

Studies in Chemically Modified Celluloses.

V. Affinities of Vat Dyes for Chemically Modified Celluloses

V. A. SHENAI and M. VEERAMANI, *Department of Chemical Technology, University of Bombay, Bombay, India*

Synopsis

Cotton cellulose was separately oxidized by potassium metaperiodate, potassium dichromate-sulfuric acid, and potassium dichromate-oxalic acid at two oxidation levels, and the resulting oxycelluloses were further modified by treatment with chlorous acid and sodium borohydride in order to prepare a series of chemically modified celluloses with different functional groups. These fiber substances were dyed with leuco-flavanthron at 40°C for different periods till equilibrium was reached. Adsorption isotherms were obtained with three purified vat dyes, and thermodynamic affinity of the dyes for the modified celluloses was determined, taking into consideration the adsorption of hydroxyl ions by cellulosic material and of sodium ions by carboxylate groups of oxycellulose. The presence of aldehyde and carboxyl groups is shown to decrease the rate of dyeing as well as the affinity of the dyes.

INTRODUCTION

Thermodynamic affinities of a series of vat dyes for cellulose have been obtained from equilibrium dyeing data by a number of workers,¹⁻⁶ assuming that the dyeing process is similar to the dyeing of direct cotton dyes on cellulose. Peters and Sumner³ showed that the affinity of vat dyes arises from two major types of attachment to the fiber, viz., hydrogen bonds and van der Waals forces. Vat dyes having coplanar structures have been shown to have higher affinity values than the related dyes with non-coplanar structures.⁵

Adsorption of direct cotton dyes^{7,8} and vat dyes^{1-6,9-11} on cellulosic fibers has been studied extensively for developing kinetic as well as thermodynamic interpretations for understanding the mechanism of dyeing of cellulose with these dyes. In comparison, the work reported in the literature on the adsorption of vat dyes on chemically modified celluloses and on the part played by certain groups in the modified celluloses during dyeing is limited. Detailed treatment of this subject (for direct cotton dyes) has been rendered by a number of workers.¹²⁻¹⁶ For example, Daruwalla et al.¹⁶ studied the equilibrium uptake of Chrysophenine G and Chlorazol Sky Blue FF by chemically modified celluloses containing different amounts of aldehyde, keto, and carboxyl groups and found that the

presence of carboxyl groups in the cellulose decreases the equilibrium adsorption values for both these dyes. Sadov and Kalinina¹⁵ found that when the ionization of carboxyl groups in nitrogen dioxide oxycellulose was suppressed by the formation of calcium or aluminium salts, the adsorption of direct cotton dyes by these oxycelluloses was nearly the same as that for unoxidized cellulose.

The present communication deals with the affinity of vat dyes for cellulose, oxycellulose, and further modified oxycellulose with a view to finding the effect of different functional groups on the equilibrium uptake of these dyes as well as on the affinity of these dyes for the various modified celluloses.

EXPERIMENTAL

Standard Cellulose

Carefully purified 20s single yarn made from Indian cotton was used as standard cellulose. It had the following properties: copper number,^{17,18} 0.03; cuprammonium fluidity (0.5% solution), 3.0 poises⁻¹; iodometric carboxyl value,¹⁹ 0.48 meq per 100 g dry sample.

Preparation of Oxycelluloses

Periodate Oxycelluloses. Standard cellulose was steeped in an aqueous solution of potassium metaperiodate (0.01*M*) at 30°C for 4 and 24 hr, keeping a liquor ratio of 50:1.

Potassium Dichromate-Sulfuric Acid Oxycelluloses. The oxidation of standard cellulose was carried out with 0.1*N* potassium dichromate and 0.2*N* sulfuric acid at 30°C for 2 and 24 hr.

Potassium Dichromate-Oxalic Acid Oxycelluloses. These oxycelluloses were prepared by suspending 60 g standard cellulose in 1500 ml 2*N* oxalic acid solution, followed by adding different amounts (20 ml and 100 ml) 2*N* potassium dichromate solution (finally diluting to 3000 ml) and keeping at 30°C for 4 hr.

Treatment of Oxycelluloses with Sodium Borohydride Solution.²⁰ The different oxycellulose samples were treated with unbuffered sodium borohydride solutions at 30°C for 24 hr, keeping a liquor ratio of 50:1.

