20 and 30°, dry cellulose, without going into solution, is converted to a polyanhydroglucose of a relatively low molecular weight. This product is characterized by low reducing power and the capability of being converted into glucose by boiling with dilute hydrochloric acid. Glucose, when subjected to the same treatment, undergoes a similar reaction. The process of anhydrization and recondensation of simpler sugars to polymers under the action of strong mineral acids is known as *reversion.*[144]

By analogy, the mechanism of the reaction with cellulose may be visualized as follows.

1. Hydrogen chloride adds to the glycosidic linkages of the (original) chain, chlorine being attached to the carbon atom in the 1-position and hydrogen to the bridge oxygen. The chain is thus cleaved into glucosyl chloride molecules (1-chloroglucose):



2. The second phase of the reaction consists of recondensation of the glucosyl chloride molecules, with the loss of hydrogen chloride, to "polyglucosan"; i.e., the chlorine atom in the 1-position of one glucosyl chloride molecule reacts with the hydrogen atom either in the 4-position or in another free position of a second glucosyl chloride molecule, and so forth. Thus, either 1,4-glycosidic linkages are restored or different glycosidic linkages are created.

The same hypothesis is invoked in the case of methylcellulose. Trimethylcellulose yielded a mixture of trimethyldi-, trimethyltri- and monomeric trimethylglucosan (Schlubach and Prochownick).

In contrast to its behavior with anhydrous hydrogen chloride, cellulose *dissolves* in anhydrous *hydrogen fluoride* to a clear colorless solution,[145] obviously undergoing reversion similar to that which takes place with anhydrous hydrogen chloride.[146] The polyglucosan or the

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[144] Wohl, *Ber.,* **23,** 2056 (1890); Wohl and Blumrich, *Z. angew. Chem.,* **34,** 1 (1921).

[145] Fredenhagen and Cadenbach, *Z. anorg. allgem. Chem.,* **178,** 289 (1929)

[146] Fredenhagen and Cadenbach, *Angew. Chem.,* **46,** 113 (1933).

mixture of polyglucosans thus formed has been termed *cellan.*[147] Cellan possesses no reducing power but, on hydrolysis, it is converted quantitatively into glucose. It also may be acetylated to yield a triacetate, $C_6H_7O_5(COCH_3)_3$. On saponification of the ester, the polyglucosan is regenerated. Its molecular weight, derived from measurements on the acetate in camphor (Barger-Rast method), indicates a degree of polymerization of 14. The optical rotation of cellan in liquid hydrogen fluoride is +98.4 (cellulose +0.8).

Glucose and cellobiose undergo similar changes when treated with hydrogen fluoride. The polyglucosans thus obtained show characteristics similar to those of cellan. Starch, under the same treatment, is converted into *amylan,* which is obviously isomeric with cellan.[148] The result of methylation with subsequent hydrolysis seems to indicate that it is not always the same hydroxyl through which, by the action of the hydrogen fluoride, the individual anhydroglucose units combine, but that different hydroxyls are involved.

Obviously, Schlubach's polyglucosan, Fredenhagen's product and Helferich's cellan have much in common, and it is probable that, in the action of hydrogen fluoride on cellulose (as well as on glucose) an intermediate glucosyl halide, glucosyl fluoride, is formed.[149]

Recent studies of the action of hydrogen chloride on glucose[150] show that the polyglucosan formed is composed of either 12 (freezing point method) or 70 (osmotic pressure method) anhydroglucose units. Hydrolysis of the trimethylated polyglucosan with hydrochloric acid in ethyl alcohol yielded penta-, tetra-, and trimethylglucose in a ratio of very nearly 1 : 2 : 1. Because of the lack of reducing power, the anhydroglucose units are obviously combined in a ring structure. The fact that penta- and trimethylglucose were obtained in equivalent quantities seems to suggest that the anhydroglucose molecules are possibly arranged in a branched structure, three anhydroglucose units being attached as "side chains" to every six members of the ring. Assuming a symmetrical arrangement, this would mean that every third member of the ring carries one extra anhydroglucose unit.

Among the products of the action of hydrogen chloride on glucose, a trisaccharide was isolated which showed 25.6 per cent of the reducing power of glucose. The yield was about 30 per cent of the quantity of glucose used, whereas the polyglucosan was obtained to an extent of 60 per cent. Thus, 90 per cent of the glucose had been converted. In the light of the findings of other investigators it is significant that no disaccharide could be found. The molecular structure of the trisaccharide is probably that of 6-[*d*-isomaltosido]-glucose; i.e., the carbon atoms in the 1- and 6-positions are involved in the combination of the anhydroglucose units.

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[147] Helferich and Böttger, *Ann.,* **476,** 150 (1929); Helferich and Peters, *ibid.,* **494,** 101 (1932).

[148] Helferich, Stärker, and Peters, *Ann.,* **482,** 183 (1930).

[149] See, however, Helferich and Peters, *Ann.,* **494,** 103 (1932); Helferich, Bäumlein, and Wiegand, *ibid.,* **447,** 27 (1926).

[150] Schlubach and Lührs, *Ann.,* **547,** 73 (1941).

A trisaccharide—in addition to a monomeric anhydrosugar—was also obtained by the action of concentrated hydrochloric acid upon levoglucosan.[151]

The phenomenon of reversion has been studied ever since Emil Fischer[152] observed that, by the action of concentrated hydrochloric acid, glucose is partly converted into a disaccharide which he designated as isomaltose and which later[153] was found to be isomeric with gentiobiose, both being 6-glucosidoglucoses, but the former belonging to the α- and the latter to the β-series. Both these disaccharides appear as products of the reversion of glucose. In addition, the formation of a trisaccharide was observed.[154] Because, as has been seen, Schlubach and Lührs found no indication of the presence of a disaccharide among the products of reversion, they are inclined to believe that the disaccharides observed by other investigators were possibly identical with the above-mentioned trisaccharide, 6-[α-isomaltosido]-glucose. On the other hand, Frahm,[155] using concentrated hydrochloric acid, concluded that the condensation of glucose to oligosaccharides goes no further than to the disaccharide stage, whereas the anhydrization of glucose produces essentially triglucosan. The same conclusions were drawn from the results obtained when *cellulose* was subjected to the action of concentrated hydrochloric acid.

The extent to which reversion of glucose occurs depends, among other factors, upon the water present in the system. With dilute hydrochloric acid, the yield of reversion products is small, amounting to about 5 per cent of the glucose originally present, whereas with concentrated hydrochloric acid it may reach 40 per cent and with pure hydrogen chloride, as has been seen, even 60 per cent. On dilution, the reversion products undergo depolymerization. The reversion of glucose is thus a reversible process (Frahm).

The extent to which reversion occurs is also influenced by the original glucose concentration. The higher this is, the more glucose is converted. Thus, the fact that Willstätter and Zechmeister observed very little reversion when they subjected cellulose to highly concentrated hydrochloric acid[156] is probably explained by the low cellulose concentration they employed.[157]

Obviously, the phenomenon of reversion furnishes part of the explanation for the fact that the yield of glucose obtainable on the hydrolysis of cellulose with strong acids (and likewise on the commercial saccharification of wood, etc.) under these conditions remains considerably below the theoretical. It also explains the necessity of dividing the process of hydrolysis into two steps, for the reversion products formed in the concentrated acid solution of the first phase

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[151] Reichel and Nagel, *Ber.*, **74**, 1742 (1941).

[152] Emil Fischer, *Ber.*, **23**, 3687 (1890); **28**, 3024 (1895).

[153] Berlin, *J. Am. Chem. Soc.*, **48**, 1107 (1926); Coleman, Buchanan, and Paul, *ibid.*, **57**, 1119 (1935); see also Georg and Pictet, *Helv. Chim. Acta*, **9**, 612 (1926); Zemplén and Bruckner, *Ber.*, **64**, 1852 (1931); Myrback, *Svensk Kem. Tid.*, **53**, 264 (1941).

[154] Georg and Pictet, *Compt. rend., Séances Soc. Phys. Hist., Genève*, **47**, 94 (1930); Hurd and Cantor, *J. Am. Chem. Soc.*, **60**, 2677 (1938).

[155] Frahm, *Ber.*, **74**, 622 (1941).

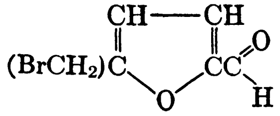
[156] Zechmeister, *Z. physiol. Chem.*, **103**, 316 (1923).

[157] Ost, *Ber.*, **46**, 2925 (1913).

undergo cleavage to glucose when this solution is diluted and heated at elevated temperature in the second phase.[158]

The Degradation of Cellulose with Other Hydrolyzing Agents

If water-free cellulose is heated in a sealed tube at 80–100° with *hydrogen chloride* which has been dissolved *in ether* or *in chloroform,* ω-chloromethylfurfural is obtained. With *hydrogen bromide,* the product is ω-bromomethylfurfural (I).[159] The presence of a CH_2Br or CH_2Cl group indicates that possibly hydroxymethylfurfural (II) was present primarily. The latter is formed by the action of dilute hydrochloric acid upon glucose (p. 437). Thus, the formation of ω-bromo- or ω-chloromethylfurfural from cellulose could be regarded as the result of three consecutive reactions: (1) hydrolysis of cellulose to glucose, (2) dehydration of glucose to hydroxymethylfurfural, and (3) bromination or chlorination to form the derivative. However, in view of the fact that the reaction is accomplished in the absence of water, it is difficult to visualize the process of hydrolysis as being involved. In the light of the behavior of cellulose with hydrogen chloride discussed above, it is more probable that the first reaction consists of the addition of halogen and hydrogen to the glucosidic linkages in cellulose. The labilized linkages would subsequently be cleaved with the loss of hydrogen chloride or bromide, resulting in the formation of anhydroglucose. In a third phase, the anhydroglucose would lose two molecules of water to form hydroxymethylfurfural, the latter being simultaneously brominated or chlorinated to form bromo- or chloromethylfurfural.



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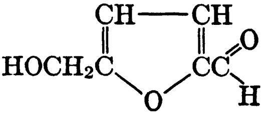

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On the assumption that hydroxymethylfurfural is essentially obtained from ketoses, Fenton and Gostling, as well as Cross and Bevan,[160] concluded that

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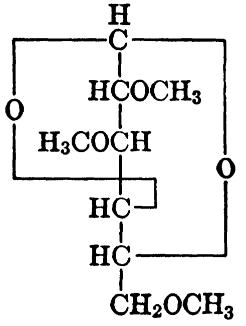
[158] Bergius, *Chem.-Ztg.,* **57,** 475 (1933); Fredenhagen and Cadenbach, *Angew. Chem.,* **46,** 113 (1933).

[159] Fenton and Gostling, *J. Chem. Soc.,* **79,** 361, 807 (1901); **83,** 191 (1903); see also Hess, *Z. Elektrochem.,* **26,** 234 (1920); Hibbert and Hill, *J. Am. Chem. Soc.,* **45,** 176 (1923). ω-Chloro- and bromomethylfurfural from *glucose* apparently were first obtained by Fischer and Negmann, *Ber.,* **47,** 973 (1914).

[160] Cross and Bevan, *J. Chem. Soc.,* **79,** 366 (1901).

cellulose consists not only of aldose but also of ketose units. Apart from the fact that the formation of ketoses on the hydrolysis of cellulose has never been observed, it has been shown that aldoses also lent themselves to the formation of hydroxymethylfurfural.[161] On sufficiently long and repeated treatment with hydrochloric acid, glucose may be entirely converted into hydroxymethylfurfural.

The result of the action of hydrogen halides upon cellulose seems to depend largely upon the conditions applied. Thus, Freudenberg and Braun,[162] on treating trimethylcellulose with ether saturated with hydrogen chloride[163] in a sealed tube at 350° for 24 hours, obtained a chloroglucose derivative, 1-chloro-2,3,6-trimethylglucose. On treatment of the chloride (dissolved in ether) with sodium metal, hydrogen was liberated and the chlorine removed; this resulted in the formation of an anhydroglucose. This anhydride probably has the structure of a 2,3,6-trimethyl-1,4-1,5-anhydroglucose.[164] It is a colorless, oily



liquid, resistant to Fehling solution, and on hydrolysis it is converted into 2,3,6-trimethylglucose.

The successive action of acetylchloride and trimethylamine upon 2,3,6-trimethyl-1,4-diacetylglucose and subsequent removal of the trimethylamine group from the product with barium hydroxide solution resulted in a mixture of anhydroglucoses (Micheel and Hess), none of which was evidently identical with that described above.

By the conversion of glucose into its anhydride, Hess hoped to find proof of his belief that cellulose is built up of monomeric anhydroglucose molecules held together by secondary valences only. It was thought that the "building

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[161] van Ekenstein and Blanksma, *Ber.*, **41**, 2360 (1910); Heuser and Eisenring, *Cellulosechem.*, **4**, 20 (1923).

[162] Freudenberg and Braun, *Ann.*, **460**, 290 (1928).

[163] It is not stated that the hydrogen chloride was freed of water, but it probably was.

[164] See also Micheel and Hess, *Ber.*, **60**, 1898 (1927); Hess and Littmann, *Ber.*, **66**, 774 (1933); *Ann.*, **506**, 298 (1933) regard Freudenberg's anhydride as a mixture of methylated glucal and hydroglucal.

unit" of cellulose, glucosan, could possibly be synthesized by subjecting glucose to a process of anhydrization and that the glucosan molecules thus formed would be capable of spontaneous aggregation to cellulose. However, these hopes could not be realized. Indeed, Freudenberg and Braun's trimethylanhydroglucose ("trimethyl glucosan") being a liquid, differs essentially from trimethylcellulose and shows no tendency to aggregation. Moreover, the anhydroglucose units in the polyglucosans which, as has been seen, result from the action of hydrogen halides upon glucose (and cellulose) and those which Pictet and co-workers obtained on heating of anhydro-, mono-, and disaccharides in the presence of dehydrating means [165] are, no doubt, linked by *primary* valences.

Whereas *acetyl bromide* alone has little effect upon cellulose, in a mixture with hydrogen bromide it reacts to form acetobromocellobiose and acetobromoglucose.[166] However, the yields are rather small, the main reaction being that of acetylation, resulting in considerably degraded cellulose acetates. Evidently, the agent which accomplishes the degradation to the cellobiose and glucose derivatives is the hydrogen bromide, and the hydroxyl groups thus liberated are acetylated and brominated.

On the other hand, it has been claimed that acetyl bromide, if allowed to act on cellulose with the exclusion of moisture and at low temperature, results in the formation of trihexosan.[167] It would seem that the mechanism involved is comparable to that by which Schlubach and co-workers have explained the formation of polyglucosans by the action of hydrogen chloride upon cellulose.

A mixture of acetyl chloride and hydrochloric acid acts on cellulose in a manner similar to that of acetyl bromide-hydrogen bromide, although less violently. Again the chief product of reaction is considerably degraded cellulose acetate.[168] In addition, acetochlorocellobiose has been isolated.[169]

By the action of phosphorus pentabromide upon triacetylcellulose at 90–100°, a small amount of dibromotriacetylglucose was obtained; [170] this was identical with the derivative which Fischer and Armstrong [171] had obtained earlier by treating 1,2,3,4,6-glucose pentaacetate with liquid hydrogen bromide and the molecular structure of which is now recognized as 1,6-dibromo-2,3,4-triacetylglucose [172]:

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[165] For example, Pictet and Ross, *Compt. rend.*, **174**, 1113 (1922); Pictet and Salzmann, *Helv. Chim. Acta*, **8**, 948 (1925).

[166] Zechmeister, doctoral dissertation, Zürich (1913); Karrer and Widmer, *Helv. Chim. Acta*, **4**, 700 (1921); **5**, 194 (1922); *Z. angew. Chem.*, **35**, 90 (1922); Bergmann and Beck, *Ber.*, **54**, 1577 (1921); Hess, *ibid.*, **54**, 2878 (1921); Zechmeister, *ibid.*, **56**, 573 (1923); Hess, Weltzien, and Kunau, *Ann.*, **435**, 94 (1923).

[167] Micheel, *Ann.*, **456**, 69 (1927).

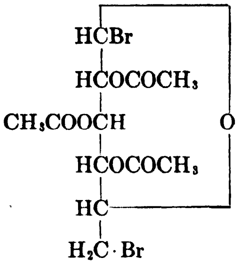
[168] Hess, *Ber.*, **54**, 2872 (1921); Hess and Weltzien, *Ann.*, **435**, 46, 111 (1923).

[169] Skraup and Geinsperger, *Monatsh.*, **26**, 1469 (1905); see also Hudson, *J. Am. Chem. Soc.*, **48**, 2002 (1926).

[170] Karrer and Smirnoff, *Helv. Chim. Acta*, **5**, 124, 187 (1922).

[171] Fischer and Armstrong, *Ber.*, **35**, 836 (1902).

[172] Karrer and Smirnoff formulated it as 1,6 dibromo-2,3,5 triacetylglucose.



The fact that this glucose derivative is identical with that which had been obtained from glucose directly,[173] makes it seem probable that cellulose, when treated with phosphorus pentabromide, is first decomposed to glucose, and that the reaction whereby the hydroxyl group in the 6-position and the aldehydic oxygen in the 1-position are replaced by bromine is of a secondary nature. With this interpretation of the result, the action of phosphorus pentabromide upon cellulose cannot be utilized for predicting which of the carbon atoms are involved in the oxygen bridges between the glucose residues in the cellulose chain. The fact that the same dibromoacetylglucose is obtained by the action of phosphorus pentabromide upon triacetyllevoglucosan and on octaacetylmaltose must be viewed in the same light. Karrer and Smirnoff had argued that a 1,6-dibromotriacetylglucose could be expected only from polysaccharides in which the individual monose residues are united through 1,6-linkages and that, hence, such linkages are operative in cellulose.

THE RATE AND THE KINETICS OF ACID HYDROLYSIS OF CELLULOSE

Different methods have been used to ascertain the extent to which degradation occurs after various periods of time. Some methods are applicable only to hydrolysis with dilute acids, i.e., to conditions under which the cellulosic material retains its solid form and other methods must be used if the cellulose is dissolved in concentrated acid. Some methods may be employed in both cases.

The methods which have been and are being widely used for pursuing the hydrolysis of cellulose in solution are the polarimetric method (optical rotation), iodine titration, and, more recently, the mercaptalation method. The latter two have also been used for following the first phase of the hydrolysis, i.e., while the cellulose is still present in solid form.

The iodine method, an end-group determination, was first applied to cellulose and cellulose modifications by Bergmann and Machemer.[174] It is derived from Willstätter and Schudel's [175] method for the deter-

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[173] See also Fischer and Sach, *Ber.*, **45**, 3763 (1912).

[174] Bergmann and Machemer, *Ber.*, **63**, 316, 2304 (1930).

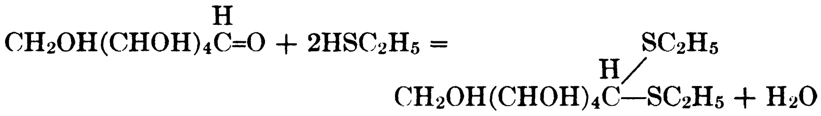
[175] Willstätter and Schudel, *Ber.*, **51**, 780 (1918).

mination of aldohexoses. Hypoiodide oxidizes these sugars to the respective carboxylic acids and is thus reduced to iodine, according to the equation:

$$\mathrm{RCHO + 2HOI \rightarrow RCOOH + H_2O + I_2}$$

The excess of iodine which has not entered the reaction is titrated with thiosulfate solution. The volume of $N/10$ iodine solution consumed by 1 gram of the sample is called the iodine number.

The mercaptalation method, based upon the reaction between aldehydic groups and ethyl mercaptan, was suggested by Wolfrom and co-workers.[176] With monosaccharides, this reaction results in the formation of mercaptals (thioacetals):[177]



$$\mathrm{CH_2OH(CHOH)_4\overset{H}{C}{=}O + 2HSC_2H_5 = CH_2OH(CHOH)_4C(H)(SC_2H_5){-}SC_2H_5 + H_2O}$$

Cellulose is hydrolyzed at 0° with a suitable concentration of hydrochloric acid under conditions of continuous mercaptalation with ethyl mercaptan. Samples of the reaction mixture are withdrawn at intervals, neutralized, and subjected to sulfur determination. The sulfur content is representative of the mixture of the mercaptalated hydrolytic fragments.

According to Freudenberg[178] and co-workers, the determination of the reducing power with Fehling solution is not suitable for ascertaining the degree of hydrolytic cleavage at time intervals. It was shown that cellobiose reduces a greater quantity of copper than could be expected from the presence of only one reducing group per two glucose residues. It is likely that, while the free reducing group of cellobiose is being oxidized, the other half of the cellobiose molecule is also attacked; the result is an increased consumption of Fehling solution. The error may be expected to be still greater with chain fragments containing more than two glucose residues, i.e., at time intervals at which the hydrolysis has not yet reached the cellobiose stage.

The results obtained by the various methods mentioned above may be shown in some examples.

Willstätter and Zechmeister[179] followed the course of the hydrolysis

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[176] Wolfrom and Georges, *J. Am. Chem. Soc.*, **59**, 282 (1937); Wolfrom, Georges and Sowden, *ibid.*, **60**, 1026 (1938).

[177] Fischer, *Ber.*, **27**, 673 (1894).

[178] Freudenberg, Kuhn, Dürr, Bolz, and Steinbrunn, *Ber.*, **63**, 1512 (1930); see also Meyer, Hopff, and Mark, *ibid.*, **62**, 1103 (1929).

[179] Willstätter and Zechmeister, *Ber.*, **46**, 2410 (1913).

of cellulose in highly concentrated hydrochloric acid by using the polarimetric method. Their results are shown in Fig. 107. The $[\alpha]_D$ values measured at a temperature of 16.2° are plotted against time. It is seen that the optical rotation of the solution is low for 1 to 2 hours after dissolution but then it rises and tends to reach a constant value. The inflection shown between the third and fourth hour is interpreted to indicate the appearance of cellobiose.

Similar inflections were observed by Sherrard and Froehlke,[180] who subjected celluloses isolated from different woods (according to Cross and Bevan's method) to hydrolysis with 41 per cent hydrochloric acid for a longer period of time. Their results are shown in Fig. 108. It is seen that, as the time of hydrolysis is extended to about 9 to 12 hours, the polarimetric values closely approach that of glucose ($[\alpha]_D$ = 100°), which indicates that the hydrolysis has reached its end point.[181]

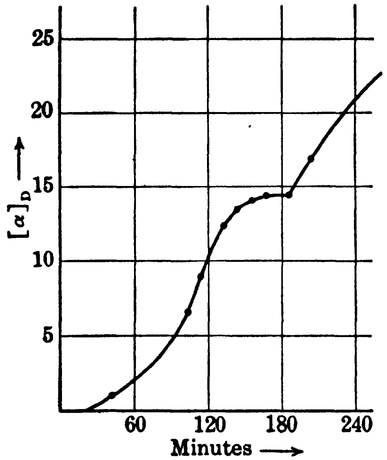

FIG. 107. Change of optical rotation of cellulose dissolved in 41 per cent hydrochloric acid with time. Willstätter and Zechmeister.

In contrast, Wolfrom and co-workers[182] [who also followed the hydrolysis of cellulose (high viscosity cotton linters) in highly concentrated hydrochloric acid polarimetrically] observed no break in the curve; nor was such a break observed by Hibbert and Percival,[183] who studied the course of hydrolysis of cellulose under the action of a hydrochloric acid-zinc chloride mixture. Wolfrom and co-workers are inclined to attribute the variations in the polarimetric curves to different methods of cellulose purification.

When they followed the hydrolysis of their various wood celluloses by determining the change in reducing power of the solution, Sherrard and Froehlke obtained the results shown in Fig. 109.[184]

To follow the hydrolysis of cellulose with strong sulfuric acid Freudenberg and co-workers,[185] for reasons discussed above, preferred

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[180] Sherrard and Froehlke, *J. Am. Chem. Soc.*, **45**, 1729 (1923).

[181] See also the more recent results of Frahm, *Ber.*, **74**, 622, 631 (1941).

[182] Wolfrom and co-workers, *loc. cit.*

[183] Hibbert and Percival, *J. Am. Chem. Soc.*, **52**, 3995 (1930).

[184] See also Frahm, *loc. cit.*, p. 632.

[185] Freudenberg *et al.*, *loc. cit.*, p. 1513.

the iodine titration method. In addition, the polarimetric method was used. Ramie cellulose (8.1 grams) was dissolved in 680 cc. of sulfuric acid (d. = 1.560, 20°); this took 40 minutes of thorough kneading. The solution was made up to 1000 cc. with sulfuric acid of the same specific gravity. The hydrolysis was allowed to proceed at 18° and 30°, 50–60 days being required to complete the reaction at 18°. Samples were taken at intervals, diluted and neutralized with alkali, and titrated with iodine solution according to the method of Willstätter and Schudel. The end point was reached when the iodine consumption had become constant and the optical rotation value had become the same as that of glucose treated under the same conditions. As an

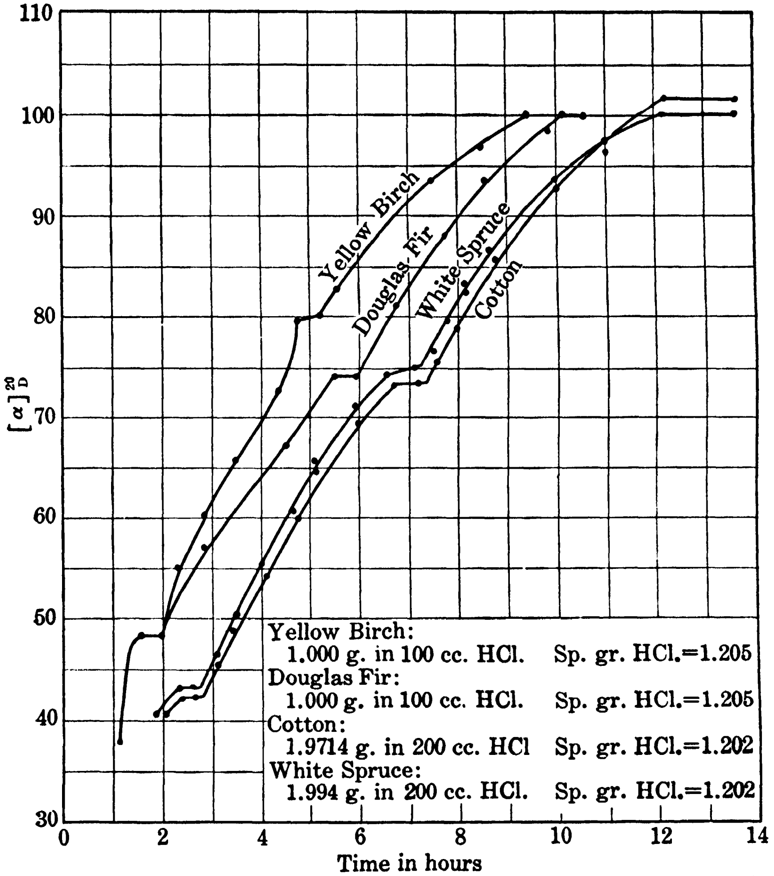

FIG. 108. Change of optical rotation of different wood celluloses dissolved in 41 per cent hydrochloric acid with time. Sherrard and Froehlke.

example, the order of magnitude of the iodine consumption was 0.5 cc. *N*/10 iodine solution at the beginning of the measurements and 19.0 cc. at the end.

