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Kyle Ward, Jr.

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## A. CELLULOSE CHEMISTRY

Kyle Ward, Jr.

### Origin and Chemical Composition

In 1956 Treiber<sup>1</sup> reviewed the various theories of cellulose formation. Since then two independent groups have concluded<sup>2,3</sup> that its synthesis, at least by Acetobacter species, takes place by a phosphate mechanism. Syntheses with cell extracts or with isolated enzymes have been reported by two investigators<sup>4-6</sup>, adenosine triphosphate being necessary in both cases. Here, too, phosphate intermediates are indicated and a study with carbon-14<sup>5</sup> indicates that the cellulose may be formed either directly from glucose or from trioses. A study of the oligosaccharides formed from various species of Acetobacter<sup>7</sup> indicates that cellobiose and, with *A. xylinum* at least, cellotriose are involved. Peat, Whelan, and Roberts<sup>8</sup>, in a study on the partial hydrolysis of lichenin, have suggested that lichenin is synthesized in nature by the polymerization of cello-triose and that this possibility should be considered with cellulose.

Akiya and Tomoda<sup>9</sup> have found a hexasaccharide in the human placenta which is broken down to glucose by  $\beta$ -glucosidase, but not by  $\alpha$ -glucosidase; previous work<sup>10</sup> had indicated a 1,4-linkage. This apparent occurrence of cellohexaose in the higher animals, if corroborated, will be unique in present records (cellulose is found only in the tunicates among the animals) and permits ontogenetic-phylogenetic speculation. However, the melting point and rotation<sup>10</sup> do not agree with reported values for cellohexaose<sup>11</sup>. The rotation agrees well with those in the maltose series of oligosaccharides<sup>12</sup> and the enzymolysis studies on this hexasaccharide might well be re-examined.

While the method of combination of the nonglucose units remaining in alkali-resistant cellulose is still not known, most of the recently published

work seems to favor sorption mechanisms. Hamilton and Quimby<sup>13</sup> have shown that by improved alkali extractions with sodium or lithium hydroxide, cellulosic residues from Western hemlock pulps can be obtained in good yields containing as low as 0.6-0.7% mannose and less than 0.1% xylan. The adsorption of xylans<sup>14</sup> and of slash-pine hemicelluloses high in mannan<sup>15</sup> by cellulose has been clearly demonstrated. In softwoods the "alkali-resistant hemicellulose" appears to be a glucomannan<sup>16-19</sup> which, in the cases of Western hemlock and of spruce, accounts for most of the mannose in the wood. The persistence of small amounts of these other units in fractionated cellulose nitrates<sup>20</sup>, has again been confirmed<sup>21,22</sup>. That this is very likely also a matter of adsorption had already been indicated by the experiments of Snyder and Timell<sup>23</sup> with cellulose and mannan nitrates. This would not interfere, of course, with Timell's proposed use of nitration for isolating the cellulose component<sup>24</sup>, both from woody<sup>25</sup> and nonwoody<sup>26</sup> tissues.

Ono<sup>27,28</sup> has continued his studies of the growth process in the cotton fiber. Russian work in this field has been recently reviewed, also<sup>29</sup>. The development of cotton cellulose grown with temperature deficiency<sup>30</sup> has been characterized, as has that of irrigated cotton as compared with rain-grown<sup>31</sup>.

#### STRUCTURE IN THE SOLID STATE

The chain configuration for cellulose II proposed earlier by Petitpas<sup>32</sup> has been confirmed by continuous x-ray photometry<sup>33</sup>. Improved techniques and applications of x-ray measurements<sup>34-38</sup> and infrared spectroscopy<sup>39-41</sup> have also been described. Janssen and coworkers<sup>42</sup> have improved the purification process in the treatment of large amounts of cellulose with ethylamine in such a way as to obtain pure cellulose I in the crystalline regions.

The evaluation of x-ray diffraction patterns requires a knowledge of the influence of the noncrystalline phase. Ellefsen and his coworkers<sup>43,44</sup> are studying this using cellulose which has undergone dry grinding in a ball mill. The spaces in the noncrystalline portion of the cellulose fiber of nettles have been recently studied by x-ray methods by the metal deposition method<sup>45</sup>. A review of methods for controlling this spacing appeared early in the year<sup>46</sup>.

