

Dyeing of Chemically Modified Cellulose. IV. Dyeing of Oxidized Celluloses with Some Reactive and Direct Dyes

A. HEBEISH, A. Z. MOURSI, A. WALY, and M. H. EL-RAFIE, *National Research Centre, Textile Research Division, Dokki, Cairo, Egypt*

Synopsis

Oxidation of cotton cellulose with potassium periodate, potassium dichromate-sulfuric acid, and potassium dichromate-oxalic acid results in creation of variable amounts of acidic and reducing groups along the cellulose molecule, being dependent upon the type of oxidizing agent used. Such groups were found to have a profound effect on the acceptability of cellulose for reactive and direct dyes. The rate and extent of dye uptake for the oxidized celluloses were significantly lower than those of the unoxidized cellulose. While presence of the acidic groups in cellulose molecules induces a negative environment thereby making approach of the dye anions to the cellulose difficult, presence of the reducing groups lowers the magnitude of cellulose reactivity as well as decreasing its adsorptive power. Further modification of the oxidized celluloses via either borohydride or chlorous acid treatment brought about modified celluloses the dyeability of which confirms the inhibiting effect of the acidic and reducing groups of those oxidized celluloses on the rate and extent of dyeing with reactive and direct dyes.

INTRODUCTION

Previous reports¹⁻³ have shown that chemical modification of cellulose via etherification, esterification, and grafting prior to dyeing with reactive and direct dyes has a considerable effect on the susceptibility of cellulose towards dyeing. The magnitude of dye uptake depends on the degree of modification as well as the nature of the substituent on cellulose. Oxidation of cellulose before dyeing with vat dyes also effected the dyeability of cellulose.⁴

The present work is undertaken for the purpose of studying the influence of creation of acidic and reducing groups along the cellulose molecules on the rate and extent of dyeing with reactive and direct dyes. For this purpose, purified cotton cellulose was subjected to oxidation with potassium dichromate-sulfuric acid or potassium dichromate-oxalic acid mixture, and the oxidized celluloses so obtained were further modified through reduction with sodium borohydride or oxidation with chlorous acid. The oxidized celluloses and their modified products were then dyed using reactive and direct dyes.

EXPERIMENTAL

Materials

Cotton Cellulose

Egyptian cotton slivers were purified by a mild alkaline scouring (2% NaOH and 0.2% wetting agent, per weight of material) for 5 hr at 110°C and 6–10 lb/in.² using a liquid ratio of 10:1.

Preparation of Oxidized Cellulose

(1) **Periodate oxidized cellulose:** The purified cellulose was immersed in an aqueous solution of potassium *meta* periodate (0.01*M*) at 30°C for 24 hr, keeping a liquid ratio of 50:1.

(2) **Potassium dichromate-sulfuric acid oxidized cellulose:** Oxidation of the purified cellulose was carried out with 0.1*N* potassium dichromate and 0.2*N* sulfuric acid at 30°C for 24 hr using a liquid ratio of 50:1.

(3) **Potassium dichromate-oxalic acid oxidized cellulose:** Purified cellulose was steeped in an aqueous solution containing oxalic acid (2*N*) and potassium dichromate (2*N*) for 4 hr at 30°C using a liquid ratio of 50:1.

(4) **Treatment of oxidized cellulose with sodium borohydride solution⁵:** The various oxidized cellulose materials mentioned above were treated with unbuffered sodium borohydride solutions at 30°C for 24 hr, using a liquid ratio of 50:1.

(5) **Treatment of oxidized cellulose with chlorous acid^{6,7}:** The oxidized samples were treated with 0.2*N* sodium chlorite solutions in 1*M* acetic acid at 30°C for 72 hr. After all the treatments described above were completed, the samples were washed with several portions of distilled water in each case until free from the impurities and dried at ambient temperature before analyzing.