The results attained by Wolfrom and co-workers by the mercaptalation method (cotton linters dissolved in highly concentrated hydrochloric acid and allowed to hydrolyze at 16°, initial cellulose concen-

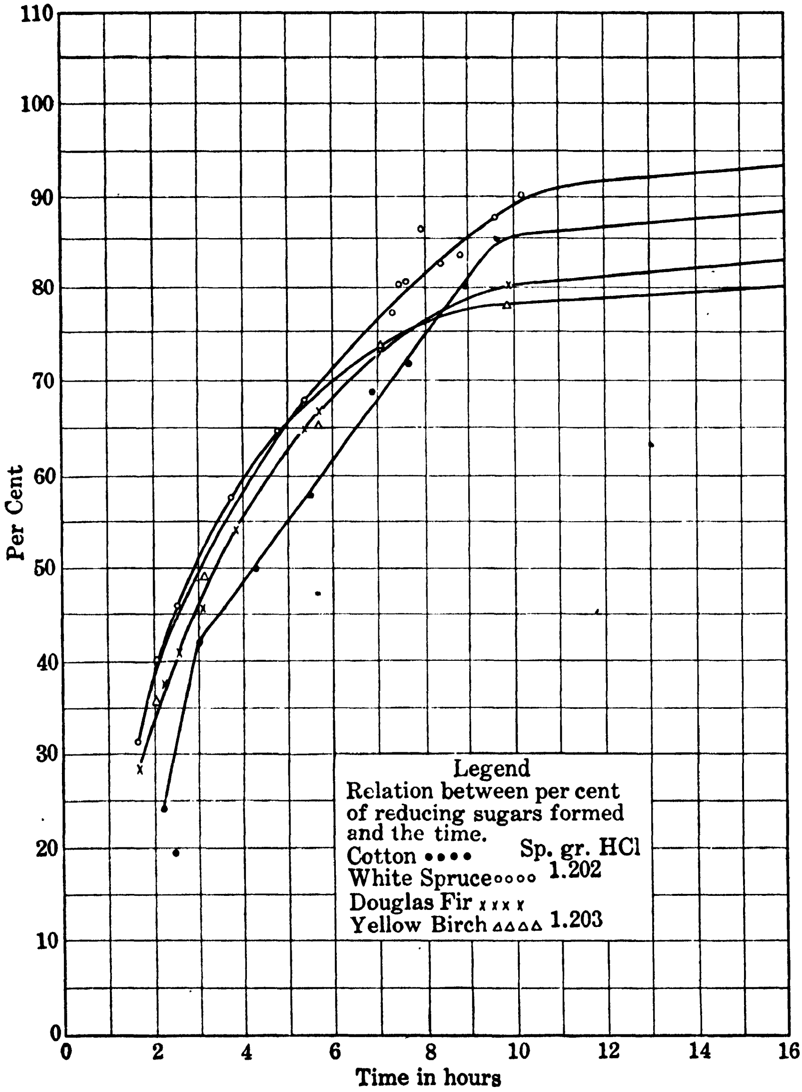

FIG. 109. Change of reducing power of various wood celluloses dissolved in 41 per cent hydrochloric acid with time. Sherrard and Froehlke.

tration 5 per cent) are shown in Table 74. It also lists the $[\alpha]_D$ values. It is seen that the increase in sulfur content of the mercaptalated products is a suitable expression of the increase in aldehyde groups and thus of the progress of hydrolysis.

TABLE 74

CHANGE OF DEGREE OF MERCAPTALATION (SULFUR CONTENT) DURING HYDROLYSIS OF CELLULOSE

Time of Hydrolysis Minutes	$[\alpha]_D$ 16°	Sulfur Content of Mercaptalated Products, %
17	. . .	0.33
20	2.00	0.35
30	3.0	0.45
45	4.5	0.94
60	6.0	0.50
75	7.4	0.66
90	9.0	1.29
105	10.2	1.37
120	11.7	1.56
135	13.0	1.42
150	14.5	1.71
165	16.0	1.69
180	17.5	2.03
Hours		
6	36.7	2.39
9	46.6	. . .
12	61.0	. . .
15	70.1	. . .
18	79.8	21.3
21	. . .	21.1
24	91.5	21.9
27.5	99.8	21.6

A similar relation was established for trimethylcellulose.[186] Again, the final rotation was found to be in good agreement with that obtained for an equivalent concentration of 2,3,6-trimethylglucose, thus indicating a substantially complete hydrolysis of the methylcellulose. 2,3,6-Trimethylglucose was isolated from the solution in the form of its diethylmercaptal.[187]

The value of such studies of the course of the cellulose breakdown may be seen in the agreement of the experimental evidence—i.e., a

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[186] Wolfrom, Sowden, and Lassettre, *J. Am. Chem. Soc.*, **61,** 1072 (1939).

[187] Wolfrom and Georges, *J. Am. Chem. Soc.*, **59,** 601 (1937).

steady increase in aldehyde groups—with the chain structure concept of cellulose.

Moreover, the experimental data may be utilized for answering the question whether the glycosidic linkages in the chains are all of the same type or whether they alternate. The hypothesis that a considerable number of β-linkages must be present in cellulose is supported by the substantial yield of cellobiose on acetolysis, a disaccharide in which the β-linkage has been established with certainty. The results which were obtained by a study of the kinetics of the hydrolysis of cellulose with strong sulfuric acid leave no doubt that the chains contain only β-linkages. A consideration of the mathematical equations which Kuhn [188] has developed for the kinetics of the breakdown of high polymer chains and their application to the evaluation of the experimental data obtained for cellulose show that the simultaneous occurrence of α-linkages (as in maltose, being, as is cellobiose, 1,4-glycosidoglucose) would reveal itself by the rate of the hydrolytic breakdown.[189] Compared with cellobiose, maltose undergoes cleavage about 1.5 times faster.[190] Thus, on the assumption that the cellulose chain contains both α- and β-linkages, the velocity constant of the hydrolytic breakdown would be higher than actually observed. It appears almost unnecessary to mention that maltose has never been discovered among the products of cellulose hydrolysis.

Similar studies were made on the kinetics of the acetolysis [191] of cellulose and the hydrolysis of cellobiose and cellotetraose with 51 per cent sulfuric acid.[192] In all cases, good agreement between the experimental and the calculated data was established.

The conclusions drawn from these investigations are substantiated further by the results of a study of the optical superposition [193] of solutions of methylated and unmethylated cellobiose and the other known free and methylated oligosaccharides, and also of cellulose and methylated cellulose.[194] The result of these studies eliminates the

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[188] Kuhn, *Ber.*, **63**, 1503 (1930); see also Meyer, Hopff, and Mark, *Ber.*, **62**, 1103 (1929); **63**, 1531 (1930); Mark, "Physik und Chemie der Cellulose," p. 296.

[189] Freudenberg, Kuhn, Dürr, Bolz, and Steinbrunn, *loc. cit.; J. Soc. Chem. Ind.*, **50**, 291T (1931); Freudenberg and Kuhn, *Ber.*, **65**, 484 (1932).

[190] Freudenberg, Dürr, and Hochstetter, *Ber.*, **61**, 1735 (1928); see also Freudenberg, Kuhn, *et al.*, *loc. cit.*

[191] Freudenberg and Soff, *Ber.*, **66**, 19 (1933).

[192] Freudenberg and Blomquist, *Ber.*, **68**, 2070 (1935); Freudenberg, *Trans. Faraday Soc.*, **32**, 74 (1936).

[193] Freudenberg, "Tannin, Cellulose, Lignin," p. 86.

[194] Freudenberg, Friedrich, and Bumann, *Ann.*, **494**, 41 (1932); Kuhn, *Ber.*, **66**, 166 (1933); Freudenberg, *ibid.*, **66**, 193 (1933); see also Mark, "Physik und Chemie der Cellulose," p. 320.

presence of other than β-linkages. In addition, the conclusion could be drawn that the configuration of the glucose residues, which represent the members of the chain between the two end units, is identical with that of the center residues of the higher oligosaccharides.

The results of subsequent investigations[195] although revealing certain differences as to the various mechanical possibilities of cleavage and as to certain other assumptions, lend further support to the hypothesis which postulates the chain structure formula for cellulose.

The experimental data on the gradual degradation of cellulose with time may be used for calculating the average chain length as it exists in the mixture of degradation products at any time during hydrolysis. Both viscosity and end-group methods may be applied to the partially hydrolyzed cellulose preparations in solid form or to the products entirely or partly regenerated from their solution in the hydrolyzing agent. If, however, regeneration is no longer possible, end-group determination methods may be used. Wolfrom's mercaptalation method may be employed in all cases.

It should be kept in mind that these methods yield only values of a first approximation. Moreover, the results of different methods sometimes differ considerably, so that a decision even on the order of magnitude might be quite difficult.

Sometimes, however, the results of different methods applied to the same series of samples are in satisfactory agreement. This has been found to be true within certain limits when the results of the mercaptalation method were compared with those derived from viscosity data.[196]

> Cotton linters were dissolved in fuming hydrochloric acid (1.205 density) and the solution maintained at 16°. To samples taken at intervals, ethyl mercaptan was added. After mechanical shaking for some time, the mercaptalated products of reaction were precipitated by pouring the solution into a suspension of sodium bicarbonate in water. The further purified precipitate was dried and subjected to sulfur analysis. For comparison, samples of nonmercaptalated products of hydrolysis were prepared in the same manner, except that the addition of the mercaptan was omitted. The viscosity of the samples was determined in cuprammonium hydroxide.

Table 75 shows the degrees of polymerization (number of glucose units) calculated from the sulfur analytical data on the mercaptalated

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[195] af Ekenstam, *Ber.*, **69**, 549, 553 (1936); Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936); Stamm and Cohen, *J. Phys. Chem.*, **42**, 921 (1938); Loebring, *Kolloid-Beihefte*, **50**, 235 (1939); Durfee and Kertesz, *J. Am. Chem. Soc.*, **62**, 1196 (1940); Mark and Simha, *Trans. Faraday Soc.*, **36**, 611 (1940); Sakurada and Okamura, *Z. physik. Chem.*, **A187**, 289 (1940); Montroll, *J. Am. Chem. Soc.*, **63**, 1215 (1941); Schulz and Lohmann, *J. prakt. Chem.*, **157**, 238 (1941).

[196] Wolfrom and Georges, *J. Am. Chem. Soc.*, **60**, 1026 (1938).

products and also those calculated from the cuprammonium viscosity data[197] on both the mercaptalated and the nonmercaptalated hydrolyzed celluloses. The agreement between the degrees of polymerization derived from sulfur analysis and from cuprammonium viscosities is remarkably good, with the exception of the first two points (20 and 30 minutes). Also, the agreement between the degrees of polymerization from the viscosity data on the mercaptalated and nonmercaptalated products is quite good. It is seen that the hydrolysis in this strong acid proceeded remarkably fast, considering that the original material had a degree of polymerization of 2008 (derived from the cuprammonium viscosity).

TABLE 75

Degree of Polymerization (D.P.) of Mercaptalated and Nonmercaptalated Hydrolyzed Celluloses

Time of Hydrolysis, Minutes	Mercaptalated Products		Non-mercaptalated Products, D.P. by Viscosity
	D.P. by sulfur content	D.P. by viscosity	
20	114	182	158
30	89	112	136
45	87	98	89
60	80	87	58
75	66	66	51
90	31	51	45
105	29	33	39
120	26	35	35
135	27	33	32
150	23	29	29
165	24	28	25

When the investigation was repeated[198] under conditions which made it possible to begin the measurements at a time when the samples were considerably less degraded than shown in Table 75, the agreement between the two methods was less satisfactory until the average degree of polymerization had dropped to about 100.

The *influence of the process of hydrolysis upon the chain-length distribution* at various stages of the process may be shown by the frac-

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[197] Using the equation of Kraemer and Lansing (see Chapter XV).

[198] Wolfrom, Georges, and Sowden, *J. Am. Chem. Soc.*, **60**, 3009 (1938).

tionation of samples taken at intervals while the process of hydrolysis is in progress.[199] An investigation of this type was carried out with the most homogeneous fraction of a commercial cellulose acetate.[200] This fraction had an average degree of polymerization of 350 (from viscosity measurements in cuprammonium hydroxide). The relatively high homogeneity of this fraction is seen from the results of further fractionation:

$$\left.\begin{array}{lr} \text{Fraction 1:} & \text{7 per cent had D.P.} = 270 \\ \text{Fraction 2:} & \text{82 per cent had D.P.} = 340 \\ \text{Fraction 3:} & \text{12 per cent had D.P.} = 400 \end{array}\right\} \begin{array}{c} \text{Calculated Average} \\ \text{D.P.} = 345 \end{array}$$

Thus, 82 per cent of the material had an average degree of polymerization of 340 and only 7 per cent were below and 12 per cent above this value.

These results are expressed in the form of a distribution curve in Fig. 110. In this figure, the degrees of polymerization of the three fractions are plotted against the quantities of the fractions in percentages. The fractions are plotted in dotted sharp-edged lines. It is seen that the two small fractions are located on each side of the main fraction. The smooth curve represents, as well as possible, the actual distribution of the material.

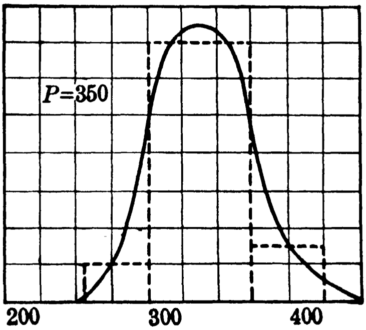

FIG. 110. Chain-length distribution curve of a fraction of cellulose acetate. Mark and Simha.

The fraction having an average degree of polymerization of 350 was subjected to acetolysis and the samples taken at intervals were fractionated and the degree of polymerization determined for each fraction. The results are shown in Table 76. The data reveal considerable heterogeneity in the first two samples (average D.P. 158 and 100) but, as the degradation progresses, a steady increase in higher degraded material and in homogeneity are observed. Thus, at the beginning and during the earlier stages of the acetolysis, an initially fairly homogeneous material is converted into a rather heterogeneous mixture but, as degradation proceeds further, the original degree of homogeneity is again approached.

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[199] Mark and Simha, *Trans. Faraday Soc.*, **36**, 611 (1940).

[200] The average degree of polymerization of the unfractionated acetate was 410.

TABLE 76

CHANGE OF DEGREE OF POLYMERIZATION AND CHAIN-LENGTH DISTRIBUTION OF CELLULOSE ACETATE DURING ACETOLYSIS

Samples Taken at 24-Hour Intervals	Average D.P. of Samples	Weight and Degree of Polymerization of Fractions of Samples									
1	158	17%	64	24%	114	26%	167	22%	206	11%	300
2	100	12%	24	26%	51	36%	98	18%	163	8%	236
3	54	13%	10	18%	44	52%	53	15%	95	2%	180
4	31	14%	14	68%	27	14%	60	4%	75	....	...

On the basis of the theoretical deliberations of Kuhn, of Flory and others, Mark and Simha worked out a statistical mathematical equation for the degradation of long-chain molecules. The application of this equation to the experimental data reported above yielded theoretical distribution curves which corresponded quite well with the experimental curves, both being obtained as described above (see Fig. 110).

The work of Mark and Simha was extended by Montroll and Simha.[201] On the assumption that all bonds connecting monomeric elements in the system have the same probability of being broken, expressions were derived for the distribution of chain lengths in the depolymerized system as a function of the original chain length and of the average number of bonds cleaved per molecule. In addition, relationships were established between the average molecular weight of the degraded product and the average number of bonds cleaved per molecule.

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[201] Montroll and Simha, *J. Chem. Phys.*, **8**, 721 (1940).

CHAPTER XII

THE THERMAL DECOMPOSITION OF CELLULOSE

Although, generally speaking, cellulose may be regarded as being resistant to moderate heat, the degree of resistance depends upon a number of factors, such as the time of exposure, the degree of polymerization of the cellulosic material, the presence or absence of impurities and products of degradation, as well as the surrounding atmosphere prevailing during the exposure.

Obviously, the *time of exposure* is a factor of major importance, for cellulose fibers which suffer a good deal in strength on long heating at relatively moderate temperature may show hardly any change on shorter exposure to a much higher temperature.[1] Thus, cellulose which has been heated to 100–110° for some hours reveals scarcely any change except a lower moisture content. However, its reducing power distinctly increases when heated at 80° for 336 hours.[2] Other changes will, of course, also be noticeable. The essential influence of the length of time upon the behavior of cellulosic materials at different temperatures has been confirmed many times by numerous investigators.

The usual belief[3] that normally bleached cotton stands heating to temperatures of 100–120° for several hours without suffering any damage to its properties must be revised in the light of newer investigations.[4] It was found that cotton showed slight signs of damage even after heating to 80–100° for a few hours; its viscosity and *alpha*-cellulose content had decreased and its copper (and iodine) number had increased. After an exposure to 100–120°, a moderate decrease in physical strength properties was noticeable, but when the temperature was from 120–140°, the decrease was quite pronounced.

The changes in viscosity, copper number and *alpha*-cellulose content which cellulose suffers under conditions of long periods of heating at

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[1] Scheurer, *Bull. Mulhouse*, **53**, 68 (1883); Koechlin, *ibid.*, **55**, 547 (1888). For additional older literature see Schwalbe, "Chemie der Cellulose," p. 25.

[2] Knecht, *J. Soc. Dyers Colourists*, **36**, 195 (1920).

[3] See the compilation of older investigations in Hess, "Die Chemie der Cellulose," p. 527.

[4] Haas, *Kunstseide und Zellwolle*, **21**, 88 (1939).

100° are shown in Table 77, the data representing averages of numerous tests made with rag paper stock.[5] The rate of change was faster when the temperature during heating was 150°. Under these conditions, the viscosity dropped from 203 to 12.9 after 48 hours and to 5.8 after 98 hours. Likewise, copper number and *alpha*-cellulose content dropped at a faster rate.

TABLE 77

CHANGE IN PROPERTIES OF RAG PAPER STOCK ON AGING AT 100° FOR VARIOUS LENGTHS OF TIME

Time, hours	0	48	852
Viscosity in cuam.	203	61.9	10.3
Copper number	0.204	0.393	1.18
Alpha-cellulose, %	97.04	96.4	93.0

The influence of the *degree of polymerization* upon the resistance of cellulosic materials to heating still lacks systematized investigation. However, it may be anticipated that the resistance decreases with decreasing degree of polymerization. Haas [6] states that viscose staple fiber, when exposed to the same conditions of heating as cotton, suffers much more damage. The sensitivity of viscose staple fiber to heating has also been demonstrated by subjecting the heated material to an alkali-solubility test. It was found [7] that the material which had been heated at 108° to constant weight (3–4 hours) was considerably more soluble in strong aqueous alkali than the same material heated at 60° or at 20° (with the aid of a current of conditioned air).

Ordinary bleached wood pulp, having on the average a lower degree of polymerization than cotton cellulose, may also be expected to suffer more damage on heating than the latter. However, alkaline refined pulps (so-called *alpha*-pulps), from which the shorter chain material (including the majority of the noncellulosic carbohydrates) have been removed, seem to display almost as good a relative resistance as rag paper stock if the results are judged by the rate of change, considering the fact that the initial values for the pulps are lower than those for the rag stock.

The loss in strength which ordinary wood pulps suffer under various conditions of heating is quite considerable, particularly during long periods of time and at high temperatures, such as 150° and 175°

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[5] Lewis, *Paper Trade J.*, **95**, No. 21, 29 (1932). The table gives a selection of the published data.

[6] Haas, *loc. cit.*

[7] Schramek and Christoph, *Kolloid-Beihefte*, **48**, 262 (1938).

(Lewis). A difference has also been established between sulfite and sulfate pulp, the former on an average suffering more, particularly in fold resistance, than the latter.[8]

The fact that cellulose suffers a decrease in viscosity on heating has been known for a long time. This effect has been utilized commercially for preparing low viscosity cellulose derivatives (for example, cellulose nitrate, p. 211). Likewise, sulfite pulp, when heated in the air, produces viscose of lower viscosity than pulp not so treated.[9]

Impurities in cellulosic materials resulting from the method of isolation seem to favor decomposition under the influence of heat. Similar observations were made with tendered cotton, particularly if the tendering was caused by overbleaching, which results in the formation of oxycellulose. On heating, such material becomes yellow and brown at a much faster rate than untendered cotton. The differences are particularly pronounced at temperatures between 150° and 175°.[10]

The effect of heating seems, at least in part, to depend also upon the *surrounding atmosphere.* It was found that the rate of attack of cotton heated at 140° in air was greatly lessened if the heating was carried out in an inert atmosphere.[11] On the other hand, comparative heating of rag paper stock and *alpha*-pulps in air, nitrogen, and oxygen did not reveal great differences in the degree of attack.[12] It may be anticipated, then, that at higher temperatures (above 140–150°) the influence of the surrounding atmosphere is overshadowed by the destructive action of the heat.

Moisture in the cellulosic material tempers the process of drying, provided it is allowed to progress at a relatively slow rate. But even slow drying of the moist material affects the reactivity of the dried fiber; its ability to reabsorb water and to swell is distinctly diminished.[13]

According to Stamm and Hansen[14] the first thermal reaction on drying is the loss of water of constitution. If this loss were due to the formation of ether linkages laterally between adjacent cellulose chains

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[8] von Possanner, *Papier-Fabr.*, **39**, 23 (1941); see also Brecht and Michaelis, *ibid.*, **38**, 173 (1940).

[9] Rassow and Wadewitz, *J. prakt. Chem.*, **106**, 299, 312 (1923).

[10] Fort, *J. Soc. Dyers Colourists*, **48**, 94 (1932).

[11] Dorée, "The Methods of Cellulose Chemistry," p. 208.

[12] Lewis, *loc. cit.*

[13] Urquhart and Williams, *J. Textile Inst.*, **15**, T138 (1924); Urquhart, Bostock, and Eckersall, *ibid.*, **23**, T135 (1932); see also Schwalbe, *Papier-Fabr.*, **24**, 33 (1926); Houtz and McLean, *J. Phys. Chem.*, **43**, 309 (1939).

[14] Stamm and Hansen, *Ind. and Eng. Chem.*, **29**, 832 (1937).

through hydroxyl groups, the loss in hygroscopicity and subsequent swelling could be explained by this substitution of the less hygroscopic ether groups for the more hygroscopic hydroxyl groups. This hypothesis would also account for the fact that heating in the presence of a large excess of water vapor causes no change in hygroscopicity, for the presence of an excess of water vapor would depress the thermal decomposition in which water is evolved and thus markedly reduce the tendency to form ether linkages. This hypothesis would furnish an explanation also of the fact that cellulose, thoroughly dried in a dry atmosphere, has lost much, if not all, of its original ability to absorb water and to swell.

De Bruyne[15] has suggested that cellulose, being strongly polar by virtue of its hydroxyl groups, loses its polar character on overdrying. This loss could be explained by Stamm and Hansen's hypothesis of the formation of ether linkages.

Before conditions are reached under which ether linkages could be formed, it may be assumed that the hydroxyl groups, being still satisfied by water, merely draw closer together on drying and finally mutually satisfy one another. On rehumidification, a great many of the bonds thus formed are broken; this would explain the fact that the processes of water absorption and swelling are to a great extent reversible with carefully dried materials.[16]

It has been observed that x-ray analysis of dried and heated cellulose fibers reveals increased orientation of chains and chain bundles in the micellar system.[17] This change should result in improved tensile strength, although the permanent elasticity (regain) may suffer. However, it would seem that this effect is counteracted by other thermal effects, for it is common experience that commercial wood pulp suffers a loss in physical strength properties even on normal drying. On the other hand, Berl and Schmidt[18] found that the x-ray pattern of cellulose did not change, even when heated to 225° in the presence of water under pressure (see also below).

As the conditions become more severe, the destructive action of heat becomes more pronounced, and more and more glycosidic linkages are broken; this effect is possibly favored by oxidation.[19] With temperatures in the neighborhood of 200°, the conditions of destructive distillation are approached.

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[15] De Bruyne, *Paper-Maker,* **99,** TS12 (1940).

[16] Stamm and Hansen, *loc. cit.;* see also Urquhart and Williams, *loc. cit.;* Kanamaru, *Helv. Chim. Acta,* **17,** 1427 (1927).

[17] Kanamaru, *loc. cit.;* Matthieu, *Trans. Faraday Soc.,* **29,** 122 (1933).