Valentine's suggested use of the sorption ratio<sup>47</sup> of celluloses for determining the amount of the noncrystalline phase has been criticized<sup>48</sup>. Stamm<sup>49-51</sup> has measured the rates of sorption and swelling both with moisture and with liquid water and has applied the B.E.T. equation calculating the free energies of adsorption per unit of contact area. Merchant<sup>52</sup> has calculated surface areas from nitrogen sorption data on pulps dried by solvent-exchange after swelling with water. He found the specific surface of never-dried samples to be about double that of samples dried from water and reswollen. The effect of temperature and the heats of wetting have been the subject of further work<sup>53-55</sup>.

Schwertassek<sup>56,57</sup> has continued his work on iodine sorption as a means of determining the fine structure of celluloses. Although opinions differ as to its validity<sup>58,59</sup> the technique has been used by a number of workers recently for this purpose<sup>59-61</sup> or for the related purpose of measuring reactivity<sup>62-64</sup>. Hess and his coworkers<sup>65</sup> have shown that above a certain concentration iodine in potassium iodide solution (or thallos ethylate in benzene) will penetrate by diffusion into the crystallites lengthwise along the crystallite axis.

The sorption of sulphuric acid<sup>66</sup> and of salts or dyes<sup>67</sup> has also been measured. The sorption of methanol has been suggested as another means of evaluating fine structure<sup>68</sup>. The structure of swollen cellulose is reported to be measurable by saturating with benzene and determining the benzene retention<sup>69</sup>.

Borruso<sup>70</sup> reported an increase in the noncrystalline fraction of cellulose, as measured by x-rays, during the beating of pulp. A similar effort was produced by alkali at less than mercerizing strengths. This effect on the x-ray diagram may also derive from a reduction in crystallite size.

Marchessault and Howsmon<sup>71</sup> have revised the previous definition of the degree of lateral order and have reviewed and compared data on the determination. The new concept is thermodynamic and takes into account the fact that celluloses differ in distributions of hydrogen-bond strengths. Nissan has attempted to relate the rheological behavior of cellulose (and other hydrogen-bonded solids) with the structure of hydrogen bonding<sup>72</sup>.

Sorkin has reviewed the swelling and solution of fibers<sup>73</sup>. Other studies dealing with swelling include the mechanism of swelling of regenerated cellulose<sup>74</sup>, the effect of swelling and drying on pore structure<sup>75</sup>, and the nature of swelling and other reactions during the parchmentization of cellulose with sulphuric acid<sup>76</sup>.

#### STRUCTURE AND THE SPINNING PROCESS

Dolmetsch<sup>77,78</sup> still considers that morphological residues exist in solutions of cellulose solutions, but his conclusions are being attacked by Frey-Wyssling<sup>79</sup> and others. Samuelson and coworkers<sup>80</sup> found fibrillar

structures in cellulose precipitated from dilute solutions of cellulose acetate and saponified, but attribute this to the ability of cellulose molecules to align themselves regularly and not to the persistence of fibrillar structure in the dilute solutions. In concentrated solutions of cellulose xanthate, however, the presence of supermolecular aggregates is confirmed by sedimentation velocity investigations<sup>81,82</sup>, but Oldsberg and Samuelson found no indication of micellar structure in dilute viscose solutions during viscosity measurements<sup>83</sup>.

Centola<sup>84</sup> considers the occurrence of lamellar aggregates in re-generated cellulose to be due partly to persistence in concentrated viscose solutions and partly to recrystallization. He considers the skin in rayons to be characterized by radial orientation of these lamellae. A comparison of thick-skinned filaments and broken-skin filaments with respect to spinning conditions and subsequent variations in lateral order has been made<sup>85</sup>. Howsmon has also recently given a brief comparative summary of this field<sup>86</sup>.

#### CHARACTERIZATION OF CELLULOSIC MATERIALS

Rutishauser<sup>87</sup> has reviewed the chemical, physical, and microscopical testing methods available for characterizing celluloses in the form of paper pulps to show the necessity for using all three types of testing. A new micro-method for estimating cellulose<sup>88</sup> has been described and the monoethanolamine method has been newly evaluated<sup>89</sup>. Another method for preparing chain length distribution curves has been proposed<sup>90</sup>.

The effect of accessibility on the determination of functional groups has been investigated<sup>91</sup>. It has been shown that there need be no fear of retention of hydrochloric acid to disturb the determination of carboxyl<sup>92</sup>. Two methods for determining calcium in cellulose have been described<sup>93,94</sup>.

