

## Studies in Chemically Modified Celluloses. II. Some Aspects of Physical Properties of Chemically Modified Celluloses

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### Synopsis

The changes in physical properties such as moisture regain, tensile strength, elongation at break, bursting strength, and resistance to abrasion of cellulose modified with different oxidizing agents such as dichromate-sulfuric acid, sodium hypochlorite in presence of leuco vat dyes, and potassium metaperiodate and of the corresponding products obtained as a result of reduction with sodium borohydride and those by oxidation with chlorous acid have been studied. Results are critically discussed in the light of existing knowledge on the changes that occur in the fine structure as well as in the chemical structure of cellulose during the mentioned modifications. It is pointed out that complex changes in physical properties of cotton cellulose brought about by chemical modification could hardly be evaluated and interpreted in terms of one or two physical or chemical parameters.

### INTRODUCTION

Oxidation of cellulose with periodate has been extensively studied.<sup>1-5</sup> The reduction with sodium borohydride results in an increase in the tensile strength and elongation at break of periodate oxycelluloses of low degree of modification.<sup>6</sup> These findings had been later confirmed by other workers.<sup>4,7-8</sup> Similar observations have also been made for dichromate-oxalic acid oxycelluloses after reduction with sodium borohydride.<sup>7</sup> In the present work, therefore, an attempt has been made to follow the changes in physical properties, brought about by reduction with sodium borohydride and by oxidation with chlorous acid of cellulose modified with different oxidizing agents such as sodium hypochlorite in presence of leuco vat dyes, dichromate-sulfuric acid; the results have been compared with those property changes produced by potassium metaperiodate oxidation. The studies are extended to investigate the effect of alkali on tensile strength of these differently modified celluloses.

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## EXPERIMENTAL

### Substrate

The modified cellulose samples were prepared from carefully purified Indian cotton yarn and cloth.

### Preparation of Chemically Modified Celluloses

Periodate oxycelluloses and dichromate-sulfuric acid oxycelluloses were prepared by steeping cotton cellulose in 0.01*M* potassium metaperiodate solution for different periods at 30°C and in aqueous solution containing 0.1*N* K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 0.2*N* H<sub>2</sub>SO<sub>4</sub> at 30°C, respectively, at a material:liquor ratio of 1:50 in both cases.<sup>3,9</sup> The modification of cotton cellulose in the presence of leuco compounds of vat dyes, namely, Cibacron Orange R, Indanthrene Yellow G, and Calco Yellow 5G, with sodium hypochlorite solution was carried out according to the method recommended by Turner et al.<sup>10</sup>

### Treatment with Sodium Borohydride and with Chlorous Acid

The various modified samples were reduced with sodium borohydride solution according to the method suggested by Head.<sup>11</sup> The oxidation of modified celluloses with aqueous sodium chlorite solution in the presence of acetic acid or phosphoric acid was carried out according to the methods described by Davidson and Nevell.<sup>12</sup>

### Treatment with Alkali

The different samples were treated with 0.125*N* sodium hydroxide solution at 60°C for 45 min, washed to neutrality, air-dried, and conditioned at 65% RH and 30°C.

### Properties of Modified Celluloses

Copper number of the samples was determined according to the modified method described by Forster et al.<sup>13</sup> The basic degree of polymerization (DP) of the samples was calculated by the method suggested by Battista<sup>14</sup> from viscometric measurements of standard cuprammonium hydroxide solutions containing the substrate.

For the determination of moisture regain values of various modified samples, 1–2 g sample was weighed and kept over phosphorus pentoxide under vacuum for 4 hr or more to reduce the moisture content below the equilibrium regain value. The sample was then conditioned at 65% RH and 30°C till equilibrium moisture uptake was attained. The per cent moisture regain was calculated on bone-dry basis after drying the sample to constant weight at 105°C.

