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A. CELLULOSE CHEMISTRY 1958

Kyle Ward, Jr.

Origin and Occurrence

Recent studies dealing with the biosynthesis of cellulose in plants and micro-organisms were reviewed in 1958 by B. A. Stone¹. This is, of course, a part of the general field of carbohydrate biogenesis, a field which was reviewed the previous year by Hough and Jones². Current research on the origin of polysaccharides usually takes one of two paths; the synthesis from simple sugars by means of cell-free enzyme systems and synthesis in the living organism. Steel and Walker³⁻⁵ have continued their researches along the former path and so have Gromet, Schramm, and Hestrin^{6,7}. Both groups are using enzyme systems from Acetobacter xylinum. The enzymes from this same organism are also being studied by Glaser^{8,9}.

In studies with the living organism, radioactively labeled sugars are used in the hope of clearing up the mechanism of formation. Cellulose synthesis has been studied in this way in barley seedlings¹⁰, spruce leaves¹¹, wheat shoots¹², and in the cambial layer of the pine¹³. With so much activity we may expect rapid progress in our knowledge of the mechanism of cellulose biosynthesis. Ono¹⁴ has presented a hypothesis for the path of cellulose biosynthesis from glucose based on his work and that of others.

In 1958¹⁵ fibers taken from fresh cowhide were found to have an outer sheath of cellulose. The occurrence of cellulose in the higher animals is reported for the first time and further developments will be awaited with interest.

Composition and Characterization

The main constituent of cellulose from any source is the glucose unit. Much importance attaches, however, to the nonglucose units in highly purified alpha-cellulosic pulps and the question of their occurrence and method of combination is

now being studied intensively. The problem of properly defining wood cellulose has recently been reviewed by Wise¹⁶. Technologically, the important problem is the removal of those constituents which interfere with the utilization of dissolving pulps. In the laboratory, methods have been worked out which produce spruce pulps containing less mannose- and xylose-containing components than can be estimated within the experimental error of our present methods^{17,18}, thereby confirming the results of Hamilton and Quimby¹⁹ on western hemlock. The specific removal of pentosans has been investigated on a variety of woods by Booker and Schuerch²⁰. It is certain that current methods of estimating "alpha-cellulose" determine a material which is not exclusively glucose units. The relationship between alkali solubility and the carbohydrate constituents of the Japanese fir (Abies sacchalinensis) has been investigated by Toda and Hamada²². The effect of composition on alkali refining was determined by Corbett and Kidd²³. Meier²⁴ has shown that mannans, glucomannans, and galactans (all containing cis-hydroxyls) may be precipitated with barium hydroxide. This should be valuable in the further scientific study of these fractions of wood holocellulose.

The chemical structure of the glucomannan compounds is being studied from a great variety of woods, various spruces²⁵⁻²⁷, western hemlock²⁹, western red cedar³⁰, pine^{31,32}, and hardwoods^{33,34}. Gillham and Timell have isolated a glucose-mannose compound from white birch. This type of compound has hitherto been found only in the softwoods.

A comparative study of cottons established galactose, glucose, arabinose, xylose, and rhamnose as the component sugars, but not mannose³⁵. In jute, on the other hand, which has been studied by a number of investigators³⁶⁻³⁹, there is evidence that mannose may be a constituent.

A new semimicromethod for determining cellulose, pentosans and lignin in wood makes use of alcoholic nitric acid⁴⁰ and a microdetermination of cellulose for use in enzyme studies utilizes the dichromate oxidation reaction⁴¹. The use of infrared spectra⁴², x-ray diffraction patterns⁴³, and activation analysis⁴⁴, is also suitable for some purposes. Timell⁴⁵⁻⁴⁷ has recently determined molecular weights of cellulose from a variety of sources and finds that, in general, they are higher than those previously reported; presumably degradation occurs during the isolation of wood celluloses. Timell found D.P.'s of 6,000 to 8,700 for woods and of about 10,000 for kapok, milkweed, and cotton.

To determine the amount of hydroxymethyl furfural in the distillate from the Tollen's pentosan determination, Bethge⁴⁸ determines total aldehyde by bromine titration and repeats the titration after extraction with chloroform. Since the distribution coefficients of furfuraldehyde and hydroxymethylfurfuraldehyde are known, the percentages of each originally present can be calculated. Bethge has done this for various woods and pulps.

Since cellulose can easily be oxidized during its isolation and purification, the determination of carbonyl and carboxyl groups becomes important. For the determination of carbonyl groups, an oxime method⁴⁹ and a modified borohydride method⁵⁰ have been recommended. Colbran and Nevell⁵¹ have confirmed their previous findings⁵² that the alkaline iodine method is not satisfactory with hydrocellulose and have found it even more unsatisfactory with periodate-oxidized celluloses.

The determination of carboxyl groups in cellulose requires that they be in the acid form. Ant-Wuorinen^{53,54} believes that washing must be done with pure CO₂-saturated water in order to avoid the interference of sorbed mineral acid. This

is disputed by Samuelson^{55,56} and his co-workers, who have presented evidence that hydrochloric acid is easily washed out. Rebek^{57,58} has reviewed methods for determining acid groups and has recommended several methods making use of the fixation of Crystal Violet Base. Two methods for determining calcium in cellulose are described, by flame photometry⁵⁹ and by titration with ethylenediamine tetraacetic acid⁶⁰.

Kirmaier⁶¹ has discussed the characterization of the quality of dissolving pulps with particular attention to the viscose pulp situation in Rumania. Komarov⁶² considers degree of polymerization the best criterion for high quality viscose pulp and Kleinert⁶³ has found a relationship between the degree of polymerization and the solubility in alkaline sodium zincate solutions. Oltus⁶⁴ describes a "rayon cellulose test" consisting of the solubility ratios in 21.5% sodium hydroxide. Pollock⁶⁵ discusses the required properties for dissolving pulps, while Slávik and Mahdalík⁶⁶ have discussed the effect of drying on these properties.

Structure in the Solid State

The internal structure of the cellulose fiber and the arrangement of the molecules are important factors influencing the properties and the relationships have been reviewed recently, both with regard to textiles^{67,68} and to paper^{69,70}.

Ellis and Warwicker⁷¹ have proposed a new chain configuration for cellulose which does not assume the two-fold screw axis. Their suggestion is based on the x-ray diagram. Mann and Marrinan⁷² have also discussed the arrangement of the unit cell of cellulose I. Their comments are based on the infrared spectrum and are in disagreement with the view of Tsuboi⁷³.

The use of infrared absorption to study the structure of cellulose and cellulose derivatives has been advanced by the development of satisfactory methods of handling the sample. Disks of finely comminuted cellulose with either potassium bromide^{74,75} or potassium chloride⁷⁶ have proved satisfactory for this purpose. Improved methods for the use of the electron microscope in fiber research have been described by Kassenbeck⁷⁷. Belford, et al.^{78,79} have used the electron microscope to study microfibrillar organization in cell walls and the deposition of metals in impregnated cellulose.

The influence of the internal structure of cellulose on both the physical and the chemical properties is still being studied by many groups. A review of the presently accepted structure of cellulose and its effect on reactivity was recently made by Bartunek⁸⁰. Ant-Wuorinen⁸¹ is continuing his investigations of the effect of accessibility on the characteristics of cellulose, varying the accessibility with alkaline treatments. Bayley and Bishop⁸² have shown that there is no correlation between the nonglucose sugar residues and the size and percentage of the crystalline region. They interpret this as additional evidence in favor of the sorption of these materials on microfibrils after the formation of the latter.