SOLUTIONS OF CELLULOSE AND CELLULOSE DERIVATIVES

Jayne is continuing his development of new solvents for cellulose. These include zincoxene<sup>95,96</sup> (a complex of zinc hydroxide and ethylene diamine), copper-alkali-biuret complexes<sup>97</sup>, various cadmium-amine complexes<sup>98</sup>, and the previously described iron-sodium tartrate complex which is particularly recommended for use in viscometry<sup>99</sup>. This application has been independently investigated by Valtasaari<sup>100</sup>, who recommends certain modifications, but agrees that the reagent has the advantages of being more odorless and more stable to oxidation than cupriethylenediamine.

Since cuprammonium and cupriethylenediamine solutions are still the standard solvents for viscometric work on cellulose itself, several groups are trying to improve and standardize procedures<sup>101-106</sup>. The two solvents proved unsuitable for fractionation to determine chain length distribution<sup>107</sup>. Since solubility in cuprammonium requires linearity, some forms of chemically modified cotton cellulose are insoluble. A method has recently been described for quantitative evaluation of this degree of insolubility<sup>108</sup>.

Some of the difficulties in using copper-complex solutions of cellulose for molecular weight determinations of cellulose are avoided by the use of a suitable derivative. The derivative used most often is the nitrate since it can be prepared without appreciable degradation. Methods have been reviewed by Lang<sup>109,110</sup>, who emphasizes the importance of the nitration method. Alexander and coworkers<sup>111</sup> have compared the use of nitrates, acetates, and xanthates, determining the factor for converting intrinsic viscosity to degree of polymerization. They have pointed out that adjustments must be made in the factor at chain lengths below D.P.

400 where it may change sharply. Moore and Epstein, too, have studied these factors<sup>112,113</sup>, using different derivatives and solvents, and comparing viscometry and osmometry. The latter has also been studied by other workers<sup>114,115</sup>. The calibration of viscosity measurements for cellulose nitrates with ultracentrifuge measurements has also been reported for D.P.'s from 20 to 10,000<sup>116</sup>. The use of the nitrate for fractionation has been studied, as to the effects of degree of substitution, temperature, and choice of precipitants<sup>117</sup>. A thermodynamic study has been made on the vapour pressures of acetone solutions of cellulose nitrate<sup>118</sup>.

The determination of the D.P. of cellulose acetate has been studied by means of viscometry<sup>119</sup>, dielectric dispersion<sup>120</sup>, and sedimentation and diffusion<sup>121</sup>. Awni<sup>122</sup> fractionated various cellulose acetates and compared fractions of comparable D.P. and different D.S. He found D.S. had no measurable influence on mechanical properties of films.

The viscometry of cellulose xanthate<sup>123</sup> and of cellulose tributyrate<sup>124</sup> is also being applied to molecular weight studies.

The solution properties of cellulose ethers are of industrial significance, but are not so frequently used in D.P. studies. The water-soluble ethers are particularly important. The effect of temperature on viscosity has been determined<sup>125</sup> for methyl, carboxymethyl, and hydroxyethyl celluloses.

As a polyelectrolyte, sodium carboxymethylcellulose has particularly interesting solution properties. The uniformity of substitution along the chain has been shown to influence the solution rheology strongly<sup>126,127</sup>. Inagaki<sup>128,129</sup> has used this compound in his study of the effect of added

ions on the second virial coefficient in polyelectrolyte solutions. In certain ionic solutions, such as 6% sodium hydroxide, the molecules of sodium carboxymethylcellulose solution behave like those of other derivatives<sup>130</sup>, and the solutions can be used for measurements of D.P.<sup>131</sup> and of polydispersity<sup>132</sup>. The conductivity of solutions of the potassium salt of carboxymethylcellulose in aqueous potassium chloride has also been used to measure the effect of added ions<sup>133</sup>.

A viscometric study<sup>134</sup> of the axial ratio of the ether-esters produced by esterifying methylethyl cellulose with a series of acids ranging from caproic to palmitic produced the interesting result that agreement between the experimentally determined lengths and widths and those calculated could be obtained only by assuming that all acyl groups are situated on the same side of the cellulose chain.

