

## Birefringence, Density, and Tensile Characteristics of Oxycelluloses

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### Synopsis

Investigations have been carried out on the changes in the characteristics such as refractive index, density, single fiber breaking strength, and moisture regain of cotton fibers brought about as a result of oxidation with sodium metaperiodate and potassium dichromate-oxalic acid. The study has also been extended to sodium chlorite-treated and sodium borohydride-reduced oxycelluloses obtained from these oxycellulose products. Results indicate that in case of sodium metaperiodate oxidation, birefringence and density first increase, reach a maximum and then decrease sharply as oxidation is continued, while breaking strength decreases in the initial stages, reaches a minimum, and then increases in the later stages. With dichromate-oxalic acid oxidation, birefringence increases sharply during the initial stages of oxidation and after reaching a maxima, decreases as oxidation progresses, while there is a rapid increase in the values of density during the initial stages followed by a slow rise as oxidation is continued. In case of dichromate-oxalic acid oxycelluloses, breaking strength decreases continuously with the progress of oxidation. Results are interpreted in terms of changes in gross morphology and fine structure of cotton as a result of oxidation and subsequent chlorite and borohydride treatments.

Changes due to chemical modifications in gross and fine structure of cotton and regenerated cellulosic fibers in relation to physical characteristics have been studied by such different techniques as x-ray diffraction, plane and polarized light microscopy, electron microscopy, infrared spectroscopy, etc. As compared with the considerable information available in the literature regarding the fine structure of cellulosic fibers, useful data in the case of chemically modified cellulose obtained by employing optical techniques are rather limited. Kanamaru<sup>1</sup> has studied the changes in the refractive indices of cellulose oxidized with sodium hypochlorite and potassium permanganate, whereas Patel<sup>2</sup> has carried out optical investigations on oxycelluloses obtained as a result of the action of sodium metaperiodate-sodium chlorite, dichromate-sulfuric acid, and sodium hypobromite on ramie cellulose. Tensile strength characteristics of oxycelluloses have been studied by Clibbens and Ridge,<sup>3</sup> Davidson,<sup>4</sup> and Nevell and Zeronian.<sup>5</sup>

In the present study, systematic investigation has been undertaken regarding changes in the gross morphology and fine structure of cotton fibers

brought about as a result of oxidation with sodium metaperiodate and potassium dichromate-oxalic acid. The study has also been extended to sodium chlorite-treated and sodium borohydride-reduced oxycelluloses obtained from the above oxycellulose products. Important characteristics studied include refractive index, spiral angle, density, single fiber breaking strength, and moisture regain.

### EXPERIMENTAL PROCEDURES

Good quality Indian cotton (Nandayal N-14) was carefully purified according to the standard procedure. Purified cotton had copper number of 0.01 and DP of 2000 as determined from intrinsic viscosity of its solution in cupriethylenediamine.

All chemicals used were of Analar grade.

#### Preparation of Periodate, Periodate-Sodium Chlorite, and Periodate-Sodium Borohydride Oxycelluloses

Periodate oxycelluloses were prepared by steeping purified cotton in the dark at 30°C. in a solution of  $\text{NaIO}_4$  of 0.01*M* or 0.1*M* concentration at pH 5.3-5.6 for different periods, the liquor-to-material ratio being kept at 50:1. Oxygen consumed by the sample during oxidation was estimated by titrating an aliquot of solution with a standard solution of sodium arsenite after the addition of  $\text{NaHCO}_3$  and KI according to the method of Muller and Friedberger.<sup>6</sup> After the completion of oxidation, samples were washed rapidly with distilled water till free from periodate ions, squeezed under vacuum, and air-dried. A part of each oxycellulose was treated with a solution of  $\text{HClO}_2$ , 0.1*M* with respect to  $\text{NaClO}_2$  and 0.5*M* with respect to phosphoric acid at 30°C. for 18 hr. or 0.2-0.4*M*  $\text{NaClO}_2$  and 1-2*M* acetic acid at 30°C. for 72 hr., at a liquor-to-material ratio of 50:1 according to the method used by Davidson and Nevell.<sup>7</sup> Samples were washed till free from  $\text{HClO}_2$  and air-dried. Another portion of each periodate oxycellulose was reduced with aqueous solutions of  $\text{NaBH}_4$  of concentrations 0.01*M* or 0.05*M* at 30°C. for 48-72 hr., depending on the extent of oxidation, according to the method recommended by Head.<sup>8</sup> The reduced oxycelluloses were washed, steeped in dilute acetic acid, washed free of acid, and air-dried.

#### Preparation of Dichromate-Oxalic Acid, Dichromate-Oxalic Acid-Chlorite, and Dichromate-Oxalic Acid-Borohydride Oxycelluloses

Purified cotton was suspended in 2*N* oxalic acid at 30°C. and different amounts of 2*N*  $\text{K}_2\text{Cr}_2\text{O}_7$  solution were added rapidly to the suspension. Samples were agitated continuously throughout the course of reaction with a view to permitting oxidation to proceed at a uniform rate. Oxidized samples were washed till free from acid and air-dried. A part of each oxycellulose was subjected to the same standard  $\text{HClO}_2$  treatment and another to  $\text{NaBH}_4$  treatment as was employed in the case of periodate oxycelluloses.

All the oxidized samples were stored in the dark in an atmosphere of 75% R.H. at 30°C.

### Determination of Copper Number

Copper number of the samples was determined by the method of Clibbens and Gaeke as modified by Heyes.<sup>9</sup>

### Determination of Refractive Indices

For the determination of refractive indices, the well known Becke line method as used by Meredith<sup>10</sup> was adopted using a Leitz Ortholux-Polarizing microscope with heating stage. A series of liquids ranging in refractive index from 1.516 to 1.600, increasing in steps of 0.001 were prepared by mixing  $\alpha$ -monobromonaphthalene and liquid paraffin of known refractive indices. The standardization of the liquid mixtures were carried out at a temperature of 30°C. with the help of an Abbé refractometer. Refractive index measurements of the fibers parallel ( $n_{\parallel}$ ) and perpendicular ( $n_{\perp}$ ) to the fiber axis were also carried out at 30°C. In all, 15 fibers per sample were tested. Birefringence was calculated from the difference,  $n_{\parallel} - n_{\perp}$ .

The spiral angle  $\theta$  was calculated from eq. (1)

$$\cos^2 \theta = \frac{(n_{\parallel}^*)^2(n_{\parallel} - n_{\perp}^*)(n_{\parallel} + n_{\perp}^*)}{n_{\parallel}^2(n_{\parallel}^* - n_{\perp}^*)(n_{\parallel}^* + n_{\perp}^*)} \quad (1)$$

which is deduced from the geometry of ellipsoid of the cellulose crystallites.<sup>11</sup> The values  $n_{\parallel}^* = 1.595$  and  $n_{\perp}^* = 1.529$  represent the values obtained for ramie, the most perfectly oriented natural cellulosic fiber.