[18] Berl and Schmidt, *Ann.,* **461,** 192 (1928).

[19] It has also been suggested that, at the earlier stages of decomposition, hydrolysis may occur (Haas, *loc. cit.*).

According to Dole,[20] cellulose lacks the property of thermoplasticity, i.e., it decomposes and chars before melting, because the cohesive forces between the chain molecules are too strong to be broken down at temperatures below the decomposition temperature. In contrast, the introduction of ester or ether groups weakens the cohesive forces to a point where the fiber melts before being decomposed. In other words, cellulose esters and ethers are thermoplastic.

The Destructive Distillation of Cellulose

As the term indicates, destructive distillation[21] involves the decomposition of cellulose at an elevated temperature and the simultaneous distillation of the reaction products. The products are aqueous, of tar-like consistency, and gaseous. The aqueous distillate and the tar are obtained on condensation through cooling. The gases may be collected in various replacement devices.

The reaction products are the result not only of a profound decomposition of the cellulose, but also of secondary and tertiary reactions. Therefore, no conclusions regarding the molecular structure of cellulose can be drawn from the results of so violent a process. The results of the various studies[22] on the destructive distillation of cellulose may be summarized as follows.

The aqueous distillate begins to form at about 200°, depending to a certain extent upon the rate of temperature elevation. When the temperature is increased above 200°, tar begins to appear, and gases are evolved to a considerable extent. At about 270°, the reaction becomes violent, and the formation of the decomposition products reaches its maximum. The fact that the reaction is distinctly exothermic, a rise in temperature as high as 80° having been observed, seems to indicate that secondary and tertiary reactions occur to a considerable extent at this point. After the violent reaction has passed, further elevation of the temperature results only in a slow formation of distillation products, and at 470° the process comes to a standstill. The residue in the distillation vessel consists of coke.

The aqueous distillate contains relatively small amounts of acetic and formic acids, acetone, methylethyl ketone and other ketones.

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[20] Dole, *Am. Dyestuff Reptr.*, **30,** p. 332 (1941); see also Stillwell, "Crystal Chemistry," McGraw-Hill Book Co., New York (1938).

[21] Other terms are "pyrogenic decomposition" and "pyrolysis."

[22] Ramsay and Chorley, *J. Soc. Chem. Ind.*, **11,** 872 (1892); Cross and Bevan, "Cellulose," Longmans, Green and Co., London (1910), p. 68; Büttner and Wislicenus, *J. prakt. Chem.*, **79,** 177 (1909); Klason, von Heidenstam, and Norlin, *Z. angew. Chem.*, **22,** 1205 (1909).

The tar consists chiefly of phenols; in addition, carbolic acid,[23] small amounts of cresol, and traces of toluene [24] have been found.

Apart from the products mentioned so far, a number of other compounds have been isolated in small quantities, partly from the aqueous distillate and partly from the tar or from both sources. The chief products are: furfural,[25] ω-hydroxymethylfurfural, maltol, δ-valerolactone,[26] methylfuran, 2,5-dimethylfuran, and tri- and tetramethylfuran.[27]

The presence of phenols, as well as of furan and pyrone derivatives (such as maltol), indicates that, under the influence of the high temperature and possibly with the aid of other products of decomposition which may act as catalysts, aliphatic chains are transformed into ring-structured aromatic compounds, a transformation which is known to occur with many other aliphatic substances.

More recently some aromatic hydrocarbons, namely, benzene and diphenyl, have been isolated.[28]

The evolution of gases, 75 per cent of which consists of carbon dioxide, is most violent between 270 and 350°. With further elevation of the temperature, more carbon monoxide than carbon dioxide is evolved. Toward the end of the reaction, methane [29] and small amounts of ethylene and formaldehyde [30] also appear. Although Klason and coworkers and other investigators found no hydrogen among the gaseous products, this gas was observed by Sarasin, as well as by Erdmann and Schaefer.

The yields in which the various products of distillation are obtained depend quite essentially upon the rate of heating, as well as upon the methods used for the separation of the mixtures. For this reason, the results of the various studies are not strictly comparable. An example of what may be expected from the destructive distillation of cotton is shown in Table 78, which is taken from the work of Klason, von Heidenstam, and Norlin. (The yields are calculated on the dry cellulose.)

The coke, provided the distillation was actually completed, has a composition quite similar to that of anthracite coal, except that its hydrogen content is somewhat lower (Klason). According to various investigators the coke still shows the structure of the original fiber (Wislicenus).[31]

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[23] Wichelhaus, *Ber.*, **43**, 2922 (1910).

[24] Sarasin, *Arch. sci. phys. nat.; Chem. Zentr.*, II, 528 (1918).

[25] Cross and Bevan, *loc. cit.*

[26] Erdmann and Schäfer, *Ber.*, **43**, 2398 (1910).

[27] Sarasin, *loc. cit.*

[28] Smith and Howard, *J. Am. Chem. Soc.*, **59**, 234 (1937).

[29] Sarasin, *loc. cit.*; Hawley and Aiyar, *Ind. Eng. Chem.*, **14**, 1055 (1922).

[30] Erdmann and Schäfer, *loc. cit.*

[31] See also Tropsch, *Brennstoff-Chemie*, **5**, 288 (1924).

TABLE 78

DESTRUCTIVE DISTILLATION OF COTTON CELLULOSE—
YIELDS OF REACTION PRODUCTS

	%
Water	34.52
Acetic acid	1.39
Acetone	0.07
Tar	4.18
Other organic substances	5.14
Carbon dioxide	10.35
Carbon monoxide	4.15
Methane	0.27
Ethylene	0.17
Coke	38.82

Bergius[32] has explained the lower hydrogen content of the cellulose coke by overheating caused by the exothermic heat developed during the thermal decomposition. To avoid overheating, Bergius allowed the "coalification" of cellulose to take place in the presence of certain amounts of water. Under these conditions and with the temperature raised to 300° in a closed system (corresponding to a pressure of 100–150 atmospheres), a cellulose coal was obtained, the hydrogen content of which was the same as that of natural anthracites.

The object of Bergius' much discussed experiment was to show that of the constituents of wood, cellulose is the main source of *natural* coal. He thus believed that he demonstrated that the extremely slow process of natural coalification may be accomplished in the laboratory within a relatively very short time.

Franz Fischer and his school, who contended that the only source of natural coal is the lignin constituent of the wood, whereas the cellulose (and the noncellulosic carbohydrates) fall prey to the activity of bacteria and thus are entirely destroyed, were not able to reproduce Bergius' results.[33] However, Berl[34] showed that the transformation of cellulose into a coal identical with anthracite may be actually accomplished under certain conditions. On the other hand, lignin and cellulose, when heated together, yielded a product similar to lignite which could not be transformed into anthracite.[35] Berl thus concluded that the natural anthracite is formed from plants rich in cellulose and poor in lignin (as

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[32] Bergius, *Z. angew. Chem.*, **25**, 1171 (1912); *Z. Elektrochem.*, **18**, 660 (1912); *Chem.-Ztg.*, **37**, 977, 1236 (1913); "Die Anwendung hoher Drucke, etc.", Knapp, Halle a. S. (1913); *Naturwissenschaften*, **16**, 1 (1928).

[33] Tropsch and von Phillippovich, in Fischer, *Ges. Abhandl. Kenntnis Kohle*, 7, 84 (Gebr. Borntraeger), Berlin (1925), and numerous other publications in these volumes. See also Bone, "Coal, etc. Constituents and Uses," Longmans, Green and Co., London (1936).

[34] See the compilation by Berl, *Papier-Fabr.*, **31**, 141 (1933).

[35] See also Heuser, *Z. angew. Chem.*, **26**, 393 (1913).

well as in waxes and fats), whereas lignite is formed from plants which are rich in lignin and contain appreciable quantities of waxes and fats.

The once rather passionate polemics between the two schools of thought which ascribed the formation of natural coals to either one or the other of the two main constituents of wood have practically ceased at the present time.[36] In the meantime, numerous results have been accumulated to show that a number of the aromatic constituents of natural coals could very well arise from cellulose. In this connection, the reader is referred to the numerous publications by Berl and co-workers on this subject, particularly on the origin of bituminous coals.[37]

Likewise, the isolation of benzene and diphenyl from the products of the thermal decomposition of cellulose favors the concept that cellulose is an essential source of the aromatic structures in bituminous coals. The temperature (200–300°) at which, according to Smith and Howard, the transformation of the aliphatic compound into aromatic C_6 ring structures occurs may conceivably be reached during natural coalification.[38] Moreover, the yield of the aromatic hydrocarbons is of the same order as that obtained by similar treatment of bituminous coal from a Pittsburgh seam.

Whereas it is thus possible to convert cellulose into coal which closely resembles the natural product by thermal decomposition, the participation of bacteria, fungi, and other micro-organisms in the natural formation of coal cannot be overlooked. A considerable portion of the cellulose waste (including noncellulosic carbohydrates and lignin) which nature produces is decomposed by micro-organisms to various intermediates before it is completely burned to carbon dioxide and water. This fact seems to suggest that the products of the biological transformation take part in the formation of natural coal side by side with those portions of the cellulose and the lignin which remain partly or entirely undecomposed during this biological deterioration. It would appear that it is this mixture of cellulose, lignin, and their biological decomposition products (together with the cell material from the micro-organisms) which is exposed to elevated temperature and pressure during further periods of geochemical development and is thus the source of natural coal.

The thermal decomposition of cellulose has been studied also in an attempt to ascertain the part which the various constituents of wood play in the formation of products on its destructive distillation. For a long time, this process was the main and almost the sole source of the commercial manufacture of acetic acid, acetone, and methyl alcohol. Today, these compounds are prepared synthetically and the process of destructive wood distillation has lost much of its earlier importance, except for the manufacture of charcoal and possibly phenols.[39]

In comparing the results which have been obtained by the destructive dis-

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[36] Rudge, *J. Soc. Chem. Ind.*, **54**, 499 (1935).

[37] See especially the following publications: Berl and Schmidt, *Ann.*, **493**, 97, 135 (1932); **496**, 283 (1932); Berl, Schmidt, and Koch, *Ang. Chem.*, **45**, 517 (1932); Berl and Keller, *Ann.*, **501**, 84 (1933); Berl and Koerber, *Ind. Eng. Chem.*, **32**, 676 (1940); *ibid., Anal. Ed.*, **12**, 245 (1940); Berl, Biebesheimer, and Koerber, *Ind. Eng. Chem.*, **33**, 672 (1941).

[38] Lewis, *J. Inst. Fuel*, **9**, 235 (1936).

[39] Klar, *Holz Roh- u. Werkstoff*, **1**, 135 (1937).

tillation of cellulose and lignin, it is seen that lignin yields a greater quantity of tar and aromatic compounds[40] and that methyl alcohol is formed essentially from lignin, but not from cellulose.[41] Cellulose itself yields methyl alcohol only on hydrogenation in the presence of catalysts.[42]

The question whether the noncellulosic carbohydrates are responsible for the higher yield of acetic acid obtained from the destructive distillation of hardwoods has not yet been definitely answered.[43]

The process of coalification of cellulose in the presence of water, mentioned earlier in this chapter, was studied also by x-ray investigation.[44] It was found that the x-ray pattern of the heated cellulose remained practically unchanged up to a temperature of 225°, except for a certain disturbance of the orientation of the micelles. Above 250°, the pattern disappeared; this shows that the crystalline structure of the fiber had been destroyed at this temperature. The optical anisotropy of the original fiber disappeared after a temperature of 225° had been reached.

The Destructive Distillation of Cellulose in the Presence of Various Agents

The action of heat upon cellulose suspended in organic liquids, such as benzene or toluene, seems to take a different course. Under such conditions, cellulose appears to be more resistant. When heated at 250–260° and about 45 atmospheres for 35 hours, the suspensions produced 12–13 per cent benzene-soluble products, leaving a coke-like residue. It is noteworthy that under these conditions practically no gases were formed.[45]

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[40] Heuser and Skiöldebrand, *Z. angew. Chem.*, **32**, 41 (1919); Pictet and Gaulis, *Helv. Chim. Acta*, **6**, 627 (1923), on the distillation of spruce lignin *in vacuo*.

[41] Heuser and Skiöldebrand, *loc. cit.;* Heuser and Schmelz, *Cellulosechem.*, **1**, 49 (1920); Katzen, Muller, and Othmer, *Ind. Eng. Chem.*, **35**, 302 (1943). On the destructive distillation of wood, small amounts of methyl alcohol might be formed from noncellulosic carbohydrates, Ritter and Kurth, *Ind. Eng. Chem.*, **25**, 1250 (1933); see also van Beckum and Ritter, *Paper Trade J.*, **108**, No. 7, 27 (1939), who found about 1 per cent methoxyl in holocellulose from hardwood. On destructive distillation, this methoxyl could appear as methyl alcohol.

[42] Fierz-David and Hannig, *Helv. Chim. Acta*, **8**, 900 (1925); *J. Soc. Chem. Ind.*, **44**, T942 (1925); Bowen, Shatwell, and Nash, *ibid.*, **44**, T507 (1925); Waterman and Perquin, *Rec. trav. chim.*, **46**, 638 (1927).

[43] Heuser and Scherer, *Brennstoff-Chemie*, **4**, 97 (1923); Heuser and Brötz, *Papier-Fabr.*, **23**, *Special Number*, 69 (1925); Othmer and Schurig, *Ind. Eng. Chem.*, **33**, 188 (1941). On the destructive distillation of wood, see also Schorger, "The Chemistry of Cellulose and Wood," The Chem. Catalog Co., New York (1926), and Hawley and Wise, "The Chemistry of Wood," The Chem. Catalog Co., New York (1926), new edition in preparation.

[44] Berl and Schmidt, *Ann.*, **461**, 192 (1928).

[45] Fischer and Schneider in Fischer, *Ges. Abhandl. Kenntnis Kohle*, **3**, 289 (1925); Tropsch and von Phillippovich, *ibid.*, **7**, 91 (1925).

In this connection the behavior of cellulose when heated in alcohol is of interest.[46] It was found that cotton and cotton linters suspended in pure alcohol remained practically unattacked when the suspension was heated in a sealed glass tube at 180° for 4 hours. However, when heated in water under the same conditions, the materials became so brittle that they could be rubbed between the fingers into small fragments. Their *alpha*-cellulose contents had decreased considerably, cotton showing only 92.2 and cotton linters as little as 52.6 per cent after the treatment. Likewise, the copper number of the treated materials had increased. On the other hand, alcohol-water mixtures exerted effects which ranged between those obtained with the separate liquids, and these effects became more pronounced as the water content of the mixture was increased. In view of the probability that water is dissociated to a considerable extent[47] at 180°, it would appear that the effect is that of hydrolysis and that the presence of alcohol depresses the hydrolytic effect, perhaps by some sort of chemical association between the water and the alcohol molecules.

The effect of water is considerably intensified in the presence of certain salts. Thus, wood pulp heated in an aqueous solution of magnesium chloride in an autoclave at 180° for 12 hours was transformed into coal having a composition ranging between that of lignite and that of anthracite. The effect of the magnesium chloride (which is hydrolytically dissociated to a considerable extent under these conditions of temperature and pressure) is probably due to the action upon the cellulose of the hydrochloric acid thus formed. This action results in the formation of glucose which, in a subsequent phase of the reaction, undergoes dehydration. This view is supported by the fact that other salts, such as calcium chloride, being less dissociated under the conditions employed, were unable to effect this far-reaching transformation.[48]

The heat of combustion of cellulose is about 4200 calories per gram. The values for the specific heat[49] of cellulose vary from 0.366 to 0.41.

The Destructive Distillation of Cellulose in Vacuo

The violence of the destructive distillation of cellulose is much lessened, if the reaction is carried out *in vacuo*.[50] The fact that very

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[46] Kleinert, *Cellulosechem.*, **18**, 114 (1940).

[47] Noyes, Kato, and Sosman, *Z. physik. Chem.*, **73**, 20 (1910).

[48] Schwalbe and Schepp, *Ber.*, **57**, 319, 881 (1924); **58**, 2500 (1925).

[49] Fleury, *Compt. rend.*, **130**, 437 (1900); Dietz, *Papier-Fabr.*, **43**, 3119 (1912).

[50] Pictet and Sarasin, *Helv. Acta*, **1**, 87 (1918).

little tar is formed seems to indicate that, under these conditions, secondary and tertiary reactions take place to a much smaller extent. Likewise, less coal is formed (about 10 per cent against 20–40 per cent under ordinary conditions). The main product is a brown and oily substance which gradually solidifies and partly crystallizes. The purified product thus obtained[51] had the empirical formula $C_6H_{10}O_5$ and very nearly the molecular weight which this formula requires (162); it did not reduce Fehling solution but was converted into glucose when boiled with dilute acid, indicating that it consisted of an anhydroglucose. Its physical properties and its molecular structure were recognized as those of β-levoglucosan. The product was thus identical with that which had been obtained by earlier investigators on the cleavage of certain glucosides—for example, picein (a spruce wood glucoside), which splits into piceol (*p*-hydroxyacetophenone) and levoglucosan under the influence of strong bases.[52]

Pictet and Sarasin realized a yield of about 30 per cent of levoglucosan calculated on the weight of the cellulose. This figure could be somewhat improved by Venn,[53] who found that the yield depended upon the pretreatment of the cellulosic material. The best yield—40 per cent—was obtained from hydrocellulose (Egyptian cotton boiled in 2 per cent hydrochloric acid for 1 hour), whereas purified cotton yielded only 35 per cent.

The fact that levoglucosan, if distilled under normal conditions, yields reaction products similar to those which are obtained on the destructive distillation of cellulose seems to suggest that levoglucosan is an intermediate of this reaction. Obviously the use of a vacuum prevents subsequent destruction.

The lack of reducing power shows that the aldehyde group is involved in an oxygen linkage with one of the free hydroxyl groups in the 2-, 3-, 4-, or 6-position, the 5-position being excluded by the amylene oxide linkage. The 1,6-linkage, as shown in formula II and made probable by previous investigations,[54] is best supported by the result of the hydrolysis of trimethyllevoglucosan which results in the formations of 2,3,4-trimethylglucose.[55] Thus, in levoglucosan, none of

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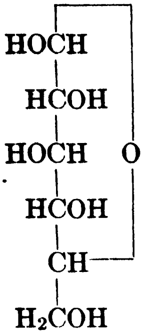
[51] See also Venn, *J. Textile Inst.*, **15**, T414 (1924).

[52] Tanret, *Bull. soc. chim.*, [3] **11**, 949 (1894); see also Vongerichten and Müller, *Ber.*, **39**, 241 (1906).

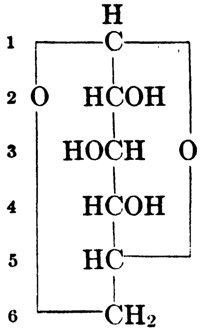
[53] Venn, *loc. cit.*

[54] Pictet and Cramer, *Helv. Chim. Acta*, **3**, 640 (1920); Karrer and Smirnoff, *ibid.*, **5**, 124 (1922); Zemplén and Csurös, *Ber.*, **62**, 993 (1929); Josephson, *ibid.*, **62**, 313 (1929).

[55] Irvine and Oldham, *J. Soc. Chem. Ind.*, **119**, 1744 (1921).



I. GLUCOSE



II. 1,6-ANHYDRO-*β*-*d*-GLUCOPYRANOSE

the hydroxyls in the 2-, 3-, or 4-position is involved in the second oxygen linkage, and the only possibility remaining is the 1,6-arrangement.

The *β*-configuration is derived from the fact that levoglucosan is obtained from *β*-*d*-glucose and *β*-*d*-glucosides and not from the *α*-modification of these sugars.[56]

The formation of levoglucosan from *glucose*—on distillation *in vacuo* —makes it probable that cellulose, when subjected to this process, produces glucose as the primary reaction product and that this is subsequently dehydrated to levoglucosan.

This interpretation of the formation of levoglucosan as the result of a secondary reaction would also lead to a better understanding of the fact that the oxygen bridges in levoglucosan are in different positions than are those prevailing in the mother compound. If we imagine the glucose residues in cellulose to be taken out of their natural combination, we may regard them as 1,4-anhydro-1,5-glucoses, i.e., as units from which the elements of water have been eliminated at the carbon atoms 1 and 4 (see formula on p. 528). The transformation of 1,4-anhydroglucose units into 1,6-anhydroglucose seems to indicate that it is actually the glucose rather than the cellulose as such which undergoes the process of anhydrization. This view is supported by the observation that glucose undergoes transformation into a number of isomeric anhydrides, depending upon the experimental conditions. In this connection the reader is referred to E. Fischer's 3,6-anhydro-1,5-glucose [57] and to Brigl's 1,2-anhydro-1,5-glucose.[58]

It would thus appear to be objectionable to ascribe the 1,6 linkage to the anhydroglucose units in cellulose, as was suggested at the time when the dis-

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[56] Karrer, *Helv. Chim. Acta,* **3**, 258 (1920); Pictet, *ibid.,* **3**, 649 (1920); Irvine and Oldham, *loc. cit.,* p. 1757.

[57] Fischer and Zach, *Ber.,* **45**, 456, 2068, 3761 (1912); Ohle, Vargha, and Erlbach, *ibid.,* **61**, 1211 (1928).

[58] Brigl, *Z. physiol. Chem.,* **122**, 245 (1922). The 1,4-anhydro-1,5-glucose which Freudenberg and Braun and Micheel and Hess believed to have obtained by different methods from 2,3,6-trimethylglucose would also serve as an example, if its existence were definitely established; see Hess and Littmann, *Ber.,* **66**, 774 (1933); *Ann.,* **506**, 298 (1933).

covery of levoglucosan gave a new impetus to the speculation on the molecular structure of cellulose.[59] Another argument against such conclusions is furnished by the fact that starch yields the same levoglucosan as cellulose.[60] Thus, it is probable that, on the destructive distillation of starch, β-*d*-glucose is formed in a primary reaction, but is subsequently transformed into the anhydride.

The destructive distillation *in vacuo* of methylcellulose yielded methyllevoglucosan.[61] Cellulose methylated to an extent of 2 methyl groups per glucose residue yielded 50 per cent (calculated on "dimethylcellulose") of dimethyllevoglucosan. On boiling with dilute sulfuric acid, dimethylglucose was obtained. Methylcelluloses with a methoxyl content below or above the dimethyl stage yielded methylated levoglucosans with correspondingly less or more methoxyl, indicating that the products thus obtained, probably including the dimethyllevoglucosan, were mixtures.

It is apparent that the methoxyl groups in methylcellulose are resistant to thermal decomposition *in vacuo*. Reilly made no attempt to ascertain the position of these groups or to determine the type of the second oxygen ring in the methylated levoglucosans. Assuming that, in a methylcellulose preparation containing 43.7 per cent methoxyl (Reilly's experiment #4), most of the cellulose is fully methylated to 2,3,6-methylcellulose, one would expect that trimethyllevoglucosan (which was probably the main portion of a preparation with 42.3 per cent CH_3O) would not have the 1,6 but rather the 1,4 oxygen ring, because the 6-position in the cellulose was shielded by methoxyl. Likewise, Reilly's "dimethyllevoglucosan" (or at least that portion which was homogeneous) was probably a dimethylated 1,4-anhydro-1,5-glucose.

Levoglucosan, like other glucosans, tends to undergo polymerization when heated *in vacuo* at about 150° or under normal atmospheric conditions in the presence of zinc chloride at the same temperature. Thus, a dilevoglucosan and a tetralevoglucosan and, at elevated atmospheric pressure, a hexa- and an octalevoglucosan have been obtained.[62] When heated with zinc powder at 250° *in vacuo,* levoglucosan yielded tri-, tetra-, and heptalevoglucosans.[63] Likewise, polymerization has been observed to occur if levoglucosan is heated in the presence of benzene or other inert organic liquids.[64]

As would be expected, the physical properties of these polyglucosans change with their degree of polymerization; for example, with increasing molecular weight their solubility decreases, whereas their melting point increases. These polyglucosans may or may not have a constitution similar to those which are formed when glucose undergoes the process of reversion in the presence of highly concentrated halide acids (p. 523) or when cellulose is subjected to the action of these agents, as nothing seems to be known about the position of either their glycosidic or their anhydro-oxygen linkages. The relation between these various

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[59] See for example Heuser, "Lehrbuch der Cellulosechemie," 3rd ed., p. 225.

[60] Pictet and Sarasin, *loc. cit.;* Zemplén and Gerecs, *Ber.*, **64,** 1545 (1931).

[61] Reilly, *Helv. Chim. Acta,* **4,** 616 (1921); see also Hess and Wittelsbach, *Z. Elektrochem.*, **26,** 237, 251 (1920).

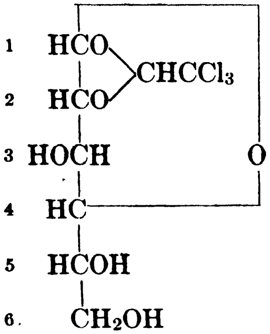
[62] Karrer and Salomon, *Helv. Chim. Acta,* **5,** 108 (1922); Pictet and Ross, *ibid.*, **5,** 876 (1922); Pictet and Georg, *ibid.*, **9,** 612 (1926).

[63] Irvine and Oldham, *J. Chem. Soc.*, **127,** 2903 (1925).

[64] Pictet and Ross, *loc. cit.;* Pictet and Salzmann, *Helv. Chim. Acta,* **8,** 984 (1925).

types of glucosans and any relation they might have to cellulose still have to be established.

Levoglucosan adds chloral (Cl_3CCHO) to form mono- and dichloralglucoses (chloraloses).[65] The molecular structure of the monocompound, according to White and Hixon,[66] is represented by the following formula, proof of which has been furnished by W. Freudenberg and Vajda.[67]



The product is thus β-chloralglucose—i.e., the same product which may be obtained directly from glucose by condensing it with chloral in the presence of concentrated sulfuric acid, whereby one molecule of water is liberated.