#### REACTIONS OF CELLULOSE

Several reviews of cellulose reactions and cellulose derivatives appeared in 1957 which are worth listing here. These include discussions of the natural macromolecular structure<sup>135</sup>, the chemistry of cellulose degradation<sup>136</sup>, the biological degradation of cellulose derivatives<sup>137</sup>, and the preparation and applications of soluble fibers by modification of cellulose<sup>138</sup>.

#### Hydrolysis

The relationship between hydrolysis of cellulose and its fine structure is still being investigated and generalized views appeared last year from four countries. After pointing out in 1956 that the parallel

processes of chain scission, recrystallization, and solution occur<sup>139</sup>, Ant-Wuorinen now goes on to explain hydrolysis as occurring in three stages, on the basis of crystallite disappearance and the phenomenon of level-off D.P.<sup>140</sup>. First recrystallization occurs, then the separation of micellar aggregates into molecules and finally actual chain scission. Daruwalla and Subramaniam emphasize the role of recrystallization<sup>141</sup>. Sharples<sup>142</sup> has presented a convincing picture of the later stages of hydrolysis, based on hydrolytic attack at the crystallite ends and on an exponential distribution of crystallite lengths which could arise from random arrangement of amorphous regions in the original fiber. Husemann<sup>143</sup>, however, remains unconvinced of random attack and concludes that periodic weak links of a chemical nature occur. The present conclusion is based on the occurrence not only of carbonyl groups but also of carboxyl groups at the beginning of the hydrolysis when air is present. Freudenberg<sup>144</sup> has reviewed his earlier work on homogeneous hydrolysis. Hydrolysis by water alone at 100-225°C. has been shown to be due to acids formed in the initial stages causing a drop in pH<sup>145</sup>.

The hydrolysis of natural cellulosic materials is closely tied to the nature of hemicellulosic components. The production of acetone on acid distillation of jute<sup>146</sup> probably arises from the hydrolyzed sugars. Quick has described a simplified chromatographic procedure for hemicellulose studies<sup>147</sup>.

### Oxidation

The chemical reactions occurring during oxidation may be of several types and for most oxidizing agents different types occur randomly along the cellulose chain. Schurz<sup>148</sup> has reviewed the nature of various oxidation reactions. Ströle has used a modified method of carbonyl determination with

acid chlorite to re-examine a number of oxycelluloses<sup>149</sup> and has confirmed the results of Davidson and Nevell who have shown that acid chlorite does not completely oxidize the carbonyl groups of hydrocelluloses<sup>150</sup>. The oxidation of these end-groups with alkaline hypiodite<sup>151</sup> has also been shown to be complicated by the effect of potassium iodide concentration.

Henderson<sup>152</sup> has shown that aqueous chlorine at pH 4.5 produces considerable amounts of an arabinose carbonate ester from the model compound, methyl  $\beta$ -glucoside, and a similar reaction along the chain from cellulose confirming to some extent earlier observations of Kaverzneva<sup>153,154</sup>. This has a theoretical bearing on overbleaching with hypochlorite, which continued to be of interest<sup>155-158</sup>. Kazeniak<sup>159</sup>, working at pH 9, obtained quite a different type of reaction (2,3-scission) with methyl 4-methylglucoside.

Huffman<sup>160</sup> has studied the periodate oxidation of cellulose, reducing and methylating the product and isolating methoxyacetaldehyde and 1,4-dimethyl-erythritol from the hydrolyzate of the methylated material. Mester<sup>161,162</sup> has continued his study of formazans from oxycelluloses.

Atmospheric oxidation is greatly accelerated by various types of irradiation. Photo-oxidation in the presence of light is presently being studied by model compounds. One hypothesis<sup>163</sup> calls for the removal of hydrogen from cellulose, at least in the presence of photoexcited dye molecules, followed by addition of oxygen to give a peroxy radical which will produce either a chain scission or an unstable carbonyl group, but there is no general accepted theory<sup>164</sup>. Nuclear radiation has also been shown to attack cellulose primarily through oxidation<sup>165,166</sup>, the main product being an oxycellulose of the acidic type<sup>167</sup>.

Air oxidation occurs with especial ease in the presence of alkali. This can be either bane or boon depending on the industry involved. In the hot alkaline refining of dissolving pulps<sup>168</sup> it can be detrimental by producing alkali-sensitive linkages with subsequent degradation<sup>169</sup>; these effects can be partially remedied by chlorous acid oxidation or borohydride reduction<sup>170</sup>. However, the aging process in the manufacture of viscose rayon depends on a controlled oxidation of this type which produces both carbonyl and carboxyl groups. Samuelson has studied the effect of adding hydrogen peroxide to the alkali<sup>171</sup> and the eventual destruction of the cellulosic fragments dissolved in the waste liquor<sup>172</sup>.

