

Studies in Chemically Modified Celluloses. XI. Hypochlorite Oxidation of Cellulose in the Presence of Chromium Oxide

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Synopsis

In the dyeing of mineral Khaki on cotton fabrics, which are mainly used for military uniforms in India, a mixture of Fe_2O_3 and Cr_2O_3 is deposited in the fabric. When these garments are laundered using bleaching powder solution, the chromium oxide is likely to accelerate the oxidation of cotton cellulose. This aspect has been studied by oxidizing cotton yarn with sodium hypochlorite solution in the presence of chromium oxide, varying the chromium content, the pH of the oxidizing medium, and the concentration of the oxidizing agent. The properties of these chemically modified celluloses indicate that chromium oxide does accelerate the hypochlorite oxidation of cellulose and that the maximum extent of acceleration takes place when the oxidation is carried out at pH 7. The oxidized products were further modified separately by treatment with chlorous acid and sodium borohydride, and the effects of these agents on the properties of the oxidized products were studied.

INTRODUCTION

Military uniforms are extensively made from cotton cloth dyed with mineral Khaki, involving the deposition of chromium oxide (Cr_2O_3) and ferric oxide (Fe_2O_3) in a particular proportion and generally topped with vat olive green or vat Khaki dye. In this case, a substantial amount of chromium oxide is present in the cloth. Earlier work¹⁻⁶ carried out in this laboratory during the last decade had established that when cotton yarn in which hydroxides and/or carbonates of various metals such as iron, manganese, cobalt, nickel, and copper are present in a lower state of oxidation is oxidized with sodium hypochlorite solution, the cotton cellulose undergoes accelerated oxidation to various extents, depending on the metal, the amount of the metal hydroxide, the pH, and the concentration of the oxidizing solution. This accelerating activity was found with ferrous hydroxide and not with ferric hydroxide. Because military uniforms dyed with mineral Khaki are laundered using bleaching powder solution, it is to be expected that the presence of Cr_2O_3 (of the mineral Khaki) in the cloth may cause accelerated oxidation of cellulose during laundering with bleaching powder solution, especially since the chromium may exist in a higher state of oxidation in CrO_3 or Cr_2O_7 . In order to verify this, cotton yarn in which various amounts of $\text{Cr}(\text{OH})_3$ were deposited was treated with sodium hypochlorite solution buffered to different pH values and containing different concentrations of sodium hypochlorite for a short period. As was done in the earlier studies,¹⁻⁶ the resulting oxycelluloses were further modified separately by treatments with chlorous acid and sodium borohydride, and the effects of these agents on properties such as copper number, iodometric carboxyl value, cuprammonium fluidity, and alkali solubility were studied.

EXPERIMENTAL

Standard Cellulose. Yarn (20's) made from Indian cotton was purified by the method described earlier.⁶ It had the following properties: copper number,^{7,8} 0.03; iodometric carboxyl value,⁹ 0.63 meq/100 g dry sample; and cuprammonium fluidity (0.5% solution),¹⁰ 2.4 poises⁻¹.

Sodium Hypochlorite Solution. A stock solution of sodium hypochlorite was prepared by bubbling chlorine gas through 12% sodium hydroxide solution at 0–5°C.

Buffers.¹¹ The following buffers were used: (i) mixtures of 0.2*N* acetic acid and 0.2*N* sodium acetate (pH 3.72–5.57); (ii) mixtures of 0.1*M* sodium hydroxide and 0.1*M* potassium dihydrogen phosphate (pH 5.8–8.0); and (iii) mixtures of 0.1*M* boric acid and 0.1*M* sodium hydroxide (pH 7.81–10.0).

Hypochlorite Oxidation of Cellulose in the Presence of Cr₂O₃. Cotton yarn (20 g) was impregnated with chromium sulfate, Cr₂(SO₄)₃, solution, followed successively by squeezing, treating with sodium hydroxide solution, washing free of sodium hydroxide, and treating with sodium hypochlorite solution by the procedure described earlier.⁴

Further Modifications of Oxycellulose Samples. Samples of oxycellulose prepared as above were separately treated with chlorous acid¹² and sodium borohydride¹³ solutions.

