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Studies in Chemically Modified Celluloses. VII. Periodate Oxidation of Cellulose Dyed with Reactive Dyes

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Synopsis

Periodate oxidation of cellulose and cellulose dyed with reactive dyes at 32°C in the presence and absence of various concentrations of alkali metal chlorides and sulfates has been studied. The extent of oxidative degradation undergone by cellulose and assessed in terms of copper number and cuprammonium fluidity of the oxidized dyeing, the oxygen consumption during the oxidation, and the rate constant were shown to be markedly increased by the presence of the salts in the oxidizing solution. Borohydride and chlorous acid treatment were used to further modify the periodate oxycelluloses, and the effect of these treatments on the properties was studied.

INTRODUCTION

Sodium periodate is a specific oxidizing agent for the rupture of α-glycol-type compounds. When it acts on cellulose, the secondary hydroxy groups attached to the C-2 and C-3 carbon atoms of the anhydroglucose units of the cellulose macromolecule are oxidized, resulting in the cleavage of C-2–C-3 bond with the formation of a dialdehyde. The periodate does not attack cellulose at other sites to any significant extent. If one or both of these secondary hydroxy groups are chemically modified, the extent of periodate oxidation of the modified cellulose is likely to decrease. For example, if cellulose is dyed with a reactive dye and if the dye reacts with the secondary hydroxy groups also (in addition to the reaction with the primary hydroxy groups, which is known to take place to a major extent), periodate oxidation of such dyed cellulose must be inhibited by the modification of the α-glycol structure of cellulose by blocking one or both of the secondary hydroxy groups. In order to verify this, Shenai and Narkar[1] studied the periodate oxidation of cotton cellulose dyed with a series of commercial reactive dyes belonging to different chemical classes and found that cellulose underwent oxidation at a slower rate (assessed in terms of rate constant, percentage accessibility to periodate ions, copper number, and cuprammonium fluidity of the oxidized products) in the presence of the reactive dyes than in their absence. They also found that increasing

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the concentration of the same dye on the fiber, decreased the extent of periodate oxidation of cellulose. Lower rate constants and lower percentage accessibility for periodate ions in the presence of a bifunctional reactive dye than those with a monofunctional reactive dye indicated crosslinking of cellulose macromolecules during dyeing with the former dye.

Based on these observations, they concluded that a reactive dye reacts with the secondary hydroxy groups also, in addition to the known reaction between the dye and the primary hydroxy groups of cellulose. However, the lower rate of periodate oxidation of cellulose in the presence of the reactive dye may also arise as a result of another phenomenon, viz., ionization of the sulfonate groups of the reactive dye, irrespective of the site at which the dye has reacted with cellulose. The ionization of these sulfonate groups increases the negative charge on the cellulose substrate; and as a result, the periodate anions are repelled, which can lead to a lower rate of periodate oxidation of cellulose. If this is the case, the addition of an electrolyte such as sodium chloride or sodium sulfate to the periodate solution used for the oxidation should decrease the negative charge on the fiber by the adsorption of the cation of the added electrolyte at the sulfonate ion, resulting in the partial suppression of ionization of the sulfonate groups. The rate and extent of periodate oxidation of cellulose should then increase, compared to the periodate oxidation carried out in the absence of the added electrolyte. The present communication deals with this aspect of oxidation of cotton cellulose dyed with reactive dyes. The effects of varying the electrolyte type as well as electrolyte concentration are also reported.

EXPERIMENTAL

Standard Cellulose

The fiber material selected was 20s single yarn prepared from Indian cotton. After careful purification, it had the following properties: copper number[2,3] 0.01, and cuprammonium fluidity[4] (0.5% solution), 3.12 P^{-1}.

Dyestuffs and Chemicals

Commercial dichlorotriazinyl dyes, Amaryl Orange G(I) and Amaryl Brilliant Yellow 6G(II) (Amar Dye-Chem, Bombay), and monochlorotriazinyl dyes, Procion Brilliant Blue H-GR (III) and Procion Brilliant Red H-8B (IV) (ICI (India) Pvt. Ltd., Bombay), were chosen for the study.

Potassium periodate and lithium sulfate were of chemically pure quality, while the other salts were of Analar quality.

Dyeing Procedure

Cotton yarn (30 g) in the hank form was dyed with 3% shade in each case by the exhaustion method, keeping a liquor ratio of 30:1. The dyeings were soaped at the boil thrice to ensure the complete removal of the unfixed hydrolyzed and reactive dye forms. This was confirmed by the inability of 50% aqueous pyridine at 95°C for 30 min to strip any dye from the dyeings after soaping.