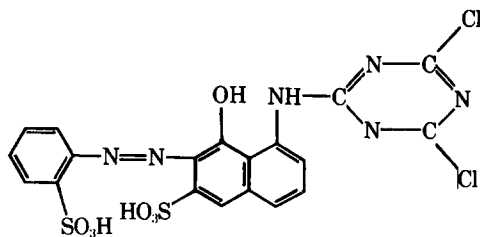
Dyestuffs

Four dyes were used throughout this investigation. Of these two belong to fiber-reactive dyes and the other two belong to direct dyes. The reactive dyes used were Procion Brilliant Red M2B (C.I. 18158) and Procion Brilliant Orange MG (C.I. 17907). Chemical structure of these two reactive dyes are represented below as (I) and (II), respectively. The direct dyes used were Solophenyl Orange TGL (C.I. 40220) and Chlorantine Fast Red 6BLL (C.I. 29065). Chemical structure of these two direct dyes are represented as (III) and (IV), respectively. All the dyes were used without further purification.

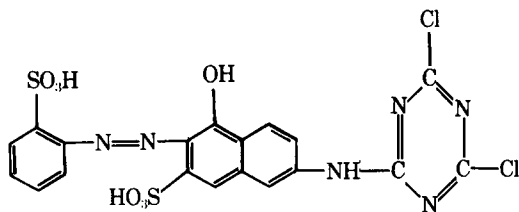
Dyeing Procedures

Dyeing with reactive dyes: The following solutions were first prepared: solution I, 2 g/liter reactive dye; solution II, 100 g/liter Glauber's salt; and solution III, 200 g/liter sodium carbonate.

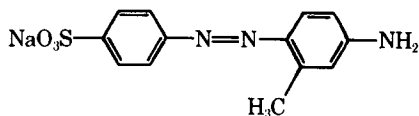
Dyeing was carried out as follows. The cellulose (1 g) was held on a stainless steel hook. The hook was then immersed in a solution containing 20 ml of so-



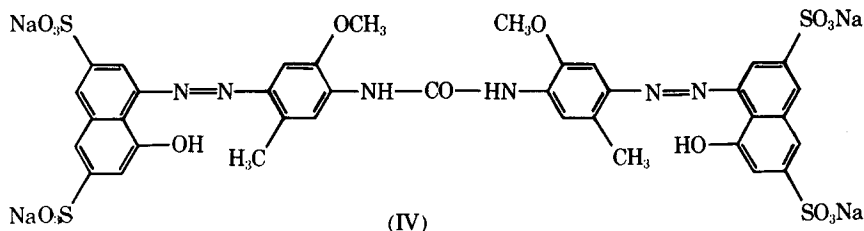
(I)



(II)



(III)



(IV)

lution I in 50 ml of distilled water. Solution II (30 ml) was gradually added with continuous shaking over a period of 10 min. The pH of the dyeing bath was then adjusted to pH 9.2 using solution III (1 ml, sodium carbonate 20%). The dyeing operation was performed for different periods of time ranging from 10 to 60 min at 20°C. Following the dyeing step, the sample was washed thoroughly with water, given a light soaping (5 ml/liter nonionic wetting agent) at the boiling point for 30 min. Finally, the sample was thoroughly washed and air dried.

Dyeing with direct dyes: Solutions prepared were solution I, 1 g/liter direct dye, and solution II, 100 g/liter Glauber's salt.

Dyeing was performed by holding the cellulose (1 g) on a stainless steel hook which was then immersed in a solution containing 50 ml of solution I in 850 ml of distilled water. Solution II (100 ml) was gradually added with continuous shaking. Dyeing was allowed to proceed at 90 °C for different lengths of time ranging from 10 to 60 min. Finally the sample was thoroughly washed and dried as described above.