Analysis of Oxycelluloses and Further Modified Oxycelluloses. Copper number, iodometric carboxyl value, cuprammonium fluidity, and alkali solubility¹⁴ of all the oxycellulose and further modified oxycellulose samples were determined. The basic D.P. values of these samples were determined from the cuprammonium fluidity values using the Battista equation.¹⁵

RESULTS AND DISCUSSION

Effect of Chromium Content

In this set of experiments, cotton hanks were impregnated with chromium sulfate solution (10–60 g/l.) and, after converting it into Cr(OH)₃ and washing the excess sodium hydroxide, were oxidized with sodium hypochlorite solution (3 g/l. available chlorine) buffered to pH 7.0 at 30°C for 10 min, keeping a material-to-liquor ratio of 1:50. The oxygen consumed by the yarn and the deposited Cr(OH)₃ were calculated by determining the available chlorine in the solution before and after the oxidation. The various properties of the oxycelluloses thus formed were determined. The results are given in Table I.

It is seen that the presence of chromium hydroxide in the yarn during the hypochlorite oxidation accelerates the oxidation of cellulose and that, with increasing chromium hydroxide content, the extent of oxidation of cellulose, assessed either in terms of oxygen consumed or in terms of the different properties of the resulting oxycellulose, increases. In the case of cuprous hydroxide-accelerated and nickelous hydroxide-accelerated oxidation of cellulose, when the copper and nickel contents were varied from 1 to 12 g/l. (as cuprous chloride) and 1–10 g/l. (as nickel sulfate), respectively, a substantial degree of oxidation of cellulose was achieved. A similar extent of oxidation was achieved with the chromium system with 10 to 60 g/l. chromium hydroxide (as chromium sulfate), indicating that chromium hydroxide is much less effective in accelerating the

TABLE I
Effect of Chromium Hydroxide Concentration on the Properties of Oxycellulose Prepared at 30°C and pH 7.0

Concn. of $\text{Cr}_2(\text{SO}_4)_3$ in treating solution, g/l.	Conc. of NaOCl_2 , g/l. available Cl_2		Oxygen consumption, m.atoms/100 g cellulose	Copper number	Carboxyl value, meq/100 g sample	Alkali solubility, %	Cuprammonium fluidity, p^{-1}	Basic D.P.
	Initial	Final						
0	2.944	2.777	11.85	3.16	0.84	9.45	19.85	799
10	2.984	2.494	34.40	8.48	3.36	18.90	38.95	331
20	2.949	2.239	51.35	10.68	5.32	22.95	43.24	294
30	3.019	2.175	58.12	11.50	6.16	24.90	44.48	279
40	2.984	2.105	62.85	13.27	6.72	25.65	46.58	259
50	2.984	2.038	67.61	14.92	7.28	26.05	—	—
60	3.019	2.056	71.15	15.50	7.84	27.00	—	—

hypochlorite oxidation of cellulose. However, chromium hydroxide was found to be more effective than ferrous hydroxide (195 g/l. ferrous ammonium sulfate) and manganous hydroxide (250 g/l. of manganous chloride) in this respect.

As in the earlier studies,^{4,6} a comparison of copper number and iodometric carboxyl value of chromium hydroxide-accelerated oxidation of cellulose shows that the oxycellulose formed is predominantly of the reducing type (with high copper number and substantial alkali solubility). As was observed earlier,^{2,4,6} in the present case the copper number and the iodometric carboxyl value were also found to be linearly related to the gross oxygen consumption.

