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ORIGIN AND OCCURRENCE

That step in the biosynthesis of cellulose where the microfibril first appears has been studied on young wood with the electron microscope\(^1\). Additional information on this step has been given by Colvin's observation\(^2\) that ethanol extracts of *Acetobacter xylinum* contain some material which in the presence of water develops typical microfibrils of cellulose. This final step is accelerated by a thermolabile extracellular substance but does not require the presence of bacterial cell walls.

Further details have been published of the nature of the conversion of radioactive carbon dioxide\(^3,4\) or sodium carbonate\(^4\) into the carbohydrate constituents of pinewood. A more active holocellulose was obtained from trees injected with sodium carbonate than from those exposed to carbon dioxide. \(^{14}\text{C}\) has also been introduced into flax cellulose by biosynthesis in an atmosphere of \(^{14}\text{CO}_2\).\(^5\) Where \(^{14}\text{C}\)-labelled glucose was injected into the cotton boll, it has been shown by fragmentation of the cellulose that some glucose had broken down and been resynthesized by the Embden-Meyerhof pathway\(^6\).

The occurrence in mammalian connective tissue of a polysaccharide with the characteristic x-ray diffraction pattern of cellulose has been corroborated. Cruise and Jeffery\(^7\) have confirmed the findings of Hall et al.\(^8\), in most respects. They do not agree, however, that the cellulose forms an outer sheet on certain protein fibres but, rather,
that a certain type of fibre appears to be predominantly polysaccharide. They have obtained x-ray patterns from individual isolated fibres and these, coupled with microscopic observations, form the basis for their views.

COMPOSITION

Differences in behaviour between highly purified cellulosic pulps from wood and from cotton are of importance to the rayon industry and have been investigated for some time. Kraessig and Howard have recently proposed a comprehensive program of basic study in this field, aimed partly at differences in composition and partly at differences in fine structure in the two pulps.

One of the main differences in composition is the long-established presence of mannose units in wood, especially in sulphite dissolving pulps from softwood. There is good evidence that this is due to the presence of glucomannans, which have been isolated from a variety of woods. It is possible by suitable extraction procedures to remove the non-glucose polymers to levels below the limits of our experimental methods. Conversely, the pulping process may be modified to retain more glucomannans, which may be desirable for certain paper pulps.

It is to be noted in this connection that very slight amounts of non-glucose sugars may be formed during hydrolysis of cellulose and subsequent chromatography. Saeman et al., observed two spots moving more rapidly than glucose during paper chromatography of glucose solutions which had been boiled with acid; Matsuzaki et al., have
attributed this to acid epimerization of the glucose. The amounts formed are extremely small and do not always appear on chromatograms. The authors believe that they may interfere where only traces are present, but not in ordinary investigations. Improvements in analyzing for the constituent sugars continue to appear.

In 1954 before the present development of sugar determination by paper partition chromatography had become widespread, Steinmann and White found a statistical correlation between the mannose content of cellulosic pulps and the titration of these pulps with lead tetraacetate. Roudier and Nick have re-examined this oxidation, determining the mannose and xylose content of pulps before and after oxidation. This has also been done by Matsuzaki and Ward and by Detrick. In all cases it is found that accessibility and end groups affect the oxidation of pulps as well as the mannose content, but the correlation found by Steinmann and White is corroborated by all workers. All of the mannose is not oxidized under the conditions used by any of these workers. Choudhury has determined the effect of hemicelluloses on the accessibility to acid of jute fibers.

Greatly increased activity in the study of the structure of the noncellulosic polysaccharides of wood and other plant materials has recently been reviewed by Roudier, by Hamilton and his coworkers, and by Hirst. Many individual contributions in this field have been made in regard to various species of pine, beech, birch, larch, kapok, jute, etc.
STRUCTURE IN THE SOLID STATE

For many years crystal structures based largely on x-ray diffraction data have been accepted for the various forms of cellulose. More recently information has also been obtained from infrared spectra \(^{43,44}\), particularly from polarized infrared radiation \(^{45,46}\). As Jones \(^7\) has shown, some of our classical unit cells for the cellulose crystal must be modified to account for the newer data. In the past year proposals to account for the various hydrogen bonds indicated by the infrared spectra have been advanced by Mann and Marrinan \(^46\) and by Liang and Marchessault \(^48\).

These new data \(^45\) confirm the observation that the crystal modification of bacterial and Valonia cellulose I is somewhat different from that of the usual cotton and wood cellulose I. A new crystalline modification of cellulose resembling cellulose I has been observed by Ellefsen \textit{et al.}, from acid-treated cellulose \(^9\).

