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THE OXIDATION AND (METHYLTHIO)METHYLATION OF COTTON BY METHYL SULFOXIDE–ACETIC ANHYDRIDE

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ABSTRACT

Methyl sulfoxide–acetic anhydride oxidizes some of the cellulosic hydroxyl groups of cotton yarn to aldehyde and ketone groups, while etherifying other hydroxyl groups with (methylthio)methyl groups. The ratio of oxidation to (methylthio)methylation of the cellulose is influenced by the reaction temperature, the reaction time, and the ratio of methyl sulfoxide to acetic anhydride employed. The (methylthio)methyl groups may be cleaved by boiling the cotton in aqueous solutions of acetic acid.

The total carbonyl content of the oxidized cellulose was determined by conversion into the polyoxime. The ratio of aldehyde to ketone groups in the oxidized cellulose was determined by further oxidation with chlorous acid; the carboxyl groups produced were measured spectrophotometrically by a method involving adsorption of Methylene Blue.

INTRODUCTION

Chemical modification of cotton for the purpose of endowing it with certain physical properties not inherent in the native polymer has been the goal of many intense research efforts. The two most common approaches to modification of cotton fiber are based upon (*1*) direct reaction with various reagents to form ether, ester, or acetal derivatives, and (*2*) polymerization, within the fiber, not involving a significant amount of covalent-bond formation to the cellulose backbone. An indirect approach of particular interest to us involves the use of reagents that chemically alter cellulose to generate new reactive sites along the chain, in the hope that the products would be cellulose-based precursors possessing almost the same physical properties as cotton, but able to undergo a much broader range of chemical reactions.

The present article reports some promising observations regarding functional alterations of untreated cotton yarn. Specifically, we have observed that mixtures of

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methyl sulfoxide with acetic anhydride (reagent *A*) oxidize cotton to introduce carbonyl groups along the chain. Accompanying the oxidation was the formation of *O*-(methylthio)methylcellulose at a degree of substitution (d.s.) about equal to, or greater than, the d.s. for the carbonyl group, depending on the reaction conditions. Experiments on the adsorption of Methylene Blue showed that there was a very low content of carboxyl group in yarn treated with reagent *A*; this demonstrated that the oxidation of cotton by the reagent is highly selective.

Reagent *A* has been extensively employed in prior studies as a selective oxidant for the synthesis of aldehydes and ketones from their respective alcohols[1,2]. Although various carbohydrate derivatives[3–5] have been subjected to the reaction, there are no previous literature reports on the use of this reagent for the oxidation of native cotton. The present paper describes some of our observations on the reaction of reagent *A* with cotton yarn.

RESULTS AND DISCUSSION

The effect of reaction conditions on the ratio of products: formation of carbonyl group versus *(methylthio)methyl ether.* — The infrared (i.r.) spectra (potassium bromide discs) of cotton before and after treatment with reagent *A* are shown in Fig. 1. The only perceptible difference between these spectra is a shoulder at $\sim 1725\ \mathrm{cm}^{-1}$ on the ascending limb of the band at $1614\ \mathrm{cm}^{-1}$ (water of hydration) in the spectrum of the treated cotton. The disc used to obtain Fig. 1B was dried, and it then gave the spectrum shown in Fig. 1C; this spectrum clearly showed carbonyl absorption at $\sim 1725\ \mathrm{cm}^{-1}$. Further evidence that aldehyde or ketone groups had been generated along the cellulose chain was the ready reaction of the treated cotton with the Schiff reagent, (2,4-dinitrophenyl)hydrazine, semicarbazide, and hydroxylamine. The most convenient, qualitative test for carbonyl groups is the addition of a few drops of the Schiff reagent to a small amount of yarn immersed in water; a positive test consists in the yarn's turning a distinct violet color within 15–20 min.

In addition to the oxidation of cellulose by reagent *A*, a significant proportion of (methylthio)methyl ether (Cell-OCH_2SMe) was also formed, as indicated by the sulfur content of the product.