Hearle⁸³ has proposed a structure to account for the properties of regenerated cellulose. He regards the ordered regions as continuous fringed fibrils (rather than fringed micelles) composed of molecules diverging from the fibril at different positions along its lengths.

Nissan⁸⁴ has continued his studies of hydrogen bonding in fibers and has developed a theory of the beating process based on rearrangements of the hydrogen bonds. By measuring bound water, Voitsekhovskii⁸⁵ has shown an increase

in the hydrophilic nature of cellulose during mercerization and beating and a decrease during drying of the paper web.

Nakao, et al.⁸⁶, have measured the effect of various treatments of cellulose upon the alkali solubility. Under the various treatments of hydrolysis, ultraviolet radiation, nitration, and denitration, the alkali solubility is shown to be markedly affected by changes in the lateral order but very little by changes in the degree of polymerization. Linters pulps show more homogeneous distribution and higher lateral order than do rayon pulps from wood.

Kouris, Ruck, and Mason⁸⁷ have shown the effects of various methods of drying upon the x-ray crystallinity of wood cellulose fibers. No change was observed when the fibers were dried from water but a lower crystallinity was obtained when they were dried from benzene. The heats of wetting suggest changes in the accessibility with different drying methods. In the case of drying from water, recrystallization can occur and this appears to be true with the lower alcohols to some extent.

Heikens, et al.⁸⁸, have presented a hypothesis explaining the small angle x-ray scatter of dry and wet cellulose. According to them, submicroscopic vacuoles in dry cellulose contribute appreciably to the small angle x-ray scatter. In the wet state, these vacuoles are filled with water and contribute less so that the density difference of the crystalline region and the noncrystalline region is high and becomes the main factor whereas in dry cellulose it is negligible. This hypothesis is quite reasonable. It seems possible that in the wet state these vacuoles are also smaller due to swelling of the surrounding microfibrils.

Gupta^{89,90} has investigated the x-ray diagrams of jute treated with caustic soda. In general, he has repeated the earlier observations of Mukherjee and Woods⁹¹ in regard to the effect of various conditions of washing upon the crystallite orientation. There is more cellulose I produced when the caustic soda is washed out with hot water than with water at room temperature. The swelling action of sodium hydroxide falls off above concentrations of 20%. The explanation is the same as that of the previous workers, namely, a possible stabilizing effect of the lignin in the jute fiber.

Measurements of accessibility by moisture sorption and of crystalline content by means of density measurements have been made for a number of regenerated cellulose fibers⁹². The difference between the accessibility and the crystallinity has been interpreted as due to differences in the average cross-sectional area of the crystalline regions. An effort has been made to correlate the results with the properties of the various fibers.

Schwertassek⁹³ continues his studies of the measurement of accessibility by means of iodine sorption. He has corroborated Hess⁹⁴ that the penetration of iodine into the ordered regions of cellulose as well as into the less ordered regions occurs if concentrations of iodine greater than 8-12% are sorbed. In order to obtain values for degree of order, modified methods and conversion tables must be used, which are given. Hess et al.⁹⁵⁻⁹⁸, have found that iodine enters the crystalline regions; that is, changes the x-ray pattern when more than eleven or twelve per cent is added. The iodine in the noncrystalline regions can be removed by washing with water, but the other iodine migrates, moving along the fiber axis. Electron micrographs and small angle x-ray reflections show an alternation along the fiber axis of crystalline and noncrystalline zones with some lateral alignment of similar

structures. This is true of both native and regenerated cellulose as well as of other fibers and Hess believes that the order seems determined by physical rather than chemical factors. In Fortisan fibers which are highly oriented and show a pronounced structure, there is a small period of 100 to 200 A. and a very distinct large period of 650 to 800 A.

Further work has been reported on improved pilot plant processes for cotton decrystallization^{99,100}. Methods for removing ethylamine from the decrystallized cotton are compared. Extraction with hexane is tedious and both cellulose I and cellulose III are present in the residual material. A simpler method of removal consists of evaporation. Very slow evaporation leaves essentially pure cellulose III in the remaining crystalline region while rapid evaporation leaves cellulose I. Intermediate rates of evaporation produce mixed lattices.

Most of the material dealing with the solid state structure of viscose rayon probably belongs in the chapter on rayon, but there are some studies which have such significance for cellulose chemistry that they should be included here also. Kanamaru¹⁰¹ and his co-workers have studied the stabilization of viscose rayon by swelling with dilute acid and heat treatment and the effect on the elasticity, strength, elongation, crystallinity, and moisture sorption of the fibers. The effects were most prominent for swelling baths in the pH range favoring maximum hydration of cellulose II, that is, 3.0-5.0, and at temperatures near the glass transition temperature, 60-70°. The authors give a good discussion of the matter, pointing out that the glass transition temperature of Ueberreiter¹⁰² is for dry rayon and that the wet materials must have a lowered transition temperature due to plasticization. They infer that heat treatment has caused an increased development of order in the nonordered regions.

Gjønnes, et al.¹⁰³, have concluded that the concept of amorphous cellulose is not necessary for explaining the x-ray diffraction patterns of cellulose I, but that the reflexions from cellulose II cannot be exclusively from crystalline regions. Even here, differences in the degree of perfection of the best-ordered regions seem to constitute a better explanation than the ratio of crystalline to amorphous material.

It is interesting that, while Gjønnes is discounting the existence of noncrystalline material, Mikhailov¹⁰⁴ is discarding the idea of crystallinity. Since the heat content of native and hydrate cellulose does not change significantly over a wide range of fiber orientation and is independent of D.P. or fiber history, and since there is a continuous, unbroken change when transforming the fiber by repeated xanthation and regeneration with mineral acids (without destruction of fiber structure), Mikhailov concludes that phase differences can be ruled out in the structure of the two forms of cellulose and that native cellulose differs from regenerated cellulose in the configuration of sugar units along a molecular chain rather than in any crystalline differences. In fact, Mikhailov accepts Kargin's views that regenerated cellulose is essentially noncrystalline throughout, even when highly oriented. It should be pointed out that the "native cellulose" of Mikhailov regenerated from viscose rayon is generally considered to be a different crystal form, cellulose IV, rather than the cellulose I of naturally occurring material. (This transformation to cellulose IV has recently been shown by Jullander and Rånby¹⁰⁵ to take place with mercerized wood pulp also.)

Nelson¹⁰⁶, on the other hand, also using heats of solution and heats of combustion, has studied the hydrolysis of samples of cellulose I, II, and III and, on the more usual assumption of a two-phase structure in celluloses, has used her

determinations to calculate the heats of combustion and solution for the amorphous cellulose and for each of the three crystal lattice types.

It has been shown that regenerated cellulose may show different fine structures depending upon the D.P. This is due to the crystallization tendency working in opposition to the inhibiting effect of molecular length, according to the interpretation of Schurz and Zimmerl¹⁰⁷. Centola¹⁰⁸⁻¹¹⁰, has extended his ideas on the formation of the skin in viscose rayon to other fibers than regenerated cellulose.