In addition to information as to the nature of the crystalline regions of cellulose, the x-ray also indicates the relative amounts of crystallinity \(^50\). There is, however, no agreement as to the exact interpretation of the x-ray diagram in this regard. Ant-Wuorinen thinks that his crystallinity index is a measure of the average degree of order and not of the percentage of completely crystalline material \(^51\). Additional methods have been proposed in the past year for evaluating the x-ray diagram \(^50,52,53\).
Heikens et al., have continued the investigation of the x-ray small-angle diffraction of cellulose. They find that with water-swollen materials the scattering is due to crystallites embedded in a homogeneous mixture of noncrystalline cellulose and water. In dry cellulose the scatter is largely due to the submicroscopic vacuoles, which are filled with water in the swollen state.

Cellulose I may be converted to cellulose II, III, or IV by suitable treatment. Ziifle et al., have compared the physical properties of the first two conversion products. Jullander and Rånby have measured the changes of physical properties in wood pulp during conversion to cellulose IV by heat treatment. Kanamaru has studied heat treatment of viscose rayon at 60-200°C. Yurugi found earlier an unusual x-ray pattern in high-tenacity rayon which he attributes to partial formation of cellulose IV. Centola stresses the fact that changes in the crystal structure of cellulose (regeneration from solution, heat treatment, etc.) are insufficient to explain the concomitant property changes. He supports an earlier hypothesis of Petitpas and Mering that accompanying rearrangements of the macromolecular chains are responsible for the changes in physical and chemical properties. Howsmon and Marchessault have found that the recrystallization of ball-milled cellulose can occur either as cellulose I, II or IV. Their results indicate that radicals are produced during milling. This recrystallization has also been studied by Korol'kov.

Molecular and crystallite orientations are known to have marked effects on the properties of cellulosic materials. Recent articles discuss
this from the standpoint of cotton, mercerized cotton and rayon. Cumberbirch and Harland find D.P. more important than previously suggested for the mechanical properties of cellulose acetate filaments.

Ant-Wuorinen and Visapää have studied the effect of various chemical treatments on the fine structure of cellulose. Of interest is the fact that calcium thiocyanate solutions will convert wood cellulose, but not linters, to cellulose II. The authors explain this as a result of the low crystallinity of the former, which permits more complete swelling and complex formation.

It has been indicated previously that structural reversals along the cotton fibre represent regions of high order. X-ray diffraction patterns taken along the fibre by a microtechnique show that qualitatively the crystalline pattern at the reversal is more distinct than that between reversals.

Nakai has published a series of papers on the structure of regenerated cellulose fibres and the formation of skin and core types in rayon. In his studies he has shown changes due to recrystallization after spinning, comparing the iodine absorption and the hydrolysis method of measuring order. The formation of different types of structure in rayon fibres is attributed to the different rate of gelation of the xanthate and to various orienting effects. Other work in this field of general importance to the field of cellulose chemistry includes that of Cumberbirch on the structures of high denier model filaments and of
Kato on the use of reactive dyes in staining techniques for differentiation of structure. A new type of rayon fibre, the so-called "polynosic" fibre, has been announced. It is stated to have a homogeneous structure, resembling that of natural cellulosic fibres, but adequate description has not yet appeared in the literature.

The effect of changes in the fine structure of cellulose upon the mechanical properties has been discussed by a number of workers both in regard to natural cellulosic fibres and to regenerated rayons. Borgin has carried out a series of experiments on the surface properties of cellulose and its behaviour with water. In this connection recent work by Jayme and Hunger showing electron micrographs of microfibrils in dried and hornified pulps is also of interest. Mishchenko et al. have compared various methods for determining specific surface area and concluded that the most reliable methods are nitrogen sorption and ion-exchange.

SORPTION AND SWELLING

Early last year Downes et al. showed that the moisture sorption of wool was greater under integral sorption than under interval sorption. Beever and Valentine have presented results to show that this is also true for cellulose and cellulose acetate. This seems to indicate that the shape of the sorption isotherm will depend on the magnitude of the humidity increment during the various stages of adsorption.

In 1958 a symposium on the sorption of moisture by wood was held in Stockholm. These papers have now been published as a unit. They
include discussions of the exact determination of a new sorption theory, of the rate of sorption, of the sorption of the individual components, of sorption at the fibre saturation point, of sorption at elevated temperatures and vapor pressures, and of the sorption of wood impregnated with salts.

Van den Akker et al., have also studied the cellulose-water system with especial interest in high humidities and have concluded that there is no real fibre saturation point for pulps and fibre masses. Stamm agrees that a definition of fibre saturation point based on equilibrium with the atmosphere is not productive. He proposes a new definition for the concept.

Clemson has measured the moisture regain changes in stretched viscose yarn and finds that the moisture content increases with extension of the yarn. This is in contrast to the behaviour of cotton fabrics and yarns where the regain is reduced on account of the inhibition of free swelling by compression of the fibres. It would be interesting to measure the moisture content of individual fibres of cotton under tension.