Periodate Oxidation of Undyed and Dyed Cotton

Periodate oxidation was carried out with 0.01*M* potassium periodate at 32°C, for different periods (1–48 hr) in the presence and absence of a series of electrolytes of different concentrations (0.05, 0.1, and 0.2*M*), keeping a liquor ratio of 50:1. The oxidation was carried out in the dark. Periodate consumption during the oxidation was determined periodically by titrating an aliquot against 0.1*N* sodium arsenite solution. The extent of oxygen consumed by the dyeing is expressed as oxygen atoms per 100 anhydroglucose units (AGU).

Analysis of Oxidized Dyeings

The oxidized dyeings were analyzed for their copper number and cuprammonium fluidity. The accessibility of dyeing to periodate ions was calculated from the oxygen consumption values by the method of Goldfinger et al.[5] and Timell.[6] The alkali-sensitive links present in the periodate oxycellulose samples were stabilized by treating the samples with 0.05*M* sodium borohydride solution[7] at 30°C for 24 hr, followed by washing free of the residual borohydride and its decomposition products and air drying. The periodate oxycellulose samples were treated with 0.2*M* sodium chlorite[8] in 1*M* acetic acid at pH 3 for 72 hr at 28°C, keeping a liquor ratio of 50:1. The chlorous acid-treated samples were washed with distilled water, steeped in 0.5*N* hydrochloric acid for 15 min, and washed free from the acid before air drying.

RESULTS AND DISCUSSION

Periodate Oxidation of Cellulose Dyed with Reactive Dyes

Purified cotton yarns, dyed separately with four reactive dyes, were oxidized with 0.01*M* potassium periodate at 32°C for 4–48 hr in the absence and presence of various concentrations of potassium sulfate. Similar experiments were carried out in the presence of chlorides of sodium and potassium and sulfates of sodium and lithium.

The oxygen consumed by the dyeings (atoms of oxygen/100 AGU) was determined by the method described earlier. Undyed cotton yarn was also oxidized under similar conditions. The extent of chemical modification undergone by cellulose was assessed in terms of copper number. The results in the case of oxidation carried out in the presence of potassium sulfate are given in Table I.

It is seen that for each time of oxidation carried out in the absence of any added salt, inhibition of periodate oxidation takes place in the presence of the dye. The extent of inhibition is different for different dyes. When

TABLE I
Periodate Oxidation of Cellulose Dyed with Reactive Dyes at 32°C in the Presence of Potassium Sulfate

Dye	Concn. of K_2SO_4, *M*	Oxygen consumption, atoms of oxygen/100 AGU, after				
		4 hr	8 hr	16 hr	25 hr	48 hr
—	0.00	1.540	2.500	3.959	4.839	6.541
	0.05	2.861	4.250	5.937	6.808	7.889
	0.10	3.150	4.850	6.380	7.100	8.022
	0.20	4.25	5.030	6.500	7.240	8.075
		(9.95)[a]	(11.90)	(15.20)	(17.20)	(19.20)
I	0.00	1.490	2.300	3.700	4.623	6.496
	0.05	2.847	4.050	5.729	6.493	7.853
	0.10	3.131	4.570	6.100	6.900	7.980
	0.20	4.053	4.930	6.210	7.150	8.066
		(9.70)	(11.80)	(14.55)	(16.90)	(19.10)
II	0.00	1.431	2.100	3.147	4.157	6.236
	0.05	2.755	3.950	5.467	6.445	7.810
	0.10	3.079	4.220	5.802	6.780	7.950
	0.20	3.920	4.750	6.000	7.002	8.040
		(9.63)	(11.20)	(14.20)	(16.60)	(19.03)
III	0.00	1.404	2.060	3.135	3.989	6.215
	0.05	2.713	3.870	5.300	6.400	7.766
	0.10	3.061	4.140	5.700	6.756	7.920
	0.20	3.914	4.670	5.967	6.981	7.980
		(9.607)	(10.95)	(14.10)	(16.50)	(18.90)
IV	0.00	0.998	1.600	2.440	3.578	6.027
	0.05	2.309	3.750	5.100	6.215	7.700
	0.10	3.021	4.050	5.596	6.747	7.890
	0.20	3.887	4.600	5.900	6.900	7.950
		(9.30)	(10.81)	(13.90)	(16.22)	(18.70)

[a] The values given in parenthesis are the copper numbers of the corresponding oxycellulose samples.

the copper number of the oxycellulose samples was plotted against the corresponding oxygen consumption values, a straight line passing through the origin was obtained, and this straight line had a slope of 2.33. This constancy of the relation between copper number and oxygen consumption suggests that the mode of oxidation of cellulose by periodate is the same, irrespective of whether the reactive dye is present on cellulose or not. The same type of oxycellulose is formed in proportion to the amount of oxygen consumed by the dyeing (specifically by cellulose, since the dye was not oxidized as noted visually) in the absence or presence of any of the reactive dyes studied in the present investigation.