Treatment of Oxycelluloses with Chlorous Acid.^{21,22} The oxycellulose 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 sample was washed with fresh changes of distilled water in each case till free from the impurities and dried at 30°C before analyzing.

Analysis of Chemically Modified Celluloses

Copper number of these celluloses was determined by the standard method.^{17,18} For the estimation of carboxyl value, all the chemically modified 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 30°C. The carboxyl value was determined by iodometry.¹⁹

Vat Dyes

Three vat dyes-Caledon Yellow GN (flavanthron), Caledon Gold Orange G (pyranthron), and Indanthren Yellow FFRK (1,1'-dianthrimide monocarbazole) were selected for the study and were purified by the method suggested by Venkataraman.²³ The method involved extraction of water-soluble impurities by boiling water, dissolution of the dye in concentrated sulfuric acid, followed by filtration and reprecipitation by dilution at 0-5°C and vatting and reoxidation, followed by washing with distilled water and drying at 110°C.

Affinity of Vat Dyes for Cellulose and Modified Celluloses. Affinity values of the three vat dyes for cellulose and modified celluloses were determined by the method followed by Fowler et al.¹ and modified by Peters and others.²⁻⁴ The initial concentration of the dye in the dyebath was varied (12.5-75 mg/l.), and the dyeing was carried out at 40°C till equilibrium was attained (24 days), in the presence of sodium hydroxide (0.2*N*) and sodium hydrosulfite with a total sodium ion concentration of 0.4667*N*. The dyeing was carried out in a 250-ml Pyrex conical flasks, the air above the dye solution being blown out with a current of oxygen-free nitrogen and then closing the flasks with rubber stoppers, followed by sealing with hard wax. The flasks were occasionally shaken. Following this technique, the dyebaths were in good condition at the end of the requisite period (up to 30 days).

Estimation of the Dye in the Exhaust Dyebath. The dye liquor usually showed signs of oxidation following the withdrawal of cotton yarn, and it was found necessary to bubble oxygen-free nitrogen through the dye liquor and to make small additions of sodium hydroxide pellets and sodium hydrosulfite before estimating the dye in the exhaust dyebath. A portion of the dye liquor was suitably diluted with a solution containing sodium hydroxide (10 g/l.) and sodium hydrosulfite (12 g/l.), and the dye was colorimetrically estimated using Amil Hilger Biochem absorptiometer. The exhaustion of the dyebath (and hence the dye uptake) was calculated.

RESULTS AND DISCUSSION

Oxidation of Cellulose

Oxidation of cellulose is known to produce different functional groups such as alkali-sensitive reducing groups, enediol groups, carboxyl groups, lactones, etc. The carboxyl groups are formed in different positions of the anhydroglucose units of cellulose macromolecules. Sodium borohydride reduces the aldehyde, keto, enediol, and lactone groups, while chlorous acid oxidizes aldehyde groups to carboxyl groups. Thus, it is possible to produce chemically modified celluloses by treating standard cellulose with

TABLE I
 Properties of Chemically Modified Celluloses

Sample no.	Duration of oxidation, hr	Oxygen consumption, milli atoms/100 g cellulose	Copper number				Carboxyl value, meq/100 g	
			Oxycellulose	Chlorous acid-treated oxycellulose	Borohydride-treated oxycellulose	Oxycellulose	Chlorous acid-treated oxycellulose	Borohydride-treated oxycellulose
1	4	10.0	4.18	0.36	0.11	1.68	12.28	0.48
2	24	27.5	15.93	0.63	0.25	3.78	37.76	0.71
3	2	7.9	2.83	0.73	0.04	0.92	2.60	0.68
4	24	35.0	19.68	2.68	0.75	11.32	26.96	2.63
5	4 ^a	—	3.34	0.32	0.06	1.38	8.93	0.33
6	4 ^b	—	15.50	1.16	0.16	6.34	36.40	1.27

^a With 20 ml 2N K₂Cr₂O₇.

^b With 100 ml 2N K₂Cr₂O₇.

selected oxidizing agents, followed by borohydride or chlorous acid treatment so as to produce different functional groups in certain positions in the anhydroglucose units of cellulose macromolecules.

Standard cellulose was oxidized by using three oxidizing agents at two levels of oxidation by the methods described above; the reducing and acidic properties of these oxycellulose samples were determined before and after borohydride or chlorous acid treatment. The results are given in Table I.