Cooper and Ashpole have studied the heat of absorption of cellulose deduced from calorimetric measurements. The differential heat of absorption, which gives information about the absorbing regions of the fibre, varies from fibre to fibre (this does not necessarily infer differences in the energies of the water cellulose bonds). Kawai has studied the sorption of water vapor by cellulose and high polymers at
high humidities and concludes that the simple theory of sorption as a process of solution of water in the disordered regions of the polymer does not explain his experimental evidence. Morrison et al.\textsuperscript{119}, conclude from a study of the thermodynamics of the cellulose-moisture system that the hysteresis of the sorption isotherm is an entropy phenomenon. Several indirect methods of measurement of hydration and moisture content have been described\textsuperscript{120-125}.

For some time Ant-Wuorinen\textsuperscript{126} has contended that mineral acid is very tenaciously held in trace amounts by cellulose fibres and that this can interfere with analytical determinations, in disagreement with the work of Samuelson and others\textsuperscript{127}. In his latest paper Ant-Wuorinen states that no Donnan equilibrium can be assumed with cellulose fibres immersed in dilute acid and that the carboxyl groups in such fibres are undissociated under these conditions.

Archer and Mason\textsuperscript{130} have measured the permeability of cellophane to the vapors of benzene, ethanol, methanol and water. The latter parallels the sorption isotherm over adsorption-desorption cycles. Kaila and Sihtola have shown that substitution of cellulose increases sorption of low-molecular weight acids\textsuperscript{129}.

Corroborating their previous work, Belford et al.\textsuperscript{131} find that copper ion uptake by cellulose from solutions of copper salts follows the Langmuir adsorption while electron diffraction diagrams indicate a regular pattern of metal ion and a corresponding regular arrangement of the cellulose molecules on the outer surface of the microfibrils. They also point out that this type of adsorption can hardly be connected with
carboxyl content and question the validity of carboxyl determination by ion-exchange methods. On the other hand, Davidson and Spedding have found that the absorption of copper from sodium cuprate solutions by cotton cellulose does not follow the Langmuir adsorption isotherm but the Freundlich isotherm, and that the limiting copper uptake is higher than that required for the Normann compound.

Wedell has found that the adsorption of carbon black by cotton depends upon the moisture content of the system, but that desorption is affected little by humidity.

The sorption of a great many different types of molecules on cellulose has been studied during the past year, including formaldehyde, glycerol, locust bean and guar gums, starch and cellulose derivatives, various types of aromatic compounds, melamine-formaldehyde condensates and urea-formaldehyde condensates. Giles and Hassan have extended to dyes their earlier conclusions that cellulose adsorbs organic compounds of various types by hydrogen bond formation in the absence of water, but from aqueous solvents by van der Waals' forces alone.

Bartunek has attempted a unified interpretation of the phenomenon of swelling with particular reference to cellulose. Thode and Guide have also given a thermodynamic interpretation of the swelling of cellulose in organic liquids. Shukalova et al. have measured the kinetics of aqueous swelling of cuprammonium rayon. Ingmanson et al. have studied the theory of the various effects of beating on cellulose, including fibre swelling and increase of surface.
Denoyelle \(^{151}\) has studied particularly the swelling of cellulose in soda solutions, but draws certain more general conclusions. He believes that the Donnan equilibrium cannot explain the swelling of polyelectrolyte gels but that swelling results rather from a balance between cohesive and solvating forces. As mentioned above, Ant-Wuorinen \(^{128}\) also is skeptical of the establishment of a Donnan equilibrium with dilute acids.

Kato and Yamada \(^{152}\) have also studied the effect of sodium hydroxide on cellulose—in this case, rayon—and two sets of workers have compared the physical properties, after removal of the swelling agent, of cellulose swollen with alkali and with ethylamine \(^{58,153,154}\).

The swelling of cellulose in phosphoric acid has been studied under the microscope by Koshizawa \(^{155}\). In addition to other solvents, phosphoric acid has also been used to swell fibres for examination in the swollen state under the electron microscope \(^{156}\).

**CELLULOSE SOLUTIONS**

Dolmetsch \(^{157,158}\) still questions whether dilute solutions of cellulose or its derivatives are true molecular dispersions. He believes that the nitrate viscosity permits only limited conclusions as to the true chain length of cellulose, that the ratio of nitrate D.P. to cuprammonium D.P. measures the presence and extent of ordered crystalline substance, and that even highly diluted cuprammonium solutions of cellulose are not as finely subdivided as diluted viscose after xanthation with excess carbon disulphide.
Structured aggregates of insoluble material and gel particles can, of course, exist in technical solutions of cellulose and its derivatives. Schuerch has suggested some methods for preparing clear solutions of cellulose derivatives.

The extensive study of the past several years on various metal complexes as cellulose solvents has been reviewed by Calistru. There has also been further work on many of these solvents: sodium beryllate and zincate, sodium iron tartrate, cadoxene (cadmium-ethylene-diamine) and sodium-copper-biuret.