The effect of the reaction time on the oxidation and (methylthio)methylation of cotton cellulose yarn is shown in Fig. 2. The total content of carbonyl group (aldehyde+ketone) is reflected by the increase in nitrogen content after reaction of the respective samples of oxidized yarn with hydroxylamine reagent. The content of sulfur (determined by X-ray fluorescence measurements) is also shown in Fig. 2.

For comparing the two processes on a molar basis, the actual percentage of nitrogen found was multiplied by 2.3 (the approximate ratio of the atomic weights of sulfur and nitrogen). Figure 2 shows that, assuming complete conversion[6,7] of $\rangle C{=}O$ into $\rangle C{=}N{-}OH$, the levels of oxidation and (methylthio)methyl ether formation are about the same at reaction times up to ~1 day, after which the latter reaction predominates. Although the reason for inhibition of the oxidation at longer

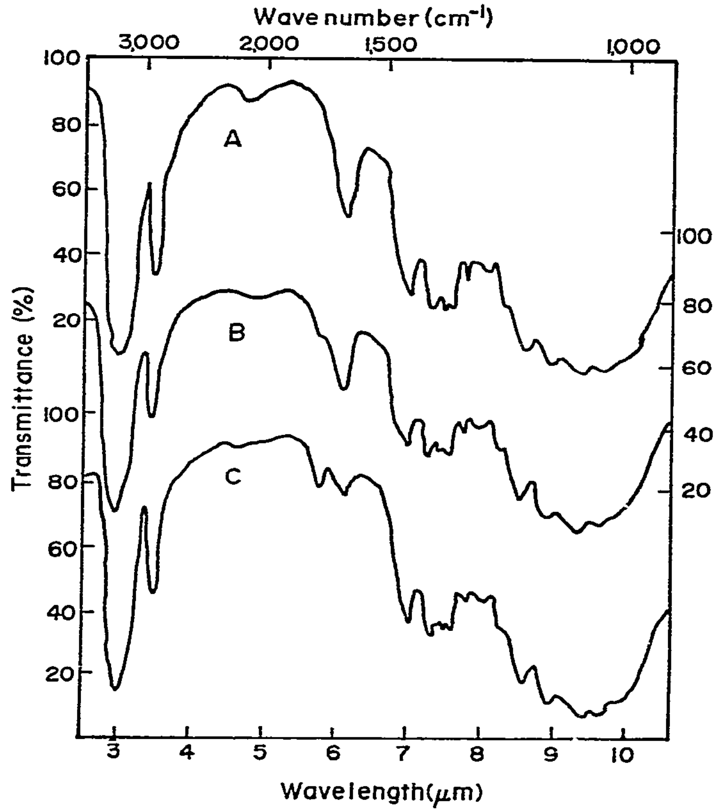

Fig. 1. Infrared spectra of cotton before and after oxidation with methyl sulfoxide–acetic anhydride (reagent *A*): (A) native cotton, (B) native cotton treated with reagent *A* (3:2 v/v) for 24 h at 25°, (C) same KBr disc as for (B), but dried for 24 h *in vacuo* at 50° over phosphorus pentaoxide.

times is unclear, the low d.s. (<0.1) at which it ceases is noteworthy. This result contrasts with the much greater extent of oxidation observed when 6-*O*-tritylcellulose (derived from regenerated cellulose) is treated with reagent *A* (0.6–0.8 carbonyl group per D-glucose residue) under conditions similar to those employed in this investigation[4].

With regard to the formation of the (methylthio)methyl ethers of cellulose, it is known[2,8] that oxidative procedures employing reagent *A* give (methylthio)methyl ethers as byproducts, but, in our investigation, this reaction occurred to an extent (relative to that of carbonyl formation) that was unexpected on the basis of previous results[1,4,9].

Table I shows the effect, on the distribution of product, of varying the proportion of acetic anhydride and the reaction temperature; increase in the concentration of the acetic anhydride above 17% does not lead to any significant increase in carbonyl groups, but favors formation of the (methylthio)methyl ether. From the experiment conducted at 8°, it appears that low temperatures favor the oxidation.