The refractive index  $n_{\text{iso}}$  (i.e., the refractive index of the fiber in the isotropic state) of all the oxycellulose samples was calculated by using the equation recommended by Hermans:<sup>12</sup>

$$n_{\text{iso}} = \frac{1}{3} (n_{\parallel} + 2n_{\perp}) \quad (2)$$

In this case the values of  $n_{\parallel}$  and  $n_{\perp}$  used were the values of refractive indices at 25°C. which were deduced from those experimentally obtained at 30°C. by the application of a correction factor of 0.0005/°C. so as to express the relationship between refractivity and density of the oxycelluloses at an identical temperature of measurement.

### Determination of Breaking Strength

A representative hand sliver was prepared for each of the oxycellulose samples. Single fiber breaking strength (in grams) was determined on 100 fibers per sample by use of a Ball's magazine hair-break tester with test gauge length of 10 mm. at a constant rate of loading of 1.4 g./sec. and at 65% R.H. The relative breaking strength for each oxycellulose sample was calculated considering the breaking strength of untreated cotton as 100%.

### Determination of Density

Density measurements were made in a density gradient tube at 25°C., by use of a mixture of carbon tetrachloride and xylene according to the method recommended by Preston and Nimkar.<sup>13</sup>

### Determination of Moisture Regain

Moisture regain of oxycellulose sample was determined in the present investigation under the condition of desorption. After the oxidation of cellulose was over, it was washed several times with distilled water and was sucked dry on a sintered glass crucible. The sample, 0.5–1 g., was transferred to a weighing bottle and was kept under vacuum in a desiccator over a saturated solution of NaCl (75% R.H.) at 30°C. till equilibrium moisture uptake was attained. The sample was weighed accurately and then heated in an electric oven at 106–108°C. to constant weight. Percentage moisture regain was calculated on the basis of oven-dry sample weight.

### Determination of Morphological Changes

To determine the changes in the average ribbon width, convolutions, and structural reversals, light and polarized microscopy techniques as employed by Betrabet et al.<sup>14,15</sup> were adopted.

## RESULTS AND DISCUSSION

Cotton fibers are composed mainly of macromolecules of cellulose which are disposed in the fiber substance in such a way as to display a number of characteristics which collectively can be termed supermolecular structure. The term supermolecular structure is generally used to express the physical arrangement resulting from multiform associations and organizations of molecules in the fiber. In addition to the structural aspects, the gross morphology of the fiber itself should be considered before coming to conclusions regarding optical and mechanical behavior of the cotton fiber. On this basis, changes in the supermolecular structure brought about as a result of oxidation of cotton with specific oxidizing agents have been discussed in the following.

According to Jackson and Hudson,<sup>16</sup> metaperiodate oxidation of cellulose results preferentially in the oxidation of hydroxyl groups at carbon atoms 2 and 3 of the glucose units to dialdehyde groups with carbon-carbon bond cleavage at the points of oxidative attack. Recently, Ivonov et al.<sup>17</sup> have, however, shown that oxidation of cellulose by sodium metaperiodate does not result only in reaction at  $\alpha$ -glycollic groupings but also in the conversion of the primary alcoholic groups to the aldehyde groups. In addition to this main reaction, breakdown of cellulose chains also takes place on account of non-Malaprade side reactions as indicated by the fact that cuprammonium fluidity of oxidized samples never reaches the same value as that of the original cotton, even when alkali-sensitive linkages are stabilized by reduction with NaBH<sub>4</sub> solution. Furthermore oxidation of cellulose with periodate is a permutoid reaction, and as indicated by Davidson<sup>4</sup> as well as Nevell,<sup>18</sup> the x-ray diagram becomes more and more diffused with progressive oxidation, suggesting thereby the gradual breakdown of crystalline regions. Periodate oxycellulose also contains hemiacetal crosslinks between aldehyde groups formed at 2 and 3 carbon atoms and the primary alcoholic groups at

TABLE I  
Birefringence, Density, Moisture Regain, and Single Fiber Breaking Strength of Periodate-NaBH<sub>4</sub>, and Periodate-NaClO<sub>2</sub> Oxycelluloses

Sample no.	Oxygen consumption, atoms/100 glucose units	Moisture regain, %	Refractive index for sodium D line at 30°C.		Birefringence ( $n_{  } - n_{\perp}$ )	Spiral angle $\theta$	Density $d$ , g./ml.	$n_{iso} - 1/d$	Single fiber strength	
			$n_{  }$	$n_{\perp}$					Breaking load, g.	Relative breaking strength, %
Control	Nil	8.56	1.5722	1.5290	0.0432	35.1°	1.5452	0.3501	5.51	100.0
Periodate oxycelluloses										
A <sub>1</sub>	1.10	8.71	1.5748	1.5220	0.0528	32.8°	1.5466	0.3472	3.56	64.6
A <sub>2</sub>	1.60	8.95	1.5750	1.5220	0.0530	32.6°	1.5478	0.3471	3.04	55.2
A <sub>3</sub>	2.35	9.21	1.5760	1.5219	0.0541	31.7°	1.5481	0.3472	2.78	50.4
A <sub>4</sub>	3.07	9.34	1.5792	1.5228	0.0564	28.5°	1.5480	0.3483	2.99	54.3
A <sub>5</sub>	4.60	9.51	1.5782	1.5220	0.0562	29.5°	1.5473	0.3479	1.50	27.3
A <sub>6</sub>	6.65	9.78	1.5780	1.5220	0.0560	28.5°	1.5466	0.3479	1.07	19.4
A <sub>7</sub>	15.15	10.82	1.5746	1.5230	0.0516	33.0°	1.5420	0.3487	1.91	34.7
A <sub>8</sub>	27.40	12.02	1.5669	1.5230	0.0439	39.9°	1.5320	0.3493	1.96	35.6
Periodate-NaBH <sub>4</sub> oxycelluloses										
B <sub>1</sub>	1.10	8.54	1.5746	1.5220	0.0526	33.0°	1.5467	0.3471	4.50	81.7
B <sub>2</sub>	1.60	8.60	1.5750	1.5220	0.0530	32.6°	1.5480	0.3471	4.25	77.1
B <sub>3</sub>	2.35	8.74	1.5768	1.5220	0.0548	30.9°	1.5484	0.3474	3.80	69.0
B <sub>4</sub>	3.07	8.81	1.5801	1.5223	0.0578	31.2°	1.5486	0.3481	3.21	58.3
B <sub>5</sub>	4.60	8.65	1.5789	1.5221	0.0568	28.8°	1.5469	0.3481	2.06	37.3
B <sub>6</sub>	6.65	8.59	1.5788	1.5220	0.0568	28.9°	1.5467	0.3480	1.40	25.4
B <sub>7</sub>	15.15	8.55	1.5764	1.5242	0.0522	31.2°	1.5430	0.3494	1.41	25.6
B <sub>8</sub>	27.40	8.54	1.5690	1.5242	0.0448	38.0°	1.5320	0.3502	1.41	25.6
Periodate-NaClO <sub>2</sub> oxycelluloses										
C <sub>1</sub>	1.10	8.57	1.5747	1.5220	0.0527	32.9°	1.5471	0.3472	3.61	65.5
C <sub>2</sub>	1.60	8.60	1.5750	1.5220	0.0530	32.6°	1.5492	0.3469	3.55	64.4
C <sub>3</sub>	2.35	8.59	1.5768	1.5221	0.0547	33.9°	1.5487	0.3472	3.10	56.3
C <sub>4</sub>	3.07	8.61	1.5796	1.5230	0.0566	28.2°	1.5487	0.3482	3.00	54.4
C <sub>5</sub>	5.49	8.59	1.5783	1.5242	0.0541	29.4°	1.5488	0.3485	2.12	38.4
C <sub>6</sub>	11.50	8.74	1.5778	1.5240	0.0538	29.9°	1.5490	0.3482	1.37	24.9
C <sub>7</sub>	15.15	8.92	1.5760	1.5242	0.0518	31.7°	1.5490	0.3480	0.92	16.7