Cyrot has reviewed various methods for measuring the polydispersity of high molecular weight cellulosics. He also describes a method for measuring intrinsic viscosity of nitrated cellulose.

It was shown last year that cellulose nitrates containing carbonyl groups may be insoluble. Virkola has continued this work and demonstrated that carboxyl groups have a similar effect. Ellefsen and Vardheim have also studied the effect: they believe that cross-linking occurs after nitration, not during that process.

The methods for determining intrinsic viscosity have been discussed by various workers. Edelmann and Horn have investigated the use of iron-sodium tartrate solvents for measuring degree of polymerization by viscometry.

The viscosity of cellulose solutions is of importance in both the textile and the paper industry. Treiber et al. have discussed
the viscosity of technical viscose solutions, in particular the viscosity-concentration relationship. Dahm has discussed the relation between pulp viscosity and paper strength in bleached kraft pulps.

Earlier work on the molecular weight of ethylcellulose solutions has been extended to measurements of the temperature dependence of viscosity and to correlations of critical frequency with D.P. in solvents of low dielectric constants. Cumberbirch et al., describe a detailed study of chain-length distribution in secondary chemical acetates. Vink has prepared celluloses of low polydispersity by saponification of fractionated cellulose acetate. Marx-Figini has developed an improved method for fractional precipitation of cellulose nitrate. Yagami has compared fractional precipitation and solution methods and has determined the molecular weight distribution of the hemicelluloses dissolved during the viscose steeping process. Nakao et al., have also studied the fractional solution of nitrated pulps, and have found that fibre structure has a more pronounced influence than does the D.P. and that, therefore, the fractional solution curve is not representative of chain-length distribution in cellulosic fibres. Abadie-Maumert has measured the effect of cyclohexane addition on the precipitation of cellulose nitrate from acetone by water. Almin has successfully applied the Craig countercurrent techniques to fractionation of cellulose acetate, making use of immiscible phases of multicomponent solvent systems.
REACTIVITY OF CELLULOSE

Hydrolysis

The seven-year industrial expansion plan for Russia includes increasing utilization of wood by saccharification. As a result, there have been many publications covering studies in this field: hydrolysis under various conditions, the study of mechanisms, the manufacture of crystalline glucose, trihydroxyglutaric acid and levulinic acid, studies of the effect of acid concentration and of structure on rate, the control of pH, continuous apparatus, and the effect of temperature. Hajny, in reviewing wood hydrolysis, concludes that in the United States economical utilization must await upon uses for the lignin and the hemicellulose sugars. Zedet has also reviewed the field of cellulose hydrolysis.

The studies of Marchessault and Ränby on the hydrolysis of cellulose in phosphoric acid add further corroboration to the idea that the so-called weak links in cellulose are effects due to oxidation and to an activating effect of the carbonyl or carboxyl groups so produced. Higgins et al. have decided from their studies of the kinetics of acid degradation of cellulose that the most reasonable explanation of the decreasing rate lies in the gradually varying order of molecular arrangement. Parisot et al., indicate that pentoses in the chain may induce sensitivity to hydrolysis, but the pentoses may originate from oxidation also, as has been indicated by studies of Kaverzneva, Henderson, Daniel, Theander and Bešlik.
Rogovin and Pogosov treated cellulose with 95% hydrofluoric acid. Cotton cellulose was completely hydrolyzed in five minutes to products of low degree of polymerization.

The effects of heterogeneous acid hydrolysis on the properties of the partially hydrolyzed fibre have been studied from a number of different points of view. Achwal et al., have suggested that changes are due to solution of hydrolyzed material and to recrystallization of the remaining cellulose. Hosoi et al., have made similar studies, working, however, with wood holocelluloses in which there are considerable amounts of noncellulosic polysaccharides. Matsuzaki and Sobue have compared a dissolving pulp from wood and a raw cotton cellulose with regard to the properties of the residual crystallites and conclude that the peeling of cellulose chains from crystallite surfaces may be the main action. Graeser and Liesebach have demonstrated the hydrolysis (tendering) of cellulose due to finishing with formaldehyde resins.

The deterioration of book paper may have various causes, but hydrolysis is a major factor. Langwell has described a test for use by librarians to indicate the presence of sulphur dioxide in the atmosphere of rooms used for paper storage. Barrow and Sproull have concluded that in modern book paper the acidity of the paper itself is the major factor and have suggested a stabilizing process of impregnation with the carbonates of alkaline earths.
Oxidation

Theander has reviewed the conclusion to be drawn about cellulose oxidation from studies on the glucosides as model compounds.\textsuperscript{230,231}

Three groups have studied the oxidation of cellulose with nitrogen dioxide, investigating the conditions of reaction and the mechanism.\textsuperscript{232-235} Inano and Machida\textsuperscript{236} have described a method of preparing D-glucuronic acid from cellulose, using the "celluronic acid" prepared with sodium nitrite and concentrated phosphoric acid. An attempt to introduce three carboxyl groups per glucose unit resulted in a product containing 50.8\% carboxyl (75\% of theory).\textsuperscript{237}