Since the oxycelluloses formed are of the reducing type (hence have high alkali solubility), the cuprammonium fluidity values (and the D.P. values calculated from them) are not the true values, as during the dissolution of the oxycelluloses in the cuprammonium hydroxide solvent, and further depolymerization takes place due to the high alkalinity of the solvent. The fluidity values (Table V) determined after subjecting the oxycelluloses to sodium borohydride treatment, which stabilizes the alkali-sensitive reducing groups present in the oxycelluloses, represent the true extent of depolymerization undergone by the cellulose during the oxidation.

Effect of Varying the pH of the Oxidizing Medium

The pH of maximum acceleration of hypochlorite oxidation of cellulose in the presence of various metal hydroxides has been shown¹⁻⁶ to vary from 6.1 for ferrous hydroxide to 7.5 for cuprous hydroxide, the value for other metal hydroxides being 7. In order to study this aspect of the chromium system, cotton yarn was oxidized for 10 min at room temperature with sodium hypochlorite solution (3 g/l. available chlorine), buffered to different pH values, after depositing chromium hydroxide (prepared from 20 g/l. chromium sulfate) keeping a material-to-liquor ratio of 1:50. The various properties of the oxycelluloses thus formed were determined before and after the oxidation, and the results are given in Table II.

It is seen that the maximum extent of oxidation of cellulose, assessed in terms of copper number, carboxyl value, cuprammonium fluidity, and alkali solubility, or extent of oxygen consumption takes place at pH 7.

As found in the earlier studies,¹⁻⁶ the iodometric carboxyl values in the present case also were linearly related to the copper number at all the pH values studied, indicating that the same type of oxycellulose was formed at all these pH values. Further, carboxyl value and copper number are linearly related to the gross oxygen consumption. A straight-line relationship was also obtained between the alkali solubility values and the copper number, suggesting that the resistance of the oxycelluloses formed to the boiling alkali solution decreases with increasing number of reducing groups formed during the accelerated oxidation.

Effect of Concentration of Oxidant

The concentration of the oxidant has been found to affect the normal, unaccelerated oxidation of cellulose. To investigate the effect of this factor in the accelerated oxidation of cellulose, the oxidation of cellulose was carried out by varying the concentration of the hypochlorite (2 to 6 g/l. available chlorine), buffered to pH 7, after impregnating the cellulose with chromium sulfate solution

TABLE II
Properties of Oxycelluloses Prepared at Different pH Values, Using 20 g/l. $\text{Cr}_2(\text{SO}_4)_3$

pH of NaOCl solution	Concn. of NaOCl, g/l. available Cl_2		Oxygen consumption, m.atoms/100 g cellulose	Copper number	Carboxyl value, meq/100 g sample	Alkali solubility, %	Cuprammonium fluidity, p^{-1}	Basic D.P.
	Initial	Final						
4.05	2.917	2.569	24.5	6.57	3.03	11.52	34.21	432
5.20	2.951	2.499	31.85	8.25	3.60	16.64	38.37	365
6.00	2.986	2.499	34.30	8.61	4.50	19.20	41.65	318
7.00	2.986	2.222	53.90	10.76	5.25	23.04	44.42	281
8.00	2.986	2.610	26.95	6.78	3.26	15.36	35.74	385
9.00	2.951	2.777	12.25	4.32	1.38	8.96	21.82	728
10.00	2.986	2.917	4.90	1.63	0.96	5.12	9.05	1413

(20 g/l.), followed by treatment with sodium hydroxide and then washing this alkali. The oxygen consumed during the oxidation was determined in each case, and the oxycelluloses thus formed were analyzed for their various properties. The results are given in Table III.

It is seen from these properties that cellulose undergoes degradation continuously with increasing oxidant concentration. When copper number and carboxyl values were plotted against oxygen consumption, straight lines were obtained, suggesting that the reducing and acidic groups are formed in direct proportion to the oxygen consumption.

Effect of Chlorous Acid on the Properties of Oxycelluloses

As in the case of earlier studies,¹⁻⁶ the oxycelluloses prepared under different conditions in the presence of chromium hydroxide were also treated with chlorous acid (sodium chlorite and acetic acid), and the different properties of these further modified oxycelluloses were determined. The results are given in Table IV.