The breaking load and elongation at break of different samples conditioned at 65% RH and 30°C were measured with Zellweger Uster single-thread tester. A few samples were also tested on a Moscrop single-thread

tester for breaking load. The results of the breaking load of different samples were calculated and expressed as percentage of the breaking load of the original unmodified yarn. The mean breaking load of a sample was calculated from about 140 readings in each case. The bursting strength of modified cloth samples conditioned at 65% RH and 30°C was measured on a Goodbrand hydraulic bursting tester. All the results of bursting strength of the modified samples are expressed as percentages of the bursting strength of the unmodified sample.

The abrasion resistance of samples was tested on a Martindale wear-testing machine, where the sample rubs against emery cloth in every direction. The extent of abrasion was determined by comparing the bursting strength of the samples both before and after a definite number (15) of rubs.

## RESULTS

### Cellulose Modified with Potassium Metaperiodate

Figure 1 illustrates the results obtained and shows the changes taking place in the breaking load of cellulose yarn during progressive potassium metaperiodate oxidation and also as a result of subsequent chlorous acid oxidation. The strength of the yarn falls steeply in the early stages of periodate oxidation, but in the later stages the rate of loss in strength slows down considerably. The modified yarn is found to retain about 35% of its original strength, even though the oxygen consumption increased to 48 milliatoms/100 g sample. The chlorous acid oxidation results in a loss in strength of cellulose modified with periodate. On the other hand, the results of reduction with sodium borohydride show an increase in the breaking strength and extensibility of cellulose modified with periodate (Fig. 2). The change in the percentage relative breaking load that takes

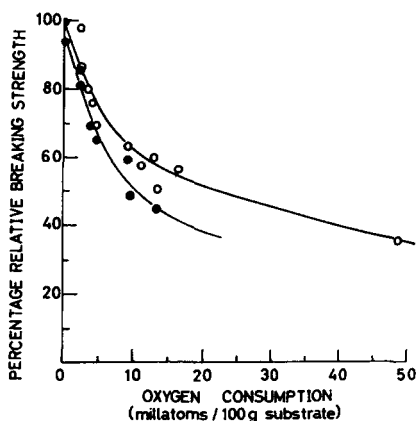


Fig. 1. Effect of chlorous acid treatment on tensile strength of periodate oxycelluloses: (O) periodate oxycellulose; (●) chlorous acid-treated periodate oxycellulose.

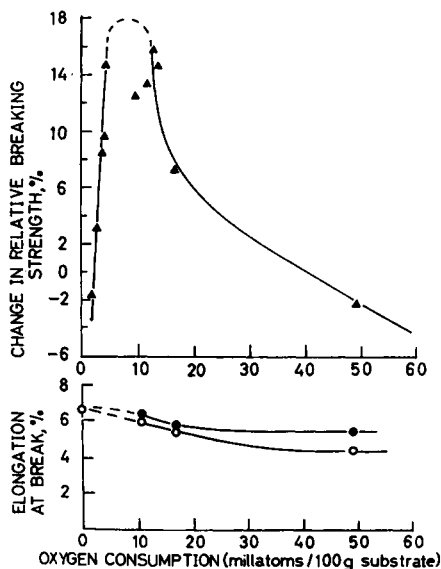


Fig. 2. Influence of  $\text{NaBH}_4$  reduction on tensile strength and elongation at break of periodate oxycelluloses: (▲) change in tensile strength as a result of  $\text{NaBH}_4$  reduction of periodate oxycellulose; (○) elongation at break for periodate oxycellulose; (●) elongation at break for  $\text{NaBH}_4$ -reduced periodate oxycellulose.

place as a result of borohydride reduction of periodate oxycellulose is plotted against the degree of modification of cellulose with potassium metaperiodate in Figure 2, which is rapid during the initial stages of modification, reaches a maxima around an oxygen consumption of 10 milliatoms/100 g sample and then drops thereafter.