Analysis: The copper number of the various oxidized celluloses was deter-

mined according to a reported method.⁵ For the determination of carboxyl groups, all the oxidized celluloses were rendered cation free by steeping them in 0.5*N* hydrochloric acid at 30°C for 2 hr, followed by washing free of acid and drying at ambient temperature. The carboxyl content was determined by a method described elsewhere.⁶

Dye uptake was determined colorimetrically by dissolving the dyed sample in 72% sulfuric acid.^{7,8}

RESULTS AND DISCUSSION

To start with, purified cotton cellulose was oxidized independently with three oxidizing agents, viz., sodium *meta* periodate, potassium dichromate-sulfuric acid, and potassium dichromate-oxalic acid according to the methods described above. The changes in the chemical structure, assessed by the copper number and carboxyl groups, and brought about by oxidation are illustrated in Table I.

The various oxidized celluloses so obtained were further modified by subjecting them to either sodium chlorite under acidic conditions (i.e., chlorous acid) or sodium borohydride treatment. Chlorous acid treatment is used to convert the aldehyde and keto groups to carboxyl groups without attacking the cellulose at other sites.⁹ As can be seen in Table I, chlorous acid oxidizes most of the reducing groups (assessed in terms of the copper number), producing a substantial amount of acidic groups.

Sodium borohydride treatment, on the other hand, almost completely removes the reducing groups present in the oxidized celluloses. Besides this, a substantial decrease in the carboxyl content is observed after the borohydride treatment (Table I). The decrease in carboxyl content suggests (a) that the calcium acetate method⁶ gives the total number of acidic groups, including the lactones, if present in the oxidized cellulose and (b) that a certain amount of acidic groups, that are free carboxyl groups, remain unaffected by the borohydride treatment. Thus,

TABLE I
Properties of Oxidized Celluloses

Substrate	Copper number	Carboxyl content m eq/100 g
Potassium periodate oxidized cellulose	9.3	9.47
Potassium periodate oxidized cellulose treated with chlorous acid	1.68	20.50
Potassium periodate oxidized cellulose treated with borohydride	0.5	1.32
Potassium dichromate-sulfuric acid oxidized cellulose	2.36	1.84
Potassium dichromate-sulfuric acid oxidized cellulose treated with chlorous acid	0.40	3.47
Potassium dichromate-sulfuric acid oxidized cellulose treated with borohydride	0.28	1.32
Potassium dichromate-oxalic acid oxidized cellulose	3.2	2.37
Potassium dichromate-oxalic acid oxidized cellulose treated with chlorous acid	1.15	4.47
Potassium dichromate-oxalic acid oxidized cellulose treated with borohydride	0.16	1.58

the carboxyl values of the oxidized celluloses treated with borohydride shown in Table I may be taken as representing free carboxyl groups present therein.

RATE OF DYE UPTAKE OF REACTIVE DYES

Dyeing of purified cellulose and the various oxidized cellulose samples with two reactive dyes, viz., Procion Brilliant Red M5B and Procion Brilliant Orange MG was carried out at 20°C for different periods of time according to the method described in the experimental section. Figure 1 shows the percent of dye uptake versus duration of dyeing of periodate oxidized celluloses and their modified samples, whereas Figures 2 and 3 show the same relation for dichromate-oxalic acid and dichromate-sulfuric acid oxidized celluloses together with their modified celluloses, respectively.

Obviously, regardless of the dye used, Figures 1-3 reveal one common feature, i.e., the rate and extent of dyeing are maximum for purified cellulose and minimum for chlorous acid-treated oxidized celluloses, which acquire high carboxyl content. However, the rate and extent of dyeing for chlorous acid-treated periodate oxidized cellulose with the marked acidic groups are substantially lower than the corresponding modified celluloses derived from dichromate-sulfuric acid and dichromate-oxalic acid oxidized celluloses. Furthermore, in case of oxidized celluloses themselves, the dyeing occurs more slowly in comparison with the purified cellulose. This could be interpreted in terms of presence of carboxyl and aldehydic groups; the latter are nonreactive with the dye.^{4,10} Moreover, the carboxyl groups ionize and repel the similarity charged dye anions. That is, ionization of the cellulose carboxyls increases the negative surface potential of