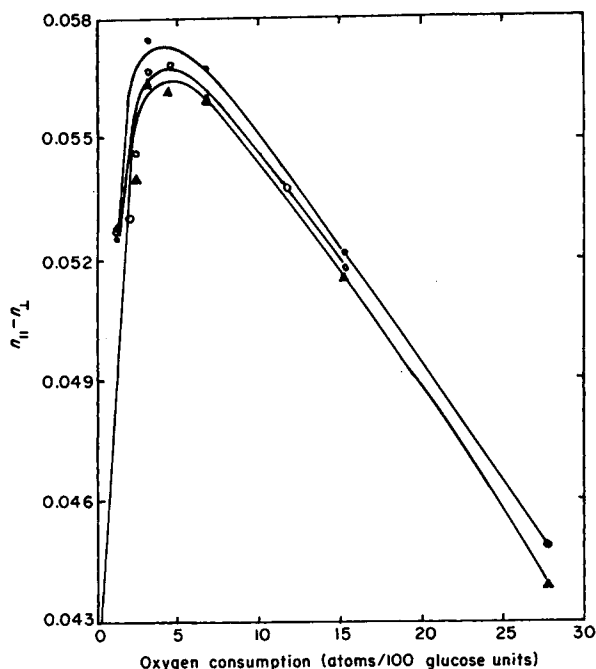


Fig. 1. Effect of periodate oxidation, periodate-chlorite, and periodate-borohydride treatments on birefringence of cotton fiber: (▲) periodate oxycellulose; (○) periodate-chlorite oxycellulose; (●) periodate-borohydride oxycellulose.

position 6 in the glucose unit, the proportion of these links increasing with increasing degree of oxidation. This conclusion has been substantiated by the results of Anthony,<sup>19</sup> who found that the solubility of nitrates of periodate-oxidized cellulose in acetone decreases and the molecular weight increases with progressive oxidation. The presence of hemiacetal or hemiacetal crosslinkages has been suggested by Mack and Reeves<sup>20</sup> from the result of measurement of dry wrinkle-recovery angles of fabrics treated with periodate. When the periodate oxycelluloses are oxidized further with  $\text{NaClO}_2$ , the aldehydic groups in the periodate oxycelluloses are oxidized to carboxyl groups, whereas reduction with  $\text{NaBH}_4$  leads to the conversion of the aldehyde groups to primary alcoholic groups. When periodate oxycelluloses are oxidized with  $\text{NaClO}_2$  or reduced with  $\text{NaBH}_4$ , the products obtained do not contain any crosslinkages. Thus, in interpreting the results of birefringence, density, and breaking strength measurements, several factors such as gross morphology of cotton as well as the effects of chemical reactions involved in the modifications of cellulose chain molecules must be considered.

Results of the present study indicate that with progressive oxidation, values of  $n_{\parallel}$  for all the three types of oxycellulose increase sharply during the initial stages, followed by maxima at oxygen consumption between 4 and 6 atoms per 100 glucose units (copper number = 12) and a rapid de-

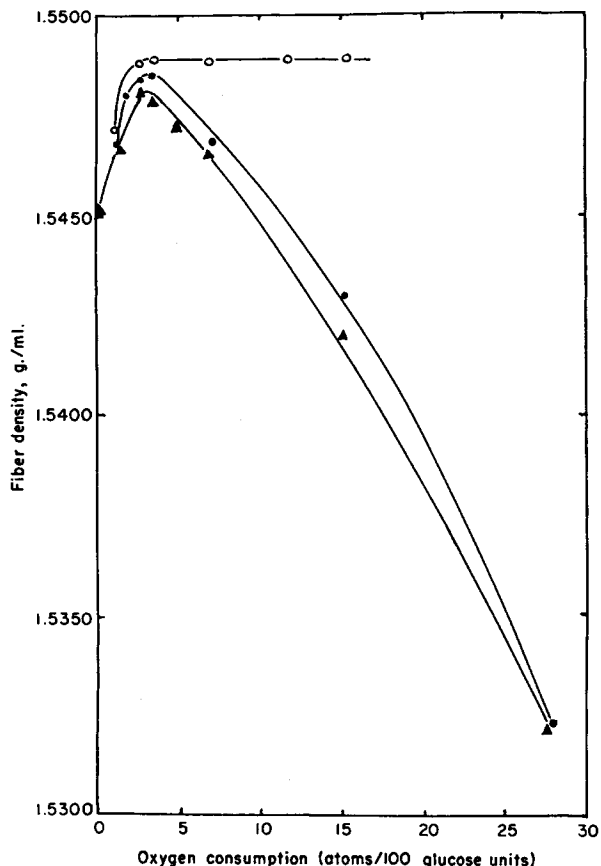


Fig. 2. Effect of periodate oxidation, periodate-chlorite, and periodite-borohydride treatments on fiber density of cotton: (▲) periodate oxycellulose; (O) periodate-chlorite oxycellulose; (●) periodate-borohydride oxycellulose.