The results of moisture-regain values, i.e., hygroscopicity, of cellulose modified with potassium metaperiodate are illustrated in Figure 3. The

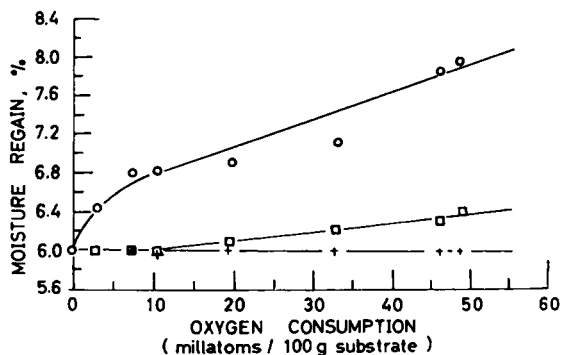


Fig. 3. Effect of chlorous acid oxidation and of borohydride reduction on moisture regain of cotton cellulose modified with potassium metaperiodate: (○) periodate oxycellulose; (□) chlorous acid-oxidized periodate oxycellulose; (+) borohydride-reduced periodate oxycellulose.

TABLE I  
Effect of Periodate Oxidation and of Subsequent Borohydride Reduction on Bursting Strength of Cellulose Before and After Abrasion

Substrate	Oxygen consumption, milliatoms/100 g sample	Copper number	DP	Relative bursting strength		Decrease in bursting strength due to abrasion, % <sup>a</sup>	Increase in bursting strength as a result of NaBH <sub>4</sub> reduction, %	
				Before abrasion (A)	After abrasion (B)		Before abrasion	After abrasion
Cellulose	0.00	<0.005	2460	100.00	72.49	27.51		
Periodate oxycellulose (I)	8.95	4.12	449	69.05	47.49	31.22		
Periodate oxycellulose (II)	13.89	6.37	393	56.18	37.08	34.00		
Periodate oxycellulose (I) reduced with NaBH <sub>4</sub>	—	<0.005	1478	77.67	53.43	31.21	12.48	12.51
Periodate oxycellulose (II) reduced with NaBH <sub>4</sub>	—	<0.005	1426	67.41	48.95	27.38	19.98	32.02

<sup>a</sup> Calculated as  $100(A - B)/A$ .

hygroscopicity of cellulose increases with the degree of periodate oxidation, while subsequent reduction with sodium borohydride results in its decrease to a value not different from that of the unmodified cellulose. The chlorous acid oxidation of periodate-modified samples also shows similar results. However, the hygroscopicity of chlorous acid-treated periodate oxycelluloses is slightly higher than that of the corresponding borohydride-treated samples or unmodified cellulose. Thus, the effect of oxidation with chlorous acid or reduction with sodium borohydride on the hygroscopicity of periodate oxycelluloses is to decrease it considerably.

The interesting behavior shown by periodate oxycelluloses after reduction with sodium borohydride led to extending the investigation to study the effect on other properties such as bursting strength and resistance to abrasion. The typical results of the changes in bursting strength and

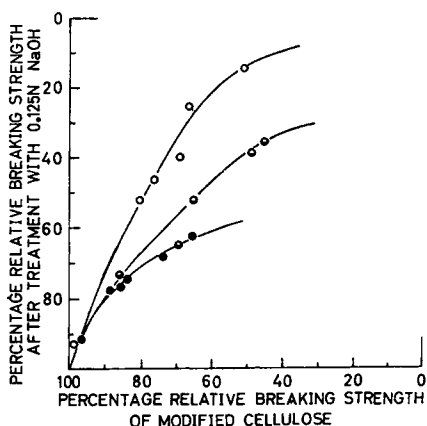


Fig. 4. Effect of 0.125N NaOH treatment at 60°C for 45 min on the relative breaking strength of (O) periodate oxycellulose, (◐) chlorous acid-treated periodate oxycellulose and (●) borohydride-reduced periodate oxycellulose.

abrasion resistance of cotton fabrics due to oxidation with potassium metaperiodate and subsequent reduction with sodium borohydride are summarized in Table I. From the results, it is seen that the bursting strength of the cloth decreases with the degree of periodate oxidation with a simultaneous increase in copper number and a decrease in DP and resistance to abrasion. The effect of abrasion, in general, is to decrease the bursting strength of the samples. The borohydride reduction results in the elimination of reducing groups with a simultaneous apparent increase in DP of periodate-oxidized samples due to the stabilization of the alkali-sensitive linkages in them. Further, it is very interesting to note that the bursting strength of the periodate oxycelluloses increases after borohydride reduction, depending upon the extent of oxidation. The bursting strength of the borohydride-reduced and abraded periodate oxycelluloses is more than that of the corresponding abraded periodate oxycelluloses. It may be also

remarked that the resistance to abrasion of reduced periodate oxycellulose (II) is not different from that of the unmodified sample (Table I).