#### Other Types of Degradation

The rigid separation of atmospheric oxidation and thermal degradation is very difficult, except in the strictest exclusion of oxygen, which is itself difficult. Oxidation is accelerated by heat and is one of the major reactions occurring in the complicated processes usually grouped as "thermal degradation." The thermal degradation mechanisms have been reviewed by Aubry<sup>173</sup>.

It is convenient to include with the nonoxidative processes the question of degradation during storage and aging because of the commonly used accelerated aging tests. Kleinert<sup>174</sup> has compared the heat-accelerated aging of rayon with prolonged storage in the dark and found the former much more severe. Berkley has presented data<sup>175</sup> to show that cotton stored in the bale since 1862 had undergone no appreciable deterioration. Demus<sup>176</sup> and Veith<sup>177</sup>, however, working from 100-290°C. and from 70-250°C. respectively, have shown that essentially the same reactions are involved throughout the

range and that the difference is largely one of rate. Veith concluded that even vacuum drying cannot remove moisture and gas completely, because of increased damage not only with increased temperature, but also at longer times.

With oxidation reduced to a minimum, cellulose decomposes on heating in vacuum to yield levoglucosan. The yields increase with crystallinity (packing density) of the cellulose<sup>178,179</sup> because of inhibition of the secondary reactions of hydrolysis, dehydration and oxidation. Heat treatment of cellulose in kerosene at 200°C. yields a product rapidly hydrolyzable with dilute acid<sup>180,181</sup>.

Demus, in the article previously cited<sup>176</sup>, found 290°C. the minimum ignition temperature of cellulose. This is in agreement with the carbonization studies of Kudo and Yoshida, who concluded<sup>182</sup> that cellulose begins to decompose at about 280°C. with complete decomposition around 300-350°C.

The importance of microbiological degradation arises from the prevalence of cellulolytic organisms in the air, the soil<sup>183</sup> and the water, especially in sewage polluted water<sup>184</sup>. Cellulolytic bacteria contribute to the degradation of cotton during weathering and storage<sup>185</sup>. A modified staining test has been described<sup>186</sup> for the detection of fungal growth on cotton and cellulosic textiles.

Enzymes have been isolated from some of these organisms<sup>187-190</sup>.

Myrothecium verrucaria has been shown to produce more than one cellulolytic enzyme fraction<sup>190</sup> and the existence of such multiple enzyme systems has been

cited as a likely cause for past confusion in the field of the celluloses. One of the effects of the grinding of wood in the vibratory ball mill is to render the cellulose very sensitive to cellulolytic enzymes<sup>191</sup>. This effect of fine structure on enzymolysis would be expected from past work and is in agreement with a recent study comparing the kinetics of enzymolysis and acid hydrolysis<sup>192</sup>.

Wolfrom has improved the preparation of the polymer-homologous series of  $\alpha$ -<sup>193</sup> and  $\beta$ -D-oligosaccharide acetates<sup>194</sup> from cellobiose through cellohexaose. Alcoholysis has been further studied and the rate related directly to the accessible surface area<sup>195,196</sup>. The thorough study by the British Rayon Research Association of the alkaline degradation of cellulose to form saccharinic acids continues<sup>197-199</sup> and two main reactions have been shown to occur, one proceeding to complete degradation to simple saccharinic acids, the other a stopping reaction which gives an alkali-stable product. These results should be useful in many fields, including pulping and purification both of pulps and textiles.

#### Cellulose Nitrate

Bonnet<sup>200</sup> has interpreted his most recent experiments to mean that the main factors affecting the rate of cellulose nitration are diffusion and swelling, the latter varying with the composition of the nitrating bath.

In the usual nitration procedure, cellulose nitrate requires a stabilizing treatment to remove sulphate acid ester. A study using  $S^{35}O_4$  as a tracer confirms the presence of the residual sulphur within the fibrous structure<sup>201</sup>. It can be completely removed only at the expense of degradation of the cellulose nitrate. A recent patent<sup>202</sup> describes a nitration method

requiring no stabilization; magnesium nitrate is used as a catalyst instead of sulphuric acid. An evaluation of suggested methods for determining sulphate acid ester in unstabilized cellulose nitrate resulted in the approval of several methods as satisfactory<sup>203</sup>.