Various dichloralglucoses (with a second chloral radical probably on the oxygen atoms in 5- and 6-positions) were obtained by the action of chloral hydrate [$Cl_3CCH(OH)_2$] on cellulose in the presence of concentrated sulfuric acid. Obviously, the formation of the chloral derivatives is preceded by hydrolysis of the cellulose to glucose.[68]

That chloral actually enters the cellulose chain if it is allowed to act in the presence of organic bases, such as pyridine, has been claimed in a patent.[69] The cellulose goes into solution and the solution, being of viscous consistency, may be cast into films, etc.

Provided that, during this reaction, no glycosidic linkages are broken (this, however, is doubtful), chloral must be expected merely to combine with a pair of neighboring free hydroxyl groups, i.e., in an acetal fashion (as, for example, in the 5- and 6-positions of dichloralglucose) and not also in a semi-acetal fashion (as in the 1- and 2-posi-

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[65] Pictet and Reichel, *Helv. Chim. Acta,* **6,** 621 (1923).

[66] White and Hixon, *J. Am. Chem. Soc.,* **55,** 2438 (1933).

[67] W. Freudenberg and Vajda, *J. Am. Chem. Soc.,* **59,** 1955 (1937).

[68] Ross and Payne, *J. Am. Chem. Soc.,* **45,** 2363 (1923).

[69] German patent 408,821, Bad. Anilin-und Sodafabrik, & Ruppel and Meyer (1925).

tions of monochloral glucose). Experimental evidence of this assumption is still to be established, however.

HYDROGENATION OF CELLULOSE

A number of studies on the action of hydrogen upon cellulose are included under this heading, although the reaction does not always involve actual hydrogenation but simply means thermal decomposition of cellulose in a hydrogen atmosphere, the latter serving to prevent or at least to diminish further breakdown of the products of the primary reaction.

Attempts have not been successful to introduce into, or add hydrogen to, cellulose—that is, to subject the "aldehyde" cellulose to the process of reduction (the reverse of oxidation)—without simultaneously degrading it. At room temperature or at those elevated temperatures at which cellulose remains still unattacked, no reaction seems to take place. But when the temperature is raised to a point at which the thermal decomposition of the cellulose begins, hydrogen is consumed (indicated by the fall in pressure of the closed system). This fact seems to show that the hydrogen reacts with the thermal decomposition products rather than with cellulose itself.

It would appear that results on the action of hydrogen on cellulose at a high temperature were first reported by Bowen, Shatwell, and Nash.[70] They found that, whereas hydrogen alone, even at a temperature of 440° and a pressure of 120–130 atmospheres, had little influence upon the results of the thermal decomposition, the presence of a catalyst (nickel salt) caused considerable hydrogen consumption. As a result, practically all the cellulosic material used (cotton yarn) was converted into liquids and gases. The chief difference from results obtained in the absence of hydrogen under these conditions may be seen in the fact that no coal-like residue (or very little of it) was obtained. The composition of the liquid fraction and the gases was similar to that of the fractions from mere destructive distillation, except that the tar (which was lighter in color) contained less phenols and more hydrocarbons.

The necessity of the presence of a catalyst to effect substantial hydrogen consumption was also recognized by Fierz-David and Fierz-David and Hanning.[71] Indeed, when cellulose (or wood) was sub-

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[70] Bowen, Shatwell, and Nash, *J. Soc. Chem. Ind.*, **44**, 507T, 526T (1925).

[71] Fierz-David, *Chemistry & Industry*, **44**, 942 (1925); Fierz-David and Hannig, *Helv. Chim. Acta*, **8**, 900 (1925); see also Waterman and Perquin, *Rec. trav. chim.*, **45**, 638 (1926).

jected to the action of hydrogen at 450–470° and a pressure of 150–200 atmospheres without a catalyst, the whole hydrogen admitted could be ultimately recovered, and the reaction products were practically the same as when hydrogen was absent. However, if cellulose was impregnated with nickel hydroxide, which is reduced to metallic nickel in the early stages of hydrogenation, it was practically entirely liquefied and volatilized to yield tar, aqueous distillate, and gas. With wood pulp, a small quantity of residue (3.5 per cent) remained. A small amount of methyl alcohol (probably less than 0.5 per cent on the weight of the cellulose) was observed (p. 549).

Frohlich, Spalding, and Bacon[72] obtained similar results with sulfite pulp but could not confirm the formation of methyl alcohol. When hydrogen was replaced by nitrogen, a considerable solid residue (14 per cent) remained at the end of the reaction.

The results of a more recent study on the hydrogenation of cellulose seem to indicate that the presence of a *metal* catalyst is not essential for the consumption of hydrogen. Boomer, Argue, and Edwards[73] subjected absorbent cotton suspended in tetralin to the action of hydrogen at 325–350° and a pressure of 180–275 atmospheres, but in the absence of a metal catalyst. It was found that tetralin, when present in sufficient excess, promoted the complete conversion of cellulose (and wood) into liquids and gases (chiefly hydrocarbons). These results seem to justify the conclusion that tetralin not only acts as a hydrogen carrier but also fulfills the function of a catalyst. The consumption of hydrogen was found to be relatively large (2.5–3.7 per cent of the weight of the wood). With cellulose, the gases consisted chiefly of methane and ethane. Some of the tetralin was dehydrogenated to naphthalene.

Summing up the results of the various investigations, it would seem fairly safe to draw the following general conclusions: The hydrogen essentially fulfills two functions. The fact that, in the presence of a catalyst, considerable quantities of hydrogen are consumed shows that hydrogenation takes place. The increased formation of hydrocarbons, as compared with the results of destructive distillation alone, seems to indicate the nature of this reaction. Simultaneously, the hydrogen protects the primary products of the thermal decomposition against further breakdown.

The reaction takes a different course if hydrogen is allowed to act upon cellulose at elevated temperature and pressure *in the presence of*

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[72] Frohlich, Spalding, and Bacon, *Ind. Eng. Chem.*, **20**, 36 (1928).

[73] Boomer, Argue, and Edwards, *Can. J. Research*, **B13**, 337 (1935).

alkali. By subjecting cellulose (isolated from cotton hull fibers) to a pretreatment with 7 per cent sodium hydroxide solution under 80–90 pounds per square inch of steam pressure (corresponding to about 162°) for 2 hours and exposing the pretreated alkali-containing material to the action of hydrogen in the presence of Raney nickel to 250° and a pressure of 325–380 atmospheres, it was entirely converted into a colorless liquid.[74] With a hydrogen consumption of 8.11 moles, 300 grams of cellulose produced 3.31 moles of gaseous hydrocarbons (chiefly methane), 0.15 mole of carbon dioxide, and 2.39 moles of acidic material.

Among the acids were lower fatty acids, including acetic and possibly propionic and one or both of the butyric acids, as well as hydroxy acids, such as lactic, dihydroxyvaleric, and hydroxycaproic, and their lactones.

As has been seen (p. 491), the formation of these and similar hydroxy acids is the result of the action upon cellulose of aqueous alkali at elevated temperature and pressure. In the process of hydrogenation, the hydrogen seems to protect these acids against further breakdown and, moreover, to replace a number of their hydroxy groups with the result that normal acids and those with a limited number of hydroxy groups are formed.[75]

At this point, the results of earlier studies by Berl and Biebesheimer[76] on the treatment of cellulose with alkali followed by hydrogenation may be mentioned, although they are not quite comparable with those just discussed. The object of these studies was to furnish experimental evidence for the hypothesis that natural petroleum has its origin in cellulose. This hypothesis postulates that, under natural conditions of elevated temperature and pressure and in the presence of alkali (originating from lime rocks), cellulose is converted into an asphalt-like material (protoproduct), which subsequently undergoes hydrogenation (the hydrogen being supplied from various natural sources) and liquefaction to yield petroleum.

The experiment consisted in treating cotton linters with *N* sodium hydroxide solution at 310–330° and under a pressure of 180–220 atmospheres for 2 hours. Under these conditions, the cellulosic material was transformed into gases and a tar-like liquid which acquired an asphalt-like consistency on standing. In a second phase, the asphalt-like material (protoproduct) was subjected to the action of hydrogen at 420–460° and at 100 atmospheres of pressure for several hours. As a result, an oil was obtained, which had the appearance, the odor, and the physical properties of natural petroleum and consisted chiefly of hydrocarbons, i.e., compounds which constitute the natural petroleum.

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[74] Henze, Allen, and Wyatt, *J. Org. Chem.*, **7**, 48 (1942).

[75] Allen, Wyatt, and Henze, *J. Am. Chem. Soc.*, **61**, 843 (1939).

[76] Berl and Biebesheimer, *Ann.*, **504**, 38 (1933); see also Berl and Schmidt, *ibid.*, **496**, 153, 291 (1932).

Hydrogenation of cellulose has also been attempted by allowing reducing agents other than molecular hydrogen to act upon cellulose. Willstätter and Kalb [77] subjected cotton to the action of hydriodic acid in the presence of red phosphorus at 250° and obtained (calculated on the weight of the cellulose employed) 12 per cent solid and 8 per cent liquid hydrocarbons and, in addition, an ether-insoluble residue (not further characterized). The rest, it must be assumed (although no mention of it is made), was transformed into gases. The nature of the hydrocarbons was not ascertained, except for the ratio of carbon to oxygen which in both the solid and the liquid portions was found to be very nearly the same (the average value of x in CH_x was 1.6).

The statement that lignin (isolated from wood with highly concentrated hydrochloric acid, "Willstätter lignin," see p. 522) gave the same products on a similar treatment would appear surprising in the light of the difference between the molecular structure of the two substances, unless the assumption is made that aliphatic chains are transformed into aromatic compounds under the action of the high temperature. Indeed, Willstätter and Kalb regarded their reaction products as a mixture of polycyclic hydrogenated ring compounds rather than one of olefinic chains. The formation of the hydrocarbons does not seem to proceed over hexyl iodide as an intermediate (which is obtained on the reduction of hexitol and of glucose under relatively mild conditions); it is believed that another intermediate is formed which submits to polymerization by condensation between carbon atoms.

Mention may also be made of the transformation of cellulose under the action of nascent hydrogen as reported by Fischer and Schrader.[78] A mixture of cellulose, sodium formate, and water was heated in a sealed tube at 400° for 3 hours. The reaction products consisted of an ether-soluble tar and a solid residue, representing, respectively, 12.9 and 3.2 per cent of the original ash-free dry cellulose. The composition of these products was not ascertained.

The transformation of cellulose waste into hydrocarbons by way of hydrogenation appears to be of commercial interest as a potential source for the production of liquid fuel.

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[77] Willstätter and Kalb, *Ber.*, **55**, 2637 (1922).

[78] Fischer, "Conversion of Coal into Oils," Van Nostrand, New York (1925), p. 183.

CHAPTER XIII

THE DECOMPOSITION OF CELLULOSE BY BIOLOGICAL PROCESSES

Nature has provided for continuous transformation of cellulose waste into other substances and finally into carbon dioxide and water by the activity of micro-organisms. The micro-organisms which achieve this transformation are aerobic and anaerobic, mesophilic and thermophilic bacteria, fungi, and protozoa. Depending upon the nature of the organism concerned, a variety of intermediates appears before the destruction has reached its final stage. These intermediates are chiefly aliphatic fatty acids; in some cases alcohols are also formed. The formation of these products is accompanied by the appearance of considerable quantities of gases.[1]

THE DECOMPOSITION OF CELLULOSE BY BACTERIA

The production of fatty acids seems to be confined to the activity of anaerobic bacteria, for the relatively few investigations which concern the decomposition of cellulose by aerobic bacteria have brought forth no unequivocal evidence of the formation of such acids. It is likely that, where their formation has been observed,[2] anaerobic bacteria were also active, for the considerable oxygen consumption of the aerobes may create conditions which favor the simultaneous growth of anaerobic bacteria.

Under the action of essentially aerobic bacteria, cellulose is converted into a more or less colored mucilage. This characteristic change of the cellulosic material, apparently first observed with rather impure cultures by van Iterson,[3] was confirmed by later investigators who used cultures less contaminated with other organisms. Such cultures were developed by Hutchinson and Clayton[4] and by Winogradsky[5] and

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[1] For a detailed account of the subject see Thaysen and Bunker, "The Microbiology of Cellulose, Hemicelluloses, etc.," Oxford University Press (1927).

[2] Kroulik, *Zentr. Bakt.*, II, **36**, 343 (1913).

[3] van Iterson, *Zentr. Bakt.*, II, **11**, 689 (1904).

[4] Hutchinson and Clayton, *J. Agr. Sci.*, **9**, 143 (1919).

[5] Winogradsky, *Ann. inst. Pasteur*, **43**, 549 (1929).

consisted essentially of a *Spirochaeta* type, later named *Cythophaga hutchinsoni.*

These earlier studies were more recently extended under still more suitable conditions by Walker and Warren.[6] In contrast to previous investigations, it was found that about two-thirds of the cellulose used was converted into carbon dioxide. The rest consisted mainly of cellulose mucilage. Again, no fatty acids could be detected. By abundant oxygenation, it was possible to achieve a 50 per cent decomposition of cellulose (used in the form of cotton wadding) in about 8 days. The mucilage is looked upon as oxycellulose of the nonreducing (acidic) type because on boiling with hydrochloric acid it yielded considerable amounts of furfural and uronic acids (14 per cent). From the hydrolysate of the mucilage, xylose could be isolated in the form of its osazone. Cellulose acetate was not attacked.

The intermediate formation of oxycellulose has been assumed by some previous investigators.[7] Likewise, Lüdtke[8] found that the acidity of cellulose (and of wood) increases under the action of certain fungi, i.e., those belonging to the *Polyporus* and *Merilius* types. This increase in acidity may be explained by the oxidation of potential reducing and hydroxyl to carboxyl groups.

The oxycellulose theory has been criticized by Norman and Bartholomew[9] and by Norman and Fuller[10] on the ground that such an oxidative attack presupposes the existence of an oxidative exo-enzyme system, which is highly improbable. They regard the oxycellulose of Warren and Walker and previous investigators rather as a microbial gum containing both uronic acid and pentose groups. Stanier[11] has added the argument that the soil *Cytophagas* attack and grow also at the expense of cellobiose and glucose and that there is thus every reason to consider that the actual mechanism consists of hydrolysis (or phosphorolysis) with the ultimate production of reducing sugars which enter the cell and there undergo oxidative decomposition whose sole products are carbon dioxide and cell material.

Nature seems to accomplish the bacterial decomposition of cellulose more frequently under anaerobic conditions.

The first successful attempt to isolate certain individual groups of

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[6] Walker and Warren, *Biochem. J.*, **32**, 31 (1938); see also *J. Soc. Chem. Ind.*, **53**, 452 (1934), and particularly Stanier's [*Bact. Revs.*, **6**, 143 (1942)] compilation and studies on the *Cythophaga* group.

[7] Kalnins, *Acta Univ. Latviensis*, Series I, **11**, 221 (1930); Simola, *Ann. Acad. Sci. Fennicae*, **34**, No. 6, 1931, both references being quoted by Norman, "The Biochemistry of Cellulose, etc.," Clarendon Press, Oxford (1937), p. 31.

[8] Lüdtke, *Biochem. Z.*, **285**, 89 (1936); see also Falck and Haag, *Ber.*, **60**, 225 (1927).

[9] Norman and Bartholomew, *Proc. Soil Sci. Soc. America*, **5**, 242 (1940).

[10] Norman and Fuller, *Advances in Enzymology*, **2**, 239 (1942).

[11] Stanier, *Bact. Revs.*, **6**, 176 (1942).

bacteria which operate under anaerobic conditions is ascribed to Omeliansky,[12] whose name marks a turning point in the history of the biological decomposition of cellulose. By using a technique of successive inoculations and different temperatures, Omeliansky succeeded in separating the cellulose-decomposing bacteria from river mud into certain groups. The results permitted the distinction of two types of decomposition, which differ in the nature of the gases produced. Whereas one type produces only methane, the other yields no methane but only hydrogen. In both cases, the main products of decomposition are carbon dioxide and fatty acids. With the methane type of decomposition, Omeliansky obtained about 6 per cent methane, 43 per cent carbon dioxide, and 50 per cent fatty acids (essentially butyric acid). The hydrogen type of decomposition yielded 4 per cent hydrogen, 21 per cent carbon dioxide, and 67 per cent fatty acids (consisting chiefly of acetic, formic, butyric, and valeric acids). The accumulation of acids decreases the rate of decomposition, and eventually the reaction ceases altogether.

Whereas these two cultures of mesophilic bacteria decompose cellulose at a very slow rate, weeks and months being required to transform even relatively small quantities of cellulose, certain *thermophilic* bacteria—those which operate best at temperatures between 55 and 65°—cause decomposition within a much shorter time. This observation, which seems to have been made first by MacFaden and Blaxall,[13] has been confirmed by numerous subsequent investigators.[14] The process of decomposition seems to be similar to the hydrogen type observed by Omeliansky, although Langwell and Hind [14] claimed that methane is also formed. Among the liquid products of decomposition are, in addition to those obtained by the activity of mesophilic bacteria, lactic acid and ethyl alcohol. The finding of Pringsheim [14] and of Kroulik,[14] namely, that butyric acid is formed only on the decomposition by mesophilic bacteria, could not be confirmed in more recent investigations.[15]

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[12] Omeliansky, *Compt. rend.*, **121**, 633 (1895); particularly *Zentr. Bakt.*, II, **8**, 193 (1902); 370, 703 (1903); **15**, 673 (1906); **36**, 339 (1912).

[13] MacFaden and Blaxall, *Trans. Jenner Inst. Prev. Medic.*, Series II, 162 (1899).

[14] See, for example, Pringsheim, *Z. physiol. Chem.*, **78**, 288 (1912); also *Zentr. Bakt.*, II, **38**, 513 (1913); Langwell and Hind, *J. Inst. Brewing*, **29**, 302 (1923); also Kroulik, *Zentr. Bakt.*, II, **36**, 339 (1913).

[15] Peterson, Scott, and Thompson, *Biochem. Z.*, **219**, 1 (1930); Tomoda, *J. Soc. Chem. Ind., Japan*, **35**, 534 (1932); **39**, 57 (1936); Tomoda and Yamaura, *ibid.*, **36**, 436 (1933).

Another type of decomposition of cellulose is produced by the activity of denitrifying bacteria. van Iterson[16] observed that certain bacteria decompose cellulose if they are allowed to act in the simultaneous presence of inorganic nitrate. Whereas the anaerobic bacteria, which cause the methane or the hydrogen type of decomposition, seem to derive their oxygen demand from the cellulose, the denitrifying bacteria obtain the oxygen from the nitrate. As a result, nitrogen is evolved, the nitrate being transformed to carbonate. Cellulose itself is decomposed under these conditions exclusively to carbon dioxide and water. After a time, the process is delayed by alkalinization of the system, owing to the formation of carbonate. No fatty acids seem to be produced.

It would appear that, from the agricultural point of view, the presence of such bacteria in the soil is undesirable, because they deprive it of necessary nitrogen. Koch[17] has shown that this undesirable effect may be counteracted by the simultaneous presence of nitrogen-binding bacteria, such as occur in dunghills. These bacteria, which draw their nitrogen demand for the synthesis of their protein constituents not from the nitrate but from the air, are capable of depressing the chemical reduction of the nitrate by the denitrifying bacteria. An essential result, however, seems to be some sort of symbiotic activity by which the nitrogen-binding bacteria, in decomposing the cellulose to sugar, furnish the denitrifying bacteria with a source of energy.[18]

Recently, our knowledge of the mechanism of biological nitrogen fixation has been definitely advanced through the application of physical-chemical techniques to investigations of the responsible enzyme system.[19]

The tendency of the cellulose-decomposing bacteria to symbiosis has been frequently observed.[20] On the other hand, some bacteria are known which decompose cellulose only in the presence of other available carbohydrates. It was found, for example, that *Mycobacterium agreste,* an organism not regarded as a cellulose decomposer, causes in cereal straw (which is rich in pentosans) a loss of about 14 per cent in 24 days, nearly half of which was shown by analysis to

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[16] van Iterson, *Zentr. Bakt.,* II, **11,** 689 (1904).

[17] Koch, *Zentr. Bakt.,* II, **27,** 1 (1910).

[18] See the compilation in Pringsheim, "Die Polysaccharide," Springer, Berlin (1931), 3rd ed., p. 142. See also Waksman and Skinner, *J. Bact.,* **12,** 57 (1926); Heukelekian and Waksman, *J. Biol. Chem.,* **66,** 323 (1925); Waksman and Gordon, *Soil Sci.,* **45,** 199 (1938); Gray, *Can. J. Research,* **C17,** 154 (1939). For a detailed account of the subject, see Waksman, "Principles of Soil Microbiology," Williams and Wilkens, Baltimore (1932).

[19] Wilson, "Biochemistry of Symbiotic Nitrogen Fixation," University of Wisconsin Press, Madison (1940); see also *Ergeb. Enzymforsch.,* **8,** 23 (1939); *J. Am. Chem. Soc.,* **58,** 1256 (1936); Burk and Burris, *Ann. Rev. Biochem.,* **10,** 587 (1941).

[20] See for example Clausen, *Zentr. Bakt.,* II, **84,** 20 (1931); Meyer, *ibid.,* II, **92,** 1 (1935).

be due to the decomposition of cellulose.[21] Similar observations were made with a number of fungi.[22]

The results of the decomposition of cellulose as reported by earlier investigators must be valued in the light of the fact that no method was available for preparing actually pure cultures of the organisms. It would appear that a solution of this important problem was found in 1926 by the discovery of the so-called "washing" method by Khouvine.[23] This technique makes use of the fact that the cellulose bacteria attach themselves firmly to the fiber, whereas other bacteria and organisms present are attached only loosely to the surface. Thus, on washing, the latter organisms are removed. Moreover, the cellulose-decomposing bacteria develop before the others become active, and their spores are more heat-resistant.

Somewhat later, Smieszko[24] developed a technique for preparing pure cultures which is likewise based upon the faster development rate and the greater heat-resistance of the cellulose-decomposing bacteria.

Because of the lack of pure cultures, the conclusions drawn from the earlier investigations cannot be generalized. In fact, the results of more recent investigations seem to make it necessary to revise the picture in various respects. Khouvine and other contemporary investigators[25] are inclined to believe that the number of cellulose-decomposing bacteria is much smaller than hitherto assumed and that all bacteria observed to decompose cellulose belong to only one or a few different forms. Moreover, pure cultures of the methane-decomposition type, such as those of *Bacterium cellulosae dissolvens*, which Khouvine isolated from feces,[26] as well as other forms of these cellulose bacteria yield no methane at all; nor has hydrogen always been observed (R. Meyer). Where methane is formed, its presence is explained by the occurrence of metabiotic phenomena (Clausen), or, quite differently, by chemical combination of carbon dioxide and hydrogen with the liberation of water and organic acids as intermediates.[27]

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[21] Shrikhande, *Biochem. J.*, **27**, 1563 (1933), quoted by Norman, *loc. cit.*

[22] Norman, *Ann. Applied Biol.*, **18**, 244 (1931).

[23] Khouvine, *Compt. rend. soc. biol.*, **94**, 1072 (1926); see also the compilation by Khouvine in "Actualités Scientifiques et Industrielles," No. 164, II, "Cellulose et Bactéries, Decomposition et Synthèse," Hermann et Cie., Paris (1934).

[24] Smieszko, *Zentr. Bakt.*, II, **88**, 403 (1933).

[25] Khouvine, *loc. cit.*; Pochon, *Compt. rend. acad. sci. U.R.S.S.*, **202**, 1538 (1936); R. Meyer, *Arch. Mikrobiol.*, **5**, 185 (1934).

[26] Khouvine, *Compt. rend. soc. biol.*, **94**, 1072 (1926).

[27] Symons and Buswell, *J. Am. Chem. Soc.*, **55**, 2028 (1933); see also Hess, "Die Chemie der Cellulose," p. 555.

The bacterial attack is accelerated in cellulosic materials with a larger surface, for example, cellulose regenerated from its solution in cuprammonium hydroxide, or cellulose fibers in finely divided form (ground to a powder, etc.).[28] Conversely, a reduced accessibility of the cellulose, for example, in lignified materials, is a governing factor. Indeed, some bacteria, which readily decompose cellulose, seem to be without effect on wood. This behavior has led to the belief that cellulose in wood is chemically combined with lignin and that this combination prevents the cellulose bacteria from attacking the cellulosic constituent. Olson, Peterson, and Sherrard [29] showed that the cellulose constituent in wood was attacked only after practically all the lignin had been removed (to less than 1 per cent of the original).

However, in contrast to these findings are those of Virtanen, Koistinen, and Kiuru,[30] which seem to show that the inability of certain bacteria to attack lignified materials is due merely to the *mechanical* inaccessibility of the cellulosic constituent. It was found that spruce wood which had been only partly cooked with calcium bisulfite liquor and had retained most of its lignin (24.4 against 28.3 per cent originally) could be decomposed to an extent of 35 per cent, and wood still containing 18.5 per cent lignin, to an extent of 80 per cent. These results seem to show that, although cooking facilitates the subsequent attack, the lignin need not be removed. Indeed, even uncooked wood was attacked to the extent of 20 per cent if it was offered in a ground state, and the degree of decomposition increased with the fineness of the disintegrated material.

The attack of cellulose by bacteria is facilitated also in cellulosic materials of a low degree of polymerization.[31]

THE DECOMPOSITION OF CELLULOSE BY FUNGI

Although a wide range of fungi has been found capable of attacking cellulose, little is known of the products of reaction. Evidently, carbon dioxide is the main product, but, in general, acids are not formed.

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[28] Walker and Warren, *Biochem. J.*, **32**, 31 (1938); see also Stanier's studies [*Bact. Revs.*, **6**, 143 (1942)] on the action of *Cythophaga* on bacterial cellulose produced by *Acetobacter xylinum* (pp. 36, 560).

[29] Olson, Peterson, and Sherrard, *Ind. Eng. Chem.*, **29**, 1026 (1937); see also Peterson and Smieszko, *Zentr. Bakt.*, II, **88**, 410 (1933), on the different behavior of wood pulps.