The effect of hot alkali (0.125*N* NaOH at 60°C for 45 min) on tensile strength of periodate oxycelluloses along with the corresponding borohydride-reduced products and chlorous acid-oxidized products has also been investigated. The results obtained are shown in Figure 4. The tensile strength of alkali-sensitive periodate oxycelluloses suffers a considerable loss on treatment with alkali. However, the decrease in tensile strength of corresponding chlorous acid-treated or borohydride-reduced periodate oxycelluloses on treatment with alkali is significantly less. The loss in tensile strength of borohydride-reduced periodate oxycelluloses on alkali treatment is much less compared to those samples treated with chlorous acid. Thus the stabilization of alkali-sensitive linkages in periodate oxycelluloses can be brought about by treatment with chlorous acid and more so by treatment with sodium borohydride.

### Cellulose Modified with Dichromate-Sulfuric Acid

Cotton yarn oxidized with potassium dichromate in the presence of sulfuric acid loses its fibrous form rapidly and it is difficult to handle a highly oxidized substrate. The variation with oxygen consumption of relative breaking load of yarn modified with dichromate-sulfuric acid is shown in Figure 5. The strength of the substrate decreases progressively with

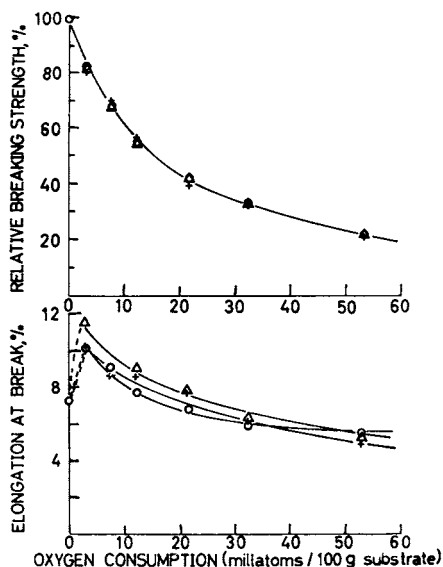


Fig. 5. Effect of chlorous acid oxidation and of borohydride-reduction on breaking strength and elongation at break of cotton cellulose oxidized with dichromate-sulfuric acid: (○) dichromate-sulfuric acid oxycellulose; (+) chlorous acid-oxidized dichromate-sulfuric acid oxycellulose; (Δ) borohydride-reduced dichromate-sulfuric acid oxycellulose.

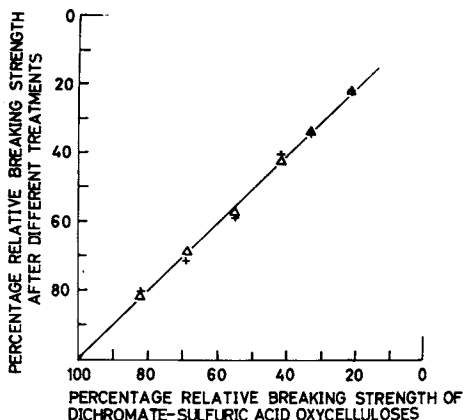


Fig. 6. Relation between initial relative breaking strength and that after chlorous acid oxidation or after borohydride reduction of dichromate-sulfuric acid oxycelluloses: (+) chlorous acid oxidation; ( $\Delta$ ) borohydride reduction.