The oxygen consumption values were analyzed according to first-order reaction kinetics by plotting log $(a-x)$ against the time of reaction t, where a and x are the periodate concentrations initially and at time t, respectively, and x is expressed as a percentage of a. The slopes of the straight lines were determined, and the rate constants k were calculated

TABLE II
Rate Constants for Periodate Oxidation of Reactive Dyed Cellulose at 32°C in the Presence of Salts

Salt	Concn. of salt, M	Rate constant k in the presence of dye, $hr^{-1} \times 10^3$				
		None	Dye I	Dye II	Dye III	Dye IV
None		43.18	32.82	26.49	25.33	24.87
		(3.08)[a]	(2.75)	(1.98)	(1.69)	(1.00)
NaCl	0.05	51.13	49.89	44.01	39.90	38.00
	0.10	57.01	50.37	48.37	47.79	46.09
	0.20	60.45	52.40	55.82	50.90	49.51
		(5.12)	(4.90)	(4.57)	(4.34)	(4.23)
KCl	0.05	54.13	52.25	49.12	47.22	44.68
	0.10	62.19	57.57	54.43	53.55	50.66
	0.20	63.11	58.72	55.27	54.13	51.82
		(5.34)	(4.99)	(4.90)	(4.79)	(4.72)
Li_2SO_4	0.05	65.63	60.71	52.97	49.51	49.06
	0.10	72.54	66.79	59.88	56.65	55.27
	0.20	77.71	67.36	61.02	57.01	56.89
		(6.15)	(5.81)	(5.72)	(5.55)	(5.50)
Na_2SO_4	0.05	70.81	66.01	56.79	50.66	52.85
	0.10	74.85	71.97	66.22	61.60	57.57
	0.20	80.61	74.85	66.79	63.33	62.19
		(6.33)	(6.15)	(5.86)	(5.83)	(5.79)
K_2SO_4	0.05	72.54	66.37	59.09	56.79	55.27
	0.10	80.61	72.90	67.94	66.09	59.88
	0.20	83.49	77.71	68.52	67.94	66.79
		(6.39)	(6.26)	(5.99)	(5.94)	(5.86)

[a] The values given in parenthesis are the percentage accessibilities of the corresponding oxycellulose samples for periodate ion.

from these slopes. The results for the oxidation of the dyeings carried out in the presence of various concentrations of the added salts are given in Table II.

As shown by Goldfinger et al.,[5] oxygen consumption values provide a means to calculate the percentage accessibility of cellulosic materials to periodate ions. The periodate oxidation of cellulose results in the rupture of C-2–C-3 bond with the formation of a dialdehyde and one oxygen atom, i.e., one periodate molecule is utilized per anhydroglucose unit. The extent of oxidation apparently is 100% when 100 atoms of oxygen are consumed by 100 AGU. The oxygen consumption A at time t may be expressed as a percentage of the total amount of oxygen consumed at the 100% level. When log C (where $C = 100 - A$) is plotted against t, two straight lines, both with negative slopes, the first one being steeper than the other, are obtained. When the second portion is extrapolated to zero time, the log C intercept can be read. From this value of C, $100 - C$ is obtained, which gives the percentage accessibility of the cellulose sample to periodate ion. The oxygen consumption data were analyzed according to