[30] Virtanen, Koistinen, and Kiuru, *Suomen Kemistilehti*, **B11**, 30 (1938), quoted from *Papier-Fabr.*, **38**, Abstracts, p. 22 (1940).

[31] Grassman, Stadler, and Binder, *Ann.*, **502**, 24 (1933).

The older literature[32] describes a number of *Aspergillus, Monilia,* and other types which decompose cellulose. van Iterson[33] counted about 35 different types out of a culture on filter paper which had been moistened with a weakly acid solution of monobasic potassium phosphate (KH_2PO_4) and exposed to air. The development of the spores is often accompanied by the formation of deeply colored pigments, a phenomenon which seems to be generally characteristic of the activity of fungi and also of certain cellulose-decomposing *Actinomycetes.*[34]

According to Pringsheim,[35] most of van Iterson's fungi are able to attack cellulose only to a limited extent. However, some of them, having a habitat similar to those which cause the well-known *dry rot,* attack cellulose profoundly and, under suitable conditions, destroy it completely within a few weeks.[36]

Unlike bacteria, the fungi develop their greatest activity in the forests, particularly on the foliage resting on the ground and on the dead trunks of the trees, as well as on the woodwork of buildings, etc.

Falck[37] distinguishes between two characteristic types of wood decomposition by fungi: the destructive and the corrosive. The *destructive* type, caused, for example, by *Merilius domesticus* and known as "dry rot" and "brown rot," grows chiefly on the woodwork of buildings, etc., and gradually destroys the cellulose, leaving the lignin unaffected. This attack is accompanied by a yellow to deep brown discoloration of the wood. The *corrosive* type, caused, for example, by *Polyporus annosis,* and known as "white rot," grows chiefly on living trees and first attacks the lignin and only in the later stage the cellulose. This stage, however, is not reached until almost all the lignin is removed, during which time the cellulose does not seem to have been attacked at all. No discoloration is observed; on the contrary, the color of the wood is brightened and the cellulose appears a pure white.

The removal from wood of the cellulose (and of the noncellulosic carbohydrates) by the action of *Merilius domesticus* (and possibly other species) seems to suggest a method by which lignin in its original form could be isolated from wood, in contrast to the preparations which are obtained by chemical methods and which seem to contain the lignin in a more or less modified form. No doubt, it would be of equal value if, by the reverse biological process, cellulose practically free of lignin could be isolated, for, as has been seen, no

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[32] Newcombe, *Ann. Botany,* **13**, 49 (1899); Wehmer, *Zentr. Bakt.,* II, **2**, 140 (1896); Went, *Jahrb. wiss. Botan.,* **36**, 611 (1901).

[33] van Iterson, *loc. cit.*

[34] Krainsky, *Zentr. Bakt.,* II, **41**, 649, 673 (1915).

[35] Pringsheim, "Polysaccharide," 3rd ed., p. 135.

[36] Schwalbe and af Ekenstam, *Cellulosechem.,* **8**, 13 (1927).

[37] Falck and Haag, *Ber.,* **60**, 225 (1927); see also Schwalbe and af Ekenstam, *loc. cit.;* Falck, *Cellulosechem.,* **11**, 198 (1930); Campbell, *Biochem. J.,* **24**, 1235 (1930); **25**, 2023 (1931); **26**, 1829 (1932).

chemical method seems to exist by which cellulose may be extracted in its original form and with its original chain length.

The two types of destruction discussed above (together with those which are caused by certain thermophilic bacteria and *Actinomycetes*[38]) take part in the formation of the humus of the soil.[39]

It is probable that the "humification" of lignin and cellulose in wood and cellulose waste is a step preparatory to the subsequent process of coalification which takes place under high temperature and pressure. The results of Berl and Körber[40] indicate that probably the activity of the cellulose-decomposing bacteria ceases when the transformation of cellulose into "cellulose humic acids" begins.[41]

THE NATURE AND THE INTERMEDIATE STAGES OF DECOMPOSITION

It is commonly believed that the decomposition of cellulose by bacteria and fungi is caused by enzymes which these micro-organisms secrete.[42] This belief is derived from Buchner's classical experiment, according to which the liquid pressed out of the organism has the same effect as the living organism itself. Buchner's technique has been applied to cellulose-decomposing organisms by various investigators. We may refer to the studies of Kohnstamm,[43] Went,[44] and van Iterson[45] with fungi and to those of van Senus[46] with bacteria. In all cases, decomposition was accomplished by the respective extracts.

The fact that van Iterson was able to identify glucose as an intermediate in a process which eventually leads to the formation of gases and acids suggested that the decomposition of cellulose by bacteria and fungi or their enzymes probably comprises two main reactions: (1) the cleavage of the cellulose chain into sugars and (2) the fer-

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[38] Falck, *Cellulosechem.*, **9**, 1 (1928).

[39] Waksman and Reusser, *Cellulosechem.*, **11**, 209 (1930).

[40] Berl and Körber, *J. Am. Chem. Soc.*, **60**, 1596 (1938).

[41] For an account of the decomposition of lignin and lignified plant material, see also Bray and Andrews, *Chem. & Met. Eng.*, **18**, 528 (1918); Bray, *Paper Trade J.*, **78**, No. 23, 58 (1924); Johnson and Lee, *ibid.*, **76**, No. 5, p. 53 (1923); Campbell, *loc. cit.*; Norman, *Science Progress*, **30**, 442 (1936); Schulze, Theden, and Vaupel, on x-ray analysis of wood under the action of fungi and bacteria, *Holz Roh- u. Werkstoff*, **1**, 75 (1937).

[42] For a detailed account of the subject of enzymes, the reader is referred to Waksman and Davidson, "Enzymes," Williams and Wilkens Co., Baltimore (1927), and to Tauber, "Enzyme Chemistry," John Wiley and Sons, New York (1937).

[43] Kohnstamm, *Beih. Bot. Zentr.*, **10**, 90 (1901).

[44] Went, *J. Botany*, **36**, 611 (1901).

[45] van Iterson, *loc. cit.*

[46] van Senus, "Koch's Jahresbericht über Gärungsorganismen und Enzyme" (1890), p. 136.

mentation of the sugars to gases and aliphatic acids, different enzymes being responsible for the breakdown in either reaction.

The method by which van Iterson identified glucose and which has been successfully used by subsequent investigators, is based upon the fact that certain antiseptics destroy the enzymes of fermentation without affecting the enzymes of hydrolysis.

Pringsheim[47] found iodoform most suitable for checking the fermentation phase and in this way identified not only glucose but also cellobiose among the reaction products. He interpreted these results to mean that, during the first phase of cellulose decomposition, two enzymes are operative, namely, cellulase, which degrades cellulose to cellobiose, and cellobiase, which cleaves the latter into glucose. Indeed, he succeeded in separating the activity of these two enzymes by raising the temperature of the reaction to a point at which the activity of the cellulase is destroyed (67°), whereas the cellobiase is still operative at this temperature. Under these conditions, only cellobiose was formed.

The accumulation of glucose as a result of checked fermentation has since been demonstrated by various investigators (e.g., by Woodman and Stewart,[48] who employed Pringsheim's method, and by Kalnins[49] and others, who used various modifications).

Grassmann and co-workers[50] separated the two enzymes (cellulase and cellobiase) by using Willstätter's[51] method of preferential adsorption with a commercial enzyme extract prepared from *Aspergillus orycae* and followed the saccharification of cellulose (regenerated from its solution in superconcentrated hydrochloric acid) by iodine titration. They were also able to establish, more firmly, the specific action of the two enzymes and thus to throw considerable light upon the rôle which they seem to play in the first phase of the biochemical decomposition of cellulose. It was found that the action of cellobiase is not confined to the cleavage of cellobiose, rather that it is capable of splitting also the oligosaccharides—i.e., cellotriose, cellotetraose, and cellohexaose. However, its activity ceases with cellodextrin. On the other hand, cellulase seems chiefly to hydrolyze fragments with a higher degree of polymerization. Whereas cellodextrin and even cellohexaose

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[47] Pringsheim, *Z. physiol. Chem.*, **78**, 266 (1912); see also Pringsheim, "Die Polysaccharide," 3rd ed., p. 152.

[48] Woodman and Stewart, *J. Agr. Sci.*, **18**, 713 (1928).

[49] Kalnins, *loc. cit.*

[50] Grassmann, Zechmeister, Tóth and Stadler, *Ann.*, **503**, 167 (1933); see also Grassmann, Stadler, and Bender, *ibid.*, **502**, 20 (1933).

[51] Willstätter, Kraut, and Erbacher, *Ber.*, **58**, 2458 (1925).

are still attacked, the action on cellotri- and cellotetraose is very limited, and cellobiose is not affected at all. Thus, the areas of the specific attack by the enzymes seem to overlap each other at the hexaose stage (molecular weight = 1000). To express this difference between the two enzymes more adequately, the former is termed "oligosaccharase" and the latter "polysaccharase." Polysaccharase thus splits the cellulose chain no further than to about the hexaose stage, after which further cleavage is brought about by the oligosaccharase. The activity of polysaccharase seems to be governed by the reducing power of the fragments formed. When the reducing power has increased to a certain point, the enzymatic activity ceases.[52]

It would certainly be of great interest if methods could be devised which would permit the isolation of the oligosaccharides from the products of enzymatic hydrolysis. The results obtained thus far seem to justify the conclusion that the biochemical decomposition of cellulose passes through the same stages as the hydrolysis with acids.

Little is known of the nature of the *second phase* of the biochemical decomposition of cellulose. Obviously, the view that this phase is also governed by the activity of specific enzymes appears to be supported by the fact that the fermentation of *glucose* itself may be directed so as to give different products of fermentation by using different organisms or enzymes. Whereas yeast or the yeast enzyme, zymase, converts glucose essentially into alcohol and carbon dioxide, other organisms and enzymes give rise to the formation of other products. A more recent example is the fermentation of glucose (as it is obtained from the hydrolysis of wood) by the anaerobic bacterium *Clostridium felsineum*, which results chiefly in the formation of butyl alcohol and some isopropyl alcohol.[53]

In recent years the industrial utilization of cellulose waste by biochemical processes has come into prominence.[54]

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[52] See also Stapp and Bortels, *Zentr. Bact.*, II, **90**, 28 (1934); Stanier, *loc. cit.*

[53] Sjolander, Langlykke, and Peterson, *Ind. Eng. Chem.*, **30**, 1251 (1938). For an account of the numerous complex reactions involved in the process of sugar fermentation, the reader is particularly referred to the work of Neuberg and his school [Neuberg and Kobel in Abderhalden's "Handb. Biochem. Arbeitsmethoden," IV, 1, p. 593 (1936)], and of Meyerhof, *Ergeb. Enzymforsch.*, **4**, 208 (1935); *Helv. Chim. Acta*, **18**, 1030 (1935); *Ergeb. Physiol.*, **39**, 10, 65 (1938). See also Raymond, in Gilman, "Organic Chemistry" (1943), 2nd ed., p. 1654; also Fontaine, Peterson, McCoy, Johnson, and Ritter, *J. Bact.*, **43**, 701 (1942).

[54] Langwell and Lynn, *J. Soc. Chem. Ind.*, **42**, 279 (1923); Sarles, Fred, and Peterson, *Zentr. Bakt.*, II, **85**, 401 (1932); May and Herrick, "Production of Organic Acids from Carbohydrates by Fermentation," *U. S. Dept. Agr. Circ.* **216**, Government Printing Office, Washington, D. C. (1932); Scott, Fred, and

The Digestion of Cellulose

Cellulose is digested by cattle and other ruminants and also by horses, but not by swine or human beings. Some insects and termites are also capable of digesting cellulose. It is generally believed that the digestion is accomplished by the symbiotic activity of various types of bacteria which live in the intestines of animals and that the reaction products are the same as observed *in vitro*. This has been demonstrated with bacteria isolated from the intestinal flora of various animals and, strangely enough, of men also. Thus, *Bacterium cellulosae dissolvens*,[55] operative in the human intestines, decomposes cellulose *in vitro* to carbon dioxide, hydrogen, ethyl alcohol, and acetic and butyric acids.[56] It is interesting to note that this organism does not attack sugars. Allowed to act in an impure culture, its efficiency in decomposing cellulose is five times as great as in a pure culture.

The ability to digest cellulose is apparently not confined to bacteria in the animalic intestines. It is believed that certain fungi also play an important part. A fungus, related to *Aspergillus niger*—i.e., *Aspergillus cellulosae*—has been isolated from the rumen of cattle and has been found to be a very efficient cellulose decomposer.[57]

Whether enzymes are responsible for, or take part in, the process of digestion of cellulose in the intestines of cellulose-digesting animals, insects, etc., seems to be still an open question. In certain cases, cellulose-decomposing enzymes have been found in the intestinal juices of snails and certain crustacea.[58] Glucose was found among the products of reaction. The intestinal juice of *Helix pomatia* proved particularly

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Peterson, *Ind. Eng. Chem.*, **22**, 731 (1930); Bernauer, "Gärungschemisches Praktikum," Springer, Berlin (1936); Fontaine, Peterson, and Ritter, paper presented before the Cellulose Division of the American Chemical Society at Cincinnati, Ohio (April, 1940); Prescott and Dunn, "Industrial Microbiology," McGraw-Hill Book Co., New York (1940); "Anaerobic Fermentation," Illinois State Water Survey, Bull. 32, Urbana, Illinois (the year of publication is not given).

[55] Khouvine, *Ann. inst. Pasteur,* **37**, 711 (1923); *Compt. rend. soc. biol.*, **94**, 1072 (1926); Khouvine, "Cellulose et Bactéries," p. 14.

[56] It is generally assumed that also in the intestines of the cellulose-digesting animals the first phase of the breakdown yields glucose and that the glucose is resorbed and utilized [Woodman and Stewart, *J. Agr. Sci.*, **18**, 743 (1928); Woodman, *Biol. Rev., Cambridge Phil. Soc.*, **5**, 273 (1930)].

[57] Ellenberger, *Z. physiol. Chem.*, **96**, 236 (1915); Hopffe, *Zentr. Bakt.*, II, **83**, 374, 531 (1919).

[58] Biedermann and Moritz, *Pflügers Arch. ges. Physiol.*, **73**, 219 (1898).

effective with filter paper [59] but cotton cellulose was affected only after pretreatment with zinc chloride or strong alkali or after reprecipitation from its solution in cuprammonium hydroxide.[60]

These older observations were confirmed a number of years later by Karrer and co-workers and extended in various directions. Among the enzymes contained in the intestinal juice of *Helix pomatia,* one was found which was capable of degrading lichenin [a carbohydrate which resembles cellulose and may be obtained from Iceland moss (*Cetraria Islandica*[61])] quantitatively to glucose.[62] It has been called lichenase. Whereas this enzyme was ineffective with cellulose, another enzyme, derived from the same source, converted cellulose—provided the cellulose was in its regenerated form (as viscose and cuprammonium rayon)—completely into glucose.[63] Cellulose in the form of medical cotton and even filter paper was more resistant, only 30 per cent of these types being converted into glucose, even under most suitable conditions.[64] As mentioned earlier (p. 116), this difference has been used to demonstrate the greater reactivity of cellulose in its mercerized form.

Termites,[65] the most dreaded wood-destroying insects, with few exceptions, digest cellulose only with the aid of certain intestinal flagellated *protozoa,* probably assisted by *bacteria* and *spirochaetes.* Cleveland[66] showed that the termites die from starvation after the *protozoa* have been killed (for example, by exposing the termites to oxygen gas), but that they continue to live if they are refaunated with *protozoa.*

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[59] Bierry and Giaja, *Compt. rend. soc. biol.,* **77,** 2 (1914); Billard, *ibid.,* **76,** 566 (1914).

[60] Seillère, *Compt. rend. soc. biol.,* **61,** 205 (1906); **63,** 515 (1907); **68,** 107, 989 (1910).

[61] Lichenin is regarded as consisting of unbranched β-glucopyranose chains, comprising 80–160 units [Carter and Record, *J. Chem. Soc.,* 664 (1939); Hess and Lauridsen, *Ber.,* **73,** 115 (1940)].

[62] Karrer, Joos, and Staub, *Helv. Chim. Acta,* **6,** 800 (1923); Karrer, Staub, Weinhagen, and Joos, *ibid.,* **7,** 144 (1924).

[63] Karrer, *Z. angew. Chem.,* **37,** 1003 (1924); Karrer and Illing, *Kolloid-Z.,* **36,** Supplement, 91 (1925).

[64] Karrer and Schubert, *Helv. Chim. Acta,* **9,** 893 (1926).

[65] Kofoid *et al.,* "Termites and Termite Control," Berkeley University Press (1934), 2nd ed.

[66] Cleveland, *Biol. Bull.,* **46,** 177 (1924); **54,** 231 (1928); see also Buchner, "Holznahrung und Symbiose," Springer, Berlin (1928).

CHAPTER XIV

THE CHAIN STRUCTURE OF CELLULOSE

In the preceding chapters, experimental evidence has been presented which leads us to visualize the individual cellulose molecule as a chain composed of glucose residues united by 1,4-glycosidic linkages of the β-type. The following is a brief review and summary of the various facts which have contributed to the establishment of this structure.[1]

A. FACTS SHOWING THAT CELLULOSE IS COMPOSED OF GLUCOSE RESIDUES

1. Upon hydrolysis with inorganic acids, cellulose is almost quantitatively converted into glucose (Ost, 1910; Monier-Williams, 1921; p. 520). The losses are due partly to the reversion and partly to the decomposition of the glucose under the influence of the strong acid.

2. Cellulose is completely converted into glucose also under the action of the enzyme from *Helix pomatia* (Karrer, 1925, p. 570).

3. The partial breakdown of cellulose—by interrupting the hydrolysis or acetolysis—yields cellobiose octaacetate (Skraup, 1901, p. 515). In the light of the probability that a chain consisting of glucose or cellobiose residues yields less than 100 per cent cellobiose, and considering the fact that losses due to further cleavage of the cellobiose thus formed are considerable, the maximum yield of 51 per cent actually obtained (Hess and Friese, 1927, p. 516) is in good agreement with the molecular chain concept (Freudenberg, 1921, p. 516).

4. Still earlier interruption of the hydrolysis or acetolysis of cellulose yields cellodextrin, now recognized as a mixture of oligosaccharides of an average chain length of about 30 glucose residues. Further

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[1] For a more detailed account of the historical development the reader is referred to Freudenberg, "Tannin, Cellulose, Lignin" (1933), p. 90; Haworth, "The Constitution of Sugars" (1929); Haworth, *J. Soc. Dyers Colourists* (1934), Jubilee Number, p. 16; Heuser, *Paper Trade J.*, Nov. 21, 28, December 5 (1935); also *Am. Dyestuff Reptr.*, **25**, 83, 116, 315 (1936); Davidson, *J. Textile Inst.*, **27**, P144 (1936); Haworth, *Ann. Rev. Biochem.*, Vol. 5, Stanford Univ. Press, California (1936); Heuser in Gilman, "Organic Chemistry" (1938), 1st ed., p. 1534; see also 2nd ed., p. 1701 (1943).

degradation yields the lower oligosaccharides: cellotriose [Bertrand and Benoit, 1923, Ost, 1926 (p. 513); Willstätter and Zechmeister, 1914 and 1929 (p. 513)]; cellotetraose (Willstätter and Zechmeister, 1914 and 1929); and cellohexaose. (Zechmeister and Tóth, 1931, p. 514). The physical properties of this series of degradation products, beginning with glucose and ending with cellohexaose, change progressively in the direction of cellulose.

5. The end product of the hydrolysis of the oligosaccharides and of cellobiose is glucose.

B. FACTS SHOWING THAT THE GLUCOSE RESIDUES ARE JOINED THROUGH 1,4-GLYCOSIDIC LINKAGES

1. Carefully isolated cellulose possesses practically no reducing power but develops this property on hydrolysis. This fact and the formation of cellobiose in a yield approaching that theoretically possible indicate that the type of linkage between individual glucose residues is of a glycosidic nature, i.e., it involves the potential aldehyde group of one glucose molecule and one of the hydroxyl groups of another.

2. Esterification and etherification lead to derivatives in which only 3 hydroxyl groups are substituted, provided substitution takes place without far-reaching degradation (Ost, 1900–1919, p. 228; Denham, 1913, p. 379).

3. Upon hydrolysis of trimethylcellulose, trimethylglucose is obtained in a yield of 80 to 91 per cent of the theoretical, the rest being dimethylglucose, the formation of which is due to incomplete methylation of the cellulose (Irvine and Hirst, 1923; Hess and Weltzien, 1925, p. 412).

4. The 3 methoxyl groups in trimethylglucose (resulting from the hydrolysis of trimethylcellulose) are in the 2-, 3-, and 6-positions (Denham, 1917; Haworth and Leitch, 1918; Irvine and Hirst, 1922; also Hess and co-workers, 1921, p. 417). The structure of the trimethylglucose is identical with that obtained on the hydrolysis of fully methylated cellobiose. On the assumption that the methoxyl groups in cellulose do not change their position on hydrolysis, the results show that the hydroxyl groups are also substituted in trimethylcellulose in the 2-, 3-, and 6-positions. Hence, in cellulose, these 3 hydroxyl groups are not involved in the glycosidic linkages. This elimination leaves either of the hydroxyl groups in the 4- and 5-positions for combination with the potential aldehyde group in the 1-position of another glucose residue.

5. Since the hydroxyl in the 5-position in glucose is involved in the amylene oxide ring (pyranose, 1,5-structure, Haworth and Hirst, 1925, 1926, p. 24), and since the molecular structure of cellobiose is that of a 1,5-glucosido-1,4-glucose (Haworth, 1926; Zemplén, 1926, p. 517), it is highly probable that the glucose residues in cellulose are united through 1,4-glycosidic linkages.

6. This probability is further supported by the fact that the glucose residues in the oligosaccharides (cellotriőse and cellotetraose) are also united through 1,4-glycosidic linkages. This is derived from the result of the cleavage of methylcellulose, of methylated cellodextrin and of methylated oligosaccharides with subsequent remethylation of the reaction products. Partial acetolysis of trimethylcellulose, followed by saponification of the acetyl groups and remethylation of the restored hydroxyl groups, leads to decamethylcellotriose and tridecamethylcellotetraose (Freudenberg *et al.*, *Ann.*, **494**, 41 (1932). Partial hydrolysis of fully methylated cellodextrin yields (besides tetramethylglucose) completely methylated cellotriose. The latter may be broken down and remethylated to give octamethylcellobiose and a one-third proportion of tetramethylglucose. Thus, four contiguous units originating from cellulose are found to be united in the same manner as cellobiose. Complete hydrolysis of the fully methylated cellotriose and cellotetraose yields mixtures of 2,3,6-trimethylglucose and 2,3,4,6-tetramethylglucose in the proportions required by three and four membered chains of glucose residues joined by 1,4 linkages (Haworth, Hirst, and Thomas, 1931, p. 514).

7. The simultaneous occurrence in cellulose of 1,5-glycosidic linkages as in disaccharides of the furanose type—for example, sucrose—is improbable, for such linkages undergo cleavage much more easily than would be expected from so resistant a compound as cellulose.

8. Likewise, the absence of isocellobiose among the products of restricted hydrolysis or acetolysis precludes the presence of other than 1,4-glycosidic linkages (Meyer and Mark, 1928, p. 519).

C. Facts which Classify the Individual Glucose Residues as Having the β-Configuration and the β-Configuration Only

1. Derivatives of cellobiose and cellotriose may be synthesized by allowing 2,3,6-trimethyl-β-methylglucoside to react with the chlorohydrins of fully methylated glucose and fully methylated cellobiose. Because these derivatives have been synthesized from components in which the mode of linkage is known, their glucose units are joined by

β-glycosidic linkages (Freudenberg, 1932, p. 514). It is probable, therefore, that the same mode of linkage is also operative in the other oligosaccharides and in cellulose itself.

2. The results of a study of the kinetics of the hydrolysis of cellulose with sulfuric acid eliminate the presence of other than β-linkages (Meyer, Hopff, and Mark, 1929; Kuhn, 1930, and Freudenberg *et al.*, 1932, p. 536). The presence of a substantial number of 1,4-α-linkages—as in maltose, which undergoes cleavage at a rate one and one-half times faster than cellobiose—would have revealed itself when the course of hydrolysis was being followed. Further, maltose would have to be among the products of hydrolysis, and it is not.

3. Likewise, the results of the evaluation of the optical rotation and the optical superposition of the free and the methylated oligosaccharides fail to supply any evidence for the presence of α-linkages (Freudenberg, 1932, p. 536).

The molecular chain structure of cellulose is also in agreement with the results of x-ray analysis. It will be recalled that the length of the identity period of the elementary cell in the direction of the fiber axis (*b*-axis, 10.3 Å) is identical with the length of two pyranose residues which are combined with each other as in cellobiose and connected with other glucose residues at their ends (Sponsler and Dore, 1926; Meyer and Mark, 1928; Haworth, 1926, pp. 24–27).

Whether the individual chains are open or united through their end groups is still a matter of discussion. Whereas degraded cellulose, by its reducing power and the formation of tetramethylglucose, reveals its chain molecules to be open, carefully isolated cellulose possesses practically no reducing power, nor does it yield tetramethylglucose, provided no degradation takes place during the process of methylation. The lack of such indications has led to the belief that the chains in native cellulose are either so long that the proportion of tetramethylglucose to trimethylglucose becomes too small to be detected or that the chains are united through their end groups (Hess and co-workers, 1937–1940, p. 415).