Sorption and Swelling

Recent measurements on solvent-exchanged cellulose have shown that the total surface (as measured by nitrogen sorption isotherms) can be increased by wet ball milling from 100 to 200 sq. m. per g. The most common pore diameter, 38 A., did not change and the total pore volume, 32-44 A., changed only slightly. Thode, Swanson, and Becher¹¹¹, conclude that these pores are related to the packing of microfibrils.

Valentine^{112,113}, has continued his study of moisture sorption. He has earlier recommended the ratio of the moisture sorption of a polymer to that of its completely amorphous form as a measure of the noncrystalline fraction. Methods for determining the sorption of the amorphous form are discussed, with particular reference to cellulose. One method involves measurement of accessibility, to D₂O, for instance, and extrapolating the relationship between accessibility and sorption to 100 per cent accessibility. The second method also involves extrapolation; in this case a random copolymer is studied in the completely amorphous form and sorption plotted against degree of substitution. Assuming that the partially substituted cellulose acetates

(homogeneously deacetylated) were completely amorphous, he has estimated the absorption isotherms of amorphous cellulose and of amorphous cellulose triacetate.

Sorption isotherms for cotton have been determined on Indian cottons covering a wide range of fiber properties¹¹⁴. Determination of the sorption isotherms at 25° on eucalyptus wood and on the individual components of this wood lead to the conclusion that the total sorption of the wood arises 47% from cellulose, 37% from hemicelluloses and 16% from lignin¹¹⁵. Wink, et al.¹¹⁶, have described a procedure for determining sorption isotherms at high temperature and have determined the isotherms for wood pulp at 200°F.

The uptake of copper by cellulose from aqueous solutions as a function of concentration indicates that this is an absorption phenomenon in accordance with Langmuir's isotherm¹¹⁷. Electron diffraction patterns of such cellulose indicate a regular two-dimensional array on the surface of the microfibril which implies a high degree of order of the cellulose molecules at this surface.

Sexsmith¹¹⁸ has made a study of the absorption of cationic surfactants, high molecular weight quaternary ammonium halides, on cellulose and oxycellulose. He finds that three mechanisms are involved; ion exchange with carboxyls in the material, micellar association, and a mechanism similar to the fixation of methylene blue at high salt concentrations. He advances a theory for substantivity in the concentration range of micelle formation and a mechanism for the adsorption of anionic surfactants.

The swelling of cellulose in water plays an important role in the use of this material both in textiles and in paper^{119,120}. In the latter field, the measurement of the swelling of pulps by water retention after centrifugation has recently

been improved¹²¹ and is recommended as a standard method. The reproducibility of swelling methods on viscose rayon has also been studied but the errors due to sampling and technique of measuring could not be separated¹²². The swelling pattern of jute filaments with increase in moisture sorption closely resembles the regain isotherms except that hysteresis is prominent only at high relative humidities. Chakravarty¹²³ gives an explanation of this hysteresis.

Ollagnier¹²⁴ has shown how swelling and contraction of cellulose during wetting and drying can be explained in terms of capillary forces. McKenzie^{125,126} has been making a thorough study of the effect of swelling on the bonding of paper-making fibers. He has shown that swelling changes the fiber structure and in this way, the number of hydroxyl groups which are available for bonding. Improvements in beating efficiency are obtained on swelling with aqueous ethylenediamine but the situation is more complicated on swelling with alkali. While there is an improvement in beating rate with dilute alkali, the rate decreases at higher concentrations. There are other factors involved here besides swelling, such as extraction of materials by the alkali, surface aggregation of the microfibrils, and a phase change from cellulose I to cellulose II.

The swelling behavior of cellulosic fibers in acids has been studied from two points of view, swelling with sulfuric acid from that of the parchментizing reaction¹²⁷ and swelling with phosphoric acid from that of morphology¹²⁸. It seems as if a transverse morphological structure exists in the outer layer of the secondary wall which is readily hydrolyzed by acid. The swelling of wood in the lower alcohols and carboxylic acids, and in glycerine, pyridine, and water has been studied by Kumar¹²⁹. In general, the swelling is greater with the smaller molecules in a homologous series and correlates well with the surface tension of the liquid.

Cellulose Solutions

Jayme and Bergmann¹³⁰ have continued the study of the iron-sodium-tartrate solution as a solvent for cellulose, pointing out its applicability for fractionation and for viscosity measurements. Strepikheev, et al.¹³¹, have also been studying new solvents for cellulose and found complete solution in three quaternary ammonium bases--dimethylphenylbenzyl, triethylbenzyl, and triethylfurfural quaternary ammonium hydroxide.

Sodium zincate is used for determining the percentages of viscose rayon and cotton in blended yarns and fabrics¹³². Kleinert¹³³ has suggested that this solution can be used for the investigation of dissolving pulps as well. The soluble portion is essentially equivalent to that part of the cellulose which is less than 200 D.P. However, there is some degradation by the sodium zincate. Recent investigations on solubility in alkali have also been made^{134,135}.

The evaluation of cellulosic materials by determining the viscosity of solutions is, of course, a standard method, but there is no unanimity as to the solvent and the procedure to be used. Within the past year methods have been described for the determination of xanthate viscosity^{136,137}, cupriethylenediamine viscosity¹³⁸⁻¹⁴⁰, cuprammonium viscosity¹⁴¹, and benzyltriethyl ammonium hydroxide viscosity¹⁴². Where degrees of polymerization are to be determined, the use of cupriethylenediamine seems to be increasing.

The relation between intrinsic viscosity and degree of polymerization requires evaluation of two constants. Recent values for these constants have been determined for cellulose in copper ethylenediamine¹⁴³ and in cuprammonium¹⁴⁴, for cellulose triacetate in chloroform¹⁴⁵ and in alcoholic methylene chloride¹⁴⁴, for

secondary acetate in acetone and aqueous acetone¹⁴⁴, for cellulose nitrate in acetone and butyl acetate^{144,146-148}, and for ethyl cellulose in various solvents¹⁴⁹ Schurz¹⁵⁰ has reviewed the matter of non-Newtonian viscosity and has discussed various approximation formulae and measurements of the flow curve.

Particularly at high D.P.'s, the methods of obtaining intrinsic viscosity are not satisfactory. Cram and Whitwell¹⁵¹ have studied various methods of calculating intrinsic viscosity and concluded that values based on zero shear rate are required to obtain independence from viscometric procedures. If intrinsic viscosity is not the objective, they recommend comparison of samples on the basis of apparent viscosity at a single high concentration and as low a standard shear as practical. Horio, et al.,¹⁵² recommend a single point method on a dilute solution at as low a velocity gradient as possible. Davison¹⁵³ also uses a single measurement. Fleury and Reitzer^{122,154} have studied the determination statistically and find that the variations are due in a minor degree to sampling but largely to variations in the determination itself.

Flory, et al.,¹⁵⁵ have investigated the intrinsic viscosities of cellulose acetate at degrees of substitution 2.86 and 3.00 and of cellulose nitrate as functions of temperature, solvent, and molecular weight. Large negative temperature coefficients are characteristic and due to increases in chain flexibility. The variations in intrinsic viscosity with solvent are also due to changes in chain flexibility brought about by solvent interaction.