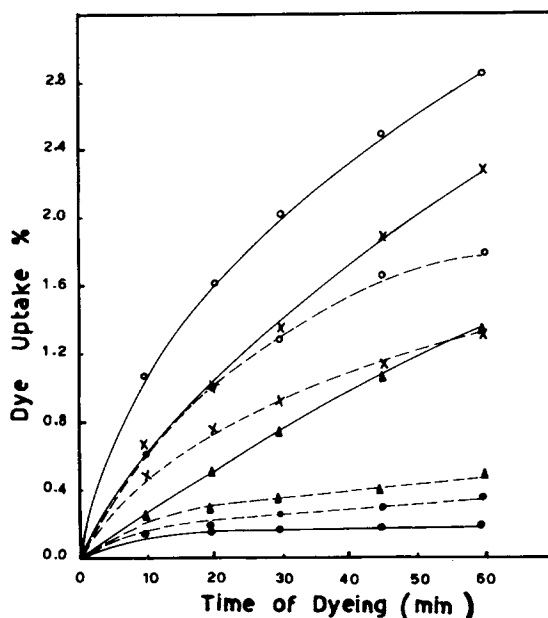


Fig. 1. Dyeing rate curves for periodate oxidized cellulose and its modified celluloses. (—) Procion Brilliant Red M2B; (- - -) Procion Brilliant Orange MG; (○) unmodified cellulose; (▲) periodate-oxidized cellulose; (●) periodate-oxidized cellulose treated with chlorous acid; (×) periodate-oxidized cellulose treated with borohydride.

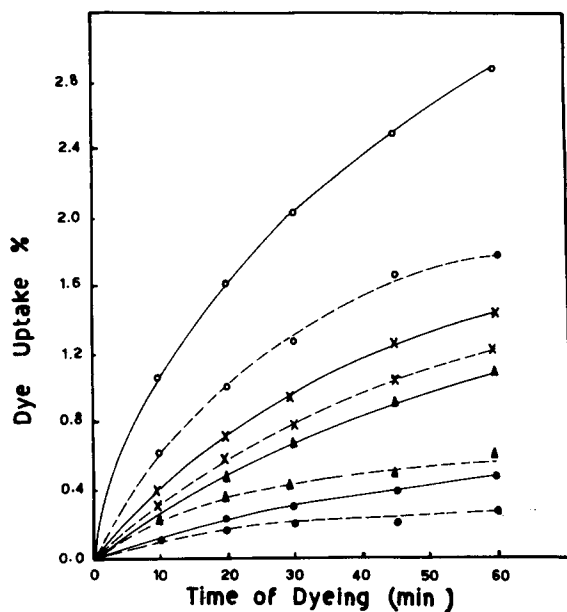


Fig. 2. Dyeing rate curves for dichromate-oxalic acid oxidized cellulose and its modified celluloses. (—) Procion Brilliant Red M2B; (· · · ·) Procion Brilliant Orange MG; (O) unmodified cellulose; (▲) dichromate-oxalic acid oxidized cellulose; (●) dichromate-oxalic acid oxidized cellulose treated with chlorous acid; (X) dichromate-oxalic acid oxidized cellulose treated with borohydride.