CHAPTER XV

THE MOLECULAR WEIGHT OF CELLULOSE

The question of how many glucose residues compose the chain molecules of cellulose as it exists in the plant is still unanswered, because methods for isolating cellulose without any degradation are still lacking. Further, even the shortened chain length of cellulose preparations as they result from the isolation by common methods is by no means a definite figure, for the various methods which have been suggested for ascertaining the chain length produce values which deviate from each other, in some cases considerably. No doubt seems to exist, however, about the postulation that the individual chain molecules of which cellulose is composed vary in length for, as has been seen, the cellulosic material isolated from the plant and subjected to various treatments or conversions may be separated into several fractions, each of which shows a chain length different from the original, whichever method of assay is employed. Hence, the chain length of any cellulose preparation represents an average figure and, as yet, it has not been possible to separate cellulose or cellulose derivatives into as many fractions as there are different chain lengths in the original aggregate. In other words, even portions resulting from a far-reaching fractionation, although more homogeneous than the original material, are still composed of chains of different length.

Not only from the scientific aspect, but also in view of the various commercial uses of cellulose and cellulose derivatives, a knowledge of the chain length distribution in a given preparation is of importance, for, as has been demonstrated by various examples, the chain length distribution influences the behavior and the usefulness of cellulose and cellulose derivatives to a considerable extent.

Provided that the chain molecules of a polymer are not branched by side chains, the average chain length of the aggregate equals its molecular weight. With cellulose derivatives, in which 1, 2, or 3 hydroxyl groups are substituted by other groups, the assumption may be made that the side chains thus formed comprise only a relatively small percentage of the total. This may be true when these groups are short or small. But when these groups become longer and heavier, as for example in the higher fatty acid esters, the side chains comprise a substantial portion of the total. Whether this fact enters the relationship between chain length and molecular weight depends, as will be seen in the following sections, upon the method selected for the determination of the average chain length.

The average chain length, i.e., the average number of glucose residues comprising the chains of the aggregate, is also expressed by the term "degree of polymerization." Conversely, the molecular weight, as it may be obtained directly or indirectly by physical methods, may be converted into the degree of polymerization by dividing the molecular weight by the weight of the single anhydroglucose unit (162).

The methods used for the determination of the average chain length of cellulose and its molecular weight may be divided into chemical and physical methods. The chemical methods will be considered first.

The Chemical Methods

The chemical methods are based upon the assumptions that the chains in cellulose isolated from its various sources are open and that the end groups of the terminating units may undergo certain reactions. The end-group determinations make use of the fact that the two end groups are different from the groups in the repeating glucose residues and represent certain percentages of the total chain. As the ratio of end groups to normal groups necessarily changes with the chain length, a small end-group content of a given preparation indicates a long average chain length and *vice versa.*

A glance at the structural formula of cellulose reveals the existence of two possibilities. One may determine either (1) the number of potential reducing groups of the chains in proportion to the number of the nonreducing groups or (2) the number of tetrahydroxy glucose units in proportion to the number of trihydroxy, i.e., normal glucose units.

End-Group Determinations Based Upon the Potential Reducing Group

The potential reducing groups in cellulose may be estimated either by the method which is used for the determination of the copper number or by allowing alkaline hypoiodite solution to act upon cellulose. In both cases, the potential aldehyde groups are oxidized to carboxyl groups, and the equivalent quantity of the agent consumed in this reaction is a measure of the reducing power of the cellulosic material under investigation.

In the *action of Fehling solution,* the quantity of cuprous oxide resulting from the reduction of cupric oxide is equivalent to the reducing power of the cellulosic material. Mark[1] has given the following example of the calculation.

On the assumption that each chain possesses only one reducing group, 1 molecule of cuprous oxide is formed per chain and n glucose residues produce $(0.8E/n) = p$ parts of Cu_2O, where E is the weight of the sample in grams and p is the copper number. Assuming a chain length of 150 glucose residues and that the reducing groups of all chains present in cellulose actually react, 100 grams of sample would give a value of $p = 0.533$ gram.[2] Inversely, if the copper number is known, the chain length, n, may be calculated from $n = (80/p)$.

On assumptions similar to those made when using the copper number, the chain length of the sample may be calculated from the *iodine number* (p. 530), using the expression $n = (123.6/I)$.

The chain lengths obtained by using these methods without special precautions are of doubtful value. The heterogeneous nature of the reactions makes it difficult to obtain accurate figures. Furthermore, it is possible that all the end groups do not possess reducing power because some of them may have been oxidized to carboxyl groups. Thus, a low copper or iodine number would indicate that the chains are longer than they actually are. On the other hand, the presence of even very small amounts of highly reducing portions (which no longer can be considered as cellulose chains) would influence the result in the opposite direction.[3] A similar influence must be expected from the presence of small amounts of reducing noncellulosic impurities. In all such cases, too high copper or iodine numbers and, hence, too short average chain lengths would result.[4]

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[1] Mark, "Physik und Chemie der Cellulose," p. 192.

[2] Davidson [*J. Textile Inst.,* **27,** P155 (1936)] has directed attention to the fact that the copper number of glucose corresponds to the consumption of from 2.5 to 4 atoms of oxygen per mole of glucose according to the composition of the alkaline copper solutions, whereas Mark based his calculations upon the consumption of one atom per reducing group of cellulose. The copper number thus calculated by Mark for a chain of 150 glucose units was probably too low.

[3] *Purified* hydro- and oxycellulose, which have been shown to possess a very small reducing power or practically none at all but in which, nevertheless, the chains are shortened considerably, would, of course, not lend themselves to the application of a method which is based upon the estimation of reducing groups.

[4] Weltzien and Nakamura, *Ann.,* **440,** 290 (1924); Hess, Dziengel, and Maass, *Ber.,* **63,** 1922 (1930); Hess and Sakurada, *ibid.,* **64,** 1183 (1931); see also Staudinger, "Die hochmolekularen organischen Verbindungen," p. 460; Mark, "Die

An important advance in the application of the copper number method was made by Richardson, Higginbotham, and Farrow.[5] They found that a certain "threshold amount" of a reducing substance has to be present before any precipitation of cuprous oxide occurs. If a certain small amount of glucose is added to the reagent, the reducing power of the test samples becomes constant. Glucose thus required 4.6 and maltose 5.2 atoms of oxygen per mole. When the modified method was applied to starch preparations, molecular weights from 500 to 1500 were obtained, i.e., values which are in good agreement with those derived from osmotic pressure data.

Neale[6] has applied this modification to bleached cotton yarn and cloth, as well as to a number of hydrocellulose preparations and to a sample of commercial cellophane. In all cases, good to fair agreement was observed with the molecular weights as derived from viscosity measurements, using Staudinger's equation. A comparison for the two bleached cotton samples is shown in Table 79.

TABLE 79

DEGREE OF POLYMERIZATION OF COTTON FROM END-GROUP COPPER NUMBER AND FROM VISCOSITY DETERMINATIONS

	Reducing Power * (Richardson *et al.*)	CHO Calculated. Millimoles per 100 Grams	D.P. from End-Group Assay	D.P. from Viscosity Measurements
Bleached cotton yarn	1.5	0.24	1400	1260
Bleached cotton cloth	3.4	0.54	740	720

* Grams of copper reduced by 100 grams of material.

Likewise, essential improvements have recently been incorporated in the iodine method. Its principal criticism, namely, that the consumption of iodine does not cease after a certain time but proceeds more or less indefinitely, seems to have been overcome. Harris and co-workers[7] showed that the side reactions which are responsible for the indefinite iodine consumption may be controlled and that, accordingly, a correction may be made. It was found that under such conditions the iodine number yields molecular weights which are of the

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Physik und Chemie der Cellulose," pp. 193 and 196, and Machemer, *Trans. Faraday Soc.*, **29**, 47 (1933).

[5] Richardson, Higginbotham, and Farrow, *J. Textile Inst.*, **27**, T131 (1936).

[6] Neale, *Chemistry & Industry*, **55**, 602 (1936).

[7] Martin, Smith, Whistler, and Harris, *Am. Dyestuff Reptr.*, **30**, 628 (1941); *J. Research Natl. Bur. Standards*, **27**, 449 (1941).

same order of magnitude as the values derived from viscosity data. This is shown in Table 80 which refers to carefully purified cotton [essentially according to the procedure described by Corey and Gray (p. 3)] and to a number of hydrocelluloses prepared therefrom by the action of hydrochloric acid of increasing concentration.

TABLE 80

COMPARISON OF MOLECULAR WEIGHTS CALCULATED FROM VISCOSITY MEASUREMENTS AND DERIVED FROM IODINE NUMBERS

Molecular weights from viscosities	307,000 *	224,000	187,000	133,000	99,000	73,000	60,000	58,000
Molecular weights from iodine numbers		189,000	189,000	160,000	121,000	97,000	70,000	65.000

* Purified cotton.

Since the iodine solution oxidizes aldehyde to carboxyl groups, an independent check of the corrected value obtained with iodine may be made by estimation of the carboxyl groups thus formed. For this purpose, titration with silver *o*-nitrophenolate (p. 586) appears to be most suitable. When this method was applied to the preparations mentioned above, a satisfactory check was obtained.

The *mercaptalation* method (pp. 531, 535) may be used for calculating the chain length from the sulfur content of the mercaptalated cellulose by using the expression:

$$\text{D.P.} = \frac{100 \times 25}{\%\,\text{S} \times C_6H_{10}O_5} - \frac{40}{\%\,\text{S}}$$

In the case of methylcellulose, the data obtained on hydrolysis and mercaptalation were subjected to a mathematical analysis (following the lines laid down by W. Kuhn, p. 536) to determine the degree of polymerization of the original cellulosic material. The original material was an acetone-soluble acetate which had been subjected to one methylation only, according to the method of Haworth and co-workers. The degree of polymerization thus calculated for the acetate was found to be 400 ± 70. It was in fair agreement with the degree of polymerization derived from viscosity measurements by using the Kraemer constant (see later), namely, 350 ± 35.

End-Group Assay Based Upon the Formation of Tetramethylglucose

The first step of the tetrahydroxy method by which the end group of the chain, carrying an additional free hydroxyl group, is determined and which was suggested by Haworth and Machemer (p. 416) consists in separating the mixture of tri- and tetramethylglucose (obtained on the hydrolysis of fully methylated cellulose) by distillation in a high vacuum. Subsequently, tetramethylglucose is purified and quantitatively estimated. The yield furnishes a means of calculating the average chain length. A methylcellulose preparation yielded 0.6 per cent tetramethylglucose. The calculation resulted in an average chain length ranging between 100 and 200 glucose units, corresponding to a molecular weight between 10,000 and 32,000.

This rather wide range is explained when it is considered that the cumbersome operations of separating the methyl sugars and of purifying the tetramethylglucose involve certain losses which, in view of the generally very low yield of tetramethyl sugar, might result in considerable error, even if the procedures are carried out with the greatest degree of perfection.[8] Moreover, the error may be expected to increase with increasing chain length of the cellulosic material being investigated.

In view of the confusion which entered into the early interpretation of the above values it cannot be stressed too much that these values must not be generalized. In other words, they refer solely to the preparation which was used by Haworth and Machemer and which was obtained by the exhaustive methylation of cellulose acetate. The acetate had been prepared from cotton linters with acetic anhydride in the presence of an acid catalyst. The cellulose constituent in the methylcellulose was thus considerably degraded. Therefore, Haworth and Machemer's values can by no means be ascribed to cellulose as it exists in the plant.

In the light of the reservations which must be made, it would appear doubtful whether the tetrahydroxy method will give even approximate values with less degraded cellulosic materials. The highest value more recently recorded by Haworth and co-workers[9] for cotton sliver, methylated fifteen times in a nitrogen atmosphere, was 700 glucose units, corresponding to a molecular weight of about 113,000. However, on the assumption that no degradation takes place on methylation in

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[8] Neumann and Hess, *Ber.*, **70**, 721 (1937); Hess and Grigorescu, *ibid.*, **73**, 499 (1940); see also Neumann, *ibid.*, **70**, 734 (1937).

[9] Haworth, Montonna, and Peat, *J. Chem. Soc.*, 1899 (1939).

a nitrogen atmosphere,[10] the molecular weight should have been higher. In fact, this material tested by the osmotic pressure method gave a value of about 250,000.[11] (Considering the nature of the raw material used, even this figure appears still too low, and the conclusion may be drawn that possibly not all the oxygen was removed from the system during the methylation operations.) Haworth and co-workers have pointed out that the amount of tetramethylglucose was too small to bring the chain length value of 700 within the limits of experimental error. "It is more accurate to state that tetramethylglucose was undoubtedly present, and the amount of it isolated corresponded to a minimum chain length of 700 glucose units."

Earlier (p. 417), attention was directed to the observation that in certain cases no tetramethylglucose was obtained, if methylation was carried out in a nitrogen atmosphere, whereas the viscosity and osmotic pressure data gave proof of the fact that the chains had been shortened. However, when the methylations had been carried out in air, subsequent procedures produced tetramethylglucose. Haworth has explained[12] this apparent paradox by the assumption that, in nitrogen, the end groups which must have been formed on the breakdown of the chains have become involved in some form of "recombination," so that no end groups remain. Since on methylation in air subsequent hydrolysis reveals the presence of end groups, air is said to operate to inhibit this recombination.

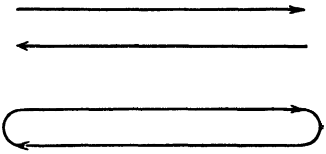

FIG. 111. Looping of cellulose chains. Haworth.

This concept would imply that pairs of chains align themselves so that the potential reducing groups of two chains point in opposite directions. Thus, recombination of the end groups may occur through glycosidic condensation between potential reducing groups and hydroxyl groups in opposite locations, so that a pair of chains could be linked together to form two loops at the ends. This is illustrated in Fig. 111.

Since it is hardly conceivable that the chains should align themselves under any circumstances, Haworth believes that the only reasonable assumption at present is that the chains are held together by some intermediate bonds at various positions along their length. In this way the chains would always be in a position which would permit the closure of their ends.

Under conditions which would shorten the chain length, a pair of chains may break at or near the cross linkages, and the ends of the shortened chains would loop up automatically as depicted in Fig. 112. This would explain the fact that Haworth and co-workers could isolate, from methylated cellulose,

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[10] Staudinger and Scholz, *Ber.*, **67**, 84 (1934); Staudinger and Reinecke, *Ann.*, **536**, 47 (1938).

[11] Haworth, Hirst, Owen, Peat, and Averill, *J. Chem. Soc.*, 1885 [1886, Table I], (1939).

[12] Haworth, *J. Soc. Chem. Ind.*, **58**, 917 (1939).

preparations with as low a molecular weight as 35,000, corresponding to some 190 methylated units, and yet these products revealed no end groups on hydrolysis. In experiments where air was present during the early stages of methylation, subsequent hydrolysis of the preparations thus obtained revealed the presence of end groups. In these cases, the molecular weight as calculated from viscosity or osmotic pressure data were found to be almost invariably lower than indicated by the end-group values. On the hypothesis of the existence of cross linkages, it is assumed that air may inhibit to some extent the closure of ends of pairs of chains. Thus, completely and partially closed loops would exist side by side, and this could account for the difference in the two values.

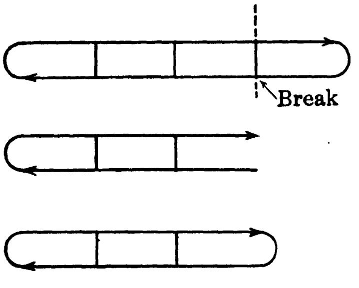

FIG. 112. Looped cellulose chains with cross linkages. Haworth.

The concept of the cross linkages would imply that they are pre-existent in cellulose itself. On this assumption, Haworth and his school visualize cellulose not as a formulation of single chains continuing without lateral primary valence bonds, but necessarily contemplate the existence of many such covalent bonds uniting the chains laterally, these bonds possibly occurring at intervals of 25–30 glucose units.

Looping bonds or "polymeric bonds" are also postulated by the Haworth school for other polysaccharides, such as starch,[13] glycogen, and xylan.

On the assumption that the cross linkages are operative between hydroxyl groups of opposite chains some hydroxyl groups would be blocked—for example, to methylation—unless the cross linkages were ruptured during this process. This possibility reminds us of the explanation which Karrer has offered to account for the observation that cellulose cannot be fully methylated unless hydrolysis has preceded, or takes place simultaneously, with methylation (p. 389).

According to Haworth, the cross linkages may be responsible also for the fact that cellulose is insoluble in water, because they would suppress the solubilizing effect of the hydroxyl groups in their accessible positions along the chains. In contrast, lichenin (p. 570), although having a molecular structure similar to that of cellulose, is soluble in water, possibly because cross linkages between individual chains are absent.[14]

It remains to be seen how the concept of the presence of cross linkages of the *primary* valence type can be brought into accord with the results of the studies of the kinetics of the degradation of cellulose which seems to preclude the presence of other but 1,4-glycosidic linkages of the β-type (p. 536).

The difference between chain length values calculated from end-group assay and those derived from physical methods[15] has led Haworth (probably only temporarily) to the belief that cellulose consists of chemical molecules of not more than about 200 glucose residues and that these chemical units are aggre-

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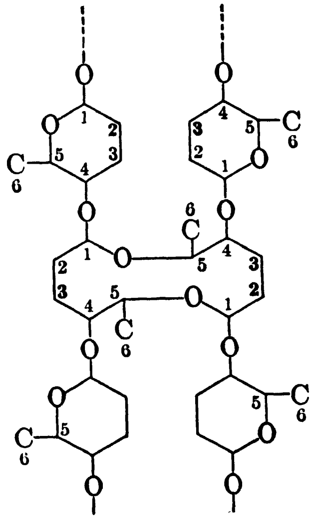
[13] Bawn, Hirst, and Young, *Trans. Faraday Soc.*, **36**, 880 (1940).

[14] See also Percival and Granichstädten, *Nature*, **150**, 549 (1942).

[15] Hirst, *J. Textile Inst.*, **27**, P167 (1936); Haworth, *loc. cit.*, pp. 922, 923; see also Staudinger and Husemann, *Ber.*, **70**, 1455 (1937).

gated to larger physical units, the size of which is measured by physical methods of molecular weight determination.[16] Such a concept of the structure of cellulose, which would seem to be a compromise with the earlier and much contested "small units" concept of Hess (p. 528), would imply that "disaggregation" could take place without chemical attack. However, this implication would conflict with the experimental evidence which shows that a substantial decrease in viscosity (indicating that "disaggregation" has occurred) is always accompanied by an unmistakable change in chemical properties.

Hess and Steurer[17] likewise observed considerable discrepancies between molecular weights derived from end-group determinations (tetramethoxy method) and those calculated from viscosity measurements (using Staudinger's equation), and have offered an explanation which also is based upon the assumption that the individual chains are laterally connected by cross linkages. It is suggested that during some stage of cellulose development, some of the pyranose rings of parallel aligned chains may open and thus furnish the bonds between chains in lateral direction at various places.[18] Obviously these bonds are believed to be of the primary valence type. The intermeshing bridges are shown in the formula below.



If such intermeshing bridges are maintained when cellulose is dissolved, the viscosity of the solution must necessarily be related to the unseparated units of chain molecules. The use of such viscosity data for the calculation of the molecular weight would yield a higher value than could be derived from end-group assay the result of which is not affected by cross linkages, and, hence, under-

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[16] Haworth, Hirst and Waine, *J. Chem. Soc.*, 1299 (1935); Haworth, *Chemistry & Industry,* **54**, 865 (1935); see also Davidson, *J. Textile Inst.*, **27**, P168 (1936).

[17] Hess and Steurer, *Ber.*, **73**, 669 (1940).

[18] *Vernetzungsbrücken* ("intermeshing" bridges)—cross linkages by which a net-like structure is produced. The quoted term is used in the abstract of Hess and Steurer's publication in *Chem. Abstr.*, **35**, 618 (1941).

goes no change whether or not the intermeshing bridges are ruptured when the methylcellulose is subjected to the hydrolysis step during which the normal oxygen bridges are cleaved.

It will be recalled that the presence of these two types of bonds was also postulated to explain the difference between the two sets of molecular weight data shown by methylcellulose which had been irradiated with ultraviolet light (p. 487). On the assumption that ultraviolet light waves rupture the cross linkages at a faster rate than the normal glycosidic linkages, the molecular weights derived from viscosity data would be lower for some time than those resulting from end-group assay.

Hess and Steurer believe that the existence of such intermeshing bridges may explain also the observation that, on spreading of cellulose derivatives upon the surface of a liquid (p. 607), homogeneous monomolecular layers are sometimes obtained, whereas in other cases the layers are not homogeneous and are thicker than would correspond to the thickness of one molecule. It is conceivable that a three-dimensional arrangement of chains, as a result of the existence of cross linkages, would prohibit the spreading out of the material in a homogeneous monolayer. Thus, the different behavior of cellulose preparations in this respect might furnish another method of distinguishing between the two types of linkages.

The relation of Hess and Steurer's suggestion to Haworth's cross linkage concept is quite obvious, although essential differences exist. It remains to be seen to what extent these differences may be reconciled, and, more important, how any cross linkage concept in which a second set of *primary* valences is involved can be brought into agreement with the results of the investigations of the kinetics of cellulose decomposition.

End-Group Assay Based Upon Carboxyl Content

The determination of the acidity of cellulose would furnish a means of chain length estimation only if the assumption could be made that the reducing end groups of *all* chains in the system are present as carboxyl groups and that none of the hydroxyl groups of the chains has undergone oxidation to carboxyl groups. Actually, however, these assumptions are not or only very seldom fulfilled. If only a limited number of the reducing groups were converted into carboxyl groups, the calculation would produce too high a figure for the average chain length. On the other hand, if hydroxyl groups have become oxidized (this may occur when cellulose is isolated and purified by processes which include, for example, a treatment with alkali in the presence of air), the carboxyl content would be high and the calculation of the chain length would result in too low a figure.

To illustrate this situation, the ideal case of the ω-hydroxydecanoic acid polymer may be invoked. This compound is an inner ester in which only one carboxyl group is attached to the end of the chain:

$$HO[-(CH_2)_9CO-O-]_n(CH_2)_9COOH$$

Although in a compound of this type, the acid hydrogen is only one part in about 25,000, no difficulties were encountered in determining the acidity by titration. The chain length calculated from the value thus obtained was in very good agreement with that derived from ultracentrifugal data.[19]

Nevertheless, various attempts have been made to calculate the average chain length of cellulosic materials of the most widely different types from their alkali-binding capacity. Whereas some investigators have recognized the deficiency of this technique, others have claimed that the values obtained are a true expression of the average chain length of cellulose in general. Strangely enough, in some cases good agreement between the degree of polymerization derived from the acidity values and that calculated from other methods was obtained.

Whereas, Lüdtke[20] has expressed the opinion that the carboxyl content resulting from the titration of cellulose in the presence of calcium acetate (p. 429) cannot be ascribed solely to carboxyl end groups, Neale,[21] using his method of titration in the presence of sodium chloride (p. 430) obtained carboxyl contents, which, converted into chain length, agreed quite well with values derived from viscosity measurements (using Staudinger's equation).

It would appear that no significance can be attached to the chain length value which Schmidt[22] calculated from the results of the conductometric titration of the acidity of cellulose preparations (p. 430). It is claimed that the carboxyl content is a constant figure (0.28 per cent CO_2, calculated on the weight of cellulose), regardless of the source of the cellulosic material. Accordingly, cellulose would always possess a chain length of 96 glucose residues. This constancy is, of course, highly improbable. Incidentally, Neale and Stringfellow were unable to confirm Schmidt's results.[23]

Another attempt to calculate the average chain length of unmodified cotton from its carboxylic end group content was recently made by Sookne and Harris.[24] Most of the cationic ash is associated with the pectic substance (p. 434). However, after the pectin has been

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[19] Carothers and van Natta, *J. Am. Chem. Soc.*, **55**, 4714 (1933).

[20] Lüdtke, *Biochem. Z.*, **285**, 78, 94 (1936); *Trans. Faraday Soc.*, **33**, 881 (1937); see also Rabinow and Heymann, *J. Phys. Chem.*, **45**, 1154 (1941).

[21] Neale, *Chemistry & Industry*, **55**, 602 (1936).

[22] Schmidt and co-workers, *Cellulosechem.*, **13**, 129 (1932); *Ber.*, **67**, 2037 (1934); **68**, 542 (1935); **69**, 366 (1936); **70**, 2345 (1937).

[23] Neale and Stringfellow, *loc. cit.*, p. 888; see also Haworth, Hirst, and Oliver, *J. Chem. Soc.*, 1917 (1934).

[24] Sookne and Harris, *J. Research Natl. Bur. Standards*, **25**, 47 (1940); *Textile Research*, **10**, 405 (1940).

removed, there remains a small acid-binding capacity; this is assumed to be equivalent to the carboxyl end groups of the cellulose chains.

As an example, it was found that the maximum quantity of acid bound by a sample of raw cotton (from which only the wax had been removed by extraction with organic solvents) amounted to 0.066 milliequivalent per gram. The pectin content, determined directly and indirectly, accounted for 0.056 M-eq./g. The difference between these two values, 0.010 M-eq./g.,[25] is ascribed to the carboxylic end groups of the cellulose constituent. From this figure, an average chain length of 600 glucose residues, corresponding to a molecular weight of 100,000, was derived.

The value of 0.010 M-eq./g. was confirmed by determining the silver- and calcium-binding capacity of cotton which had been entirely freed of pectin and of cations by electrodialysis.[26] Silver acetate and silver *o*-nitrophenolate and calcium acetate (i.e., salts of weak acids) were used. The samples were immersed in the aqueous solutions of the salts, and the quantities of silver and calcium bound were determined by titration and by electrodialysis. The reactions are exchange reactions. The combination of the ash-free fiber with a silver salt may be expressed by the following equation:

$$\mathrm{RCOOH} + \mathrm{AgA} \rightarrow \mathrm{RCOOAg} + \mathrm{HA}$$

where COOH represents the acidic groups of the fiber, and AgA the silver salt. The base-binding capacity of the ash-free and depectinized cotton was the same for both types of salts. This identity of the two values, when monovalent and divalent ions were used, is a strong indication that the binding of these ions actually results from an acid-base reaction, as shown in the equation, and not from some indefinite absorption process. This conclusion was substantiated by the result of the esterification of the acidic groups in ash-free and depectinized cotton with diazomethane, which reduced the base-binding capacity of the fiber to almost zero.