The mild oxidizing power of sodium chlorite under acidic conditions has been utilized for oxidizing free aldehyde groups present in an oxycellulose without attacking the cellulose at other sites.²¹ Thus, chlorous acid treatment may be used to produce carboxyl groups in the reducing type of oxycellulose. It is seen from Table I that chlorous acid oxidizes most of the reducing groups (assessed in terms of copper number), producing a substantial amount of acidic groups. It is also seen that all the reducing groups present in the oxycelluloses, especially those prepared at higher levels of oxidation (oxycellulose samples 2, 4, and 6), are not oxidized during the chlorous acid treatment.

Sodium borohydride treatment, on the other hand, is found to remove the reducing groups present in the oxycelluloses almost completely, the copper number being decreased by 96–98%. A substantial decrease in the iodometric carboxyl value after the borohydride treatment is observed (Table I). As shown by Nabar and Shenai,²⁴ the iodometric method gives the total number of acidic groups, including the lactones, if present in the chemically modified celluloses. They have also shown that a certain amount of acidic groups, which are free carboxyl groups, remain unaffected by the borohydride treatment. Therefore, the carboxyl values of borohydride-treated oxycelluloses reported in Table I may be taken as representing free carboxyl groups present therein.

Thus, among the different chemically modified celluloses selected for the study on the affinity of vat dyes for these substrates, (1) some are of predominantly of the reducing type with low and high acidic content (periodate oxycelluloses and potassium dichromate-sulfuric acid oxycelluloses, respectively), (2) some are of predominantly acidic type with fairly low reducing properties (chlorous acid-treated oxycelluloses), and (3) the rest are of fairly low acidic type with practically no reducing properties (borohydride-treated oxycelluloses).

Rate of Adsorption of Leuco Vat Dyes

Standard cellulose and the various modified cellulose samples were dyed with leuco-Caledon Yellow GN at 40°C for different lengths of time by the method referred to earlier. The loss in concentration of the dye in the dyebath was determined colorimetrically, and the amount of the dye on the fiber was calculated. These values are plotted against the period of dyeing periodate oxycelluloses and their further modified samples in Figure 1. Similar curves were obtained for other oxycelluloses and their modified

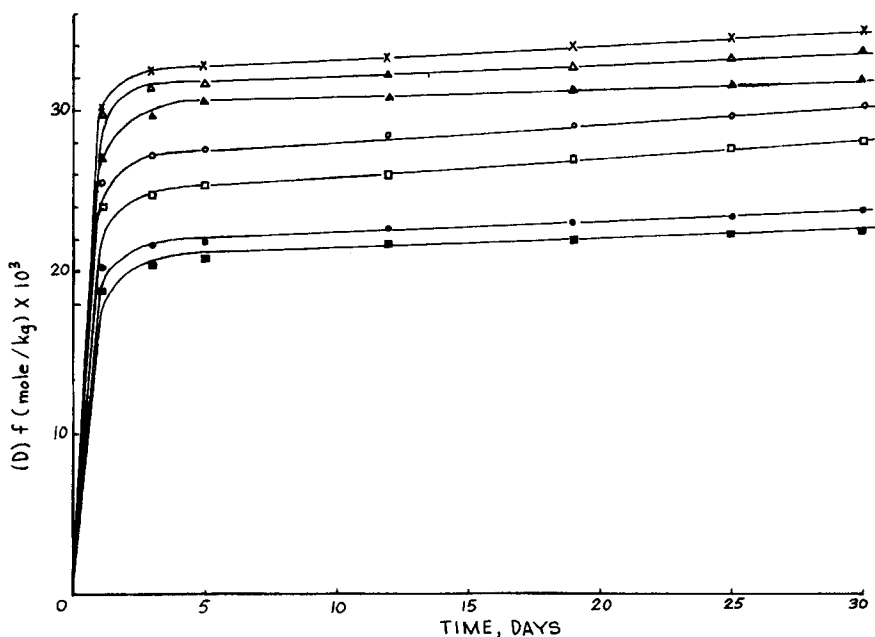


Fig. 1. Rate curves for dyeing leuco-Caledon Yellow GN on chemically modified celluloses: (×) standard cellulose; (O) KIO_4 -oxycellulose (LOL); (Δ) borohydride-treated KIO_4 -oxycellulose (LOL); (\square) chlorous acid-treated KIO_4 -oxycellulose (LOL); (\bullet) KIO_4 -oxycellulose (HOL); (\blacktriangle) borohydride-treated KIO_4 -oxycellulose (HOL); (\blacksquare) chlorous acid-treated KIO_4 -oxycellulose (HOL).

celluloses. It is seen that equilibrium adsorption takes place in each case in about 24 days, and hence this period was selected for the subsequent equilibrium dyeing experiments.