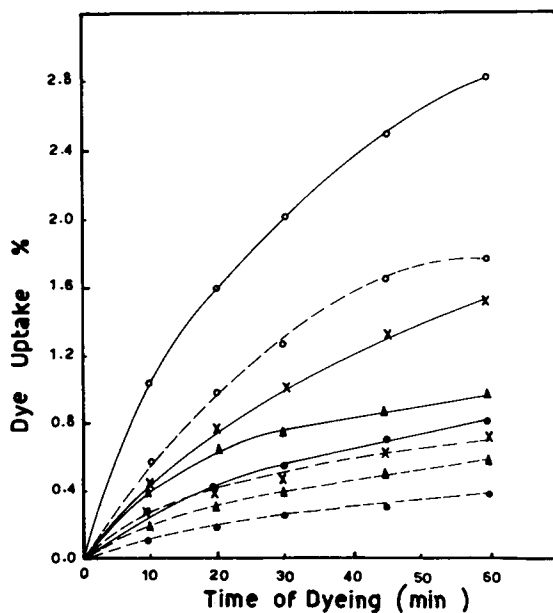


Fig. 3. Dyeing rate curves for dichromate-sulfuric acid oxidized cellulose and its modified celluloses. (—) Procion Brilliant Red M2B; (· · · ·) Procion Brilliant Orange MG; (O) unmodified cellulose; (▲) dichromate-sulfuric acid oxidized cellulose; (●) dichromate-sulfuric acid oxidized cellulose treated with chlorous acid; (X) dichromate-sulfuric acid treated with borohydride.

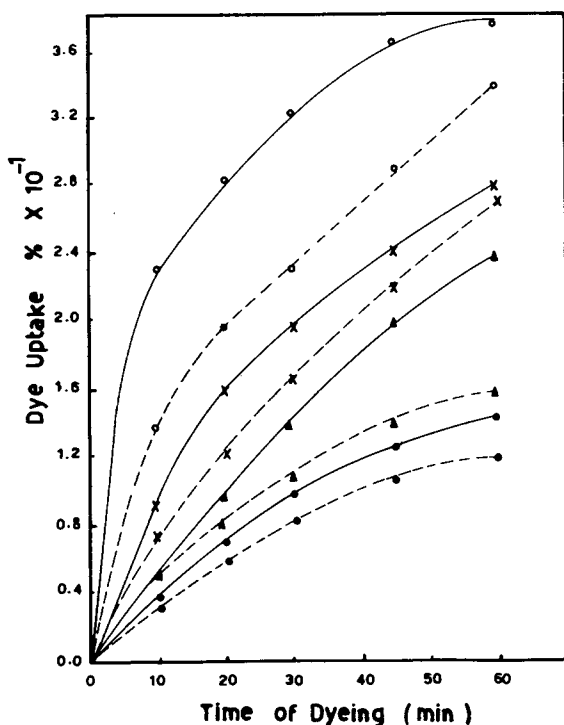


Fig. 4. Dyeing rate curves for periodate oxidized cellulose and its modified celluloses (—) Solophenyl Orange TGL; (····) Chlorantine Fast Red 6BLL; (O) unmodified cellulose; (▲) periodate-oxidized cellulose; (●) periodate-oxidized cellulose treated with chlorous acid; (X) periodate-oxidized cellulose treated with borohydride.

the substrate thereby impeding the reactive dye anion to approach the substrate. Indeed, the higher rate and extent of dyeing obtained with borohydride-treated oxidized celluloses (Figs. 1–3) where most of the acidic and reducing groups present in the original oxidized celluloses are removed, confirms this hypothesis.

An additional point of interest is that periodate oxidized cellulose which is predominantly a reducing type showed a very low rate and extent of dyeing (Fig. 1). This indicates that conversion of the secondary hydroxyl groups of the anhydroglucose unit of the cellulose molecular chain into a dialdehyde during the periodate oxidation causes an outstanding decrease in the susceptibility of cellulose towards reactive dyes.

With respect to rate of dyeing the different cellulosic substrates studied follows the order:

purified cellulose > borohydride-treated oxidized cellulose
> oxidized cellulose > chlorous acid-treated oxidized cellulose

This order is found (Figs. 1–3) regardless of the oxidizing agent used thereby qualitatively establishing the inhibiting effect of the acidic and reducing groups of these oxidized celluloses on the rate of dyeing with reactive dyes.