A. Brassard\textsuperscript{238} and Schulz et al.\textsuperscript{239} have studied the reactions occurring during the alkaline oxidation of cellulose. Kleinert\textsuperscript{240} has investigated the closely related H\textsubscript{2}O\textsubscript{2} degradation of alkali cellulose, while Michie and Neale\textsuperscript{241} have shown the catalytic action of copper during this reaction. O'Meara and Richards\textsuperscript{242} have found the major acids produced by alkaline degradation of periodate oxycellulose to be glycollic and α-dihydroxybutyric acids; they interpret this as evidence that the original scission is mainly beta-alkoxycarbonyl elimination. Rice and Johnson\textsuperscript{243} suggest that instability in oxidized cellulose arises from the formation of a 3-ketouronic acid unit, but do not state the oxidant used.

Rapson et al.\textsuperscript{244} have found that the degradative effect of sodium chlorate on cellulose is high and that this material is not promising as a bleaching agent for pulp, although Heitman\textsuperscript{245} uses it to reduce degradation during chlorine and hypochlorite bleaching.
Wacek\textsuperscript{246} has studied degradation during the sulphite pulping of wood and concludes that although mechanical action plays a part, the role of oxygen is much more important.

A number of new methods and modifications of old methods for carboxyl determination have been proposed\textsuperscript{247-257}. Schurz and Kienzl\textsuperscript{258} propose an oxidation number as a gross measure of cellulose oxidation. This is based on the iodate method for wet combustion.

Alkaline borohydrides\textsuperscript{259}, which reduce carbonyl groups and lactone groups to alcohols, may be used to reduce the bad effects of oxidation on the properties of cellulose. They have been used extensively in studying the yellowing of pulps, paper and textiles\textsuperscript{260-261}, which many believe to be related to the oxidation of the cellulose\textsuperscript{262-264}, usually during the bleach. Sihtola et al.\textsuperscript{265} have shown that carboxyl groups as well as carbonyl groups play a role in the yellowing effect. Roudier\textsuperscript{266,267} and Czepiel\textsuperscript{268} have independently proposed a nonoxidative mechanism to account for the yellowing of cellulose.

Oxidation during bleaching has been reviewed\textsuperscript{269,270}. Catalyzed oxidation during bleaching of pulps has been recommended for ensuring increased molecular-weight homogeneity\textsuperscript{271}. Degradation of linen\textsuperscript{272}, rayon\textsuperscript{273} and cotton fabrics\textsuperscript{274,275} due to bleaching agents has been measured.

Bhandari et al.\textsuperscript{276,277} have studied the effect of various hydrated metal oxides on actinic and ultraviolet degradation of cellulose, finding that hydrated oxides of manganese furnished a high degree of
protection. Czepiel has found that manganese salts also provide protection against colour reversion in dissolving pulps.

Flynn has investigated the degradation of cellulose by ultraviolet light and Jortner that of cellulose acetate. Flynn indicates that the initial process in cellulose photodegradation is the formation of carbonyl groups with liberation of hydrogen. In secondary processes carbon dioxide and carbon monoxide are evolved, D.P. drops off, and carboxyl groups are produced. Sadov and Vylcheva also find carboxyl and carbonyl groups (both ketones and aldehydes) in cellulose exposed to artificial light.

Beelik and Hamilton found a variety of sugars and oligosaccharides in the water extracts of irradiated cellulosic pulps. Three of these must have been produced by sugar transformation since they do not occur in the original pulps. These are D-arabinose, 3-β-D-glucosido-D-arabinose, and 3-β-cellobiosido-D-arabinose. It will be remembered that arabinose has also been found in the chlorine oxidation of cellulose.

Padmanabhan et al. found that ultraviolet irradiation of cellulose breaks some bonds and renders others sensitive to rupture with alkali. Some of these sensitive linkages, but not all, are also broken by storage in air or oxygen. The alkali-sensitivity would agree with the expected behaviour of Flynn's carbonyl compounds. Sippel advances the theory that weak links are produced, possibly by oxidation, from sites sensitized by unusually large stresses in the crystal lattice which cannot be distinguished before modification from the other similar lattice bonds.
Abrahamson et al.\textsuperscript{283} have studied the spectroscopy and photochemistry of cellulose-tendering dyes. Tendering activity of the dye could be directly related to the ability of the photoexcited dye to abstract hydrogen from cellulose.

The effect of gamma radiation on cotton is primarily degrading\textsuperscript{284-287}. There are increases in reducing power, carboxyl content and fluidity. Studies of the effect on wood of such irradiation are conflicting\textsuperscript{288-290}. Sharkov et al.\textsuperscript{291} have suggested that this can be used as a preliminary step in wood hydrolysis. On the other hand, it is stated that water-soluble cellulose derivatives may be cross-linked by ionizing radiation without degradation, while in aqueous solution\textsuperscript{292}.