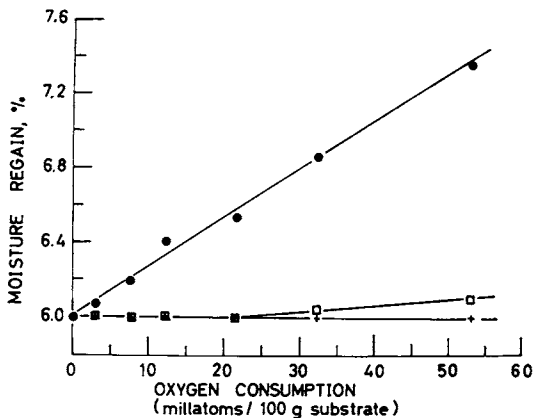


Fig. 7. Effect of chlorous acid oxidation and of borohydride reduction on moisture regain of cotton cellulose modified with potassium dichromate-sulfuric acid solution: (●) dichromate-sulfuric acid oxycelluloses; (□) chlorous acid-oxidized dichromate-sulfuric acid oxycelluloses; (+) borohydride-reduced dichromate-sulfuric acid oxycellulose.

the increasing degree of oxidation. The relation obtained between relative breaking load and oxygen consumption (Fig. 5) is similar to that found for cellulose yarn oxidized with periodate (Fig. 1), especially in the initial stages of oxidation. However, in the later stages of oxidation, a rapid fall in strength takes place for yarn oxidized with dichromate-sulfuric acid, unlike that for yarn oxidized with potassium metaperiodate, and thus at an oxygen consumption of 50 milliatoms/100 g sample, the yarn oxidized with dichromate-sulfuric acid retains only about 25% of its original strength, as compared to 35% retained by yarn oxidized with potassium



metaperiodate. The extensibility of yarn oxidized with dichromate-sulfuric acid decreases continuously with oxygen consumption after an initial rise.

Unlike periodate oxycelluloses, there is no effect on tensile strength after sodium borohydride-reduction of dichromate-sulfuric acid oxycelluloses. The changes in the extensibility of the yarn oxidized with dichromate-sulfuric acid on subsequent borohydride reduction and chlorous acid oxidation, respectively, are also shown in Figure 5. The oxidation with chlorous acid of dichromate-sulfuric acid oxycelluloses has also practically no influence on its tensile strength. In the case of periodate oxycelluloses also, this influence is of less significance. The relation between the initial relative breaking load and that after chlorous acid oxidation or after borohydride reduction is shown in Figure 6. The hygroscopicity of cellulose modified with dichromate-sulfuric acid increases almost linearly with the degree of oxidation (Fig. 7). After borohydride reduction of dichromate-sulfuric acid oxycelluloses, the hygroscopicity of the products is no different from that of the unmodified cellulose. Similar results are also obtained after oxidation of these oxycelluloses with chlorous acid. However, the hygroscopicity of highly modified samples after chlorous acid treatment is little higher than that of the unmodified cellulose. Thus, in this respect, dichromate-sulfuric acid oxycelluloses behave similarly to periodate oxycelluloses.

#### **Cellulose Modified with Sodium Hypochlorite in the Presence of Leuco Cibanone Orange R, Leuco Indanthrene Yellow G, and Leuco Calco Yellow 5G**

The present study is mainly restricted to the investigation of the effects of sodium borohydride reduction and of chlorous acid oxidation on the tensile strength of cellulose modified with sodium hypochlorite in the presence of the following three leuco vat dyes, Cibanone Orange R, Indanthrene Yellow G, and Calco Yellow 5G, with the aim of comparing the results with those obtained for periodate-modified and dichromate-sulfuric acid-modified cellulose. Typical results obtained are given in Table II. There is a significant drop in the strength of all the samples as a result of hypochlorite oxidation in the presence of leuco vat dyes, and the loss in strength depends on the pH of the oxidizing medium or alternatively on the oxygen consumed by the substrate. In the presence of Calco Yellow 5G, the loss in strength or the oxygen consumed by the cellulose yarn from the oxidizing medium is more at pH 7.48 than at pH 8.30. Similar results are obtained for DP measurements. There is no effect of chlorous acid oxidation or sodium borohydride reduction on tensile strength of these modified celluloses in presence of different leuco vat dyes. The behavior of these oxycelluloses after treatment with sodium borohydride is similar to that of dichromate-sulfuric acid oxycelluloses and differs from that of periodate oxycelluloses, where an increase in the tensile strength is observed after borohydride reduction. These oxycelluloses, however, resemble periodate and dichro-