crease thereafter. On the other hand, values for  $n_{\perp}$  decrease appreciably as compared with untreated cotton during the very early stages of oxidation and then remain more or less constant for all the three types of periodate oxycellulose, except at the very high stages of oxidation (Table I). Birefringence values follow more or less the same pattern as that of  $n_{\parallel}$  for all types of oxycellulose studied (Fig. 1). This is reflected in the values of spiral angle which decrease during the initial stages of oxidation and then beyond a stage of oxidation represented by oxygen consumption of 4–6 atoms per 100 glucose units, the fine structure of cellulose opens up considerably. Patel,<sup>2</sup> who made refractive index measurement on periodate-chlorite oxycelluloses obtained from bleached ramie found that both  $n_{\parallel}$  and  $n_{\perp}$  decreased progressively with increase in oxidation. When the degree of oxidation was small,  $n_{\perp}$  decreased to a greater extent, and afterwards  $n_{\parallel}$  was affected much more, with the result that double refraction increased at first, reached a maximum, and then decreased. The reason why Patel did

not observe the initial rise in  $n_{\parallel}$ , as was noticed in the present study, was due to the fact that oxycelluloses prepared by him were from ramie, which itself has very high degree of orientation to start with ( $n_{\parallel} = 1.5969$ ) as compared with the low value of refractive index in the case of cotton ( $n_{\parallel} = 1.5722$ ). In addition, the first stage of oxidation from which he has started the measurements of refractive indices is also fairly high. Similar to the results of birefringence of the present study, Kanamaru,<sup>1</sup> in the case of NaOCl and  $\text{KMnO}_4\text{-H}_2\text{SO}_4$  oxycelluloses, found that with progressive oxidation both  $n_{\parallel}$  and birefringence increased, but as oxidation was continued there was a reversal in the trend of birefringence.

With respect to dry density measurements, it has been found in the present study that during the initial stages of oxidation with all the oxycelluloses there is a rise followed by a maxima at an oxygen consumption of 3-4 atoms per 100 glucose units and a sharp drop in the case of periodate- and periodate- $\text{NaBH}_4$ -treated samples as oxidation is continued (Fig. 2). During the final stages of oxidation, densities of periodate oxycelluloses and the corresponding  $\text{NaBH}_4$ -treated oxycelluloses are less than those of untreated samples.  $\text{NaClO}_2$ -treated samples show the initial rise, and the values then remain more or less the same even at higher stages of oxidation. Mack and Reeves<sup>20</sup> have also observed that as the degree of periodate oxidation increases, the dry density of the fiber decreases linearly with the increase in oxidation. Similar behavior has also been noticed in the case of partially acetylated cottons, where the dry density has been shown to decrease linearly as the degree of substitution increases.<sup>21</sup> Dry density is a measure of the compactness or degree of openness of the fiber, and to some extent dry density of a fiber will rise or fall with the percentage of crystalline matter in the fiber substance. Hence, both the parameters, refractive indices and density measurements, indicate that during the initial stages of oxidation of cotton with  $\text{NaIO}_4$ , there is an increase in the degree of orientation and closeness of packing of cellulose chain molecules, but beyond a stage of oxidation corresponding to an oxygen consumption of 4-6 atoms per 100 glucose units, the fine structure of cellulose opens up appreciably. It is interesting to note that this value of oxygen consumption agrees fairly well with the value of 6 atoms per 100 glucose units representing the attack on noncrystalline regions in cotton linters as observed by Goldfinger et al.<sup>22</sup> and Timmel<sup>23</sup> during their studies on periodate oxidation of different varieties of cellulosic fibers with a view to estimating the relative proportions of crystalline and noncrystalline regions. They found that in the case of cotton, beyond this stage of oxidation, the attack proceeded to the crystalline portions.

Results of breaking strength indicate that in the case of periodate oxycelluloses, there is a drop in the relative breaking strength to about 19.4% of the original up to a stage of oxidation represented by oxygen consumption of 6-7 atoms per 100 glucose units, followed by a rise as oxidation is continued; at an oxygen consumption of 27.4 atoms per 100 glucose units (copper number 57.6) the relative breaking strength is of the order of 35.6%



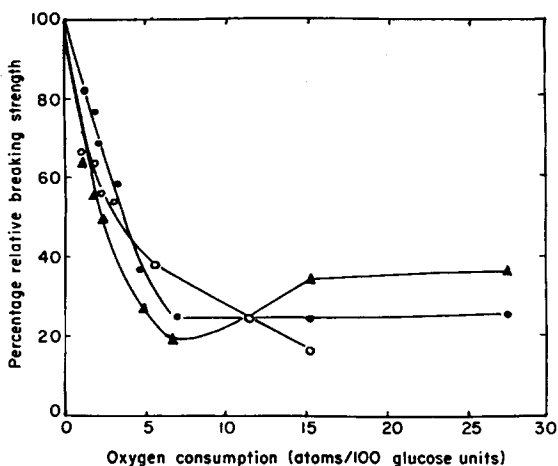


Fig. 3. Effect of periodate oxidation, periodate-chlorite, and periodate-borohydride treatments on relative single fiber strength of cotton: (▲) periodate oxycellulose; (○) periodate-chlorite oxycellulose; (●) periodate-borohydride oxycellulose.

of the original (Fig. 3). With respect to  $\text{NaBH}_4$ -treated samples, there is a decrease in breaking strength in the initial stages, and beyond oxygen consumption of 6–7 atoms per 100 glucose units, values of breaking strength remain constant, whereas in the case of  $\text{NaClO}_2$ -treated oxycelluloses, the decrease in breaking strength is continued with progressive oxidation. Both  $\text{NaBH}_4$  treatment as well as  $\text{NaClO}_2$  treatment have been found to restore a part of the strength lost by periodate oxycelluloses at each stage of oxidation up to 6–7 atoms of oxygen per 100 glucose units. The effect of  $\text{NaBH}_4$  treatment has been found to be more during the initial stages of oxidation than that in the case of  $\text{NaClO}_2$  treatment. Nevell and Zeronian<sup>5</sup> have also observed similar behavior in the tensile characteristics of yarns of different counts prepared from American cotton after periodate oxidation as well as subsequent  $\text{NaBH}_4$  reduction.