The deterioration of jute cellulose\textsuperscript{293} and of book paper\textsuperscript{229,294} on storage has been determined. Van Royen\textsuperscript{295} has indicated that aging three days at 100°C. is suitable for evaluating the comparative permanence of pulps at room temperature.

\textbf{Thermal Degradation}

In a continuation of the work of Golova\textsuperscript{296,297} on the thermal decomposition of cellulose, high yields of levoglucosan have been obtained by thermal degradation of cellulose in a stream of superheated steam\textsuperscript{298}. Sergeeva et al.\textsuperscript{299} have investigated the possibility of obtaining levoglucosan directly from lignocelluloses. The yields are good, providing that the material has been subjected to prehydrolysis to remove pentosans which inhibit levoglucosan formation.
Legrand\textsuperscript{300} has studied cellulose pyrolysis, paying particular attention to the changes in x-ray diagram. Gross and Robertson\textsuperscript{301} have calculated the self-ignition temperatures for various materials, including cotton linters. The calculated values are in reasonable agreement with measured values. Yoshimura has determined the lowering of the decomposition temperature by the addition of various inorganic salts\textsuperscript{302}.

Hessler and Workman\textsuperscript{303} have measured the chemical changes in cotton fibre induced by heat, and Grant et al.\textsuperscript{304,305} have studied the fibre damage due to overheating of seed cotton at the gin.

**Degradation by Micro-organisms**

Newman\textsuperscript{306} has found the metabolic pathway for cellulose digestion by a thermophilic micro-organism from compost to be by way of cellobiose and galactose. Nopitsch and Nobus\textsuperscript{307} have shown that *Aspergillus niger* also destroys cellulose. Ellwood and Ecklund\textsuperscript{308} have shown that bacterial action in pond-stored logs was due to anaerobic bacteria, including *Aerobacillus polymyxa*.

Efforts to separate and purify cellulolytic enzymes continue\textsuperscript{309-313}. Painter\textsuperscript{314} has made use of enzymes for degrading polysaccharides from various types of wood. If the oligosaccharides formed are immediately removed by dialysis, the yields are greatly improved.
CELLULOSE ESTERIFICATION

Nitration

Urbanski et al.\textsuperscript{315} have compared the nitration of starch and of cellulose, pointing out the important role that diffusion plays in the nitration of cellulosic fibers. The reactivity of cellulose toward nitration has also been studied by Yin and Brown\textsuperscript{316}, particularly the changes in accessibility due to wetting and drying treatments.

Petropavlovskii and Nikitin\textsuperscript{317} have prepared low-substituted cellulose nitrates, 0.4-1.6\% N. These are soluble in dilute sodium hydroxide solutions and stable. They can be regenerated as strong films with the hygroscopicity of cellophane.

\textit{Eucalyptus rostrata} does not behave toward direct nitration in the same way as other woods. The D.P. of the nitrate increases rapidly with time of nitration to a maximum and then falls off slowly. Lewin and Epstein\textsuperscript{318} question the value of direct nitration as an analytical tool in this case.

Wolfson and his coworkers\textsuperscript{319,320} have continued the study of the thermal decomposition of cellulose nitrate. With C\textsuperscript{14} as a tracer, a major fraction of the glyoxal produced was shown to be derived from C\textsubscript{2} and one of the adjacent carbon atoms; C\textsubscript{2} and C\textsubscript{5} provide some of the carbon dioxide and formic acid fragments but very little of the formaldehyde. Abe and coworkers\textsuperscript{321} have also studied this decomposition.
Infrared absorption spectra appear to confirm the existence of an addition complex between the nonesterified hydroxyl groups of cellulose nitrate and the carbonyl groups of plasticizer molecules—for instance, diphenyldiethylurea. The exact mechanism of formation is still unknown. Cellulose nitrate also reacts with butylamine. The reaction product appears to contain one nitrate group and one amino group per glucose unit.

Meyerhoff has found that the relationship between intrinsic viscosity and D.P. in nitrated cotton applied also to that in nitrated linters or wood pulp. This relationship has also been determined by Harland. Huque, in studying the solution properties of cellulose nitrate, has found that sorption of the material on the capillary walls affects the viscosity determination and its interpretation.

Several new methods have been described for the analysis of cellulose nitrate; titration, infrared and colorimetric methods. Trommell has made a study of the solubility of cellulose nitrate in alcohol-ether mixtures and finds it critically dependent on the arrangement of the nitrate and hydroxyl groups. He has also reviewed the theories of macromolecular solution.