Falconer and Purves<sup>204</sup> have found that the dinitrate obtained by treating cellulose trinitrate with pyridine and hydroxylamine has lost all the nitrate groups from the 2-position and is essentially a 3,6-dinitrate. This was established by methylation and subsequent dinitration. Hydrolysis of the resulting methyl cellulose gave 84% 2-methyl glucose and 11% 2,3-dimethyl glucose.

Gels of cellulose nitrate in diethyl phthalate and of cellulose tributyrate in dimethyl phthalate have been measured in the dilatometer to obtain glass-transition temperatures and thermal expansion data<sup>205</sup>. New measurements of creep in cellulose nitrate have also been made<sup>206</sup>.

The products of controlled thermal decomposition of cellulose nitrate have been described<sup>207,208</sup>. Ultrasonic degradation has also been studied<sup>209</sup>. All samples gave a minimum D.P. of 800 to 1000 with no evidence of weak links at shorter intervals.

#### Cellulose Acetate

Sakurada and his coworkers<sup>210-213</sup> have been studying the fibrous acetylation in both vapour and liquid phase of viscose rayon, cotton, and ramie. They find that perchloric acid catalyst speeds up the reaction much more than sulphuric acid. Iwakura and coworkers have investigated fibrous acetylation of viscose rayon with ketone<sup>214,215</sup>, but find that shrinkage occurs

with increasing degree of acetylation and that tenacity and elongation at an acetic acid value of 25% are unsatisfactory. For dimensional stabilization of wood, vapour-phase acetylation is used<sup>216,217</sup>. Liquid-phase fibrous acetylation of paper<sup>218</sup> is recommended to reduce its absorbency for use in chromatography.

For some time cotton has been partly acetylated with retention of the fibrous form. Recently this procedure has been extended to produce a fully acetylated fiber<sup>219,220</sup>. Cellulose triacetate rayon fibers are also on the market now<sup>86,221,222</sup>. At the other end of the substitution range are cellulose acetates which have been hydrolyzed much farther than the usual acetone-soluble stage<sup>223</sup>. These materials have the interesting property of solubility in water when the acetyl content is between 13 and 19%.

The relationship of pulp properties to acetylation behavior and to the properties of the cellulose acetate is very important and has recently been reviewed by Richter<sup>224</sup>. Ishikawa has continued his studies of the acetylation reaction<sup>225,226</sup> and concludes that pulps of lower reactivity may have a less stable structure<sup>227</sup>. Sumi, extending previous work on turbidity in cellulose acetate<sup>228,229</sup>, finds that pulps dried below 18% moisture may require reactivation, but that those above this moisture content can be acetylated smoothly<sup>230</sup>. This agrees qualitatively with the experience of Richter, who, however, points out that higher moisture content makes control of the industrial acetylation more difficult. Demint and Hoffpauir<sup>231</sup>, studying the effect of various pretreatments, also found reactivity decreased by excessive drying or mercerization, but increased by scouring, solvent extraction, ethylamine decrystallization, and boiling in water. Sihtola and Kaila also determined the effect of various factors

on acetylation<sup>232</sup> and agree on the beneficial effects of the higher moisture content. They also found that addition of manganese salts or silicates to the pulp improved acetylation, while sodium, copper, calcium, and iron salts were detrimental; acetylation was also better in pulps with higher carboxyl contents and lower degree of polymerization.

Julander and Jullander<sup>233</sup> found that celluloses dried by solvent exchange so as to occlude organic solvents in the fine structure were more easily acetylated in the acid-catalyzed acetylation procedure, just as Staudinger and Döhle found for acetylation with pyridine<sup>234</sup>. Richter has also had this experience<sup>235</sup>.

Engelmann has found differences in swelling during acetylation between favorable and unfavorable acetylations<sup>235</sup>, but small amounts of insoluble material remained in all cases. These were high in ash and were poorly acetylated or not at all. McKenzie and Higgins continued their investigations of reactivity<sup>236</sup> and studied the kinetics of acetylation with pyridine<sup>237</sup>. The rate of fibrous acetylation of cotton and jute has also been determined<sup>238</sup>. The improved rate produced by moisture in cotton is not observed with jute, which swells less.