Another check[27] on the value of 0.010 M-eq./g. was obtained by determining the hydrogen-ion equivalence of the cationic ash of the fiber, using a slight modification of an electrodialytic procedure which had been suggested for the determination of total cations and chloride in blood. The values found for pectin-free (and dewaxed) cotton were 0.0095 and 0.0099 M-eq./g.

Nevertheless, the chain length of about 600 glucose units represents only about one-fifth of that which similar cellulosic materials may be expected to show when subjected to other methods.

Very recently, Husemann and Weber[28] have made it seem probable that under certain specified conditions only aldehydic end groups in

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[25] Sookne and Harris, *J. Research Natl. Bur. Standards*, **26**, 205 (1941).

[26] Sookne and Harris, *J. Research Natl. Bur. Standards*, **26**, 205 (1941).

[27] Sookne, Fugitt, and Steinhardt, *J. Research Natl. Bur. Standards*, **25**, 61 (1940); *Textile Research*, **10**, 380 (1940).

[28] Husemann and Weber, *J. prakt. Chem.*, **161**, 1 (1942).

cellulose of medium D.P. may be oxidized to carboxyl groups. Indeed, the D.P. based upon the thus introduced carboxyl groups agreed fairly well with those derived from viscosity and osmotic pressure measurements.

THE PHYSICAL METHODS

Almost all physical methods for the determination of the molecular weight of chemical compounds were developed on true solutions, i.e., those in which the substance is in a state of molecular dispersion. Attempts to apply the classical methods directly to solutions in which, as with cellulose or its derivatives, the substance is merely in a state of colloidal dispersion or in a state of transition from colloidal to molecular dispersion, have, for obvious reasons, not been very successful. Even at very low concentrations, at which the ultimate degree of dispersion might have been achieved, the possibilities of determining the molecular weight of the single molecules are limited because of the tendency of such molecules to associate to larger conglomerations, a tendency which potentially increases with the length of the molecule. The difficulties are further enhanced by the influence of the solvent. Not only does the degree of dispersion depend upon the type of solvent chosen, but the solvent may also undergo interaction with the solute.

Osmotic Pressure Measurements

Because the solubility of cellulose itself is limited to those solvents which prohibit the use of the classical methods, osmotic pressure measurements can be carried out only on cellulose derivatives. In the earlier attempts to make use of this technique[29] the extrapolation to cellulose itself was, in most cases, objectionable because not enough attention was paid to the prerequisite of such a procedure, namely, that the cellulose suffers no degradation on conversion into its derivative.

Before the osmotic pressure method for the determination of the molecular weight of cellulose derivatives had come into general use, the *freezing point method* was most commonly employed. The confidence which investigators placed in this method is probably explained by the fact that it had produced

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[29] Bumcke and Wolffenstein, *Ber.*, **32**, 2493 (1899); Nastukoff, *Ber.*, **33**, 2237 (1900); Hess and Wittelsbach, *Ber.*, **54**, 3232 (1921); Hess, Weltzien, and Messmer, *Ann.*, **435**, 79 (1924); Heuser and Jayme, *Ber.*, **56**, 1242 (1923); Heuser and Hiemer, *Cellulosechem.*, **6**, 125 (1925); *Z. Elektrochem.*, **31**, 498 (1925); see also Hess, *ibid.*, **31**, 613 (1925); Heuser and Hiemer, *ibid.*, **32**, 47 (1926).

quite reliable results with other high polymers, such as polyoxymethylenes[30] and polyethylene oxides.[31] However, its application to cellulose derivatives yielded results which lacked probability and which, in fact, were later found to be irreconcilable with other experimental evidence.

In recent years, considerable efforts have been made to overcome the numerous difficulties which originally made the osmotic pressure method unsuitable for obtaining reliable values. It appears that these difficulties have now been largely eliminated and that this method may be applied to cellulose derivatives with a considerable measure of reliability.[32] In addition, methods have been developed which, as has been seen, permit the conversion of cellulose into certain derivatives practically without degradation, so that today the extrapolation from the derivative to the original cellulosic material stands on a safer basis.

A modification of the osmotic pressure method, i.e., the *isothermic distillation*,[33] was used by Ulmann[34] for the determination of the molecular weight of cellodextrin acetate,[35] of Hess and co-workers' "crystalline" cellulose triacetate,[36] and of a commercial cellulose acetate sample,[37] i.e., cellulose degradation products of very low and low degrees of polymerization. Since the interpretation of the results of these investigations and the conclusions drawn therefrom as to the molecular weight of cellulose are in disagreement with other experimental facts, they have met with sharp criticism.[38]

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[30] Staudinger and Lüthy, *Helv. Chim. Acta,* **8,** 41 (1924).

[31] Staudinger and Lohmann, in Staudinger, "Die hochmolekularen organischen Verbindungen," p. 287.

[32] For an account of the various improvements of the osmotic pressure method which have led to its present state of perfection, the reader is referred to the following publications: Duclaux and Wollman, *Compt. rend.,* **152,** 1580 (1911); *Bull. soc. chim.,* **27,** 414 (1920); Duclaux and Nodzu, *Rev. Gén. Colloïdes,* **7,** 385 (1929); Büchner and Steudel, *Proc. Akad. Wetensch. Amsterdam,* **36,** 671 (1933); Büchner and Samwel, *Proc. Akad. Wetensch. Amsterdam,* **33,** 749 (1930); Kraemer and Lansing, *J. Phys. Chem.,* **30,** 157 (1935); Dobry, *Kolloid-Z.,* **80,** 190 (1937); Duclaux, "Pression osmotique (Leçons de chimie physique appliqué à la biologie)," Hermann and Cie., Paris (1937); Haller, *Kolloid-Z.,* **78,** 341 (1937); Ostwald, *ibid.,* **80,** 195 (1937); Boissonas and Meyer, *Helv. Chim. Acta,* **20,** 783 (1937); Meyer and Wolff, *Kolloid-Z.,* **89,** 196 (1939); Carter and Record, *J. Chem. Soc.,* 660, 664 (1939); Montonna and Jilk, *J. Phys. Chem.,* **45,** 1374 (1941); Schulz, *J. prakt. Chem.,* **161,** 147 (1942).

[33] Frazer and Patrick, *Z. physik. Chem.,* **A130,** 691 (1927); Townsend, *J. Am. Chem. Soc.,* **50,** 2958 (1928); Frazer, *Colloid Symposium Monograph VII,* 259 (1930).

[34] Ulmann, "Molekülgrössen-Bestimmungen hochpolymerer Naturstoffe," Steinkopf, Dresden (1936), p. 135.

[35] Hess and Ulmann, *Ann.,* **504,** 81 (1933); *Ber.,* **67,** 2131 (1934).

[36] Ulmann, *Z. Elektrochem.,* **40,** 451 (1934).

[37] Ulmann, *Ber.,* **68,** 134, 1217 (1935).

[38] Kraemer and Lansing, *J. Phys. Chem.,* **39,** 157 (1935).

STAUDINGER'S VISCOSITY METHOD

Staudinger[39] has developed the following equation for the relationship between the viscosity of cellulose in solution and its average molecular weight:

$$\frac{\eta_{sp}}{c} = K_m \times M \qquad [1]$$

in which η_{sp} is the specific viscosity (i.e., the viscosity increase over that of the solvent); c is the concentration; M is the molecular weight; and K_m is a constant. Thus, if the value of the constant is known, the molecular weight of a given cellulosic material may be calculated simply from its specific viscosity.

The K_m

To establish the value for K_m in equation 1 for general use, the molecular weight of the cellulosic material has to be determined in some way. For cellulose derivatives, the osmotic pressure method may be used. The specific viscosity of the derivative is determined preferably in the same solvent. From the molecular weight and the specific viscosity, K_m may be calculated from the expression

$$K_m = \frac{\eta_{sp}}{cM} \qquad [2]$$

With the K_m thus established for one type of cellulose derivatives, for example, cellulose acetates, one may calculate the molecular weight of any acetate simply by inserting the specific viscosity into the equation:

$$M = \frac{\eta_{sp}}{cK_m} \qquad [3]$$

The same principle is employed if K_m for cellulose itself is to be determined. In this case, cellulose may be converted into a derivative under precautions which eliminate degradation, and the molecular weight of the derivative may be determined, for example, by the

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[39] Staudinger, "Die hochmolekularen organischen Verbindungen," Springer, Berlin (1932), p. 451.

osmotic pressure method. The result thus obtained is extrapolated to cellulose itself. The specific viscosity, however, may be directly determined on cellulose dissolved in cuprammonium solution.

To prove that the molecular weight decreases with decreasing viscosity in a linear (or approximately linear) function, Staudinger prepared homologous series of cellulose derivatives ("polyhomologous series") by gradually intensifying the conditions of degradation. For example, a polyhomologous series of cellulose acetates may be prepared by subjecting cellulose to acetylation at increasing temperatures or to acetylation mixtures of increasing sulfuric acid content, or to a combination of both conditions.

The data required for establishing the average value of K_m of the polyhomologous series are then obtained from the individual members of the series as described above and are used for the calculation according to equation 2.

For the determination of the molecular weight of a polyhomologous series of cellulose acetates, Staudinger, in his earlier work, used the freezing point method[40] and, in some cases, also Bergmann and Machemer's iodine end-group method[41] and obtained K_m values of 11.6×10^{-4} and 10.3×10^{-4}.

Provided the chain length of the cellulose constituent does not change on regeneration from the acetates, it is possible to calculate the molecular weight of the regenerated cellulose preparations from their specific viscosities. The viscosities are determined in cuprammonium solution. The molecular weight of the regenerated cellulose may then be calculated by using the following equation:

$$M_c = \frac{M_{\mathrm{Ac}}}{288} \times 162 \qquad [4]$$

in which M_c is the molecular weight to be found; M_{Ac} is the average molecular weight of the acetates as determined directly; and 288 and 162 are the molecular weights of the glucose acetate residue, $[C_6H_7O_2(OCOCH_3)_3]$, and the glucose residue, $(C_6H_{10}O_5)$, respectively.

Finally, both the viscosity values in cuprammonium solution and the molecular weights of the regenerated cellulose preparations calculated therefrom may be used for checking the K_m, if

$$M_c = \frac{M_{\mathrm{Ac}}}{288} \times 162$$

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[40] Staudinger and Freudenberger, *Ber.*, **63**, 316 (1930).

[41] Staudinger, "Die hochmolekularen organischen Verbindungen," p. 485.

is inserted into

$$K_m = \frac{\eta_{sp}}{c \times M_c} \qquad [5]$$

In this way, an average K_m of 10.2×10^{-4} was obtained.

By using the value of 10×10^{-4} for K_m in equation 1, the average molecular weights of a number of cellulosic materials were calculated from specific viscosities measured in cuprammonium hydroxide solution. Table 81 is an excerpt from Staudinger and Schweitzer's results.[42] It also gives the average degrees of polymerization as well as the average length of the chain molecules in Ångström units.

TABLE 81

MOLECULAR WEIGHTS OF VARIOUS CELLULOSIC MATERIALS (VISCOSITY METHOD)

Materials	Molecular Weight	Degree of Polymerization (D.P.)	Chain Length, Å
Purified cotton I	120,000	750	3900
Purified cotton II	112,000	690	3680
Sulfite wood pulp I	51,000	310	1610
Sulfite wood pulp II	38,000	230	1200
Cuprammonium rayon I	22,000	140	730
Cuprammonium rayon II	20,000	120	620

As may be seen from equation 1, the reliability of K_m depends upon the accuracy of the direct molecular weight determination. If the latter is not correct, the K_m value is also incorrect, and becomes doubtful as a means of merely calculating the molecular weight for cellulose derivatives and for cellulose itself from viscosity data, i.e., without checking it.

In later investigations on cellulose acetates,[43] the osmotic pressure method was used for determining the molecular weight of the acetates dissolved in chloroform. The specific viscosities were determined in *m*-cresol. From the viscosities and the molecular weights, K_m was calculated and found to be 7.4×10^{-4} for a commercial cellulose acetate (2.5 acetyl groups per glucose unit) of a low degree of polymerization (approximately 80) and 9.9×10^{-4} for a less degraded product (D.P. 330). Still other K_m values were found for triacetates of higher degrees of polymerization.

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[42] Staudinger and Schweitzer, *Ber.*, **63**, 2325, 3132 (1930).

[43] Staudinger and Daumiller, *Ann.*, **529**, 246 (1937); see also a previous publication by Staudinger and Scholz, *Ber.*, **67**, 84 (1934).

By using an equation suggested by Schulz[44] for the conversion of the osmotic pressure data into molecular weights, a K_m value of 5.3×10^{-4} was obtained.

Because chloroform was suitable only if the degree of polymerization of the triacetates was not higher than 400–500, acetates having a degree of polymerization of up to 780 (corresponding to a molecular weight of 225,000) were dissolved in *m*-cresol. The data obtained with such acetates produced a K_m of 6.3×10^{-4}.

Earlier measurements had shown that the viscosity of cellulose in cuprammonium hydroxide solution was very nearly the same as that of a triacetate prepared therefrom (in a way which precludes degradation) and dissolved in *m*-cresol, provided the concentration was the same in both cases.[45] However, more exact investigations[46] revealed that the viscosity of cellulose in cuprammonium solution was about 20 per cent lower than that of the triacetate in *m*-cresol. Consequently, the K_m value was also assumed to be 20 per cent lower, resulting in a K_m of 8×10^{-4}.

Finally, when it was considered that the K_m for the high molecular triacetates, calculated from osmotic pressure measurements, was found to be 6.3×10^{-4} (see above), the value of 8×10^{-4} was corrected accordingly. On the assumption that the ratio of the specific viscosities of cellulose in cuprammonium solution and of cellulose triacetate in *m*-cresol equals the ratio of the K_m values for cellulose and for cellulose triacetate, the latter being 6.3×10^{-4}, the former was found to be 5×10^{-4}.

A check on this result was made by regenerating the cellulose from the triacetate (without degradation) and determining the viscosity of the regenerated cellulose in cuprammonium hydroxide solution. Again, the viscosity of the regenerated cellulose preparations in cuprammonium hydroxide was found to be 20 per cent lower than that of the acetates dissolved in *m*-cresol, so that the value of 5×10^{-4} for cellulose remained unchanged.

Staudinger considers this value to be correct and, hence, all molecular weight values which previously had been obtained by using a K_m value of 10×10^{-4} had to be doubled. Using the value 5×10^{-4}, the molecular weights of a number of commercial cellulosic materials and derivatives were calculated from viscosity measurements. The values

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[44] Schulz, *Z. physik. Chem.*, **A158**, 237 (1932); **159**, 374 (1932); **160**, 409 (1932); **176**, 317 (1936).

[45] Staudinger and Schweitzer, *Ber.*, **63**, 3122 (1930).

[46] Staudinger and Eilers, *Ber.*, **68**, 1611 (1935).

thus found were 324,000 for native cellulose, 38,000 to 112,000 for cellulose triacetate, and 54,000 to 410,000 for cellulose nitrates.[47] Later determinations yielded still higher values for native cellulose, for example, 480,000.[48] More recently, even this value has been surpassed. Jurisch [49] determined the molecular weight of cotton taken from the unopened boll and obtained the value 810,000 (corresponding to a D.P. of 5000). This result seems to justify the conclusion that cotton cellulose is degraded as soon as the boll opens, obviously by the combined action of air, heat, and light.

K_m values were also determined for nitrates, for methyl- and ethylcellulose,[50] and for butyl- and benzylcellulose.[51]

Staudinger's "viscosity law" is based upon a number of suppositions. Unfortunately, they are seldom strictly fulfilled. One of the basic assumptions made by Staudinger is that the solutions of cellulose and cellulose derivatives contain these materials in the form of single molecules. The justification for making this assumption has been frequently questioned.[52] Moreover, even at a very low cellulose concentration, the possibility exists that the molecules reassociate to larger complexes.

According to Meyer,[53] the chain molecules touch each other if the cellulose or cellulose derivative concentration is above 0.1 per cent. At this concentration, the system is comparable with a "mush" rather than with a solution. Increasing difficulties in defending Staudinger's assumption also arise in the light of the possibility that the individual chains are laterally united by cross linkages of primary valence nature (see above).

Another prerequisite, namely, that the viscosity measurements are independent of the nature of the solvent and that the phenomenon of

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[47] Staudinger and Schulz, *Ber.*, **68**, 2320 (1935); Schulz, *Z. physik. Chem.*, **A176**, 323 (1936); Staudinger, *Angew. Chem.*, **49**, 804 (1936); Staudinger and Daumiller, *Ann.*, **529**, 251 (1937).

[48] Staudinger and Mohr, *Ber.*, **70**, 2296 [2309] (1937).

[49] Jurisch, *Chem.-Ztg.*, **64**, 270 (1940).

[50] Staudinger and Reinecke, *Ann.*, **535**, 47, 174 (1938).

[51] Staudinger and Reinecke, *Ber.*, **71**, 2521 (1938).

[52] McBain and Scott, *Ind. Eng. Chem.*, **28**, 470 (1936); McBain and Laing-McBain, *J. Am. Chem. Soc.*, **59**, 342 (1937); Liepatoff and Preobragenskaja, *Kolloid-Z.*, **68**, 324 (1934); see also Mark, "Physik und Chemie der Cellulose," p. 89; Lieser and Swiatowski, *Ann.*, **538**, 110 (1939), and Staudinger's reply [*Ber.*, **70**, 2514 (1937)] to earlier criticism.

[53] Kurt H. Meyer, "Die hochpolymeren Verbindungen," Akad. Verlags-Ges., Leipzig (1940), p. 243; English translation by Picken, Interscience Publishers, Inc., New York (1942); see also Kratky, *Angew. Chem.*, **53**, 153, 155 (1940).

solvation does not substantially interfere with the viscosity,[54] is by no means always fulfilled, although such influences may be greatly diminished in the case of osmotic pressure measurements.[55] Moreover, reliable viscosity data are only to be expected if the behavior of the solution does not deviate substantially from the Hagen-Poiseuille law and if the increase in viscosity with concentration occurs proportionally—in other words, if the expression η_{sp}/c_g is independent of a concentration chosen at random.[56] Finally, the viscosity of the solution must not change with the temperature.

However, even at very low concentration, the tendency of colloids (such as cellulose and its derivatives) to deviate from the laws which govern the behavior of crystalloids, in many cases, cannot be entirely eliminated.[57] As mentioned before, this undesirable tendency increases with the chain length, although, within the range of very long chains, it has a less pronounced effect upon osmotic pressure measurements.[58] Nevertheless, the final result will be that the viscosity-molecular weight relationship is not exactly linear throughout, but only within a rather limited range.[59]

Another essential assumption of Staudinger's is that the chain molecules represent stretched-out, rod-shaped units and that these "thread molecules" retain their shape in solution. This assumption

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[54] Staudinger, *Z. physik. Chem.*, **A171**, 129 (1934); Dobry, *J. Chem. Phys.*, **31**, 568 (1934); **32**, 50 (1935); Staudinger and Sorkin, *Ber.*, **70**, 2000 (1937); Staudinger and Reinecke, *Ber.*, **71**, 2524 (1938); Rogowin and Schlachover, *Angew. Chem.*, **48**, 647 (1935); see, however, Dobry, *Kolloid-Z.*, **81**, 192 (1937); also Lee and Sakurada, *ibid.*, **82**, 194 (1938).

[55] Dobry, *Kolloid-Z.*, **81**, 190 (1937).

[56] In this connection, an interesting observation by Zart [*Kunstseide*, **17**, 38 (1935)] may be mentioned, according to which the viscosity of a cellulose preparation of a molecular weight of 1000 may be increased to double its value by adding to its solution only 1 per cent of a cellulose preparation of a molecular weight of 100,000.

[57] Sakurada, *Ber.*, **63**, 2027 (1930); Sakurada and Hess, *Ber.*, **64**, 1174 (1931); **64**, 1183 (1931); Staudinger, *Ber.*, **64**, 1688 (1931); Staudinger and Husemann, *Ann.*, **530**, 1 (1937); Staudinger and Sorkin, *Ber.*, **20**, 2011 (1937).

[58] Guth and Mark, *Ergeb. exakt. Naturw.*, **12**, 115 (1933); Kraemer and van Natta, *J. Phys. Chem.*, **36**, 3175 (1932); Meyer and van der Wyk, *Z. Elektrochem.*, **40**, 446 (1934); Danes, *Kolloid-Z.*, **68**, 110 (1934); Staudinger, *Ber.*, **67**, 92, 1159 (1934); *Z. Elektrochem.*, **40**, 434 (1934).

[59] Ostwald and Riedel, *Kolloid-Z.*, **70**, 73 (1935); **81**, 198 (1937); Meyer and Wolff, *ibid.*, **89**, 200 (1939); Fordyce and Hibbert, *J. Am. Chem. Soc.*, **61**, 1912 (1939). For more recent results of studies on the viscosity-cellulose concentration relationship see Martin, paper presented before the Cellulose Division of the American Chemical Society meeting, Memphis (April, 1942); Montonna and Winding, *Ind. Eng. Chem.*, **35**, 214 (1943).

has likewise been strongly criticized.[60] Considering that the cellulose molecules in solution are subject to the Brownian movement and that the carbon-to-carbon bonds are capable of moving freely, W. Kuhn is inclined to believe that the molecules would tend to fold up, thus forming "balls of threads" of ever-changing shape and compactness.

In view of these complications, which are further augmented by the unfavorable influence of the heterogeneity of the cellulosic materials upon the viscosity,[61] the molecular weights of cellulose and cellulose derivative preparations, as calculated merely from viscosity measurements (using a rather arbitrary constant [62]) can by no means be regarded as absolute figures.[63] All that may reasonably be expected from viscosity measurements when Staudinger's equation is used is that this method permits a relative assessment of the molecular weight. With this understanding, the method has, no doubt, its merits. In fact, as has been seen in discussions in preceding chapters, the method is of considerable practical value.

A detailed description of the method of measuring the viscosities of cellulose preparations in cuprammonium hydroxide solution at very low concentration and with precautions intended to secure the exclusion of air (and light) has been given by Lottermoser and Wultsch.[64] Certain modifications of the apparatus and of the procedure will be found in detail in a publication by Heuser and Green.[65]

Kraemer's Modification of Staudinger's Viscosity Method

During recent years a method has been developed by which the molecular weight of cellulose may be determined directly, i.e., without resorting to a cellulose derivative. This is the ultracentrifugal method (see later). By using the molecular weights derived from the centrifugal data, Kraemer [66] believes that he has established a more reli-

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[60] W. Kuhn, *Z. physik. Chem.*, **A161**, 1, 427 (1932); *Kolloid-Z.*, **62**, 269 (1933); **68**, 2 (1934); *Angew. Chem.*, **49**, 858 (1936); **51**, 640 (1938); Simha, *J. Phys. Chem.*, **44**, 25 (1940); see also Sakurada, *Cellulosechem.*, **17**, 130 (1936); *Löbering, Kolloid-Beihefte*, **50**, 235 (1939); Alfrey, Bartovics, and Mark, *J. Am. Chem. Soc.*, **64**, 1557 (1942); Huggins, *Ind. Eng. Chem.*, **35**, 980 (1943).

[61] Meyer and Wolff, *Kolloid-Z.*, **89**, 196 (1939).

[62] Meyer and van der Wyk, *Kolloid-Z.*, **76**, 278 (1936); Meyer, *ibid.*, **94**, 70 (1941).

[63] See also Staudinger's attempts to overcome the difficulties listed above in Staudinger and Sorkin, *Ber.*, **70**, 1997 (1937); also Philippoff and Hess, *Ber.*, **70**, 639 (1937).

[64] Lottermoser and Wultsch, *Kolloid-Z.*, **83**, 194 (1938).

[65] Heuser and Green, *Ind. Eng. Chem.*, **33**, 868 (1941).

[66] Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

able constant to be used for calculating molecular weights from viscosity measurements.

Both molecular weight and viscosity are determined on cellulose dissolved in cuprammonium solution. The viscosities are expressed as intrinsic viscosities,[67] which represent specific viscosities extrapolated to zero concentration, thus:

$$[\eta] = \left(\frac{\log_e \eta r}{c}\right)_{c \rightarrow 0}$$

in which r is the viscosity of the solution relative to that of the solvent and c the concentration in grams of solute per 100 cc. of solution. (r is normally measured at a concentration which results in a value not higher than 1.2–1.3.)

Both the centrifugal and the viscosity data supply the basis for the calculation of the constant. The latter is defined as degree of polymerization divided by intrinsic viscosity D.P./$[\eta]$, the degree of polymerization being calculated from the ultracentrifugal molecular weight of the cuprammonium cellulose on the assumption that 1 copper atom is combined with 1 glucose residue, i.e., that the centrifugible component is the cellulose copper complex anion.

In this way, the constant D.P./$[\eta]$ has been determined for a number of cellulosic materials. For purified cotton linters, a value of 260 was found, and for a somewhat more degraded material, a value of 285. Two regenerated cellulose preparations showed 270 and 330.

Kraemer admits that the consistency of these constants is not very good, but wishes them to be considered in the light of the accuracy and consistency attainable by osmotic pressure and other methods. More consistent results might have been obtained if the ultracentrifugal data had been more completely evaluated; this, however, is a laborious procedure.

The ultracentrifugal method is also suitable for the determination of the molecular weight of cellulose derivatives.[68]

Table 82, taken from Kraemer's publication, gives the molecular weight determined in the ultracentrifuge (sedimentation equilibrium modification, see later), the degree of polymerization (D.P.), the intrinsic viscosity $[\eta]$, and the constant D.P./$[\eta]$ as defined above, for

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[67] In German publications the term *Grenzviskosität* is used; see Meyer and Wolff, *Kolloid-Z.*, **89**, 195 (1939); see also Kraemer and Lansing, *J. Phys. Chem.*, **39**, 157 (footnote 3) (1935); Hess and Philippoff, *Ber.*, **70**, 731 (1937).