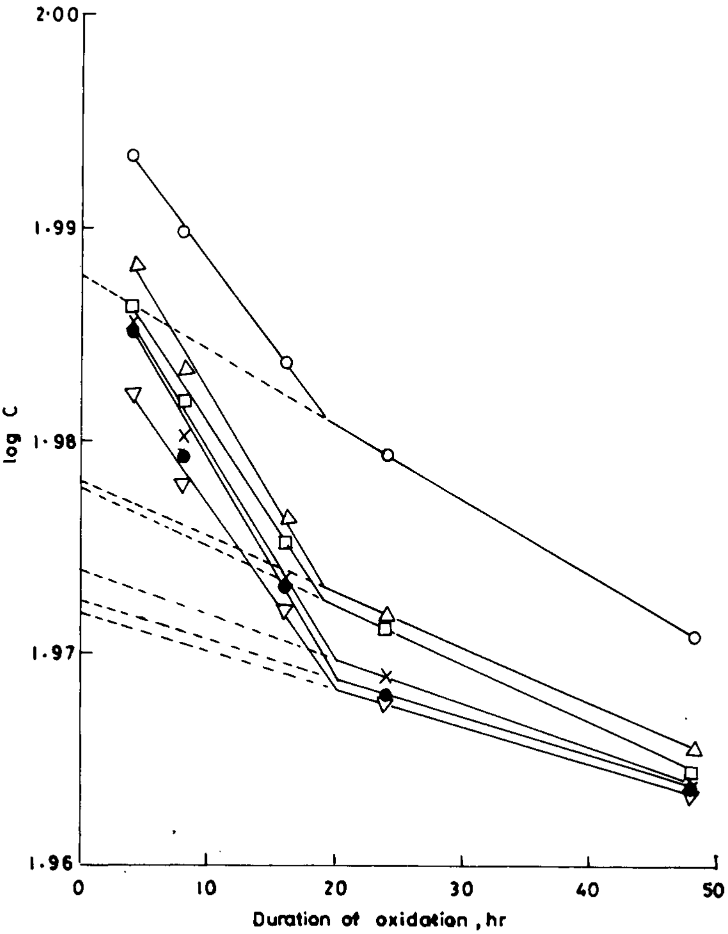

Fig. 1. Plots of log C vs. t for periodate oxidation of Amaryl Orange G-dyed cellulose at 32°C in presence of $0.2M$ salts: (○) no salt; (△) NaCl; (□) KCl; (X) Li_2SO_4; (●) Na_2SO_4; (▽) K_2SO_4.

this treatment, and the percentage accessibility was calculated in each case. The log C versus t plots for the periodate oxidation of cellulose dyed with Dye I in the absence and presence of $0.2M$ salts are shown in Figure 1. and the results are given in Table II.

It is seen from Table II that, as expected, the addition of an electrolyte ($0.2M$) increases the rate constant for the periodate oxidation of cellulose. Thus, the rate constants 52.40×10^{-3} hr^{-1} to 77.71×10^{-3} hr^{-1} were obtained when the oxidation of cellulose dyed with Dye I was carried out in the presence of $0.2M$ salts compared to 32.82×10^{-3} hr^{-1}. From the point of view of increasing the rate constant for the oxidation the salts can be arranged in the increasing order of $NaCl < KCl < Li_2SO_4 < Na_2SO_4 < K_2SO_4$. Sulfates are found to be more effective than chlorides in this respect. Both in the chloride and sulfate series, greater accelerating effect on the periodate oxidation of either undyed cotton or dyed cotton is observed with increasing atomic weight of the cation of the salt.

The accelerating effects of the salts on the periodate oxidation are also seen in the percentage accessibility of each cellulose sample to periodate ion. Each salt increases the percentage accessibility of cellulose dyed with different reactive dyes to different extents. The effect of the salt is more pronounced with monochlorotrizinyl dyes (III and IV), which cannot crosslink cellulose molecules, than with dichlorotriazinyl dyes (I and II), where there is a possibility of crosslinking the cellulose molecules, which itself might restrict the accessibility to extraneous ions. That the percentage accessibility to periodate ions is increased when the dichlorotriazinyl reactive dyes are present, when compared to the percentage accessibility of dyed cotton, during the periodate oxidation carried out in the presence of different salts is clearly seen in Table II.

Effect of Sodium Borohydride Treatment

Sodium borohydride is a powerful reducing agent. However, it does not reduce free carboxyl groups, though it does reduce lactones and enediol groups. All these groups are likely to be present in an oxycellulose. The reducing property of sodium borohydride has been widely used in characterizing the various functional groups formed in cellulose during oxidation. Shenai and Sudan[9] have shown that in a typical oxycellulose the carboxyl groups can be lactonized and then reduced by borohydride treatment and that if saponification of lactones present in the oxycellulose is carried out prior to the borohydride treatment, significant reduction in the acid content (determined either by the alkali titration method or the iodometric method[10]) does not take place. Borohydride is also known to reduce the free aldehyde groups present in an oxycellulose. In the present investigation, the oxycellulose samples prepared from dyed and undyed cellulose at 32°C in the absence and presence of 0.2*M* salts were treated with 0.1*M* sodium borohydride solutions. The copper number of these samples was determined before and after the borohydride treatment.