Acetylation

Sakurada has continued his studies of the acetylation reaction with particular attention to pretreatments with swelling liquids, especially alkali. Hamalainen et al. have shown that trifluoroacetic acid is an effective esterification promoter in the preparation of partially
acetylated cotton. Kido has determined the sorption of acetylation catalysts (\(\text{ZnCl}_2\), \(\text{H}_2\text{SO}_4\) and \(\text{HClO}_4\)) on cellulose in glacial acetic acid.

Matsuzaki, continuing his investigation of cellulose acetates from wood pulps, has determined the ultraviolet spectra of phosphoric acid solutions of unfractionated and fractionated cellulose acetate and has shown that this absorption is due to carbohydrates resulting from the hydrolysis—in particular, to xylose and to modified saccharides. The first fractions of the fractionated acetates showed greater absorption than the intermediate fractions. Machida has also studied the relationship between the properties of cellulose acetate and the hemicellulose contents of the corresponding pulps.

Several reviews and extended studies of the production of partly acetylated cotton appeared during the year. Conrad, in an extensive study, has shown that the mechanical properties of cotton fabrics, yarns and fibres are generally not improved by acetylation or other chemical substitution. According to Cumberbirch, the tenacity of a cellulose acetate filament can be computed from D.P. distribution and the relationships of tenacity and D.P. in the individual fractions.

Rogovin et al. have described an accelerated process for making cellulose triacetate. Kido et al. have studied the production of triacetate I and triacetate II and have shown that the form produced is temperature dependent. The effect of heat treatment on the swelling behaviour of cellulose triacetate has been determined.
Two new analytical methods are of interest in the field of cellulose acetate. One of these is the determination of the cellulose acetate content of double-based propellants, the other a simplified method for determining acetyl content.

The sorption isotherms of cellulose acetates of different degree of substitution have been determined. The mechanisms that govern transfer of water and of ions through cellulose acetate membranes have been formulated. There have also been new studies of the absorption of dyes by cellulose acetate.

Xanthation

Vermaas has reviewed the literature on the nature of xanthation and of the ripening of viscose solutions. He has also carried out a study of these mechanisms using ethyl xanthate as a model compound. A potentiometric method for determining the ripening degree of viscose has been described. It has also been shown that the redox potential of viscose solution depends upon the ripeness.

The properties, particularly the reactivity of the cellulosic pulp used, affect greatly the course of the reaction and the properties of the fibers. A variety of methods has been described for measuring this reactivity and many efforts have been made to correlate the treatment of the pulp with the properties. Certain dissolving pulps from wood are now claimed to approach cotton linters pulps in their properties and methods for controlling pulp quality have been reviewed.
Continued efforts are made to establish the distribution of xanthate groups in cellulose xanthate\(^ {372,373}\). Yamada et al., indicate that the distribution becomes more uniform during the ripening process\(^ {373}\).

Cellulose xanthate can be used as an intermediate for other reactions. For instance, a rayon fiber with a surface layer of cellulose thiourethane may be produced\(^ {374}\). Farrar has studied the product of the reaction of cellulose xanthate with betapropiolactone\(^ {375}\).

Additional work has been done on the particle size in viscose solution, both by the ultracentrifuge\(^ {376}\) and by light-scattering methods\(^ {377}\). The presence of a small amount of material of very high molecular weight has again been demonstrated.

**Miscellaneous Esterification**

The mechanical properties and advantages of cellulose propionate for plastics have been discussed by Paist and Jones\(^ {378}\). Iida\(^ {379-381}\) describes a new chemically modified cotton, produced by reaction with diketene to introduce acetoacetyl groups.

A mild esterification process for polysaccharides involves heating with an ammonium salt such as ammonium phthalate\(^ {382}\). Cellulose is mentioned in the discussion, but all of the examples refer to starch.

Mixed esters of cellulose acetate continue to be of interest. A method has been described for introducing halogenated groups into cellulose acetate, which can then be further reacted\(^ {383}\). Rusznák\(^ {384,385}\) has fractionated cellulose diacetate monophthalate and made molecular weight
determinations. The acetobutyrate has also been intensively investigated\textsuperscript{386}. Rogovin\textsuperscript{387,388} has determined the stability to saponification and heat of the previously described alkyl cellulose carbonates.

A method for preparing sodium cellulose sulphate with very little chain-length diminution has been described\textsuperscript{389}. On the other hand, the preparation of purposely degraded sulphates with a degree of polymerization ranging from 6 to 100 has also been studied\textsuperscript{390}.

CELLULOSE ETHERIFICATION

Croon\textsuperscript{391,392} has continued his studies of the distribution of substituents in partially methylated cellulosics. He finds\textsuperscript{391} that when cellulose is methylated with methyl chloride acting on alkali cellulose the reactivities of the 2-, 3-, and 6-hydroxyl are 5:1:2, respectively. The rates of ethylation are similar\textsuperscript{393}. He has also shown that the relative reactivity at the 2-carbon atom is greater with methyl chloride than with methyl sulphate. The flow properties of methylcellulose solution have also been determined\textsuperscript{394}. On the other hand, toward diazomethane the hydroxyls are almost equally reactive (1.2:1:1.5) with the primary 6-hydroxyl somewhat more reactive than the secondary\textsuperscript{392}.