It is also seen in Figure 1 that both the rate and extent of dyeing are maximum for standard cellulose and minimum for chlorous acid-treated periodate oxycelluloses, which are marked by high acidic content. In the case of oxycellulose itself, the dyeing takes place more slowly by the oxycellulose of a higher oxidation level than that of lower oxidation level. Dichromate-sulfuric acid oxycelluloses and dichromate-oxalic acid oxycelluloses also behaved in a similar manner with respect to the rate and extent of dyeing with leuco-Caledon Yellow GN. This may be explained on the basis that the presence of increasing amounts of carboxyl groups (after ionization) increase the negative surface potential of the substrate, thereby making it more difficult for the leuco vat anion to approach the substrate. Further evidence confirming this hypothesis is obtained from the dyeing behavior of borohydride-treated oxycelluloses, where most of the acidic groups present in the original oxycelluloses are removed. For these substrates, the rate and extent of dyeing are higher than those for the corresponding oxycelluloses.

The observation that the dyeing of periodate oxycelluloses, which are of the predominantly reducing type, leads to the conclusion that the conver-

sion of the secondary hydroxy groups of the anhydroglucose unit of the cellulose molecular chain into a dialdehyde during the peroxide oxidation is responsible for the lower rate of dyeing of these oxycelluloses with the leuco vat dye.

From the point of view of rate of dyeing, the different cellulosic fiber substances may be arranged in increasing order as follows: chlorous acid-treated oxycellulose < oxycellulose < borohydride-treated oxycellulose < standard cellulose

The same order of increasing rate of dyeing was observed in the dyeing of dichromate-sulfuric acid oxycelluloses and dichromate-oxalic acid oxycelluloses and their further modified products, thereby establishing qualitatively the inhibiting effect of the carboxyl groups of these chemically modified celluloses on the rate of dyeing with leuco vat dyes, as well as on the equilibrium dye uptake by these fiber substances.

Affinity of Vat Dyes

Theoretical

In applying thermodynamics to the dyeing of cellulosic fibers with anionic dyes, the fiber is considered as a homogeneous phase of a certain volume in which the dye is evenly distributed. For the absorption of direct dyes by cellulose, Peters and Vickerstaff²⁵ divided the fiber-dyebath system into two phases, aqueous and cellulosic, and described the activity of the dye in the fiber in terms of its concentration. They assumed that the two phases may be regarded as homogeneous and that a Donnan equilibrium exists between them, the dye anions being nondiffusing. Applying this model to the dyeing of vat dyes on cellulose from an alkaline hydro-sulfite bath in the presence of sodium chloride, Fowler et al.¹ made simplifying assumptions that only dye anions had affinity for the fiber and that all the other anions could be replaced by an equivalent quantity of chloride ions. Peters and Sumner³ modified it on the basis of the small but definite affinity of hydroxyl ions for cellulose.

When a reduced vat dye, Na_zD , is adsorbed by cellulose from the dyebath under isothermal conditions at equilibrium, the change in the standard chemical potential ($\Delta\mu^0_{\text{D}}$) per mole of the dye is given by

$$-\Delta\mu^0_{\text{D}} = RT \ln \frac{[\text{D}]_f[\text{Na}]_f^z}{[\text{D}]_s[\text{Na}]_s^z} \quad (1)$$

where $[\text{Na}]_f$, $[\text{D}]_f$, $[\text{Na}]_s$, and $[\text{D}]_s$ are the concentrations (in g ions/l.) of sodium and dye ions in the fiber and solution phases, respectively, and z is the charge on the dye anion. The cellulosic phase is considered to have an internal volume of 0.25 l./kg (for 0.2N NaOH-swollen cotton yarn). Of these quantities, $[\text{D}]_f$ and $[\text{D}]_s$ can be known from colorimetric measurements of the dyebath before and after equilibrium dyeing, and $[\text{Na}]_s$ may be taken as the original concentration of sodium ions in the bath,

since the adsorption of sodium ions may be considered negligible at the high electrolyte concentration in the dyebath.