There are several macromolecular structural features which are responsible for the peculiar behavior of cotton when subjected to mechanical forces. These include molecular chain length, polymolecularity, crystallinity, crystallite size, crystallite modification, orientation, presence of crosslinkages, chemical modifications, and gross morphology of cotton. The strength of a fiber is related to a number of supermolecular structural factors, but especially to molecular chain length and orientation. Thus, it is not possible to attribute the changes observed in the breaking load of oxycelluloses studied in terms of one or two individual factors. Chemical modification of cotton appears to have diverse effects on the tenacity. For instance, in the case of partially acetylated cottons with increasing acetyl content, there is a loss of strength in the beginning, but as the degree of substitution goes beyond 0.8, the trend is reversed and the breaking strength increases above that of unacetylated cotton at a degree of sub-

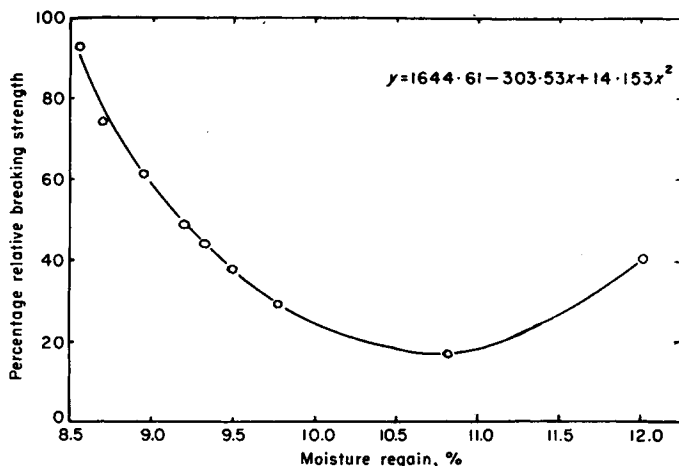


Fig. 4. Relation between moisture regain and relative single fiber strength of cotton oxidized with sodium metaperiodate.

stitution of 1.5,<sup>24</sup> a behavior somewhat similar to that observed in the present study during periodate oxidation.

In the case of periodate oxycelluloses, increasing degree of oxidation gives rise to increasing crosslinks between neighboring cellulose chain molecules with the result that the relative movement of the chains becomes more restricted and thus there is less possibility for the movement of chains to equalize distribution of stress on individual chains. This leads to high local stress concentration, and the fiber undergoes rupture. When these hemiacetal crosslinks are removed either by  $\text{NaBH}_4$  treatment or  $\text{NaClO}_2$  treatment, one of the causes of strength loss is removed, and hence a proportion of that loss is restored. Similar loss in strength and tenacity of fiber bundles is noticed when reactive resins are applied to cotton in the relaxed state and of significant interest is the fact that restoration of tenacity is more or less complete when the resin phase is removed by stripping the fiber with urea and phosphoric acid.<sup>25</sup>

The reason why the strength losses in the case of periodate oxycellulose in the initial stages are not removed completely even after  $\text{NaBH}_4$  or  $\text{NaClO}_2$  treatment is that during oxidation, non-Malaprade side reactions take place leading to chain scission which is an additional factor for loss in strength. The occurrence of non-Malaprade side reactions leading to cellulose chain breakdown is substantiated from the results of values of intrinsic viscosities of oxidized samples in standard cupriethylenediamine solution as observed in the present study which never reach the same value as that of the original cotton, even when alkali-sensitive linkages have been stabilized by borohydride treatment. With respect to the subsequent rise in the breaking strength of periodate oxycelluloses, it appears that certain other factors in addition to the formation of a rigid, three-dimensional covalent network as suggested by Nevell and Zeronian<sup>5</sup> seem to play a part.

The moisture content of periodate oxycelluloses appears to increase slowly in the beginning, but beyond a stage represented by oxygen consumption of 6.65 atoms per 100 glucose units, it increases very rapidly as observed from the results of the present study (Table I). The data on per cent moisture regain ( $x$ ) and per cent relative breaking strength ( $y$ ) were statistically analyzed, and a regression  $y = 1644.61 - 303.53x + 14.15x^2$  was worked out (Fig. 4). It was found that a general quadratic explained about 77% of variation in  $y$ , and the contribution of quadratic component was highly significant. It is, therefore, likely that beyond a certain stage of oxidation, the effect of moisture regain of the sample on the tenacity of the fiber would be appreciable. It is well known in the case of cotton fibers that higher the moisture regain of the sample, higher is the tenacity. Thus, at higher degrees of oxidation it is likely that the combined effect of crosslinking and non-Malaprade reaction in reducing the tenacity is upset by the high absorption of moisture leading to a reversal in the trend of breaking strength values. This behavior is not observed in the case of either  $\text{NaBH}_4$ -treated or  $\text{NaClO}_2$ -treated periodate oxycelluloses, because in these cases, moisture contents of the samples are close enough to that of the original cotton. Davidson and Nevell<sup>7</sup> have demonstrated that periodate oxycelluloses undergo some degradation when treated with  $\text{NaClO}_2$  and the extent of degradation increases with an increase in the initial degree of oxidation. During this treatment the material is partly converted to water-soluble fragments, presumably of low molecular weight. Thus, the observed continuous fall in breaking strength of chlorite-treated periodate oxycelluloses is in accordance with the expectation.

Gross morphological changes revealed that at higher periodate oxidation, in particular the subsequent chlorous acid treatment affected the length of the fibers rendering them brittle. However, relatively no appreciable change in the average ribbon width and the number of convolutions was observed, except in the last two highly oxidized samples where a fall in the number of convolutions was observed.

The structural reversals in cotton are reported to be the highly oriented regions and as periodate oxidation is known to attack crystalline regions of cotton fibers, changes brought about in these regions by progressive oxidation was followed up. For this study a West Indies cotton, VH8, was selected in preference to Nandyal N-14, as the former, belonging to *G. barbadense* species, contains large number of reversals in contrast to the latter, which belongs to *G. arboreum indicum*.<sup>15</sup> The untreated sample contained about 20 reversals/cm., which dropped to 14/cm. and 0.7/cm. with progressive oxidation in the samples of 7.7 and 14.0 copper number, respectively. Further treatment with  $\text{NaBH}_4$  did not induce reformation of reversals.

#### **$\text{K}_2\text{Cr}_2\text{O}_7$ -Oxalic Acid Oxycelluloses**

Oxidation of cellulose with  $\text{K}_2\text{Cr}_2\text{O}_7$  and oxalic acid has been shown to be mainly confined to the oxidation of primary hydroxyl groups to the alde-