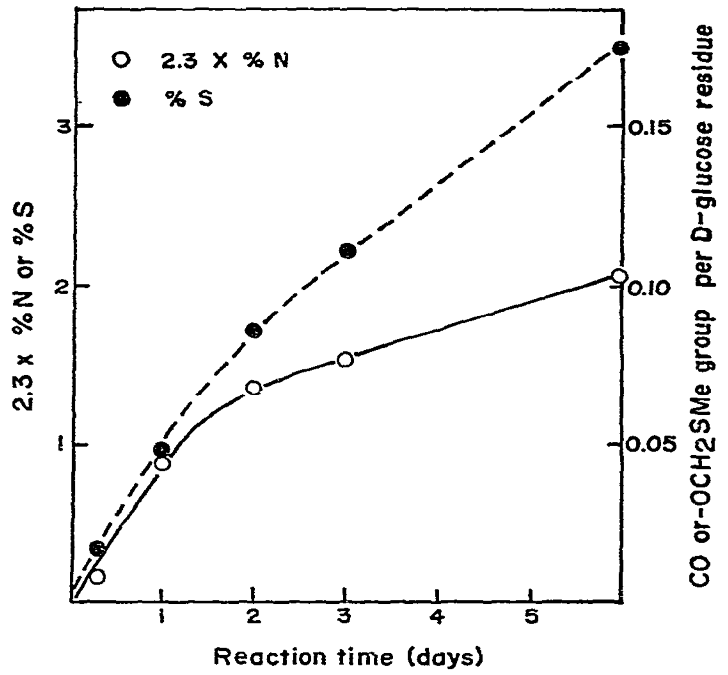

Fig. 2. Oxidation and (melthylthio)methylation of cotton yarn with methyl sulfoxide–acetic anhydride (60 ml of methyl sulfoxide plus 40 ml of acetic anhydride per 5 g of cotton) at 25° *versus* reaction time.

TABLE I

EFFECT OF CONCENTRATION OF ACETIC ANHYDRIDE, AND REACTION TEMPERATURE, ON THE OXIDATION AND (METHYLTHIO)METHYLATION OF COTTON YARN WITH METHYL SULFOXIDE–ACETIC ANHYDRIDE

Acetic anhydride (ml)[a]	*Temp. (°C)*	*Reaction time (days)*	N_{oxime} (%)	*Carbonyl (milliequivalents per* D-*glucose residue)*[b]	*S* (%)	*(Methylthio)methyl groups (milliequivalents per* D-*glucose residue)*[c]
5	25	1	0.05	6	0.23	12
10	25	1	0.29	33	0.63	32
20	25	1	0.29	33	0.78	40
40	25	1	0.39	45	0.95	48
60	25	1	0.27	31	1.15	58
40	8	3	0.58	67	0.72	36
40	58	0.3	1.08	124	2.07	105

[a] The yarn sample (5 g) was immersed in methyl sulfoxide (60 ml). [b] Calculated from % N found. [c] Calculated from % S found.

The presence of *O*-(methylthio)methylcellulose in textile materials is undesirable, as this material slowly liberates volatile compounds having an unpleasant odor (possibly, methylmercaptomethanol or methanethiol). However, we have found that the (methylthio)methyl group can be removed by acid hydrolysis under conditions that do not affect the carbonyl content. For example, on boiling with 20% acetic acid, a sample of yarn that had been treated with reagent *A* underwent an 85% diminution in the sulfur content, with no loss in carbonyl groups.

Distribution of functional groups in cotton oxidized with reagent A. — When cellulose is oxidized by reagent *A*, the possibility of production of three types of carbonyl group must be considered: aldehydic, ketonic, and carboxylic. In order to determine the percentage of each of these groups in this product, the carboxyl content thereof before and after oxidation with chlorous acid at 25° was determined[7,10].