The results are shown in Figure 2, where the copper number after borohydride treatment is plotted against that before treatment. It is seen that a straight line with a slope of 0.0425 is obtained, indicating that about 96% of the reducing groups, estimated as copper number, is removed by the borohydride treatment. It has been shown earlier that periodate oxycelluloses possess excessive alkali sensitivity and that, when cuprammonium fluidity of the oxycelluloses is determined, the fluidity values thus obtained do not represent the true degree of polymerization of the oxycelluloses. Sodium borohydride treatment has been recommended for stabilizing the alkali-sensitive groups. In the present investigation, the cuprammonium fluidity values of the periodate oxycellulose samples prepared at 32°C in the absence and presence of 0.2*M* salts during the oxidation were determined both before and after subjecting the oxycellulose

TABLE III
Effect of Borohydride Treatment on Cuprammonium Fluidity of Periodate Oxycellulose Prepared in the Presence and Absence of Reactive Dye and Electrolytes at 32°C

	Cuprammonium fluidity of oxycellulose, p^{-1}									
	No dye		Dye I		Dye II		Dye III		Dye IV	
Salt	4 hr[b]	8 hr[b]	4 hr	8 hr	4 hr	8 hr	4 hr	8 hr	4 hr	8 hr
None	46.25	62.50	46.00	61.60	45.70	60.75	45.48	60.55	44.90	59.80
	(27.00)[a]	(45.75)	(26.45)	(44.75)	(26.00)	(43.90)	(25.25)	(43.20)	(24.75)	(42.80)
NaCl	49.83	66.40	49.60	66.10	49.47	65.90	49.10	65.75	48.80	65.60
	(33.25)	(48.75)	(32.50)	(48.00)	(32.00)	(47.80)	(31.50)	(47.50)	(30.75)	(47.25)
KCl	51.48	67.00	50.68	66.80	50.50	66.75	50.20	66.68	49.75	66.37
	(35.20)	(49.25)	(34.75)	(48.90)	(33.90)	(49.00)	(33.00)	(48.80)	(32.50)	(48.00)
Li_2SO_4	52.02	68.00	51.60	67.80	51.00	67.65	50.50	67.00	50.20	66.80
	(35.75)	(51.25)	(35.30)	(50.50)	(34.50)	(50.30)	(33.90)	(9.25)	(33.00)	(48.90)
Na_2SO_4	52.75	68.10	52.00	68.10	51.60	68.00	51.00	67.40	50.75	67.25
	(36.00)	(51.60)	(35.75)	(51.60)	(35.30)	(51.25)	(34.50)	(51.10)	(34.10)	(49.80)
K_2SO_4	54.90	68.50	54.40	68.30	54.20	68.10	53.75	67.80	53.50	67.65
	(38.50)	(52.50)	(37.75)	(52.00)	(37.00)	(51.60)	(36.75)	(50.50)	(36.40)	(50.30)

[a] Value given in parenthesis is the fluidity determined *after borohydride treatment.*

[b] Duration of oxidation.