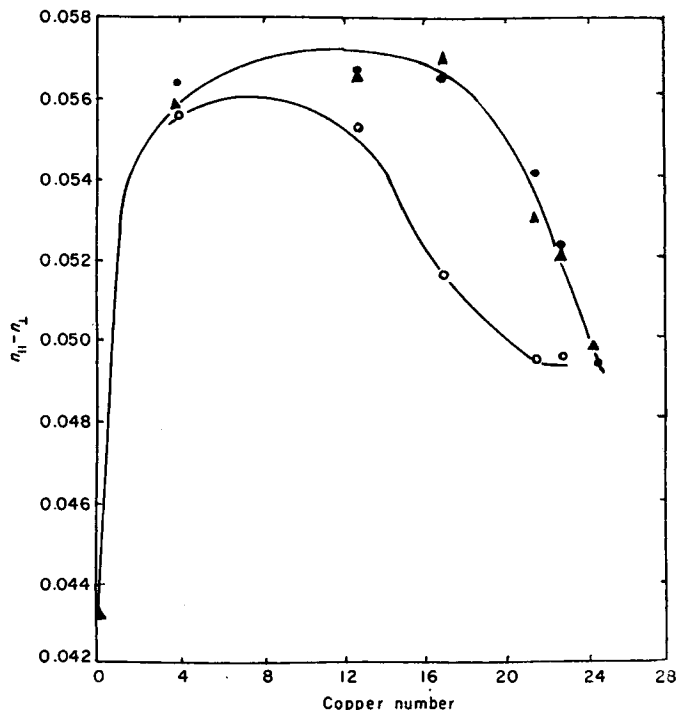


Fig. 5. Effect of dichromate-oxalic acid oxidation, dichromate-oxalic acid-chlorite, and dichromate-oxalic acid-borohydride treatments on birefringence of cotton fiber: (▲) dichromate-oxalic acid oxycellulose; (○) dichromate-oxalic acid-chlorite oxycellulose; (●) dichromate-oxalic acid-borohydride oxycellulose.

hyde groups. During this oxidation, some of the aldehyde groups formed are further oxidized to the carboxylic acid stage.<sup>26</sup> Although this reaction is mainly confined to the oxidation of primary hydroxyl groups, the results of Lindberg and Theander<sup>27</sup> on model compounds indicate that during this oxidation some of the hydroxyl groups at carbon atom 3 in the glucose unit are also oxidized to aldehyde or carboxyl. In addition to this main reaction, breakdown of cellulose chains also takes place due to the presence of acid in the reaction mixture. This has been substantiated by the fact that cupriethylenediamine fluidities of the oxidized samples never reach the same value as that of original cotton, even when stabilization of alkali-sensitive linkages has been effected. Unlike periodate oxidation, oxidation with  $K_2Cr_2O_7$  and oxalic acid is confined only to the noncrystalline regions of cellulose fibers, and the x-ray diffraction pattern of the oxidized celluloses does not change with progressive oxidation.<sup>28</sup> This behavior has also reflected in the present study, inasmuch as no change in the gross morphology i.e., the average ribbon width and number of convolutions, was observed.

Although presence of hemiacetal crosslinks between aldehyde groups and alcoholic groups in the case of  $K_2Cr_2O_7$ -oxalic acid oxycelluloses has not been detected by any investigator, such crosslinks have been found to exist

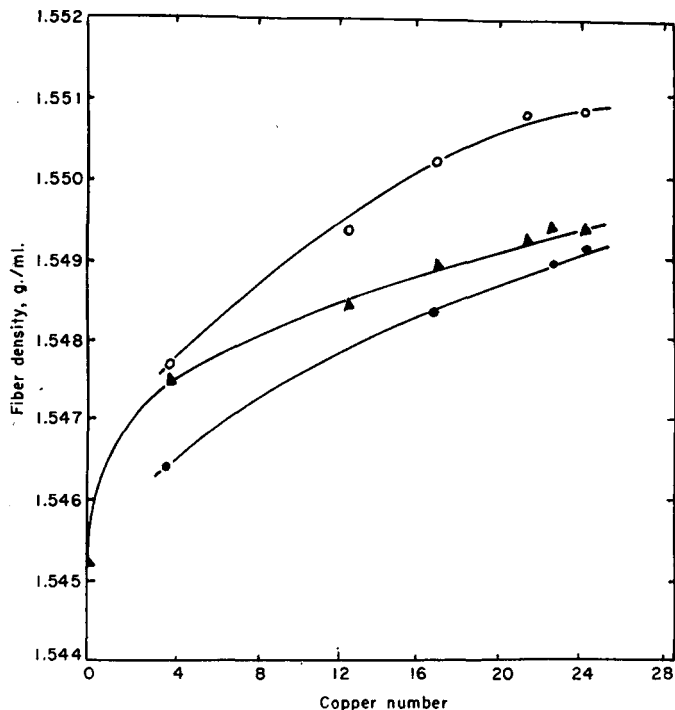


Fig. 6. Effect of dichromate-oxalic acid oxidation, dichromate-oxalic acid-chlorite, and dichromate-oxalic acid-borohydride treatments on fiber density of cotton: (▲) dichromate-oxalic acid oxycellulose; (O) dichromate-oxalic acid-chlorite oxycellulose; (●) dichromate-oxalic acid-borohydride oxycellulose.

in the case of  $\text{NO}_2$ -oxycelluloses,<sup>29</sup> wherein the oxidation has also been found to take place preferentially at the primary alcoholic groups. When the  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycelluloses are oxidized further with  $\text{NaClO}_2$ , aldehyde groups in the 6 position of glucose unit are oxidized to carboxyl groups, while reduction of these oxycelluloses with  $\text{NaBH}_4$  brings about the conversion of aldehyde groups in the 6 position once again to primary alcoholic groups.

Results of the present study indicate that with progressive oxidation of cotton with  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid,  $n_{\parallel}$  increases sharply from 1.5722 to 1.5824 at a copper number of 12.7 and then decreases to 1.5789 at copper number of 21.5. Thereafter the values for  $n_{\parallel}$  remain practically the same (Table II). The maximum value for  $n_{\parallel}$  obtained with  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycellulose, viz., 1.5824, is close enough to the limiting value of  $n_{\parallel}$  of crystalline cellulose, viz., 1.5895. Borohydride reduction or  $\text{NaClO}_2$  oxidation of these oxycelluloses does not bring about appreciable change in the values of  $n_{\parallel}$  from those observed for the original oxycelluloses. On the other hand, values for  $n_{\perp}$  in the case of  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycellulose decrease appreciably as compared with untreated cotton during the early stages of oxidation, remain more or less constant for the intermediate range

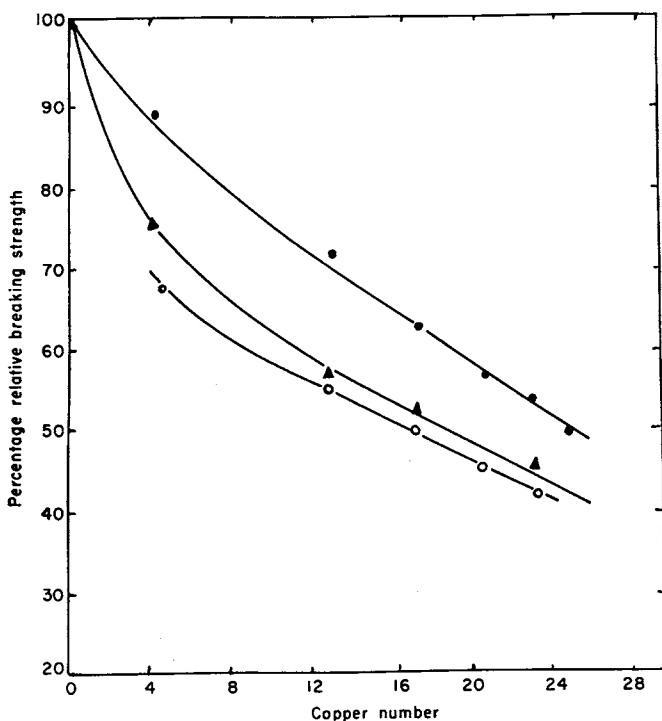


Fig. 7. Effect of dichromate-oxalic acid oxidation, dichromate-oxalic acid-chlorite, and dichromate-oxalic acid-borohydride treatments on relative single fiber strength of cotton: (▲) dichromate-oxalic acid oxycellulose; (○) dichromate-oxalic acid-chlorite oxycellulose; (●) dichromate-oxalic acid-borohydride oxycellulose.