Bartunek¹⁵⁶, has investigated the specific viscosity of cupriethylenediamine solutions of cellulose at various concentrations. He finds that if a cellulose solution is diluted a lower viscosity is obtained than if a new solution of the

same concentration is made. He interprets this in agreement with Dolmetsch's hypothesis that coarse structures are present which are dispersed more completely by further dilution. It is not certain that he has taken into account the time required for complete solvation of molecules, however.

The determination of the molecular weight distribution of cellulose is usually done by fractional precipitation of cellulose nitrate¹⁵⁷. Rånby, et al.¹⁵⁸, have studied the effect of previous extraction of low D.P. carbohydrates on such a fractionation. The extraction stabilizes the nitrated pulp and removes a great deal of noncellulosic carbohydrate material, as well as a glucan of low D.P. The authors conclude that most of the noncelluloses are mechanically held rather than chemically bound to the cellulose. The extraction improved the resolution of the fractionation.

Marx¹⁵⁹ has run molecular weight distribution of flax, cotton, and spruce cellulose by this method. Flax and cotton have two maxima, one about 9000 D.P. and the other 6000 to 7000 D.P. Spruce cellulose showed a single maximum between 5000 and 8000. The change of distribution in spruce during pulping and the resulting degradation was determined.

A comparison of water and of heptane as precipitants during this fractionation has recently been made¹⁶⁰. The conclusions are that heptane gives more reliable results with nitrates of high D.S. but is not suitable for the precipitation of nitrates of low D.S. Yagami and Kano¹⁶¹ have also studied this method and have modified it to reduce the time required to about 20% of the ordinary method.

Cumberbirch and Harland¹⁶² have described the fractionation of secondary cellulose acetate which they carried out in determining the constants previously mentioned. Witting and Krässig¹⁶³ have discussed a proposed approximation method

for calculating the molecular weight distribution of statistically or randomly degraded celluloses and have compared the results with experimental data. The Fuchs¹⁶⁴ method for fractionating polymers by preferential solution of thin films has been applied to the fractionation of cellulose derivatives and reproducible rapid results are claimed¹⁶⁵. Schurz and Streitzig¹⁶⁶ have also made measurements on molecular weight distributions by means of the flow curves of mixtures.

Scherer, et al.^{167,168}, have developed further the determination of molecular weight by measuring dielectric dispersion of solutions. Cellulose acetate and ethylcellulose were used.

Degradation of Cellulose

The Rheinau saccharification process for producing glucose and other sugars from wood has recently been modified so that prehydrolysis is no longer carried out with dilute acid at elevated temperature, but with 35% hydrochloric at 20°C.^{169,170}. Ito and Nakayama¹⁷¹ have discussed prehydrolysis of hardwoods with water at about 200°. Still another wood saccharification process has recently been discussed by Putnynya and Odintsov¹⁷². In this case the wood is saccharified with 75% sulfuric acid and the acid solution used to decompose apatite. After this utilization, the solution is worked up for glucose.

Sugars are not the only products produced by hydrolysis of cellulose. Under the proper conditions hydroxymethylfurfural¹⁷³ and levulinic acid¹⁷⁴ can be recovered. It is predicted that levulinic acid will become a commercial raw material¹⁷⁵.

In the analysis of vegetable raw material, one of the most useful recent methods is complete hydrolysis with separation of the sugars by paper chromatography. Several new methods have been described for chromatographic analysis of cellulose hydrolyzates¹⁷⁶⁻¹⁷⁹. Fellegi¹⁸⁰ has discussed the use of the method in studying cellulose and hemicelluloses. Peat, et al.¹⁸¹, have studied the reversion of glucose in acids, since these reversion products interfere in determining the major hydrolysis products.

Papers still appear every year on the kinetics of cellulose hydrolysis. Husemann and Spingler last year discussed the effect of oxygen and came to the conclusion that oxidation preceded hydrolysis. However, in 1958, they concluded, on the basis of experiments with and without metal salts¹⁸², that the cleavage of weak spots in the chain is due to hydrolysis with subsequent oxidation. Ivanov¹⁸³ reports results showing that carboxyl groups decrease the stability of the glucosidic bond in acid media. Parisot^{184,185} reviews the subject and concludes that the assumption is still controversial, but that "weak" links will explain the mechanical behavior of wet fibers.

On the other hand, Sanyer and Purves¹⁸⁶ found no clear evidence for the existence of any weak links in cotton cellulose. Krässig¹⁸⁷ concluded that the morphological structure of the fiber and accessibility considerations were responsible for preferential degradation of animal cellulose, (tunicin). Sharples¹⁸⁸ has continued his studies and confirmed that the hydrolytic mechanism of crystallite degradation involves end attack and that the mean length of the crystallites in a sample of cellulose is related to the amount of crystalline material present. Bryce and Greenwood¹⁸⁹ have reassessed the mathematics of degradation kinetics. Using data of Gibbons¹⁹⁰ on the hydrolysis of methylcellulose, they conclude that weak links are absent.

Light scattering studies have shown that oligosaccharides are not the only reversion products of glucose¹⁹¹. There is evidence of the formation and growth of a large branched polymer of 5-hydroxymethylfurfural during the hydrolysis of cellulose.

Several years ago Lemiszka and Whitwell¹⁹² proposed a stress relaxation method for determining the accessibility of fibers to hydrochloric acid. This method has been criticized by Valentine¹⁹³ and a reply made by the authors of the original paper¹⁹⁴.

Among particular hydrolytic systems studied, two might be mentioned here. Rogovin and Pogosov¹⁹⁵ have studied the hydrolysis of cellulose with hydrochloric acid. Water-soluble products with a D.P. of 15-17 are formed. Reversion is the probable explanation of this phenomenon. Malm, et al.¹⁹⁶, studied the chain breakdown of cellulose by acetic acid solutions of water and sulfuric acid. This is of interest on account of its relation to the breakdown of the cellulose chain during the process of acetylation. This breakdown depends on the quantity and uniformity of the sulfuric acid sorbed.

Grohn^{197,198} has studied the breakdown of cellulose in the vibratory ball mill and has come to the conclusion that this is probably a mechanically activated hydrolysis.

Korol'kov, et al.^{199,200}, have continued the comparison of cellulose hydrolysis and cellulose alcoholysis. They have shown that the limiting D.P. is much higher with alcohol and that the accessibility of cellulose to the alcoholic acid decreases with the size of the alcohol used. There is practically no re-crystallization during ethanolysis of cellulose and the use of this reaction for the measurement of the amorphous fraction is recommended.

Wolfson²⁰¹ has continued his studies of the polymer-homologous series of sugars obtained by acetolysis of cellulose. He has reduced the aldoses (from cellobiose through cellohexose) to produce the corresponding cellobiotols, which have been carefully characterized.

Oxidation

It is well known that no oxidation reaction in cellulose is entirely specific. In the case of sodium periodate oxidation it has recently been determined that, under the particular experimental conditions studied, carbon atom 6 oxidized to the extent of about 10% of the total reaction²⁰². If the reaction product, predominantly oxidized on the 2- and 3-carbon atoms, is further oxidized with sodium chlorite to produce 2,3-dicarboxycellulose, the resulting material shows chelating properties for metallic cations and can be used as an ion-exchange material²⁰³.