TABLE II  
 Effect of Sodium Borohydride Reduction and Chlorous Acid Oxidation on Tensile Strength of Cellulose  
 Modified with Sodium Hypochlorite in Presence of Leuco Vat Dyes

Sample	Leuco vat dye	pH of oxidation	Oxygen consumption, milliatoms/100 g sample	Relative breaking load,				DP		
				Before treatment	After reduction with NaBH <sub>4</sub>	After oxidation with chlorous acid	Before treatment	After reduction with NaBH <sub>4</sub>	After oxidation with chlorous acid	
Cellulose				100.00					2600	
Oxycellulose (I)	Cibanone	7.33	16.90	63.77	63.77	63.77	576	598	591	
	Orange R									
Oxycellulose (II)	Indanthrene yellow G	7.02	13.20	66.94	66.72	66.72	638	685	669	
Oxycellulose (III)	Calco Yellow 5G	7.48	17.60	62.77	62.77	62.77	591	630	638	
Oxycellulose (IV)	Calco Yellow 5G	8.30	7.80	84.43	86.33	—	669	677	678	

mate-sulfuric acid oxycelluloses in their behavior with regard to tensile strength after chlorous acid oxidation. It is also interesting to note that the DP of these oxycelluloses does not change much after borohydride reduction or chlorous acid oxidation.

### DISCUSSION

Potassium metaperiodate attacks at C<sub>2</sub> and C<sub>3</sub> of the glucose units of the cellulose chain molecules, resulting mainly in the conversion of secondary hydroxyl groups to aldehyde groups with a carbon-carbon bond cleavage at the point of attack.<sup>1</sup> All these groups in the periodate-oxidized cotton cellulose are not present as free aldehyde groups, as indicated from the studies of several workers.<sup>15-25</sup> From the results available it is difficult to find out the exact proportion of free or otherwise aldehyde groups in a periodate-oxidized substrate. Even if it is accepted that most of the aldehyde groups are not free, it is highly speculative in absence of an unambiguous information as to whether the suggested hemialdals or hemiacetal groupings are intermolecularly or intramolecularly bonded. Thus, it would not only be difficult to predict the changes in properties as a result of periodate oxidation and subsequent aftertreatments but also it is complicated to interpret the results in terms of chemical modification alone at this stage.

There are several factors such as molecular chain length (DP), crystallinity, orientation, crosslinkages, chemical modifications, gross morphology, hygroscopicity, temperature, etc., which are known to influence the mechanical properties of cotton fiber. It is difficult to bring about any chemical change in the cellulose chain molecules without altering the degree of crystalline order and the degree of orientation. Moreover, since it is difficult to alter the degree of crystalline order without affecting the degree of orientation, and since the effect of the former seems to be smaller than that of the latter, the exact relationship between tenacity and order is not yet clearly understood.<sup>26-28</sup> There are indications, however, that differences in perfection of order are important, and that increased order raises the ultimate strength of the fibers. Increased orientation increases the tenacity and decreases the elongation of the fiber. Thus, it is realized how difficult it is to attribute the changes observed in mechanical properties of chemically modified celluloses in terms of one or two individual factors or to the chemical modification alone, without considering the changes in the fine structure of fibers.