of oxidation, and then rise in the values beyond copper number of 16.9. The values of  $n_{\perp}$  in the case of  $\text{NaBH}_4$ -treated  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycelluloses do not change appreciably from those of the original oxycelluloses. Birefringence values for  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycelluloses follow more or less the same pattern as that of  $n_{\parallel}$  except that beyond the stages of oxidation represented by copper number 16.9, the values are found to decrease continuously (Fig. 5). In the case of  $\text{NaBH}_4$ -reduced oxycelluloses, there is not much change in the values of birefringence from those of the parent oxycellulose. Patel,<sup>2</sup> who also made refractive index measurement on  $\text{K}_2\text{Cr}_2\text{O}_7$ - $\text{H}_2\text{SO}_4$  oxycelluloses obtained from bleached ramie, found that both  $n_{\parallel}$  and  $n_{\perp}$  decreased progressively with increase in oxidation. Beyond a stage of oxidation represented by carboxyl content of 6 mmoles/100 g. cellulose, he found that, whereas values for  $n_{\parallel}$  continued to decrease, values for  $n_{\perp}$  showed a tendency to remain more or less constant.

With respect to density measurements, it has been found in the present study that the values of density show continuous increase up to a stage of oxidation represented by copper number 21.5 and there is little change thereafter when oxidation is continued further (Fig. 6). This behavior is

TABLE II

Birefringence, Density, Moisture Regain, and Single Fiber Breaking Strength of  $K_2Cr_2O_7$ -Oxalic Acid,  $K_2Cr_2O_7$ -Oxalic Acid-NaBH<sub>4</sub>, and  $K_2Cr_2O_7$ -Oxalic Acid-NaClO<sub>2</sub> Oxycelluloses

Sample no.	Volume 2N $K_2Cr_2O_7$ used, ml.	Copper number	Moisture regain, %	Refractive index for sodium D line at 30°C.			Spiral angle $\theta$	Density $d_s$ , g./ml.	$n_{100} - 1/d$	Single fiber strength	
				$n_{11}$	$n_{\perp}$	Birefringence ( $n_{11} - n_{\perp}$ )				Breaking load, g.	Relative breaking strength, %
Control	Nil	0.01	8.56	1.5722	1.5290	0.0432	35.1°	1.5452	0.3501	5.51	100.0
$K_2Cr_2O_7$ -oxalic acid oxycelluloses											
DA <sub>1</sub>	20	3.9	8.58	1.5808	1.5250	0.0558	26.9°	1.5475	0.3496	4.14	75.1
DA <sub>2</sub>	50	12.7	8.61	1.5824	1.5260	0.0564	25.2°	1.5484	0.3503	3.13	56.8
DA <sub>3</sub>	80	16.9	8.64	1.5820	1.5251	0.0569	25.6°	1.5489	0.3497	2.93	53.2
DA <sub>4</sub>	100	21.5	8.66	1.5789	1.5260	0.0529	27.8°	1.5492	0.3493	2.23	40.5
DA <sub>5</sub>	200	22.7	8.72	1.5792	1.5270	0.0522	28.5°	1.5494	0.3499	2.56	46.5
DA <sub>6</sub>	250	24.3	8.85	1.5797	1.5300	0.0497	28.1°	1.5493	0.3514	2.27	41.2
$K_2Cr_2O_7$ -oxalic acid-NaBH <sub>4</sub> oxycelluloses											
DB <sub>1</sub>	20	0.05	8.57	1.5815	1.5250	0.0565	26.2°	1.5464	0.3501	4.89	88.7
DB <sub>2</sub>	50	0.27	8.59	1.5825	1.5260	0.0565	25.1°	1.5471	0.3505	3.96	71.9
DB <sub>3</sub>	80	0.34	8.59	1.5815	1.5250	0.0565	26.2°	1.5483	0.3497	3.51	63.7
DB <sub>4</sub>	100	0.42	8.57	1.5790	1.5250	0.0540	28.8°	1.5491	0.3489	3.15	57.2
DB <sub>5</sub>	200	0.42	8.55	1.5792	1.5270	0.0522	28.5°	1.5489	0.3498	3.02	54.8
DB <sub>6</sub>	250	0.43	8.55	1.5795	1.5300	0.0495	28.3°	1.5491	0.3513	2.74	49.7
$K_2Cr_2O_7$ -oxalic acid-NaClO <sub>2</sub> oxycelluloses											
DC <sub>1</sub>	20	0.25	8.58	1.5815	1.5260	0.0555	26.2°	1.5476	0.3501	3.46	62.8
DC <sub>2</sub>	50	0.74	8.60	1.5822	1.5270	0.0552	25.4°	1.5493	0.3505	3.08	55.9
DC <sub>3</sub>	80	0.99	8.63	1.5815	1.5300	0.0515	26.2°	1.5502	0.3515	2.82	51.2
DC <sub>4</sub>	100	1.20	8.61	1.5794	1.5300	0.0494	28.3°	1.5508	0.3508	2.47	44.8
DC <sub>5</sub>	200	1.32	8.62	1.5795	1.5300	0.0495	28.3°	1.5511	0.3508	2.40	43.6
DC <sub>6</sub>	250	1.36	8.65	1.5794	1.5300	0.0494	28.3°	1.5508	0.3508	1.98	35.9

unlike that observed in the case of periodate and periodate- $\text{NaBH}_4$  oxycelluloses, where there is a rise in density during the initial stages of oxidation followed by a maxima and a sharp drop when oxidation is continued. With  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycelluloses,  $\text{NaBH}_4$  treatment brings about reduction in density, while  $\text{NaClO}_2$  treatment increases the density of oxycelluloses. Thus, the results of density measurements indicate that during oxidation of cotton with  $\text{K}_2\text{Cr}_2\text{O}_7$  and oxalic acid, there is an increase in the crystallinity of the fiber substance throughout the progress of reaction, the effects being more pronounced in the initial stages than in the later stages.