This reaction has been studied using cellobiose as a model compound. Wright²⁰⁴ has shown that periodic acid completely oxidized cellobiose in 24 hours with scission of the glycosidic linkage, but sodium periodate or potassium periodate attacks only the alpha glycol linkages. Head²⁰⁵ has presented a new mechanism for the oxidation of cellobiose with periodate. Carbon dioxide is liberated from the reducing end of the molecule and Hough and Woods²⁰⁶ have suggested the use of the reaction for determining structure. The amount of carbon dioxide produced per mole of periodic acid is dependent upon the type of glycosidic linkage. Higgins and McKenzie²⁰⁷ have studied the physical-chemical properties of periodate-oxidized cellulose and the possibility of its use in paper.

Guthrie and Honeyman²⁰⁸ oxidized methyl-4,6-O benzylidene- α -D-glycoside with periodate to produce a crystalline dialdehyde. This crystallized from nitromethane in an anhydrous form, but crystallization from alcohol produced monoalkyl derivatives which were apparently free of carbonyl groups. Their findings have been related to oxidized cellulose, considering the sugar derivative as a model compound. Nevell, in his studies of the nitrogen dioxide oxidation²⁰⁹, had noticed the retention of methanol by nitrogen-dioxide-oxidized cellulose. This occurs also with periodate oxycelluloses²¹⁰, and Nevell²¹¹ suggests that the reaction of Guthrie and Honeyman²⁰⁸ explains this retention, a cyclic hemiacetal being formed with the methanol. The same reaction has been studied by Goldstein and Smith²¹², these authors have suggested the use of the reaction for controlled introduction of cross linkages into polysaccharides. In a detailed study of the periodate oxycellulose²¹³, the polyaldehyde produced by extensive oxidation was reduced with sodium borohydride to the corresponding polyalcohol. Even after retreatment of the polyalcohol with periodate, the product still contained glucose residues and, to the authors, this indicates some cross linkage or other blocking of either the two or three hydroxyls in the original cellulose.

Infrared spectroscopy indicates significant partial oxidation at the six carbon atom²¹⁴⁻²¹⁶. The infrared spectra of nitrogen-dioxide oxycellulose indicate scission with sodium chlorate between carbons two and three.

Evidence that the nitrates of periodate-oxidized cellulose contain cross linkages produced during nitration has been presented by Anthoni^{217,218}. The same type of insoluble nitrates were observed by Parkinson²¹⁹ in his study of nitrogen dioxide oxidation and he showed that insolubility can be prevented by previous reduction with sodium borohydride. Parkinson suggests chain scission during oxidation as a contributing factor to the alkali sensitivity of the oxidation products.

Mester²²⁰ prepared formazans from celluloses which had been oxidized by periodate, ozone, or dichromate. He suggests use of the colored metal complexes of these compounds as a research tool.

Lindberg and Theander²²¹ reduced a chromate oxycellulose with sodium borohydride. D-Allose was found in the hydrolyzate in amounts which indicate that most of the keto groups in the oxidized cellulose are on the three carbon atom.

Theander²²² has also studied the oxidation of methyl- β -D-glucopyranoside with chlorine and hypochlorite at different pH's. His results corroborate those of Henderson²²³ in so far as he finds D-arabinose as one of the principal neutral reaction products with a maximum yield at about pH 4. Like Whistler, Linke, and Kazeniac²²⁴, on the other hand, his products show evidence of scission between the two and three carbon. Daniel²²⁵ has also studied the oxidation with aqueous chlorine at pH 4.5, using labeled cellulose. He found that less than 20% of his carbon dioxide came from position 1 and that only a little of the uronic acid carbon dioxide evolved with acid came from position 6. The fractions of carbon dioxide derived from different carbon atoms varied with the oxidation level.

Bowness²²⁶ has found on the basis of absorption spectra that formylfuroic acid seems to be the main product of heating uronic acids with strong mineral acids. The β -1,4 bond in oxycellulose seems to increase the reactivity, using a commercial oxycellulose, presumably nitrogen-dioxide oxidized.

The thermal breakdown of cellulose in air seems to be essentially an oxidation reaction, nonspecific and progressing from the noncrystalline to the crystalline region²²⁷⁻²²⁹.

Koshizawa²³⁰ has oxidized cellulose by chlorine dioxide solutions and considered the ultraviolet absorption spectra of the resulting material. Somsen²³¹ reacted model compounds with chlorine dioxide and found that both diacetyl and 2,3-dihydroxybutane are oxidized to acetic acid and carbon dioxide, indicating that carbon to carbon bonds are cleaved, producing carboxyls and carbon dioxide.

Kleinert^{232,233} has suggested oxidation with tosylchloramide as an accelerated simulation of the aging of alkali cellulose. In this way the behavior of dissolving pulps can be more rapidly evaluated. Accessibility of the cellulose is indicated as a factor in this oxidation. Direct study of aging of alkali cellulose has also been an active field, the effect of molecular oxygen on alkali cellulose having been studied by research groups all over the world²³⁴⁻²³⁷.

Cellulosic fibers are degraded by electrode reactions when in contact with rusting iron²³⁸. Ferrous iron definitely increases oxidative degradation by hydrogen peroxide, but ferric iron as oxide did not have this effect²³⁹.

If acidic oxycelluloses are dyed with methylene blue, a new line appears in the x-ray diffraction pattern which is identical with one present in the pattern of methylene blue chloride. Warwicker²⁴⁰ has advanced a hypothesis to account for this crystallization of the dye.

The wet strength of paper is improved by previous oxidation of the pulps. This increased wet strength is derived from the carbonyl groups and is related to the loss on alkali boiling since alkali sensitivity is an approximate measure of carbonyl content²⁴¹. This well-known sensitivity to alkalies of oxidized cellulose has recently been studied in some detail and the mechanism of alkaline degradation evaluated²⁴²⁻²⁴⁶.

Another very interesting point in regard to oxidation is the relationship of the increased carbonyl content to yellowing or color reversion in cellulosic materials²⁴⁷⁻²⁵¹. Rochas and Gavet found that rayons containing aldehyde groups became yellow but that ketone groups did not have this effect²⁵². Jullander and Brune²⁵³ find that the carbonyl groups are responsible for about 1/2 of the brightness reversion but Okada and Ida²⁵⁴ find them responsible for most of the color reversion.

Flynn et al.²⁵⁵ have studied the degradation of cellulose in a vacuum with ultraviolet light and have proposed a mechanism where alcohol groups are photolyzed to carbonyl groups with the liberation of hydrogen. By comparison with the expected changes in molecular weight, Flynn²⁵⁶ calculates that at least part of the aldehyde formation is due to reactions which do not involve chain scission. A similar mechanism is proposed by Schurz and Kienzl²⁵⁷ based on irradiation of disaccharides as model compounds. The first effect is oxidation at carbons 2 and 3, followed by enolization and further oxidation to split the ring and finally to cleave the glycoside bond. Schurz and Kienzl's experiments were made with and without the catalysis of titanium dioxide. This and other catalysts have been studied by other workers as well^{258,259}.

Belaya²⁶⁰ attributes the photochemical effect on cellulose to oxidation and hydrolysis either caused or catalyzed by ozone. In the case of jute, MacMillan and Bhattacharjee²⁶¹ believe that the main factor accelerating the degradation is volatile peroxide.

Gamma radiation rapidly degrades cellulose²⁶²⁻²⁶⁹. Carbonyl and carboxyl groups are produced and there is a considerable loss in degree of polymerization.