The value of $[\text{Na}]_f$ can be calculated from the Donnan equilibrium:

$$[\text{Na}]_f[\text{An}]_f = [\text{Na}]_s[\text{An}]_s \quad (2)$$

where $[\text{An}]_f$ and $[\text{An}]_s$ are the concentrations of anions adsorbed by the fiber from the dyebath and in the solution phase, respectively, and the requirements of electrical neutrality in the cellulosic phase is

$$[\text{Na}]_f = [\text{An}]_f + Z[\text{D}]_f \quad (3)$$

when the adsorption of hydroxyl ions by the cellulose and the absorption of sodium ions on the ionized carboxyl ions by the cellulose are considered as indicated by Sumner,²⁶

$$[\text{Na}]_f = [\text{OH}]_f + [\text{An}]_f + Z[\text{D}]_f + [\text{ACOO}]_f \quad (4)$$

where $[\text{OH}]_f$ is the hydroxyl ions adsorbed by cellulose and $[\text{ACOO}]_f$ is the carboxyl content of the cellulose (in equiv/l.).

By considering the adsorption of sodium hydroxide, the electrolyte (Na, An), and the dye independent of each other,

$$[\text{Na}]_f = \frac{K[\text{Na}]_s[\text{OH}]_s}{[\text{Na}]_f} + \frac{[\text{Na}]_s[\text{An}]_s}{[\text{Na}]_f} + Z[\text{D}]_f + [\text{ACOO}]_f \quad (5)$$

where K is defined by

$$RT \ln K = -\Delta\mu^0_{\text{NaOH}}. \quad (6)$$

A value of 10 has been obtained for K in the case of dyeing of vat dyes on cuprammonium rayon by Peters and Simons.² It is assumed in the present investigation that the affinity of sodium hydroxide ($-\Delta\mu^0_{\text{NaOH}}$) for cotton cellulose and oxycelluloses is the same as that for cuprammonium rayon, so that $K = 10$ in the present case also.

Equation (5) can be written as a quadratic equation:

$$[\text{Na}]_f^2 - \{Z[\text{D}]_f + [\text{ACOO}]_f\}[\text{Na}]_f - [\text{Na}]_s\{K[\text{OH}]_s + [\text{An}]_s\} = 0 \quad (7)$$

Solving this equation,

$$[\text{Na}]_f = \left\{ [\text{D}]_f + \frac{[\text{ACOO}]_f}{Z} \right\} \left\{ \frac{Z}{2} + \left(\frac{Z^2}{4} + \frac{[\text{Na}]_s(K[\text{OH}]_s + [\text{An}]_s)}{([\text{D}]_f + [\text{ACOO}]_f/Z)^2} \right)^{1/2} \right\}. \quad (8)$$

In eq. (8),

$$[\text{An}]_s = 2[\text{S}_2\text{O}_4]_s \quad (9)$$

Once $[\text{Na}]_f$ is known, the affinity, $-\Delta\mu^0_{\text{D}}$, can be calculated by using eq. (1).

A good criterion to see whether the system is behaving in accordance with this theory is the unit slope of the graph to be obtained when $\log [\text{Na}]_f^2[\text{D}]_f$ is plotted against $\log [\text{Na}]_f^2[\text{D}]_s$.

While studying the mechanism of alkali adsorption by cellulose, Sumner²⁶ showed that the agreement between calculated and experimental results together with the completeness with which the treatment accounts for the loss in dye substantivity as the alkali concentration increases is very strong evidence that the apparent sorption of hydroxyl ions is a neutralization with the formation of ionized cellulose hydroxyl groups.

Equilibrium Dyeing with Leuco Vat Dyes

The dyebaths containing different amounts of purified vat dyes (12.5–75 mg/l.), sodium hydroxide, and sodium hydrosulfite ($[\text{Na}]_s = 0.4667N$), and the various chemically modified celluloses were kept at 40°C for 24 days with occasional shaking. At the end of the dyeing period, the dye concentration in the exhaust dyebath was determined colorimetrically, and $[\text{D}]_f$ was calculated. From the adsorption isotherms obtained at equilibrium, the affinity values were calculated using eqs. (8) and (1). The results for the different oxycelluloses of lower oxidation level are given in Table II.