The loss in tensile strength during progressive oxidation with periodate was attributed to the combined effect of chain scission due to non-Malaprade side reactions, presence of hemiacetal crosslinkages,<sup>4,7</sup> and increase in moisture regain.<sup>7</sup> It was also contended that the change in the tensile strength of periodate oxycelluloses after borohydride reduction<sup>4,7</sup> or chlorous acid oxidation<sup>7</sup> was due to the removal of hemiacetal crosslinkages, being one of the causes of the strength loss. However, the analysis of results of Betrabet et al.<sup>7</sup> on measurement of birefringence and density of

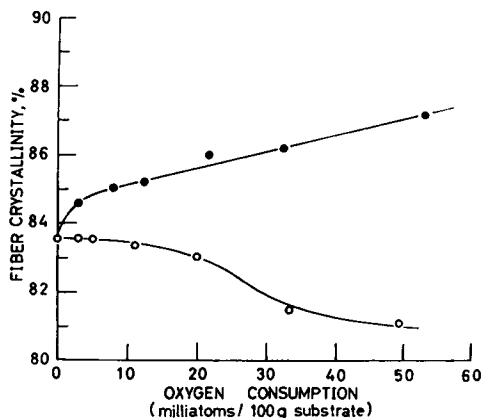


Fig. 8. Fiber crystallinity of borohydride-reduced dichromate-sulfuric acid oxycelluloses and that of borohydride-reduced periodate oxycelluloses as determined by the iodine adsorption method suggested by Hessler and Power:<sup>40</sup> (●) borohydride-reduced dichromate-sulfuric acid oxycelluloses; (○) borohydride-reduced periodate oxycelluloses.

periodate oxycelluloses and their corresponding borohydride-reduced and chlorite-treated products has revealed that the degree of orientation and the closeness of packing of cellulose chain molecules increase rapidly in the initial stage of periodate oxidation, and beyond oxygen consumption of about 24–36 milliatoms/100 g substrate, the fine structure of cellulose opens up considerably. It is in this initial region that the subsequent borohydride-reduction of periodate oxycelluloses results in a significant increase in the degree of orientation and density. But after subsequent chlorous acid oxidation, a comparatively small increase in the degree of orientation is noted with significant increase in density compared to that after borohydride-reduction. It is very interesting to note that in the present studies also, the increase in tensile strength of periodate oxycellulose as a result of borohydride reduction is observed in the same region, i.e., up to 24–36 milliatoms of oxygen/100 g substrate, and beyond this a decrease in tensile strength takes place. It has been shown by several workers<sup>29–36</sup> that as long as the orientation is low, the gain in tenacity for a given improvement in orientation is small, while if the orientation is high, a small improvement in degree of orientation produces larger increases in strength. The close similarity seen in the relation of changes in tensile strength after borohydride-reduction and oxygen consumption (Fig. 2) with that observed by Betrabet et al.<sup>7</sup> for the changes in birefringence and density after borohydride reduction of periodate oxycelluloses and oxygen consumption suggests the possible role of changes in the fine structure of the fibers on mechanical properties. The present results of the determination of crystallinity of borohydride-reduced periodate oxycelluloses from iodine adsorption as suggested by Hessler and Power<sup>37</sup> are shown in Figure 8. Chemical modification of cellulose is also known to have a diversified effect on tensile properties.<sup>38–40</sup> Dunkel<sup>41</sup> and Meyer<sup>42</sup> have estimated the

influence of various cellulose-chain components and substituents in terms of molar cohesion. Of the polar groups present in the cellulose chains, the alcoholic hydroxyl gives rise to the greatest force of lateral attraction (between chains). The sodium borohydride reduction converts the aldehyde groups to primary alcoholic groups, while chlorous acid oxidation converts them to carboxyl groups. Thus the effect of such forces in reduced periodate oxycelluloses may perhaps also influence the mechanical properties to a certain extent. If the removal of aldehyde groups alone is responsible for the observed increase in tensile strength of the modified cellulose, then either of the above treatments should bring about similar changes in tensile strength. However, the present results indicate that chlorous acid oxidation does not bring about changes similar to those caused by borohydride reduction in case of periodate oxycelluloses. Similar observations have also been made for dichromate-oxalic acid oxycelluloses by Betrabet et al.,<sup>7</sup> and they have postulated the presence of crosslinks (hemiacetal) in the oxycellulose. But in spite of this, similar changes in the fine structure of cellulose do not take place either during dichromate-oxalic acid oxidation or during subsequent aftertreatments. For example, during dichromate-oxalic acid oxidation, birefringence increases sharply in the beginning and then decreases with progressive oxidation, while density increases continuously, unlike the case with periodate oxycelluloses. In addition, birefringence and density of borohydride-reduced periodate oxycelluloses are more than those of periodate oxycelluloses, while in case of reduced dichromate-oxalic acid oxycelluloses birefringence is not different from that of the original oxycellulose but density is significantly lower in case of borohydride-reduced products than the corresponding oxycelluloses. The birefringence and density of chlorous acid-treated periodate oxycelluloses are greater than those of periodate oxycelluloses, but in the case of chlorous acid-treated dichromate-oxalic acid oxycelluloses, birefringence is lower while density is more than that of the parent oxycelluloses. Thus, it is difficult to attribute the changes observed in the breaking load of oxycelluloses studied solely to the changes in the fine structure and to isolate effects of chemical modification of cellulose.