The phototendering of fabrics in the presence of certain dyes has been further studied. No new mechanisms have been proposed²⁷⁰⁻²⁷³.

The effect of time on degradation (storage effects, weathering, aging) is of considerable practical interest. Marsh et al.²⁷⁴, have shown that many fiber properties of cotton change during weathering of the boll prior to harvesting. Regarding cotton cellulose, Goldthwait and Robinson²⁷⁵ have shown that mercerization of cotton produces improvement in the resistance to light and weathering. The effect of storage on the properties of paper²⁷⁶ and of rayon pulps²⁷⁷ have recently been further studied.

There has also been a series of studies on the changes in cellulose over the centuries by analyzing and studying the properties of α -cellulose from wood taken from peat deposits²⁷⁸⁻²⁸⁰. With increasing age of the cellulose, dehydration and hydration processes occur to produce cyclic compounds. In wood which was 140,000 years old, only about 15% of cellulose was obtained as contrasted to 38 to 44% from modern wood.

Golova et al.²⁸¹⁻²⁸⁸, have continued their studies of the formation of laevoglucosan from cellulose by thermal decomposition. They propose that this reaction does not proceed through glucose as an intermediate, but is formed by radicals produced by rupture of the 1,4-glucoside linkage. 1,6-anhydroglucofuranose was isolated as a by-product of the reaction.

Laible²⁸⁹ has reviewed recent work on the thermal degradation of cellulose and advanced the hypothesis that laevoglucosan is the important intermediate responsible for the flaming reaction. The pyrolysis reaction has recently been studied by a number of workers²⁹⁰⁻²⁹².

Kuriyama²⁹³ has presented a study of the various products produced from wood pulp and cellulose as the temperature is gradually raised from room temperature up to above 500°. Kowalski²⁹⁴⁻²⁹⁵ has made similar studies. Chars from cellulose show infrared spectra similar to those from soft coals²⁹⁶.

Microbiological Degradation

In 1957 Heyn²⁹⁷ reviewed the bacteria which decompose cellulose. He has more recently described the fungi commonly found on field cotton, including some new species²⁹⁸. Nopitsch²⁹⁹ has also discussed bacterial infection of cotton. The effect of micro-organisms on wood³⁰⁰ and on pulp and paper³⁰¹ have also been reviewed. The soil burial method used for evaluating textile preservatives has recently been closely studied by Ashcroft³⁰² and by Schmidt³⁰³. Cyrot³⁰⁴ has found that mercerized cotton resists soil burial better than unmercerized cotton.

The study of the diegestion of cellulose by the higher animals centers around the rumen microflora³⁰⁵⁻³⁰⁹. The suitability of various wood pulps as animal fodder has been studied³¹⁰. Conrad et al.³¹¹, have found that cellulose is largely converted in the intestine of the rat to absorbable degradation products, probably by the action of intestinal bacteria. Experiments have shown that earwigs also eat cellulosic textiles³¹².

Much work continues on enzyme preparations of the organisms which destroy cellulose³¹³⁻³²³, particularly from *Myrothecium* species. There is still difference of opinion as to the homogeneity of some of these enzymes.

English investigations of the alkaline degradation of polysaccharides have made considerable advance³²⁴⁻³²⁸ and are being applied to the preparation of

high-purity dissolving pulps³²⁹⁻³³¹. Interest in the same reactions in Sweden centers about the degradation during the normal alkali pulping of cellulose³³²⁻³³⁵. Bhujang and Nanjundayya³³⁶ have compared degradation by mechanical processing with degradation by alkali but mechanical degradation is insignificant in comparison.

CELLULOSE DERIVATIVES

There have been a number of reviews dealing with various phases of the reactivity of cellulose. Urquhart³³⁷ has discussed the reasons underlying differences in reactivity and suggests a theory for explaining them. Rogovin³³⁸ has reviewed the reactivity specifically of viscose pulps and Isbell, et al.³³⁹, have discussed the use of carbon-14 and tritium in the chemistry of cellulose and its derivatives. A surprising number of reviews deal with the subject of chemically modified cellulose fibers³⁴⁰⁻³⁴⁸.

Cellulose Nitrate

The military utilization of nitration-grade wood pulp has recently been discussed by Masuelli, et al.³⁴⁹. For most purposes, wood pulp is already used for nitration. Philipp³⁵⁰ has determined the effect of pulp preparation and predrying on nitration rates. Recent publications from Japan discuss nitration in acetic anhydride³⁵¹ and in phosphoric acid³⁵². Other workers have described the use of nitryl chloride³⁵³ and gaseous nitrogen pentoxide³⁵⁴ for nitration. A recently patented process³⁵⁵ uses magnesium nitrate as a catalyst, producing a nitrate which requires no stabilization.

The stabilization process itself has been investigated by Gagnon, et al.³⁵⁶⁻³⁶³. Millett, et al.^{364, 365}, have also studied stabilization and the relationship of the ion-exchange capacity (acidity) of the nitrates to that of the original pulps.

Wolfrom, et al.³⁶⁶⁻³⁶⁸, have studied the thermal decomposition of cellulose nitrate under reduced pressure. At 75 to 200 mm. a liquid mixture is formed containing water, formic acid, and various carbonyl compounds. Nitrogen is present in the form of α -hydroxynitriles. The gaseous products are predominantly carbon dioxide from carbon atom No. 1 and carbon monoxide from carbon atom No. 6. The thermal decomposition of cellulose nitrate in vacuo has also been studied by Andreev and Samsovov³⁶⁹.

Other reactions of cellulose nitrate recently investigated are decomposition with amines³⁷⁰ and interaction with various alkoxy silanes to produce cross-linked condensation products with silicon bound through two oxygen atoms³⁷¹. This reaction with silicones may occur through the free hydroxyl groups with the elimination of alcohol or through the nitrated groups with elimination of nitrous oxides.

Flory, et al.³⁷², and Meyerhoff³⁷³ have investigated the intrinsic viscosity and the flexibility of the cellulose molecules. Flory ascribes the large negative temperature coefficients and the variations with solvent to changes in chain flexibility. Takenaka³⁷⁴⁻³⁷⁶ has studied solutions and films, calculating the interaction parameter for acetone solutions of cellulose nitrate. Second order transition points and apparent activation energies of cellulose nitrates have been determined³⁷⁷. Moore and Tidswell³⁷⁸ have continued previous studies³⁷⁹ of the thermodynamic properties of cellulose derivatives. Kratky and Breiner³⁸⁰ have made small-angle x-ray measurements on cellulose nitrate solutions, confirming the relatively elongated shape of cellulose nitrate molecules. Huque, et al.³⁸¹, have studied viscosity and light-scattering data on solutions of the trinitrates and suggest that random coil configuration is attained in acetone but that a configurational transition occurs in

ethyl acetate. The values of the exponent "a" are about the same for both solvents. The thermodynamic properties of cellulose nitrate solution have also been studied by Gal'perin, and Moseev³⁸² and by Diener and Münster³⁸³.