TABLE II
Affinity of Leuco-Caledon Yellow GN for the Different Oxycelluloses

Starting concentration of dye, mg/l.	$[\text{D}]_f$, moles/l. $\times 10^3$	$[\text{Na}]_f$, g ions/l.	$[\text{D}]_s$, moles/l. $\times 10^6$	Affinity, cal/mole	Mean Affinity, cal/mole
Periodate Oxycellulose (LOL) ^a					
12.5	17.24	1.080	0.919	5782	
25.0	33.96	1.098	1.960	5733	
37.5	50.16	1.116	2.941	5744	5750
50.0	65.92	1.133	4.043	5737	
62.5	82.56	1.152	5.087	5751	
75.0	97.40	1.168	6.127	5757	
Dichromate-Sulfuric Acid Oxycellulose (LOL)					
12.5	17.72	1.042	0.800	5790	
25.0	35.32	1.051	1.720	5771	
37.5	52.84	1.080	2.610	5809	
50.0	70.24	1.096	3.510	5837	5813
62.5	87.60	1.117	4.41	5839	
75.0	104.80	1.136	5.53	5833	
Dichromate-Oxalic Acid Oxycellulose (LOL)					
12.5	17.48	1.075	0.882	5789	
25.0	34.44	1.092	1.839	5775	
37.5	51.28	1.110	2.806	5780	5786
50.0	67.88	1.128	3.798	5786	
62.5	84.24	1.147	4.828	5790	
75.0	100.36	1.165	5.882	5795	

^a LOL = Low oxidation level.

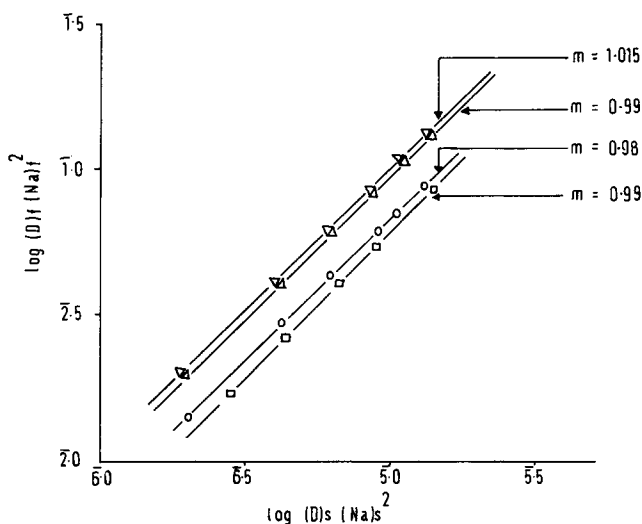


Fig. 2. Log ionic product plots for equilibrium dyeing of leuco-Caledon Yellow GN on periodate oxycellulose (LOL) (Δ) and dichromate-oxalic acid oxycellulose (LOL) (∇) and of leuco-Caledon Gold Orange G on dichromate-oxalic acid oxycellulose (LOL) (\circ) and dichromate-sulfuric acid oxycellulose (LOL) (\square).

With a view to seeing whether the present dyeing system behaves in accordance with the theory described above, $\log [Na]_f^2 [D]_f$ was plotted against $\log [Na]_s^2 [D]_s$ in Figure 2. It is seen that straight lines having a slope of nearly 1 are obtained, as expected.

The affinity values of the three leuco vat dyes for standard cellulose and the different oxycelluloses (at both oxidation levels) and the corresponding borohydride-treated products obtained in the present investigation are given in Table III. Iodometric carboxyl values and the copper numbers of these samples are also included in the table.

It is seen that with the increasing degree of oxidation with potassium metaperiodate, there is a decrease in the affinity of all the three dyes studied. This leads to the conclusion that the introduction of aldehyde groups at the C-2 and C-3 positions of anhydroglucose units of cellulose (as in periodate oxidation) does have an adverse effect on the affinity of leuco vat dyes. It is interesting to note that the reduction of the aldehyde groups to primary alcoholic groups by sodium borohydride results in an increase in the affinity value, but it does not attain the affinity for standard cellulose. This difference in the affinity values (for standard cellulose and borohydride-treated periodate oxycellulose) may be ascribed to the residual reducing and acidic groups present in the borohydride-treated periodate oxycelluloses.