Figures 1–3 also show that the magnitude of the rate and extent of dyeing depends on the nature of the dye, which, in turn, is dependent of molecular size, configuration, substituents and number, and potentiability of the solubilizing

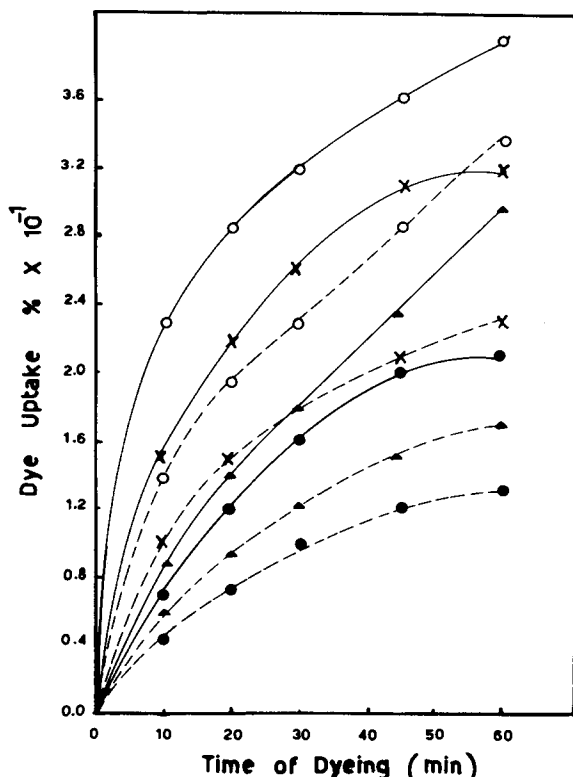


Fig. 5. Dyeing rate curves for dichromate-oxalic acid oxidized cellulose and its modified celluloses. (—) Solophenyl Orange TGL, (· · · ·) Chlorantine Fast Red 6BLL, (O) unmodified cellulose; (▲) dichromate-oxalic acid oxidized cellulose; (●) dichromate-oxalic acid oxidized cellulose treated with chlorous acid; (X) dichromate-oxalic acid oxidized cellulose treated with borohydride.

groups. Of the two dyes studied Procion Brilliant Red M2B appears to have high reactivity, though this reactivity vanishes almost completely upon using chlorous acid-treated periodate oxidized cellulose.

RATE OF DYE UPTAKE OF DIRECT DYES

Figure 4 shows dyeing rate curves for two direct dyes, viz., Solophenyl Orange TGL and Chlorantine Fast Red 6BLL, on purified cellulose and periodate-oxidized cellulose before and after treatment with either chlorous acid or sodium borohydride. As can be seen, periodate oxidation of cellulose prior to dyeing causes a significant reduction in its susceptibility towards dyeing with the said two direct dyes. This could be associated with shortage in adsorption power of cellulose as a result of conversion of some cellulose hydroxyls to aldehydic and/or carboxylic groups under the oxidation action of periodate. In addition, presence of the created carboxyl groups along the cellulose chains induces a negative environment in the cellulose thereby making approach of the dye anions to cellulose difficult. Data for a dye uptake on chlorous acid-treated periodate-oxidized cellulose (Fig. 4) which possesses a marked carboxyl content are in accordance with this since this substrate shows the lowest dye uptake. Moreover, the decrease of the acidic and reducing groups through borohydride treatment, i.e.,

borohydride treated periodate-oxidized cellulose, brought about a substantial enhancement in the acceptability of the periodate-oxidized cellulose to direct dyes, similar to reactive dyes.

Figure 5 shows the dyeing rate curves for the two direct dyes in question on purified cellulose and cellulose oxidized with dichromate-oxalic acid mixture before and after treatment with either chlorous acid or sodium borohydride. The data yield a trend which is similar to that observed with periodate-oxidized cellulose and could be explained on similar lines.