Since the reaction of cellulose with dichromate-sulfuric acid or dichromate-oxalic acid has been shown to be mainly confined to the oxidation of primary alcoholic groups to aldehyde or carboxylic acid groups,<sup>43,44</sup> it was thought that these oxycelluloses would show similar or identical behavior in mechanical properties. However, the present results have shown that neither borohydride reduction nor chlorous acid oxidation of dichromate-sulfuric acid oxycelluloses and also of oxycelluloses obtained by oxidation of cellulose with sodium hypochlorite in the presence of leuco vat dyes, affects the tensile strength. Results of the present study indicate that crystallinity of borohydride-reduced dichromate-sulfuric acid oxycelluloses increases with progressive oxidation as determined by the method suggested by Hessler and Power<sup>37</sup> (Fig. 8). In spite of changes in DP (Tables I and III), similar to dichromate-oxalic acid oxycelluloses or periodate oxycellu-

TABLE III  
Effect of Sodium Borohydride Reduction and of Chlorous Acid Oxidation on DP of Cellulose Modified with Different Oxidizing Agents

Substrate	DP		
	Before treatment	After reduction with NaBH <sub>4</sub>	After oxidation with chlorous acid
Cellulose	2600		
Periodate oxycellulose			
I	618	1873	1765
II	534	1823	1524
III	417	1543	1277
Dichromate-sulfuric acid oxycellulose			
I	829	1623	1299
II	568	1226	1169
III	421	762	659
Dichromate-oxalic acid oxycellulose			
I	685	1418	1184
II	568	1203	1094
III	421	836	726

loses, no change in tensile strength takes place after the above two treatments in case of dichromate-sulfuric acid oxycelluloses. In case of oxycelluloses obtained by accelerated oxidation, the DP does not change much after either chlorous acid treatment or borohydride-treatment. This, therefore, may point at the fact that in case of dichromate-sulfuric acid oxycelluloses and accelerated-oxidation oxycelluloses, chain scission may be more important than the changes in the fine structure and physical properties from the view point of mechanical properties. In case of periodate oxidation, chain scission due to non-Malaprade side reactions seems to be mainly responsible for the observed trend of the decrease of tensile strength in the initial stages of periodate oxidation with the simultaneous changes in other physical properties. However, during subsequent alkaline borohydride reduction, some chain scission would occur even in the initial stages of oxidation. It is known that periodate oxycelluloses of even relatively low degree of modification strongly resist mild acid attack<sup>45,46</sup> but degrade easily in mild alkaline solution.<sup>3,47</sup> This is also reflected in the present study by the influence of alkali on tensile strength of periodate oxycelluloses after reduction with borohydride or chlorous acid oxidation (Fig. 4). It may be that the observed changes in the degree of orientation and density after borohydride treatment of periodate oxycelluloses are responsible for the increase in tensile strength, especially in the initial stages of modification, besides the chemical changes. At higher stages of oxidation, the chain scission during the borohydride treatment itself may be very high, and this may account for the observed changes in the tensile

strength at later stages of oxidation. It is, however, not to be expected that such complex changes brought about by chemical modification of cotton cellulose in physical properties in the present state of knowledge could be easily evaluated and interpreted in terms of chemical changes alone.

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