Results of breaking strength measurements indicate that in the case of  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid,  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid- $\text{NaBH}_4$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid- $\text{NaClO}_2$  oxycelluloses there is a continuous decrease in the relative breaking load of all the three oxycelluloses as oxidation is continued, the decrease being more pronounced during the initial stages than during the final phase of oxidation (Fig. 7). This is in sharp contrast to the behavior observed in the case of periodate oxycellulose, where there is a sudden drop in the relative breaking strength, followed by a rise as oxidation is continued. In the case of  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycelluloses,  $\text{NaBH}_4$  treatment has been found to restore part of the strength lost by these oxycelluloses at each stage of oxidation, and the restoration of strength by  $\text{NaBH}_4$  treatment is more in the case of  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycelluloses as compared with that observed during the initial stages of periodate oxidation. Action of  $\text{NaClO}_2$  on  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycellulose results in a further decrease in the relative breaking strength.

In the case of  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycelluloses, increasing degree of oxidation gives rise both to increasing crosslinks between neighboring cellulose chain molecules as well as breakdown of cellulose chains due to the presence of acid during oxidation. This is reflected in the fact that there is an increase in birefringence and density of the fiber substance indicating fiber recrystallization, similar to that which takes place during mild acid hydrolysis, where the breaking of chains in the readily accessible regions allows the broken chain ends freedom to rotate and thus extend the already formed crystallites. Both these factors lead to a continuous decrease in the breaking strength of the oxycelluloses. Subsequent treatment with  $\text{NaBH}_4$  results in the removal of the hemiacetal crosslinks, and thus one of the causes of strength loss is removed with the result that a proportion of the loss is restored. In the case of  $\text{NaClO}_2$ -treated  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxycelluloses, there is further degradation during  $\text{NaClO}_2$  treatment resulting in further fall in breaking strength. The main difference in the behavior of breaking strength of  $\text{NaIO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid-oxycelluloses is that whereas in the case of the former, there is a subsequent rise in breaking strength beyond a specific stage of oxidation, in the case of  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxalic acid oxidation, values of breaking strength decrease progressively without showing any tendency to increase. This is due to the fact that periodate oxidation leads to intracrystalline rupture and opening up of the crystallites, thereby altering the moisture content of the oxycelluloses, and the effect of moisture



regain in the sample becomes appreciable on the tenacity of the fiber. On the other hand, dichromate oxidation is only intercrystalline, and, as indicated by x-ray diffraction measurements<sup>28</sup> and density measurements of the present study, there is no evidence of opening up of crystalline structure during oxidation. Moisture regain values of  $K_2Cr_2O_7$ -oxalic acid oxycelluloses do not increase appreciably, unlike that evidenced in the case of periodate oxycelluloses, with the result that the effect of moisture regain on the tenacity of the fiber does not come into play.

The double refraction of a cellulose fiber depends on the state of orientation of cellulose chains in the fiber substance. If the fiber substance is considered as consisting of a homogeneous mixture of crystalline and non-crystalline parts, it is to be expected that there is a definite relationship between the refractive power and the density of the fiber. If this hypothesis is to be applied to the oxycelluloses, the refractive power of the modified fibers must be expressed in terms of the refractive index of the isotropic fiber ( $n_{iso}$ ) which according to Hermans<sup>12</sup> is a parameter independent of orientation. The values of  $(n_{iso} - 1)/d$  are fairly constant at  $0.3490 \pm 0.0002$  for all the types of oxycellulose studied (Tables I and II), indicating that the correlation which exists between the refractive power and density in the case of different types of cellulose fiber also holds good for oxidation products of cellulose studied in the present work.

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### Résumé

On a examiné les changements des caractéristiques telles que l'indice de réfraction, la densité, la force de rupture d'une fibre et l'absorption d'humidité des fibres de coton. Ces changements sont provoqués par oxydation avec le métaperiodate de sodium et le mélange bichromate de potassium-acide oxalique. Cette étude a également été étendue aux oxycelluloses, obtenues au départ de ces produits, traitées par le chlorite de sodium et réduites par le borohydrure de sodium. Les résultats montrent que dans le cas de l'oxydation par le métaperiodate de sodium, la biréfringence et la densité augmentent d'abord, atteignent un maximum et puis diminuent rapidement lorsque l'oxydation est poursuivie, tandis que la force de rupture diminue au début, passe par un minimum et puis augmente. Lors de l'oxydation par le bichromate et l'acide oxalique, la biréfringence augmente rapidement au début de l'oxydation, passe par un maximum et puis diminue lorsque l'oxydation progresse, tandis que la densité augmente rapidement au début puis diminue lentement lorsque l'oxydation est poursuivie. Dans le cas des oxycelluloses oxydées au bichromate-acide oxalique, la force de rupture diminue continuellement lors du processus d'oxydation. On interprète les résultats sur la base des changements de morphologie et de la structure fine du coton provoqués par l'oxydation et les traitements subséquents au chlorite et au borohydrure.

### Zusammenfassung

Es wurde eine Untersuchung der Änderung charakteristischer Eigenschaften wie Brechungsindex, Dichte, Einzelfaserbruchfestigkeit und Feuchtigkeitenaufnahme von Baumwollfasern als Folge einer Oxydation mit Natriummetaperiodat und Kaliumdichromat-Oxalsäure durchgeführt. Die Untersuchung wurde auch auf die natriumchloridbehandelten und natriumborhydridreduzierten, aus diesen Oxyzelluloseprodukten erhaltenen Oxyzellulosen ausgedehnt. Die Ergebnisse zeigen, dass im Fall der Natriummetaperiodatoxydation Doppelbrechung und Dichte zuerst zunehmen, ein Maximum erreichen und dann bei fortgesetzter Oxydation scharf abfallen, während die Bruchfestigkeit im Anfangsstadium abnimmt, ein Minimum erreicht und dann in späteren Stadien ansteigt. Bei der Dichromatoxalsäureoxydation nimmt die Doppelbrechung während des Anfangsstadiums der Oxydation scharf zu, erreicht ein Maximum und nimmt dann bei weiterem Fortschreiten der Oxydation ab, während die Dichtewerte während des Anfangsstadiums rasch zunehmen und dann bei fortgesetzter Oxydation langsam ansteigen. Im Fall der Dichromatoxalsäureoxycellulosen nimmt die Bruchfestigkeit mit fortschreitender Oxydation kontinuierlich ab. Die Ergebnisse werden anhand von Änderungen der Grobmorphologie und der Feinstruktur der Baumwolle als Ergebnis der Oxydation und darauffolgender Chlorit- und Borhydridbehandlung interpretiert.

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