It is seen that about 60%–65% of the reducing groups (copper number) formed in the various oxycellulose samples prepared under different conditions of oxidation are oxidized to carboxyl groups by the chlorous acid treatment, indicating that the free aldehyde groups are present in the original oxycelluloses to the extent of 60%–65% of the total reducing groups. The residual reducing groups impart alkali sensitivity, as seen from the alkali solubility values. However, the alkali sensitivity of the chlorous acid-treated oxycelluloses is lower than that of the original oxycelluloses.

Effect of Sodium Borohydride Treatment on the Properties of Oxycelluloses

The reducing property of aqueous solutions of sodium borohydride has been widely used in further modifying oxycelluloses containing aldehyde, keto, enediol, and lactone groups. Free carboxyl groups are not affected by this treatment.

In the present investigation, oxycelluloses prepared by chromium hydroxide-accelerated oxidation were treated with 0.1*M* sodium borohydride solution for 48 hr at 30°C, keeping a material-to-liquor ratio of 1:50, and replacing the borohydride solution after 24 hr, followed by washing and air drying. The treated oxycellulose samples were analyzed for various properties. The results are given in Table V.

It is seen that the borohydride treatment reduced the copper number of all the oxycelluloses by 85%–95%, irrespective of the conditions of the oxidation. The residual (5–15% of the original copper number of the oxycellulose) may be due to the incomplete reduction of the reducing groups present in the oxycellulose by sodium borohydride. It is further seen that there is a considerable decrease in the cuprammonium fluidity values after the borohydride treatment of all the oxycellulose samples, indicating stabilization of alkali-sensitive reducing groups after the borohydride treatment. These fluidity values may be taken as a true measure of the depolymerization undergone by cellulose during chromium hydroxide-accelerated oxidation.

The borohydride treatment has been found to bring about a decrease of 40%–50% in the iodometric carboxyl value. This decrease may be attributed to the presence of enediol and lactone groups present in oxycelluloses which are

TABLE III
Effect of Concentration of Hypochlorite on the Properties of Oxycellulose Prepared at 30°C and pH 7, Using 20g/l. $\text{Cr}_2(\text{SO}_4)_3$

Concn. of NaOCl, g/l. available Cl_2	Final	Oxygen consumption, m. atoms/100 g cellulose	Copper number	Carboxyl value, meq/100 g sample	Alkali solubility, %	Cuprammonium fluidity p^{-1}	Basic D.P.
2.076	1.574	33.92	8.58	3.30	18.48	39.86	362
3.080	2.319	52.66	10.88	5.25	23.24	44.76	277
3.979	3.096	61.02	13.94	6.30	25.85	46.68	253
5.053	4.723	70.62	15.43	6.90	27.04	48.19	236
5.917	4.921	76.61	16.95	7.65	27.95	51.34	203