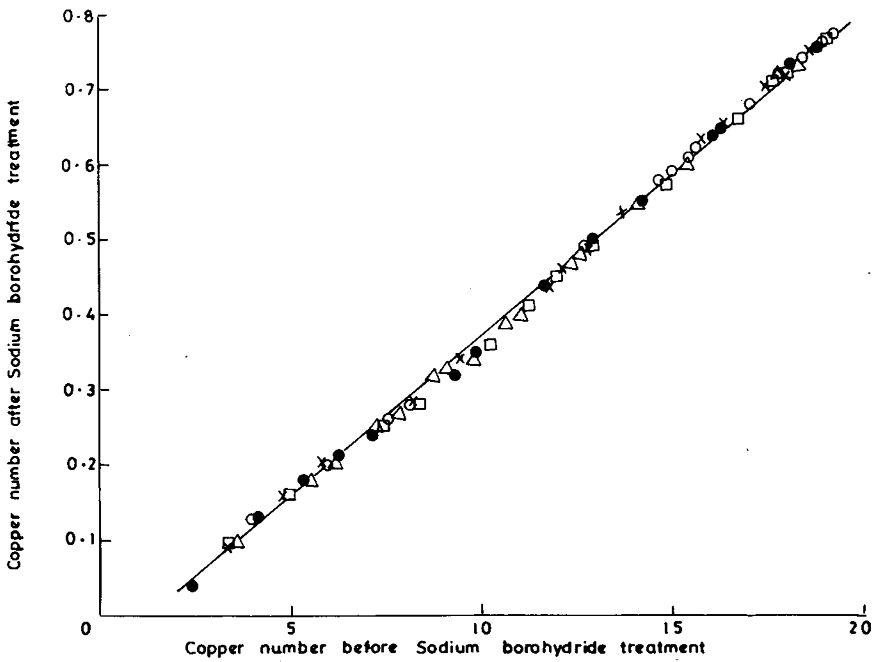

Fig. 2. Effect of borohydride treatment on the copper number of periodate oxycellulose made from reactive-dyed cellulose: (O) undyed; (Δ) Dye I; (□) Dye II; (X) Dye III; (●) Dye IV.

samples to sodium borohydride treatment. The results are given in Table III.

From Table III it is seen that the oxidative degradation undergone by cellulose, assessed in terms of cuprammonium fluidity, is more for the undyed cellulose than for the dyed ones. The effect of the added salt is pronounced, as is shown by the increasing value of the fluidity of the oxycellulose samples prepared in the presence of these salts. Further, the stabilization of the alkali-sensitive links in the periodate oxycelluloses is clearly reflected in the lower values of fluidity of brohydride-treated periodate oxycellulose samples, prepared either in the absence or presence of the dye.

Effect of Chlorous Acid Treatment

Sodium chlorite under acidic conditions is known to oxidize all free aldehyde groups present in an oxycellulose and a major portion of the potential aldehyde groups present in hydrocellulose, without attacking the samples at any other site. In the present investigation, the effect of chlorous acid treatment on the copper number of the oxycellulose samples was studied. Oxycellulose samples were prepared at 32°C in the absence and presence of different salts from dyed and undyed cellulose.

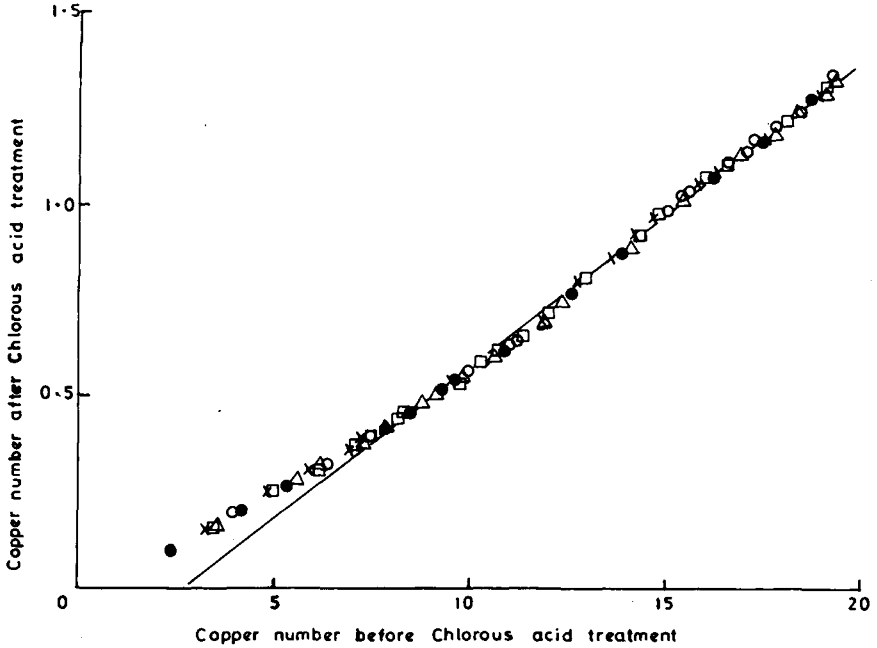

Fig. 3. Effect of chlorous acid treatment on the copper number of periodate oxycelluloses made from reactive-dyed cellulose: (O) undyed; (Δ) Dye I; (□) Dye II; (X) Dye III; (●) Dye IV.

Copper numbers of the oxycelluloses were determined before and after the chlorous acid treatment. The results are shown in Figure 3. It is seen that a straight line with a slope of 0.08 is obtained, indicating that about 92% of the total reducing groups, assessed as copper number, are oxidized by chlorous acid.

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