[68] Kraemer and Lansing, *J. Phys. Chem.*, **39**, 164 (1935); Kraemer, *Ind. Eng. Chem.*, *loc. cit.*, p. 1201.

the cellulosic materials mentioned and for some cellulose derivatives dissolved in organic solvents. The data in the table support Staudinger's hypothesis that an approximately linear relation exists between molecular weight and (intrinsic) viscosity.

TABLE 82

MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF CELLULOSE AND CELLULOSE DERIVATIVES

	Mol. Wt.	D.P.*	$[\eta]$	D.P./$[\eta]$
Celluloses in Cuprammonium Hydroxide Solution				
Purified cotton linters	300,000 †	1300	5.05	260
Purified cotton linters	270,000 †	1200	4.20	285
Purified cotton linters	200,000 †	890	3.40	260
Regenerated cellulose	110,000 †	490	1.83	270
Regenerated cellulose	90,000 †	400	1.20	330
Cellulose Acetate in Acetone ‡				
Cellulose acetate I	100,000	380	1.64	230
Cellulose acetate I	90,000	340	1.64	210
Cellulose acetate II	90,000	340	1.52	220
Cellulose acetate III	50,000	190	0.74	260
Cellulose acetate IV	68,000	260	1.23	210
Cellulose acetate V	250,000	950	3.78	250
Nitrocellulose in Acetone §				
Nitrocellulose I	102,000	390	1.40	280
Nitrocellulose II	140,000	530	2.00	265
Nitrocellulose III	160,000	600	2.20	270
Ethylcellulose in Dioxane				
Ethylcellulose I	125,000	540	1.83	300

* D.P. signifies degree of polymerization or number of glucose residues per molecule. For the celluloses in cuprammonium, they are calculated on the assumption that 1 copper atom is combined per glucose unit.

† Molecular weight of the cellulose-copper complex.

‡ About 54 per cent combined acetic acid.

§ 12 ± 0.1 per cent nitrogen.

Using the following average constants[69]—260 for cellulose in cuprammonium, 230 for secondary cellulose acetate in acetone, and 270 for nitrocellulose in acetone—Kraemer has calculated average molecu-

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[69] If Staudinger's K_m values were expressed in the same way as Kraemer and Lansing's constants, Staudinger's proportionality factors would be 100, 90, and 77 [Kraemer and Lansing, *J. Phys. Chem.*, **39**, 164 (1935)].

lar weights (weight-average molecular weights, strictly speaking[70]) of numerous cellulosic materials from intrinsic viscosities. These are shown in Table 83.[71]

TABLE 83

MOLECULAR WEIGHTS AND DEGREES OF POLYMERIZATION OF VARIOUS CELLULOSES AND CELLULOSE DERIVATIVES

Cellulosic Material	Molecular Weight	Degree of Polymerization
Native cellulose	570,000	3500
Purified cotton linters	150,000–500,000	1000–3000
Wood pulps	90,000–150,000	600–1000
Commercial regenerated cellulose	30,000–90,000	200–600
Farr and Eckerson's cellulose particles	40,000	250
Beta-cellulose	3,000–15,000	15–90
Gamma-cellulose	3,000	15
Dynamite nitrocellulose	750,000–875,000	4600–5400
Plastics nitrocellulose	125,000–150,000	800–930
One-half secondary nitrocellulose	45,000	275
Commercial cellulose acetates	45,000–100,000	275–620

These values are higher than those found by Staudinger. This difference is due to the fact that the molecular weight methods which Staudinger used give "number-average molecular weights," whereas the ultracentrifugal method gives "weight average values." However, in order that the viscosity method for estimating the degree of polymerization may give useful results for practical cases where non-uniform products are inevitably involved, Kraemer deems it essential that weight-average molecular weights be used.

THE MOLECULAR WEIGHT OF CELLULOSE NITRATES

Staudinger and co-workers have made several attempts to arrive at K_m values which could be used for calculating molecular weights for cellulose nitrates from viscosity data with some measure of reliability.[72]

The first K_m value suggested[73] was the result of an indirect and certainly not very satisfactory procedure—a comparison of the specific viscosities of a homol-

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[70] Kraemer and Lansing, *loc. cit.*, p. 165; Flory, *J. Am. Chem. Soc.*, **61**, 1912 (1939).

[71] Kraemer, *loc. cit.*

[72] In these earlier studies no attempt was made to give due consideration to the degree of substitution of the nitrate; see also Wannow, *Kolloid-Z.*, **102**, 29 (1943).

[73] Staudinger, "Die hochmolekularen organischen Verbindungen," p. 506.

ogous series of cellulose preparations in cuprammonium solution with equally concentrated solutions of the nitrates in butyl acetate, prepared from the same series. In addition, the assumption was made that the nitrates had the same degree of polymerization as the original cellulose preparations whereas, actually, under the conditions of nitration employed, some degradation had taken place. Finally, in these calculations the older, i.e., higher, value of K_m for *cellulose* (10×10^{-4}) was used (p. 591). The calculation resulted in a K_m value for cellulose nitrate of 13×10^{-4}. When, later, it was found that the specific viscosity of cellulose nitrates in butyl acetate was 1.3 times higher than in acetone,[74] the K_m value was corrected to give 14×10^{-4}.

In the meantime,[75] the original procedure had been followed, i.e., the nitrates, constituting a polyhomologous series (the degree of polymerization ranging from 90 to 800), were subjected to osmotic pressure measurements, and the molecular weights, thus ascertained directly, were used in connection with the viscosity data. The average K_m value calculated from these data was 11×10^{-4}.

In a subsequent investigation,[76] a polyhomologous series of nitrates (about 2.5 nitrate groups per glucose residue) was prepared by using phosphoric, instead of sulfuric, acid in the nitration acid to reduce the degradation of the cellulose. The osmotic pressure and the viscosity measurements were made on the nitrates dissolved in acetone. The results are shown in Table 84. It is seen that, on the average, a satisfactory agreement exists between the molecular weights determined directly by the osmotic pressure method and those derived from the viscosity data using an average K_m value of 11×10^{-4}.[77]

TABLE 84

MOLECULAR WEIGHTS OF CELLULOSE NITRATES FROM OSMOTIC PRESSURE AND FROM VISCOSITY DATA

Molecular Weight Osmotic Pressure Method	η_{sp}/c_g	$K_m \times 10^{-4}$	Molecular Weight Calculated with $K_m = 11 \times 10^{-4}$ (Average)
57,000	57.0	10.0	52,000
124,000	137	11.0	125,000
157,000	202	12.9	184,000
310,000	356	11.5	324,000

In their earlier studies, Staudinger and co-workers had found that the degree of polymerization of cellulose nitrates prepared from cotton cellulose and dissolved in an organic solvent was considerably higher than that of the original

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[74] Staudinger and Sorkin, *Ber.*, **70**, 2000 (1937).

[75] Staudinger and Schulz, *Ber.*, **68**, 2320 (1935).

[76] Staudinger and Mohr, *Ber.*, **70**, 2301 (1937).

[77] See, however, K. H. Meyer's criticism [Meyer and Wolff, *Kolloid-Z.*, **89**, 194 (1939); Meyer, *ibid.*, **94**, 70 (1941)].

cellulose dissolved in cuprammonium, both solutions being investigated at the same concentration. This difference in degree of polymerization was explained[78] on the assumption that native cellulose represents a very high molecular "ester," i.e., that it consists of normal glucose residue chains united end to end by ester linkages. These ester linkages were thought to be disrupted when native cellulose was dissolved in cuprammonium hydroxide solution or treated with alkali, for example, in the process of mercerization, but to be stable in acid and, thus, to remain unbroken during the process of nitration. Hence, the process of nitration was looked upon as a means of revealing the original, i.e., the actual, chain length of cellulose. This view appeared to be supported by the observation that cellulose which had been regenerated from its solution in cuprammonium or which had been treated with alkali yielded nitrocellulose with an unchanged degree of polymerization.[79]

However, the calculation by which the difference in degree of polymerization between the original cellulose and the nitrate was revealed was based upon the use of a K_m value of 10×10^{-4} for the original cellulose dissolved in cuprammonium hydroxide. When, instead, the value of 5×10^{-4} was used (p. 592) and thus the degree of polymerization of the original cellulose was doubled, the difference was practically eliminated. The results are shown in Table 85.[80]

TABLE 85

DEGREE OF POLYMERIZATION OF CELLULOSE PREPARATIONS AND OF CELLULOSE NITRATES PREPARED THEREFROM

Materials	D.P. of Cellulose $K_m = 5 \times 10^{-4}$	D.P. of Nitrocellulose $K_m = 11 \times 10^{-4}$	D.P. of Nitrates/ D.P. of Celluloses
Cotton linters, very severely bleached	300	320	1.1
Cotton linters, severely bleached	800	1120	1.4
Cotton linters, bleached	1300	1450	1.1
Cotton linters, slightly bleached	1600	1700	1.1
Raw cotton linters	2700	3200	1.1
Raw ramie	3400	3500	1.0

In the light of these results, it would appear that the hypothesis which once postulated the existence in cellulose itself of chain molecules united end to end

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[78] Staudinger, "Die hochmolekularen organischen Verbindungen," p. 512; *Cellulosechem.*, **15**, 66 (1934); see also Wehr, *Kolloid-Z.*, **88**, 185, 290 (1939).

[79] Similar ideas were expressed by af Ekenstam, *Ber.*, **69**, 549 (1936), on the basis of the observations that the specific viscosities of cotton cellulose in phosphoric and in sulfuric acids were considerably higher than those of the same cellulosic material dissolved in cuprammonium hydroxide and that the difference disappeared when regenerated cellulose dissolved in the acids was compared with the original material dissolved in cuprammonium hydroxide.

[80] Staudinger and Mohr, *Ber.*, **70**, 2307 (1937).

by ester linkages must be abandoned. It may be added that other investigators have explained differences in degree of polymerization between the nitrates and the original cellulosic materials by solvation phenomena, operative in the solution of the nitrate in the organic solvent.[81]

It will be recalled that Staudinger has retained the essence of his original hypothesis—the existence of ester linkages—to explain the observation that the nitrates of certain oxycelluloses showed a higher degree of polymerization than the original oxycelluloses (in cuprammonium hydroxide) (p. 470). However, in these instances, the ester linkages are thought to be the result of a chemical treatment and are no longer regarded as pre-existent in the original cellulose. It will also be recalled that, in contrast, the higher degree of polymerization of hydrocellulose nitrates (compared with the unnitrated preparations) was explained on the assumption that these products, having no ester linkages, undergo condensation under the influence of the nitration acid and thus form so-called condensation nitrates, that is, nitrated chains possessing greater average length than the unnitrated hydrocelluloses (p. 507).

THE PHOSPHORIC ACID METHOD

To obtain viscosity data for the conversion into molecular weights, af Ekenstam[82] used a solution of cellulose in concentrated phosphoric acid. In such solutions, cellulose remains stable for a period of time,[83] that is, long enough for carrying out viscosity measurements. Since the solutions are not sensitive to oxygen and light, they might be preferable to the use of cuprammonium hydroxide. On the assumption that cellulose in phosphoric (and other mineral acids) undergoes addition compound formation (p. 510), the specific viscosity of a solution of cellulose in phosphoric acid should correspond to the molecular weight of the addition compound ($C_6H_{10}O_5 \cdot 2H_2O \cdot H_3PO_4$). By dividing the molecular weight calculated from the specific viscosity of the solution by that of the addition compound (296), the degree of polymerization is obtained. The value so determined may be extrapolated to cellulose.

Some doubt arises regarding the reliability of the molecular weights which were thus determined by af Ekenstam for some cellulosic materials, for a K_m value was used which was arrived at without using data from a *direct* molecular weight determination. Similar doubt may be expressed in regard to the results obtained by Stamm and

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[81] Krüger, *Cellulosechem.*, **15**, 85 (1934); Rogowin and Schlachover, *Angew. Chem.*, **48**, 647 (1935); Wannow, *loc. cit.*

[82] af Ekenstam, "Über Celluloselösungen in Mineralsäuren," p. 67; *Ber.*, **69**, 549 (1936).

[83] See also Staudinger and Mohr, *loc. cit.*, p. 2303; Staudinger and Daumiller, *Ber.*, **70**, 2512 (1937).

Cohen,[84] for they used a K_m value (11.8×10^{-4}) which was obtained by a linear extrapolation of af Ekenstam's figures, namely, 12.4×10^{-4} at 20° and 14.7×10^{-4} at 0°. The molecular weights thus found were 113,000 for purified cotton linters (99.6 per cent *alpha*-cellulose content) and 100,000 for sulfite spruce pulp. Whereas the figure for the sulfite pulp is what might be expected, the value ascribed to the cotton linters appears rather low.

Without making an attempt to convert viscosity data into molecular weights, Schmidt-Nielsen and co-workers[85] tested the applicability of the phosphoric acid method to viscosity determinations of various cellulosic materials. The method is regarded as quite suitable for such a purpose, particularly when the viscosity of wood pulp is to be determined on a routine basis.

VISCOSITY MEASUREMENTS IN OTHER SOLVENTS

Staudinger and Daumiller[86] determined the K_m values of cellulose in a number of other solvents. On the assumption that the η_{sp}/c_g values in a certain cellulose solvent and in cuprammonium hydroxide are directly proportional to the K_m values, the K_m values were calculated for cellulose dissolved in such solvents as copper ethylenediamine, tetraethylammonium hydroxide, calcium thiocyanate, and sodium and lithium hydroxides. As an example, the η_{sp}/c_g values for copper ethylenediamine were 1.6 times higher than for cuprammonium hydroxide;

TABLE 86

K_m VALUES OF CELLULOSE IN VARIOUS SOLVENTS

Cellulose Dissolved in	$K_m \times 10^{-4}$
Tetraethylammonium hydroxide	4.2
Sodium and lithium hydroxides	about 5.5
Copper ethylenediamine	8.0
Calcium thiocyanate *	8.0
Phosphoric acid †	18–21
Sulfuric acid ‡	20
Cuprammonium hydroxide	5.0

* Calculated from earlier measurements, Staudinger, "Die hochmolekularen organischen Verbindungen," p. 492.

† Recalculated from af Ekenstam's values.

‡ Determined by af Ekenstam, "Über Celluloselösungen in Mineralsäuren," p. 71.

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[84] Stamm and Cohen, *J. Phys. Chem.*, **42,** 921 (1938).

[85] Schmidt-Nielsen *et al., Papir-J.*, **26,** 95, 109 (1938); *Papier-Fabr.*, **36,** Abstracts, p. 131 (1938).

[86] Staudinger and Daumiller, *Ber.*, **70,** 2508 (1937); see also Zimmermann, *Melliand Textilber.*, **23,** 73 (1942).

TABLE 87

SPECIFIC VISCOSITIES AND DEGREES OF POLYMERIZATION OF CELLULOSIC MATERIALS IN VARIOUS SOLVENTS

Cellulose Dissolved in	Cuprammonium Hydroxide		Copper Ethylenediamine		Tetraethylammonium Hydroxide		Phosphoric Acid	
	$\frac{\eta_{sp}}{c_g}$	D.P. $K_m = 5 \times 10^{-4}$	$\frac{\eta_{sp}}{c_g}$	D.P. $K_m = 8 \times 10^{-4}$	$\frac{\eta_{sp}}{c_g}$	D.P. $K_m = 4.2 \times 10^{-4}$	$\frac{\eta_{sp}}{c_g}$	D.P. $K_m = 18 \times 10^{-4}$
Cotton linters, very severely bleached	23.6	290	....	...	21.3	310	...	...
Cuprammonium rayon	33.8	420	55.7	430	29.6	435	119	410
Cotton, bleached	47.7	590	....	...	38.6	570	...	...
Cotton linters, severely bleached	58.8	730	92.2	710	49.2	725	205	710
Cotton linters, mildly bleached	85.6	1050	....	...	65.6	970	...	...

hence, the K_m value for cellulose dissolved in copper ethylenediamine was assumed to be $5 \times 10^{-4} \times 1.6 = 8.0 \times 10^{-4}$.

In Table 86 the K_m values of cellulose in various solvents (at 20°) are listed. The table also contains the values for cellulose dissolved in phosphoric and in sulfuric acid and in cuprammonium hydroxide.

Staudinger and Daumiller used these K_m values for calculating the molecular weights of various cellulosic materials. Table 87 contains the pertinent data for such materials dissolved in copper ethylenediamine and in tetraethylammonium hydroxide and, for comparison, the data for the same materials dissolved in cuprammonium hydroxide and in phosphoric acid. It shows that the degrees of polymerization of the various cellulosic materials are very nearly the same, irrespective of the solvent used. This result indicates that, for determining the specific viscosity of a cellulosic material and for calculating the molecular weight therefrom, any solvent may be used, provided the cellulosic material can be dispersed to an extent at which detached individual chain molecules are present in the solution. The difficulty of accomplishing this ultimate dispersion, particularly encountered with cellulosic materials of a high degree of polymerization, could probably be diminished by using them in their regenerated form.

THE ULTRACENTRIFUGAL METHOD

The ultracentrifuge supplies a means for determining the particle size of high polymers by observing the phenomena of sedimentation and diffusion. Whether the particle weight thus determined is that of the individual and kinetically independent molecules or that of aggregations therefrom, depends, as in all other cases of direct or indirect molecular weight determinations, upon the degree of dispersion that may be accomplished with the high polymers or their derivatives in suitable solvents.

The ultracentrifuge was developed for the determination of the molecular weight of high polymer colloids by Svedberg[87] and applied to proteins in particular. It appears that the molecular weight of these substances may now be determined quite reliably with this relatively new method. In addition, it is capable of directly supplying information on the degree of heterogeneity of the preparations under investigation.[88]

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[87] Svedberg, *Kolloid-Z., Supplement to Vol. 36,* 53 (1925); **51,** 10 (1930); **67,** 2 (1934); *Ber.,* **67,** 117 (1934); *Chem. Revs.,* **14,** 1 (1934); *Ind. Eng. Chem., Anal. Ed.,* **10,** 113 (1938); see also the comprehensive survey by von Mutzenbecher, *Angew. Chem.,* **51,** 633 (1938), and Svedberg and Pedersen, "Die Ultrazentrifuge," Steinkopf, Dresden (1940).

[88] See also Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York (1940), p. 303.

The phenomenon of sedimentation may be investigated in a small column of dispersed substance which is subjected to very rapid rotation. Under such conditions, one may measure either the sedimentation rate or the sedimentation equilibrium, that is, the equilibrium between the rate of settling of the dispersed particles and their diffusion in the opposite direction. The changes which take place while the dispersion is under the influence of the strong centrifugal field may be determined by optical methods, by measuring, for example, the absorption of light or the refractive index. These changes may be recorded photographically. The curves thus obtained supply the data for calculating the molecular weight.

If the substance to be investigated is polydisperse, it is possible, by means of applying centrifugal fields of varying intensity, to accomplish an accumulation of equal particles, either at the bottom or at the top of the column and thus to carry out a "molecular weight analysis." Such an analysis may be made rather accurately with the sedimentation velocity method, in which centrifugal fields of enormous intensities (150,000 and more revolutions per minute) are being used. For the calculation of the molecular weight from the data obtained, the reader is referred to Stamm's monograph and to Mark's book.[89]

Kraemer[90] has listed the advantages of the ultracentrifugal method as follows: (1) It has the same thermodynamic foundation as osmotic pressure or vapor pressure methods;[91] (2) it is, accordingly, not influenced by particle shape; (3) in general, it is not affected by solvation;[92] (4) its sensitivity increases with particle size; (5) it may be used with complex solvents, such as cuprammonium hydroxide, with which osmotic pressure measurements would be very difficult; (6) it avoids difficulties associated with the use of semipermeable membranes; (7) it permits recognition of the uniformity or nonuniformity of particle size, and it can give a quantitative rating of the degree of nonuniformity;[93] and (8) for solutes containing relatively small molecular weight contaminants, it is much less adversely affected than osmotic pressure and other methods.

Stamm[94] was the first to apply the ultracentrifugal method to cellulose dissolved in cuprammonium hydroxide. Using both the sedimentation velocity and the sedimentation equilibrium methods, he found

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[89] Stamm, "Colloid Chemistry of Cellulosic Materials," p. 29; Mark, *loc. cit.*

[90] Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1930).

[91] Tiselius, *Z. physik. Chem.*, **124**, 449 (1926).

[92] Lansing and Kraemer, *J. Am. Chem. Soc.*, **58**, 1471 (1936).

[93] Lansing and Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935); *J. Phys. Chem.*, **39**, 153 (1935).

[94] Stamm, *J. Am. Chem. Soc.*, **52**, 3047 (1930).

a rather low molecular weight for cotton linters cellulose (40,000 ± 5,000) and, against expectation, no indication of heterogeneity (polydispersity). On the other hand, various wood pulps investigated by the sedimentation velocity method showed considerable polydispersity —i.e., containing a constituent of the same magnitude as that of the cotton linters cellulose in combination with varying proportions of lower molecular weight.[95]

By applying the sedimentation equilibrium method to the same type of cellulosic materials, Kraemer and Lansing[96] arrived at much higher values (for example, 220,000 for cotton linters and 100,000 for degraded and regenerated celluloses) and were inclined to believe that during Stamm's measurements, degradation occurred and that possibly the sedimentation equilibrium was not actually attained. Recent data on both cellulosic materials and cellulose derivation are given on pp. 507 and 508.[97]

In spite of the criticism which Ulmann[98] has expressed, the ultracentrifugal method is regarded as the only absolute method of molecular weight determination that gives a correct average value.[99]

Unfortunately, the method involves the use of very expensive equipment and rather cumbersome procedures. No doubt, it would be highly desirable if the small and very simple air-driven centrifuge which has been devised by McBain and co-workers[100] could be used for cellulose and cellulose derivative solutions. Recent results on the sedimentation velocity of egg albumin in water obtained with this simple apparatus show good agreement with ultracentrifugal data recently published by Svedberg.

MOLECULAR WEIGHT BY DIFFUSION AND SPREADING MEASUREMENTS

Earlier in this book, Herzog and co-workers' results of diffusion measurements on cellulose derivatives have been mentioned (p. 198).

Herzog and Krüger[101] carried out such measurements also on cellulose dissolved in cuprammonium solution and used the data thus obtained for the calculation of the molecular weight; they found 500,000 for cotton cellulose.

Although this figure closely approaches the value as derived from ultracentrifugal data, it might have to be regarded as an incidental result. For, as Stamm[102] has pointed out, Einstein's equation upon which the calculation was

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[95] Stamm, *loc. cit.*, p. 3062.

[96] Kraemer and Lansing, *Nature*, **133**, 870 (1934).

[97] See also Polson, *Kolloid-Z.*, **83**, 172 (1938), on methylcellulose.

[98] Ulmann, *Cellulosechem.*, **16**, 114 (1935).

[99] Kraemer, *Ind. Eng. Chem.*, **30**, 1202 (1938).

[100] See, for example, McBain and Leyda, *J. Am. Chem. Soc.*, **60**, 2998 (1938).

[101] Herzog and Krüger, *Kolloid-Z.*, **39**, 250 (1926).

[102] Stamm, "Colloid Chemistry of Cellulosic Materials," p. 28.

based refers to spherical particles only and to such a low concentration that the mutual interference of the particles is eliminated. As has been seen, a rod-like shape has been postulated for cellulose particles in solution (p. 594), and Herzog and Krüger's measurements were carried out at a cellulose concentration of about 1 per cent, a concentration which is likely to impede the free diffusion of the dissolved particles.

It has been pointed out previously that both the direct and the indirect methods for the determination of the molecular weight rest upon the assumption that the cellulosic materials are dispersed in the solvent to single molecules. Positive evidence which would justify this assumption, at least in certain cases, has been derived from *spreading measurements*. By spreading the solution of certain cellulose derivatives upon a mercury or water surface, a film is obtained the thickness of which corresponds to the thickness of a single glucose chain as derived from x-ray analysis[103] (7.5 Å). Katz and Samwel, who followed the methods which were developed by Langmuir and coworkers[104] and by Adam, found that films of methyl- and ethylcellulose and cellulose triacetate, spread on a water surface, had thicknesses of the same order of magnitude, i.e., varying between 4 and 9 Å. On the other hand, Adam's attempts to spread a cuprammonium solution of cellulose into a monomolecular layer on water were not successful, obviously because precipitation occurred.

Stamm[105] has interpreted the formation of molecular layers of cellulose derivatives to mean that the cellulose molecules probably lie flat on the surface owing to their multipolar structure rather than exhibiting the end-on orientation shown by such bipolar molecules as fatty acids. The results also show that cellulose derivatives in organic solvents (and probably also cellulose itself in cuprammonium solution) must either be dissolved in the form of single molecular chains (chemical molecules) or the bundles of chains (physical molecules) must be internally sufficiently mobile to open up on the liquid surface.

It must, however, be borne in mind that not all cellulose derivatives investigated were found to give monomolecular layers, the films being sometimes much thicker than would correspond to the thickness of a single glucose residue.[106] In such cases, a three-dimensional arrangement of the cellulose chains might be responsible. Such an arrangement could result from the presence of cross linkages as suggested, for example, by Hess and Steurer (p. 583).

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[103] Sheppard and Keenan, *Nature*, **121**, 982 (1928); Katz and Samwel, *Ann.*, **472**, 241 (1929); Adam, *Trans. Faraday Soc.*, **29**, 90 (1933).

[104] Langmuir and co-workers, *J. Am. Chem. Soc.*, **39**, 1848 (1917).

[105] Stamm, *loc. cit.*, p. 32.

[106] Zocher and Stiebel, *Z. physik. Chem.*, **A147**, 401 (1930); Adam, *loc. cit.*

AUTHOR INDEX

SUBJECT INDEX

The term cellulose as such does not appear in the subject index. All entries which would normally appear as subheadings under cellulose will be found as main entries.