TABLE IV
Properties of Chlorous Acid-Treated Oxycelluloses^a

Variable	Copper number	Increase in copper number due to HClO ₂ treatment, %	Carboxyl value, meq/100 g sample	Alkali solubility, %	Cuprammonium fluidity, p ⁻¹	Basic D.P.
Variation of pH: concn. of Cr ₂ (SO ₄) ₃ , 20 g/l; concn. of NaOCl, 3 g/l. avail. Cl ₂						
pH of NaOCl solution						
4.05	2.48	62.24	6.56	9.72	31.92	479
5.20	2.96	64.12	9.12	10.93	35.42	411
6.00	3.82	55.67	9.60	12.15	37.20	382
7.00	4.32	59.84	12.08	13.37	41.85	315
8.00	2.76	59.28	8.16	11.58	33.46	447
9.00	1.61	62.45	4.03	6.07	20.55	775
10.00	0.62	61.95	2.07	3.65	7.96	1525
Variation of Concn. of Cr ₂ (SO ₄) ₃ : pH 7.0; concn. of NaOCl, 3 g/l. avail. Cl ₂						
Cr ₂ (SO ₄) ₃ concn., g/l.						
0	1.26	60.13	2.47	5.25	18.36	856
10	3.46	59.21	9.62	10.82	37.14	385
20	4.18	60.89	13.84	12.85	40.75	328
30	4.55	60.43	15.34	14.86	41.12	322
40	4.68	64.59	16.77	15.62	42.46	302
50	5.52	63.03	17.68	16.29	—	—
60	5.76	62.85	18.46	16.97	—	—
Variation of Concn. of NaOCl: pH 7.0; concn. of Cr ₂ (SO ₄) ₃ , 20 g/l.						
NaOCl concn., g/l. avail. Cl ₂						
2.076	3.42	60.13	9.55	4.58	36.41	395
3.080	4.08	62.48	12.80	10.95	40.68	326
3.979	5.32	61.69	14.84	15.72	42.34	309
5.053	5.70	63.08	15.54	16.25	43.86	289
5.917	6.25	62.89	16.52	16.89	46.58	253

^a The corresponding properties of oxycelluloses (before chlorous acid treatment) are given in Tables I, II, and III.

TABLE V
 Properties of Borohydride-Treated Oxycelluloses^a

Variable	Copper number	Decrease in copper number due to NaBH ₄ treatment, %	Alkali solubility, %	Carboxyl value, meq/100 g sample	Decrease in carboxyl value due to NaBH ₄ treatment %	Cuprammonium fluidity, p ⁻¹	Basic D.P.
Variation of pH: concn. of Cr ₂ (SO ₄) ₃ , 20 g/l.; concn. of NaOCl, 3 g/l. avail. Cl ₂							
pH of NaOCl solution							
4.05	0.89	86.48	2.05	1.71	43.57	30.84	497
5.20	1.05	67.26	3.75	2.04	43.33	32.80	486
6.00	1.31	84.78	4.10	2.38	47.10	35.86	406
7.00	1.58	85.39	5.40	3.06	41.71	40.30	335
8.00	0.92	86.58	4.75	1.87	42.65	31.68	482
9.00	0.20	95.34	1.89	0.75	45.64	19.14	827
10.00	0.05	96.95	1.54	0.47	51.02	7.28	1592
Variation of Concn. of Cr ₂ (SO ₄) ₃ : pH 7.0; concn. of NaOCl, 3 g/l. avail. Cl ₂							
Cr ₂ (SO ₄) ₃ concn., g/l.							
0	0.49	84.51	1.62	0.49	41.67	17.12	909
10	1.06	87.30	3.95	2.03	40.31	36.82	393
20	1.28	88.03	5.40	3.08	42.12	38.12	363
30	1.59	86.07	5.67	3.50	43.18	39.82	343
40	1.92	85.52	5.94	3.71	44.79	41.85	316
50	2.16	85.49	6.21	4.06	44.23	—	—
60	2.38	84.59	6.48	4.34	44.66	—	—
Variation of Concn. of NaOCl: pH 7.0; concn. of Cr ₂ (SO ₄) ₃ , 20 g/l.							
NaOCl concn., g/l. avail. Cl ₂							
2.076	0.98	86.57	3.52	1.87	43.37	35.47	413
3.080	1.21	88.65	5.28	2.85	45.70	39.48	348
3.979	1.34	90.38	5.56	3.30	47.63	41.57	317
5.053	1.67	89.19	5.80	3.95	42.75	42.12	309
5.917	1.98	88.26	6.08	4.05	47.06	43.89	287

^a The Corresponding properties of oxycelluloses (before borohydride treatment) are given in Tables I, II and III.

reducible by the borohydride treatment and both of which are estimated as acidic groups in the iodometric method of carboxyl estimation.

Thus, it may be pointed out that garments made from mineral Khaki-dyed cotton cloth should not be laundered using sodium hypochlorite or bleaching powder solution.

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