Abnormally high viscosities of concentrated solutions of cellulose acetate from certain wood pulps may be due to several factors. These are discussed by Richter and Herdle<sup>239</sup>. Watson and Henderson have shown that the phenomenon can be induced by adding mannan to the pulp before acetylation, but not by adding other low-molecular weight carbohydrates<sup>240</sup>. Several new tests<sup>241-244</sup> have been proposed for evaluating the suitability of pulps for acetylation.

The properties of partially acetylated cottons continue to be of interest. Previous studies of changes induced in the physical properties<sup>245,246</sup> have been supplemented by microscopical observations<sup>247</sup> and measurements of resistance to acid and alkali<sup>248</sup>.

Two new methods are proposed for the determination of acetyl in cellulose acetate<sup>249-250</sup>. Haskins and Sunderwirth have presented further evidence<sup>251</sup> that the free hydroxyl groups in secondary cellulose acetate occur in all three of the possible positions.

The physical properties of cellulose acetate studied within the past year includes the temperature dependence of specific volume and rigidity<sup>252</sup> and of birefringence<sup>253</sup> and the friction and conductivity<sup>254</sup>.

Rice and Johnson<sup>255</sup> have studied oxidized cellulose acetate by conversion of carboxyls to acid chlorides and subsequent decarboxylation. There is chain scission during the decarboxylation unless carbonyl groups are eliminated by borohydride reduction. The authors have also proposed the use of the shift in optical rotation in thionyl chloride (formation of the acid chloride) to measure the amount of carboxyl.

Further reactions of cellulose acetate recently patented include a new process for the acetate phthalate<sup>256</sup> and a new nonflammable mixed ester by reaction with a haloalkyl chlorophosphonate<sup>257</sup>.

#### CELLULOSE XANTHATION

The subject of cellulose xanthation and cellulose xanthates will be handled under the chapters dealing with fiber production. Nevertheless, there have been certain findings of a chemical nature which seem to belong

properly here. Such, for instance, is the series of studies by Philipp<sup>258-261</sup> on the kinetics of xanthation. The rate in excess carbon disulphide is determined mainly by the alkali bound as soda cellulose I and is much higher in the less-ordered regions. Studies with mixed xanthates<sup>261</sup> produced by mixtures of carbonyl sulphide with carbon disulphide led to the conclusion that the decrease in viscosity of viscose produced by adding polyalcohols to the mercerizing alkali can be explained by the presence of carbonyl sulphide and the formation of such mixed xanthates.

The factors governing reactivity and filterability of xanthate are many. Treiber and his coworkers<sup>262,263</sup> have reviewed the field and other investigators have studied individual aspects--the effect of fines in the pulp<sup>264</sup>, chain length distribution in sulphite pulps<sup>265</sup>, and the steep-liquor concentration<sup>266</sup>.

Barrett and Lindsley<sup>267</sup> tried to determine the location of xanthate groups in viscose by methylation with nitrosomethylmethane, followed by hydrolysis and identification of the methylglucoses. However, the methylation produced about 20% S-methyl esters which were lost during hydrolysis. Purves<sup>268,269</sup> in a similar attempt used methyl iodide for methylation. He obtained only S-methyl derivatives and here about 40% were lost during hydrolysis. Sodium and lithium hydroxides were shown to produce a lower degree of xanthation than potassium, rubidium, and cesium<sup>268</sup>. The reaction of cellulose xanthate with polyethylenimine<sup>270</sup> gives an anion exchange agent.

#### OTHER CELLULOSE ESTERS

A number of cellulose esters can be prepared using trifluoroacetic acid as an impelling agent<sup>271</sup>. The nature of the interaction of cellulose and trifluoroacetic acid has been studied by means of infrared spectrophotometry; esterification (following micellar dispersion of the cellulose structure) possibly occurs through an intermediate addition compound<sup>272</sup>.

Cellulose tricaprylate has a lower melting point than other cellulose esters. Goodman<sup>273</sup> attributes this as due to the optical length of side-chain for increasing flexibility without interfering with free rotation around the glucoside linkage.

Other cellulose esters prepared for various purposes include the isobutyrate<sup>274-278</sup>, unsaturated esters, such as the acrylate<sup>279</sup> or the crotonate<sup>280</sup> which may be further polymerized to produce cross linkages, phthalates<sup>281,282</sup> and the mixed acetate sorbate<sup>283</sup>. Cellulose mesylation<sup>284</sup> (methanesulphonation), followed by subsequent halogenation and phosphorylation can be used to produce flame resistance<sup>285</sup>. Katsuura<sup>286</sup> has determined the effect of conditions of phosphorylation on the properties, including flameproofing, of cellulose phosphate. One of the many water-soluble cellulose derivatives is an ester, the sulphate<sup>287-289</sup>.