Cellulose Acetate

In homogeneous acetylation of regenerated cellulose, preferential reaction of primary groups appears at the start, but in heterogeneous reaction, either diffusion controls the initial rate or the more rapid reaction of primary groups is compensated for by the more stable hydrogen bonding of these hydroxyls³⁸⁴. Malm, et al.³⁸⁵, have measured the rates of esterification of cellulose and of partly substituted cellulose esters with acetic, propionic, n-butyric, and isobutyric anhydrides. The rate depends on the conditions of esterification. Rogovin and Mirlas³⁸⁶ interpret the gelatinization of cellulose triacetate solution during acetylation to high structural regularity of the macromolecules and recommend adding small amounts of alkyl or acyl groups to prevent this. Kircher³⁸⁷ has described a new method for determining the rate of acetylation; methods for determining the acetyl content have also been described^{388,389}. Ishikawa's continued studies³⁹⁰⁻³⁹² of the acetylation reaction have included the use of sulfamic acid as a catalyst. In studying anomalous behavior during acetylation, Matsuzaki and Ward³⁹³ have shown that acetone solutions of the acetates of polysaccharides containing mannose groups are incompatible with those of cellulose acetate and suggest that this is related to anomalous viscosities of mannose-containing pulps.

The fibrous acetylation of cotton yarn gains in importance³⁹⁴. Bailey, et al.³⁹⁵, have found that, in such acetylation the noncrystalline areas are acetylated first. Deacetylation may proceed by either of two mechanisms. With

hydrochloric acid the amorphous regions will be deacetylated first, but with alkali deacetylation proceeds nonselectively from the fiber walls inwardly due to the swelling and penetration of the alkali. Greathouse, et al.³⁹⁶, measured the heat of acetylation during this process and Orr, et al.³⁹⁷, the mechanical properties of the product. The heat setting of cellulose triacetate has marked effects on the water imbibition and the rate of drying³⁹⁸. Recent studies have been made on the crystal structure of cellulose triacetate³⁹⁹, and the effect of heat and swelling treatments⁴⁰⁰.

Various groups have been interested in the absorption properties of cellulose acetate. Beever and Valentine⁴⁰¹ have measured moisture absorption of various cellulose acetates, and Bailey, et al.⁴⁰², iodine absorption, while Cameron, et al.⁴⁰³⁻⁴⁰⁵, have carried on an extensive study of the absorption of dyes. The thermodynamic properties of cellulose acetate have been determined in a number of solvents⁴⁰⁶⁻⁴⁰⁹.

Allen, et al.⁴¹⁰, have reacted cellulose acetate with boron trichloride. In this reaction deacetylation occurs along with complete hydrolysis, glucose being the main product in both cases. A similar reaction occurs with methylcellulose.

Cellulose Xanthate

In general, research on cellulose xanthate will be handled in the chapters on rayon, but research dealing primarily with the chemistry of the process has such a direct bearing on cellulose chemistry that it will be reviewed here also. Several good reviews of the physical chemistry of cellulose xanthation appeared during the year⁴¹¹⁻⁴¹³.

The xanthation reaction is accelerated when carried out in solution⁴¹⁴ or by a modified xanthation involving multiple sulfiding action^{415,416}. Meller⁴¹⁷ has investigated the effect of chlorous acid oxidation and of sodium borohydride reduction on the filtration properties of xanthates prepared from various pulps. Manley and Bengtsson⁴¹⁸ have isolated supermolecular particles with the ultracentrifuge from viscose solution. After redispersion, the solutions proved to be polydisperse with at least three different particle sizes, all much larger than molecular dimensions.

Tsuda and Mukoyama⁴¹⁹ have shown that the formation of cellulose IV during the spinning of viscose is increased by higher temperatures during regeneration and by higher concentration of zinc sulfate. Treiber and Rehnström⁴²⁰ have prepared analogs of cellulose xanthate using carbon diselenide instead of carbon disulfide. The reaction was extremely rapid, but very unstable products were produced with limited solubility.

Purves⁴²¹⁻⁴²³ has continued his attempts to determine the distribution of xanthate groups in sodium cellulose xanthate, and was successful with the following procedure. The xanthate was first methylated to form xanthate S-methyl esters which were then acetylated completely. During this process there was no change in the xanthate D.S. Aqueous chlorine dioxide then removed nearly all of the xanthate groups and a few of the acetyl groups. By determining the locations of the free hydroxyl groups it was found that most of them were in the six position and almost all the rest in the three position in the original xanthate.

Schurz and Zimmerl⁴²⁴⁻⁴²⁶ have continued their investigations of the diethylacetamido cellulose xanthates, measuring the molecular weights of these

derivatives by various methods. Very loose aggregations of the molecules are indicated. They assume that the same types of aggregation will explain the coagulation mechanism in viscose.

Other Cellulose Esters

Modified celluloses with ion-exchange properties have largely been ethers. However, cellulose phosphate has cation-exchange properties and has been recommended for this purpose^{427,428}. Another ion-exchange material can be made by reacting paper with succinic anhydride in the presence of pyridine to give a mono-ester⁴²⁹.

Cellulose phosphates have, of course, been used in flameproofing materials. Schiffner and Lange^{430,431} have found that flameproofing with chlormethylphosphonic acid produced less strength loss than the corresponding urea-phosphoric acid process. The addition of formaldehyde to phosphoric acid urea solution decreases the strength loss, but it is still too high for applications to rayon.

Rogovin⁴³²⁻⁴³⁴ has prepared cellulose esters of carbonic acid and mono-thiocarbonic acid. The phthalate⁴³⁵ may find some utilization since this modification imparts to wood a high degree of dimensional stability. This is unfortunately not permanent and can be used only when the wood suffers normal changes in atmospheric high humidity, not when it is wet with water.

There have been many investigations of sulfur-containing esters of cellulose. The sulfate itself can be made from the addition product of sulfuric acid and dichloroethyl ether⁴³⁶. The methanesulfonate and p-toluenesulfonate can be used as intermediates replacing the sulfonate groups with other desired groupings⁴³⁷.

Mesylation, which is apparently less impeded by steric hindrance than tosylation⁴³⁸, produces intermediates which may be further reacted to introduce phosphorus into the molecule and render it flame-resistant⁴³⁹. Viscosity data have been reported for cellulose tributyrates⁴⁴⁰, but most of the work on butyric acid derivatives involves mixed esters of acetic acid and butyric acid^{441,442}. Cellulose acetate sulfate⁴⁴³ and cellulose acetate crotonate⁴⁴⁴ have also been prepared and characterized.

Cellulose Ethers

Isbell⁴⁴⁵ has developed a micromethylation method, in order to prepare labeled ethers of polysaccharides. The method is based on the liquid ammonia method of etherification. Both Croon, et al.^{446,447}, and Derevitskaya, et al.⁴⁴⁸⁻⁴⁵¹, have confirmed their previous conclusions that the secondary hydroxyls are more reactive than the primary hydroxyls toward methylation.

The infrared spectra of cellulose change as methylation proceeds⁴⁵². The ratio of free hydroxyl to hydrogen-bonded hydroxyl increases with degree of substitution, thus confirming the accepted explanation of the water solubility of partially methylated cellulose.

Pakhomov, Golova, and Nikolaeva⁴⁵³ decomposed trimethylcellulose by heating in vacuum under the optimal conditions for converting cellulose to laevoglucosan. No trimethyl-laevoglucosan was formed, the main products being 2,3,6-tri-O-methyl-1,4-anhydro-1,5-glucopyranose and 2,3,6-tri-O-methyl-glucose.