In Figure 6 are illustrated the dyeing rate curves for the two direct dyes in question on purified cellulose and cellulose oxidized with dichromate-sulfuric acid mixture before and after subjecting it to either further oxidation with chlorous acid or reduction with borohydride. Here too, regardless of the dye used, the rate and extent of dye uptake on the substrates studied follows the order given above for reactive dyes where purified cellulose showed the highest dye uptake and chlorous acid treated-oxidized cellulose showed the lowest dye uptake. Hence the interpretation given above for the periodate oxidized cellulose and its further modified celluloses would work out for cellulose oxidized with dichromate-sulfuric acid mixture. Furthermore, the data (Figs. 4-6) clearly reveal the adverse effect of aldehydic and carboxyl groups brought about by oxidation on the dye uptake. That is, the magnitude of the dye uptake of direct dyes on cellulose depends on the degree of oxidation as well as type of oxidized

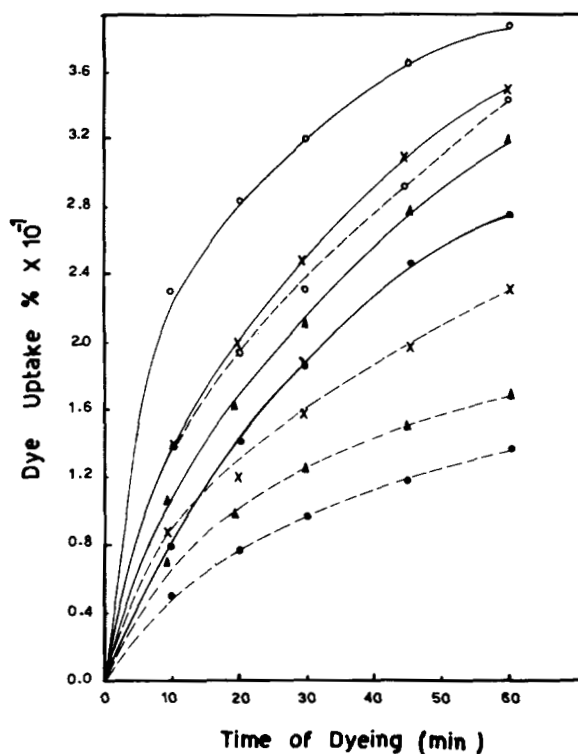


Fig. 6. Dyeing rate curves for dichromate-sulfuric acid oxidized cellulose and its modified celluloses. (—) Solophenyl Orange TGL; (▲▲▲▲) Chlorantine Fast Red 6BLL; (O) unmodified cellulose; (▲) dichromate-sulfuric acid oxidized cellulose; (●) dichromate-sulfuric acid oxidized cellulose treated with chlorous acid; (X) dichromate-sulfuric acid treated with borohydride.

cellulose used. Acidic-type oxidized celluloses with marked carboxylic groups show the lowest dye uptake.

Of the two direct dyes studied, Solophenyl Orange TGL showed much higher dye uptake than Chlorantine Fast Red 6BLL (Figs. 4–6). This is observed regardless of the substrate used, reflecting the influence of the nature of the dye, which is governed by the molecular size, substituents, steric configuration, and diffusibility of the dye, on the amount of the dye taken up by the fiber.

SUMMARY

Cotton cellulose was independently oxidized with potassium periodate, potassium dichromate–sulfuric acid, and potassium dichromate–oxalic acid, and the resulting oxidized celluloses were further modified by treatment with chlorous acid or sodium borohydride. The modified celluloses so obtained exhibit variable amounts of acidic and reducing groups, depending upon the type of oxidizing agent used and the aftertreatment given. Dyeing of these modified celluloses with some reactive and direct dyes revealed that they acquire much lower rate and extent of dyeing than the unoxidized cellulose. Regardless of the dye used, the rate and extent of dyeing follows the order:

purified cellulose > borohydride treated-oxidized cellulose
> oxidized cellulose > chlorous acid treated-oxidized cellulose

This indeed qualitatively establishes the inhibiting effect of the acidic and reducing groups created in the cellulose during oxidation on the rate and extent of dyeing with reactive and direct dyes.

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