Plisko\textsuperscript{395} has examined alkylation, especially ethylation, by means of the esters of a number of aromatic sulphonic acids. Alkylation occurs more readily in organic bases than in aqueous alkali. With aqueous alkali the ease of alkylation decreases with the size of the alkyl group.
Ferroxides formed from ethylcellulose during ultraviolet irradiation or at higher temperatures are relatively stable, but they and their decomposition products accumulate during storage, shortening the inductive periods of heat decomposition in the air. The effect of oxidation on the structural and mechanical properties of ethylcellulose solution has been investigated.

Cellulose may be carboxymethylated in different ways to achieve particular results—low-viscosity materials or low-D.S. materials. A modified method for determining the degree of substitution by the use of radioactive salts has also been published. The nitration of carboxymethylcellulose has been investigated and some of the properties of the products determined. The physicochemical properties of carboxymethylcellulose and of its fractions have been further studied, as has the ability of the sodium salt to remove and prevent redeposition of dirt in laundering. Its behaviour toward iodine (possible complexing) has also been considered as well as its use for further reaction to produce other types of cellulose derivatives.

New modifications of the cyanoethylation process continue to appear. The kinetics of the process and the properties and mechanical behavior of cyanoethylated cotton textiles have been intensively studied. The cyanoethylation process has been recommended as a means for improving the dimensional stability of paper and of wood. Cyanoethylated cotton can undergo further reaction to introduce acetate groups, amidoxime groups, or carbamoylethyl groups. Formaldehyde can be used to cross-link the latter two compounds, resulting in improved crease-resistance.
The distinction between simple cyanoethylation and graft polymerization with acrylonitrile is a slight one and much of the investigation of possible graft polymers of cellulose starts with acrylonitrile as the monomer. Various methods for inducing graft polymerization have been proposed—the use of cellulose acetate or other esters, especially esters of unsaturated acids, the irradiation of ethylcellulose to produce peroxides, the irradiation of cellulose itself with gamma radiation, or with light and a photosensitizer.

Quinchon has studied the conditions of ethylene oxide reaction with cellulose and has described a method for the determination of the degree of substitution in the resulting hydroxyethylcelluloses. Hydroxyethylcellulose can be further etherified to introduce butyl or amyl groups.

Interest in the chemical modifications of pulps to improve the properties of the paper has resulted in hydroxyethylated products being put upon the market. The identification of this type of fibre in paper requires special methods. Similar modification of the paper sheet has also been patented.

A number of miscellaneous ethers of cellulose have been investigated. These include the benzyl ether, the sulphonethyl ether, and the allylethyl ether. Of the numerous articles on the reactive dyes, only a few belong in a discussion of cellulose ethers.
McKelvey, Webre and Klein have studied reaction with some miscellaneous epoxy compounds and Rath et al., with some water-soluble bifunctional onium compounds. A number of amine derivatives of cellulose have been prepared. This is most easily done by combining the epoxy reaction with an amino compound. Partial etherifications of cotton to produce special properties include several new derivatives such as carbamoylethyl and phosphonomethyl ethers. The mechanism of introducing cross links by means of dimethylolethyleneurea has been studied.

**MISCELLANEOUS DERIVATIVES**

Both Marsh and Roff have reviewed the literature and investigated the interaction between cellulose and formaldehyde experimentally. This is of much interest in the textile field for producing crease-resistant fabrics and is also proposed for the dimensional stabilization of wood and paper. Cellulose can also be cross-linked with glyoxal. Crease- and shrink-resistant finishes for cotton may also employ acetals.

Thionyl chloride combines chlorine directly with carbon in the cellulose molecule. Sulphur can also be introduced, 6-thio-cellulose having been formed from 6-tosyl cellulose and thiosulphate with subsequent hydrolysis. Anhydrocellulose has been produced from tosyl cellulose by treatment with sodium in liquid ammonia. If cyanoethyl cellulose is similarly treated with sodium, desoxycellulose is produced to some extent. Analogs of the cellulose complex with ethylenediamine have been prepared containing three, five, six, seven and eight carbon atoms.
A series of patents discloses the formation and properties of titanium derivatives.

Cellulose thiourethane is the basis of a new synthetic fibre. This has been discussed by Frieser in his review of new fibres.

Interest in ion-exchange products from cellulose continues. If the cellulose is cross-linked previous to modification, higher capacities are obtained in the ion-exchange materials.

The preservation of cellulose against micro-organisms by treatment with copper formate is not related to the sorption complex described by Belford et al. Rose et al. could not substantiate the formation of a copper-cellulose compound by the copper formate treatment.
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