As the degree of substitution of etherified celluloses (methyl, ethyl, and hydroxyethyl) increases, so does the stability to the action of Cytophaga⁴⁵⁴. Above 6-7% methyl or ethyl groups, bacterial growth is not supported.

Methylcellulose is one of several water-soluble cellulose ethers, most of which are insoluble or sparingly so in the majority of organic solids. Manley has found that dimethyl sulfoxide is a good solvent for the nonionic cellulose ethers⁴⁵⁵.

The effect of heating on the viscosity of water-soluble cellulose derivatives has been studied, and it has been found that irreversible viscosity decreases may occur^{456,457}. The heat of wetting of these water-soluble ethers has also been determined⁴⁵⁸.

The commercial form of ethylcellulose, in contrast to that of methylcellulose, is a typical thermoplastic material with good solubility in many organic solvents. As a result, its solution properties have received wide study. Vinogradov and Manin⁴⁵⁹ have established the dependence of the dynamo-optical properties on the stress and velocity gradients and have evaluated qualitatively the nature of the thixotropic transitions. Samsonova and Frenkel⁴⁶⁰ have measured diffusion coefficients and intrinsic viscosities of commercial ethylcelluloses. Barrer, et al.^{461,462}, studied sorption and diffusion in ethylcellulose, using both hydrocarbons and water. Ethylcellulose is not very stable to heating, except in the absence of oxygen, as oxidation with atmospheric oxygen occurs quite readily⁴⁶³. The heat resistance can be improved by removing fractions containing carboxyl and also fractions which form carboxyl readily on heating^{464,465}.

Borruso⁴⁶⁶ investigated the effect of dehydration of alkali cellulose before carboxymethylation. Hayakawa and Morita^{467,468} have investigated two-stage carboxymethylations. These have no advantage over single stages for degrees of substitution below one but a considerable advantage for material of higher D.S., up to two. Reinhardt, et al.⁴⁶⁹, have applied the carboxymethylation methods of

Walecka⁴⁷⁰ to the carboxymethylation of cotton fiber, thread, and fabric. These give low degrees of substitution ranging up to 0.09. Myhre and Smith⁴⁷¹ have prepared ion-exchange papers by treating the papers with carboxymethylcellulose solutions, fixing the material on the paper by precipitation with acid.

The analysis of carboxymethylcellulose and the techniques of application have been reviewed by Wurz⁴⁷². Grant, et al.⁴⁷³, have determined the physical properties of partially carboxymethylated cotton, while Schurz and Kienzl^{474,475} have studied the optical properties and the polydispersity of carboxymethylcellulose. Although ultraviolet and infrared spectra indicated the absence of foreign groups, the x-ray diagram showed the presence of cellulose II crystallites which are believed to be the gel bodies sometimes found in sodium carboxymethylcellulose solutions. Stawitz, et al.⁴⁷⁶, have continued their studies of the retention of carboxymethylcellulose by textile fibers. This retention is greatly improved by the presence of electrolytes in the solution.

Fiedler^{477,478}, in studying preparations for improving soil structure, found that carboxymethylcelluloses with degrees of substitution above 1.2 show considerable resistance to degradation by soil micro-organisms; this is in agreement with results for textile fibers.

Carboxymethylcellulose can be further treated to produce mixed derivatives. Klimova and Kristalinskaya⁴⁷⁹ have shown that the presence of the carboxymethyl group decreases the reactivity toward acetylation and benzylation. However, the reactivity towards tosylation is not affected. Amphoteric cellulose derivatives can be prepared by reacting carboxymethylcellulose with epoxydiethylaminopropane⁴⁸⁰. Oxidation of carboxymethylcellulose with chromic acid produces alkali-soluble materials^{481,482}.

Flameproofing can be achieved by reacting the carboxymethyl group of carboxymethyl-cellulose with fireproofing compounds of antimony, zirconium, tin, etc.⁴⁸³.

Several improvements in the processes for cyanoethylating cotton have been described in the past year⁴⁸⁴⁻⁴⁸⁸. This cyanoethylated cotton can be subjected to subsequent hydrolysis to introduce free carboxyl groups⁴⁸⁹.

Froment^{490,491} has discussed the preparation and properties of hydroxyethyl- and hydroxypropylcelluloses. In both of these compounds, the substituent group may consist of a single molecule or a polyoxyethylene polymer. Methods for determining the location, distribution, and nature of the substituents have been investigated^{492,493}.

The interest in partial modification of paper pulps to produce paper of improved quality has increased greatly⁴⁹⁴⁻⁵⁰⁰. The mechanism of this effect has been discussed by Talwar⁵⁰¹ and by Higgins, et al.⁵⁰².

A number of miscellaneous cellulose ethers have been examined for ion-exchange properties. Some that have been found suitable are the sulfomethyl^{503,504}, the sulfoethyl⁵⁰³, the diethylaminoethyl⁵⁰⁵, and the triethylaminoethyl ethers^{503,506}. A number of ethers have been prepared by reaction of cellulose with various derivatives of acrylic acid. These include methyl acrylate⁵⁰⁷, ethyl acrylate⁵⁰⁸, and acrylamide⁵⁰⁹.

Choudhury^{510,511} has studied further the length-breadth ratio of various esters of methylethylcellulose. He confirms the fact that the molecules are fairly rigid rods but does not explain why the substituents are all on the same side of the chain.

Miscellaneous ethers which have received attention are the phenyl ether⁵¹², the benzyl ether⁵¹³, and the cross-linked ether which is formed from tris(1-aziridinyl) phosphine oxide⁵¹⁴. This latter compound reacts with cotton to impart both crease-proofing and flame-resistant properties.

Geiger and Nobs^{515,516} have continued their study of alcoholate groups present in alkali cellulose. The number can be determined by shaking the dry alkali cellulose with methanol in which case the alkali is removed as methyl alcoholate. The maximum number of hydroxyl groups which react with alkali depends upon what alkali is employed.

Wegmann⁵¹⁷ has reviewed the reactions of cellulose with aldehydes, aldehyde resins, and reactive dyes. The reaction with glyoxal has been studied in some detail by Head⁵¹⁸. He finds that, depending on conditions, either semiacetals or acetals can be formed. Some of the acetals are diacetals and cross-linking of the cellulose chain has certainly occurred. On the basis of the work of Hurwitz and Conlon⁵¹⁹, these cross-linkages are formed through a single carbon atom. They found that the crease recovery-strength relationships of treatments with glyoxal, glutaraldehyde, and α -hydroxyadipaldehyde were similar, if not identical, to those of formaldehyde. Irvine and Kress⁵²⁰ have recently discussed in very general terms the reaction of cellulose with acetals. More detailed reports of the nature of these acetals and the properties of the products can be expected later.

Oil- and water-repellent surfaces can be produced by the reaction of cotton with various acids containing fluorine^{521,522}. The mechanical properties of the material are little affected by this treatment.

Kramer⁵²³ has recently reviewed the reactions of isocyanates with cellulose and cellulose derivatives and the use of isocyanate derivatives in textile finishing. The thiourethanes of cellulose react with acrylic acid derivatives or with organic acids to give compounds with excellent affinity for acid dyes^{524,525}. Another type of cross-linking agent between cellulose molecules is a phosphorylamide⁵²⁶. It is suggested that this material forms a cross link between cellulose molecules through an oxygen atom at one point and a nitrogen atom at another and imparts flame-resistance to cotton.

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