The decrease in the affinity with increasing carboxyl content of the oxycellulose may be explained by the theory of Donnan membrane equilibrium as applied by Neale and Stringfellow¹² and Standing and Warwicker¹³ to

TABLE III
Effect of Chemical Modification of Cellulose on the Affinity of Leuco
Vat Dyes for Cellulose

Oxycellulose prepared with*	Subsequent treatment	Carboxyl value, meq/100 g	Copper number	Affinity, cal/mole		
				Caledon Yellow GN	Caledon Gold Orange G	Indanthren Yellow FFRK
— (Standard cellulose)	nil	0.48	0.03	-6845	-6432	-7173
KIO ₄	nil	1.68	4.18	-5750	-5597	-6614
(LOL)	NaBH ₄	0.48	0.11	-6550	-5967	-6937
KIO ₄	nil	3.78	15.93	-5566	-5423	-6486
(HOL)	NaBH ₄	0.71	0.25	-5838	-5746	-6894
K ₂ Cr ₂ O ₇ plus	nil	0.92	2.83	-5813	-5480	-6694
H ₂ SO ₄	NaBH ₄	0.68	0.04	-6052	-6076	-6964
(LOL)						
K ₂ Cr ₂ O ₇ plus	nil	11.32	19.68	-5766	-5501	-6894
H ₂ SO ₄	NaBH ₄	8.69	0.73	-5807	-5998	-6879
(HOL)						
K ₂ Cr ₂ O ₇ plus	nil	1.38	3.34	-5786	-5520	-6573
COOH	NaBH ₄	0.33	0.06	-6159	-6142	-6844
COOH						
(LOL)						
K ₂ Cr ₂ O ₇ plus	nil	6.34	15.50	-5688	-5515	-6497
COOH	NaBH ₄	1.27	0.16	-5936	-5875	-6694
COOH						
(HOL)						

* LOL = Low oxidation level; HOL = high oxidation level.

direct dyes. The dye anions are assumed to be adsorbed by the fiber; and in order to maintain electrical neutrality, these anions must have an equal number of sodium ions or other cations in their vicinity. The dyed cellulose substance is in equilibrium with the dyebath. The system consists of two phases, one being the cellulose phase and the other, the solution phase. The concentrations of the dye ions and sodium ions in the cellulose phase and the solution phase at equilibrium are related according to the Donnan membrane equilibrium as follows:

$$[D]_f = \left(\frac{[Na]_s}{[Na]_f} \right)^z \cdot [D]_s \quad (10)$$

If $[D]_s$ is maintained constant (i.e., dyeing from an infinite bath), $[D]_f$ is directly proportional to $([Na]_s/[Na]_f)^z$. If ionized carboxyl groups are present in the fiber substance, they also hold sodium ions in their vicinity, increasing $[Na]_f$ and thereby decreasing $[Na]_s/[Na]_f$. As a result, $[D]_f$ decreases. Thus, with progressive increase in carboxyl groups in the oxy-

cellulose, the equilibrium dye uptake should decrease. Since the dyeing has been carried out from an alkaline medium, all the lactones present in the oxycellulose can be considered as saponified and all the carboxyl groups are likely to be ionized. While dyeing direct cotton dyes on oxycelluloses, the number of ionized carboxyl groups, which adversely affects the equilibrium dye uptake, is generally less than the total number of carboxyl groups, as shown by Standing and Warwicker¹³ and Daruwalla et al.¹⁶ Further, some of these carboxyl groups might be present as lactones, which are unlikely to get ionized during dyeing with direct cotton dyes. Thus, all the acidic groups present in the oxycellulose may not interfere with the equilibrium dye uptake of direct cotton dyes by oxycelluloses. On the other hand, all the carboxyl groups interfere with the equilibrium dye uptake while dyeing leuco vat dyes on oxycelluloses, since these are completely ionized. The results obtained in the present investigation are in agreement with the hypothesis put forward by Standing and Warwicker.¹³

When cellulose is oxidized with potassium dichromate in the presence of sulfuric acid or oxalic acid, the oxidation is supposed to take place predominantly, though not exclusively, at the primary hydroxy groups, with the formation of aldehyde or carboxyl groups. Table III shows that with both these oxycelluloses the affinity of the three vat dyes decreases rapidly with an increase in the extent of oxidation. As with periodate oxycelluloses, borohydride treatment of these oxycelluloses also increases the affinity. As with the rate of dyeing, the affinity of the leuco vat dyes for the different modified celluloses increases in the order oxycellulose < borohydride-treated oxycellulose < standard cellulose.

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