The number of carboxyl groups in a given sample was found by spectrophotometric measurement of the amount of Methylene Blue adsorbed by a given amount of the yarn from a solution of dye of known concentration[11]. The difference in carboxyl content of the oxidized yarn (before and after further oxidation with chlorous acid) was then related to the percentage of aldehyde group originally present in the sample. As the total equivalents of carbonyl group (aldehyde + ketone) could be determined from the percentage of incorporation of nitrogen after reaction with hydroxylamine[6,7], the percentage of aldehyde groups could readily be calculated. The results of these experiments are shown in Table II. It appears that 47–62% of the oxidation occurs at C-6, producing aldehyde groups; this leaves 38–53% of the carbonyl content as ketone groups distributed between C-2 and C-3. Earlier studies[4,5] indicated that, when cellulose derivatives are oxidized with reagent *A*, very little of the diketone is formed, and that the favored point of attack is C-2.

TABLE II

CALCULATION OF THE PERCENTAGE OF ALDEHYDE GROUPS IN COTTON OXIDIZED WITH METHYL SULFOXIDE–ACETIC ANHYDRIDE

Type of cellulose used	*COOH groups (milliequivalents per* D*-glucose residue)*[a]	*Carbonyl groups (milliequivalents per* D*-glucose residue)*[b]	*Aldehyde groups (% of total carbonyl groups)*
Cotton treated with			
chlorous acid	1	0	—
reagent *A*[c]	2	50	
reagent *A* and then chlorous acid	33	—	62.4
reagent *A*[c]	2	72	
reagent *A* and then chlorous acid	36	—	47.2

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[a] Determined spectrophotometrically by Methylene Blue adsorption method (ASTM D-1926-63). [b] From oxime. [c] Oxidation of untreated yarn with reagent *A* for 2 days at 25 ± 1° (60 ml of methyl sulfoxide plus 40 ml of acetic anhydride per 5 g of cotton).

In conclusion, this investigation shows that the product obtained by treating native cotton yarn with reagent *A* (under mild conditions) contains aldehyde, ketone, and (methylthio)methyl ether groups. The last group can be removed by hydrolysis with weak acid, affording an oxycellulose having a carbonyl content of ~0.05 to 0.1 per D-glucose residue.

EXPERIMENTAL

Materials. — Cotton was loose-twist, 12/3 (tex-151), Pima, kier-boiled yarn (% N = 0.06). Methyl sulfoxide was reagent grade, and was stored over Linde 4A molecular sieves prior to use. Acetic anhydride and all other reagents and solvents were of reagent grade, and were used without further purification. Water was purified by mixed-bed, ion-exchange chromatography.

Reaction of cotton with methyl sulfoxide–acetic anhydride. — Cotton yarns were oxidized at 8, 25, and 58° for periods of 0.3 to 3 days. The yarns oxidized at 25° were immersed in reagent *A* in an Erlenmeyer flask (ground-glass stopper), and mechanically agitated. Samples treated at 8 and 58° were not agitated. The ratio of methyl sulfoxide to cotton was 12 ml per g, and the acetic anhydride was varied from 1 to 8 ml per g of cotton. At the end of the reaction, the yarn was successively extracted for 15-min periods with each of the following solvents: methyl sulfoxide (twice), hot *N,N*-dimethylformamide (twice), and ethanol (thrice). The yarn was dried for 15 min at 80°, and equilibrated overnight under ambient conditions. The change in weight of cotton treated with reagent *A* was insignificant.

Reaction of the oxidized cotton with carbonyl-group reagents. — *A. Hydroxylamine.* The ethanolic hydroxylamine reagent was prepared according to Vogel[12(a)]. Two methods were employed to convert the aldehyde and ketone groups into their oximes. The usual method consisted in immersing a sample of yarn (0.5–0.7 g) in the reagent (50 ml) for 24 h, and then washing it twice by immersion in fresh 95% ethanol (100 ml) for 2 min.

A second method (giving the same results) consisted in introducing the yarn sample and the reagent (50 ml) into a pressure tube, which was then sealed, and immersed for 2 h in an oil bath at 82°. The yarns were freed of excess of hydroxylamine by washing with tap water for 15–20 min.