#### CELLULOSE ETHERS AND MISCELLANEOUS DERIVATIVES

The relative rates of etherification of the different hydroxyl groups in cellulose are important, for they determine in large part the distribution of substituents in the cellulose ethers, and hence the properties. Rogovin and Derevitskaya<sup>290</sup> found the secondary hydroxyls to be more

reactive than the primary during methylation under various reaction conditions, confirming their previous work<sup>291</sup>, but the difference in reactivity appears more noticeable in methyl cellulose prepared from copper soda cellulose or from cellulose alcoholates. Croon and Lindberg, who are also investigating methyl celluloses<sup>292</sup>, have found that in hydroxyethylation, the primary group reacts faster and that the hydroxyethyl group itself reacts still faster, so that 25% of the ethylene oxide introduced is in the form of a graft polymer<sup>293,294</sup>. In their work on methylation<sup>292</sup>, which has not yet been published in full, the preliminary results seem to be in qualitative agreement with those of Rogovin<sup>290</sup>.

Very recently it has been shown that substitution of cellulosic hydroxyls with hydrophilic substituents produces greatly improved papermaking properties. Talwar<sup>295</sup>, following up the pioneer work of Walecka<sup>296</sup>, attributes this, in the case of carboxymethylation, to more bonds and greater bonding strength. Other treatments which improve cellulosic pulps in this way are cyanoalkylation<sup>297</sup> and hydroxyethylation. A chemically modified pulp of this type has recently been made commercially available<sup>298</sup>.

Improved methods of preparing<sup>299,300</sup> and of determining<sup>301</sup> ethyl cellulose have been described. Sorption and diffusion of organic solvents in ethyl cellulose<sup>302,303</sup> have been measured.

Carboxymethylcellulose has a variety of industrial uses<sup>304</sup>. Its use for sizing cellulosic fibers depends on retention by the fiber and this has been studied using C-14 labeled carboxymethylcellulose, both with wood pulp<sup>305</sup> and with textile fibers<sup>306</sup>. In the latter case, retention is attributed to occlusion and not adsorption. Further reaction of carboxymethylcellulose with etherifying agents produces mixed cellulose derivatives<sup>307,308</sup>.

The literature on the cyanoethylation of textile fibers continues to swell; it has been reviewed by Duflos<sup>309</sup>. More recent articles have also appeared on this process<sup>310-317</sup> and the properties of the product<sup>318-321</sup>. For analysis, Journeay and Blackmon<sup>322</sup> find the standard Kjeldahl preferable to Daul's modification<sup>323</sup>. The reaction with acrylonitrile can also be carried out so as to produce carboxyethylcellulose, if the cyanoethyl groups are hydrolyzed during the process<sup>324</sup>.

Hydroxyethylcellulose contains reactive hydroxyl groups to the same extent that cellulose does and many mixed derivatives have been prepared. Ethylhydroxyethylcellulose is a commercial product<sup>325</sup>; others recently described are hydroxyethylcellulose acetate<sup>326</sup>, the corresponding cinnamate and similar unsaturated esters<sup>327</sup> and phenylhydroxyethylcellulose<sup>328</sup>.

Cellulose reacts with activated olefinic compounds to produce ethers<sup>329</sup>, especially with acrylamide<sup>330</sup>. Some of the more unusual cellulose derivatives give products with special properties, e.g., reaction with 1,2,4-trichloro-3,5-dinitrobenzene gives a highly fungicidal ether<sup>331</sup>; reaction with a monoglycidyl ether of the aromatic series leaves a phenyl or naphthyl group in the ether which can react further for dyeing fast dyes<sup>332</sup>; the cellulose thiourethanes<sup>334-336</sup> can be spun into fibers which are highly resistant to hydrochloric acid<sup>337</sup>.

The most common procedure for etherification calls for reaction of alkali cellulose with the etherifying agent. Geiger and Nobs<sup>338</sup> have shown that acetic acid reacting with alkali cellulose produced only about half the expected amount of water. This is interpreted as meaning that half the alkali is present as a cellulose alcoholate, and the rest as an addition compound.

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