After being dried in the air for at least a day, the yarns were analyzed for nitrogen content by the Kjeldahl method. The percentage incorporation of nitrogen, which reflected the extent of oxime formation, was calculated from the difference in the values found for cotton oxidized with reagent *A* and unmodified cotton, after each had been treated with hydroxylamine reagent; *i.e.*, $\% \, N_{oxime} = \% \, N_{found} - \% \, N_{control}$. From $\% \, N_{oxime}$, the number of carbonyl groups (aldehyde + ketone) per D-glucose residue was calculated[6,7].

B. Semicarbazide. Yarns (0.5–0.7 g) were treated by immersing them in the semicarbazide reagent (50 ml; prepared as described by Vogel[12(b)]) for 24 h. They were then freed of excess of reagent by two washes with 95% ethanol for 2 min, dried, and analyzed for nitrogen content. A yarn sample that gave a % N_{oxime} of 1.62 had a % $N_{semicarbazide}$ of 3.82. This was 78% of the value expected on the basis of the nitrogen content of the corresponding oxime.

C. (2,4-Dinitrophenyl)hydrazine. This reagent was prepared by suspending (2,4-dinitrophenyl)hydrazine (25 g) in methanol (500 ml), and adding concentrated sulfuric acid (15 ml) to effect dissolution. Yarn samples (0.5–0.7 g) were treated by immersion in the reagent (50 ml) for 24 h, and freed of excess of reagent by two washes (2 min each) in 95% ethanol. The nitrogen content (Kjeldahl) of four yarn samples treated with (2,4-dinitrophenyl)hydrazine ranged from 44 to 52% of the value expected on the basis of the % N_{oxime} values for the same samples. The yarns treated with (2,4-dinitrophenyl)hydrazine were orange colored.

D. Schiff reagent. The reagent was prepared from pararosaniline hydrochloride and sodium hydrogen sulfite as described by Vogel[12(c)]. Yarns (0.5 g) oxidized with reagent *A* were immersed in an aqueous solution containing a few drops of Schiff reagent, and were dyed violet within 15–20 min. A change in color was not observed with untreated yarn.

Oxidation of oxidized yarn with chlorous acid. — For yarns oxidized with reagent *A*, the selective conversion of the aldehyde groups into carboxyl groups was accomplished by oxidation with chlorous acid by a modification of the procedure described by Ellington and Purves[10]. The yarn (~1 g) was immersed for 1 h at 25° in 30% (v/v) aqueous acetic acid (100 ml) containing sodium chlorite (6.0 g), and then washed with de-ionized water for 30 min.

Carboxyl-group determinations. — The carboxylic acid content of untreated cotton and cotton oxidized with reagent *A*, both before and after oxidation with chlorous acid, was determined by the Methylene Blue adsorption technique[11] (ASTM D-1926-63); this entails determination of the amount of Methylene Blue adsorbed by a known weight of a yarn sample. The absorbance of the Methylene Blue solution at 620 nm was measured before introduction of the yarn and after equilibration with a sample of yarn. The absorptivity experimentally determined was 5.0×10^{-4}, in agreement with literature values[13]. The equivalents of aldehyde group originally present in a sample oxidized with reagent *A* were calculated as the difference in carboxyl content before and after oxidation with chlorous acid.

In an experiment designed to check the results given by the spectrophotometric technique, the amount of Methylene Blue adsorbed by a yarn that had been oxidized with reagent *A* and then with chlorous acid was determined by measuring the percentage of nitrogen incorporated into the yarn after equilibration with a solution of Methylene Blue. The aldehyde content calculated in this way was the same as that determined from spectrophotometric measurements.

Percent of sulfur incorporation. — The percentage of sulfur in a sample of yarn oxidized with reagent *A* was determined from X-ray fluorescence measurements made on a solid wafer prepared from yarn that had been ground to 20 mesh in a Wiley mill.

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