

Behaviour of crosslinking on cotton fabric dyed with direct and reactive dyes^a

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Mercerized-bleached cotton has been dyed with direct and reactive dyes and subsequently cured with dimethyloldihydroxyethylene urea (DMDHEU) along with mixed catalyst containing magnesium chloride hexahydrate and ammonium chloride in presence of polyethylene emulsion softener. The differential behaviour of direct-dyed and reactive-dyed crosslinked cotton with respect to fastness properties, formaldehyde release, moisture regain, etc. has been discussed. Infrared, optical microscopic and X-ray diffraction studies show more crosslinking in the reactive-dyed samples as compared to that in the direct-dyed ones.

Keywords: Cotton fabric, Crosslinking, Cuprammonium dissolution, Direct dye, Formaldehyde release, Reactive dye, Wickability

1 Introduction

Finishing of cotton fabrics with resin is a common practice for improving easy care property and wrinkle resistance. The most commonly used resin dimethyloldihydroxyethylene urea (DMDHEU) reacts with two cellulose molecules to form a covalent link between them¹. Crosslinking reactions depend on the reaction of functional groups of the resin with the hydroxyl groups present in the amorphous region as well as their spatial availability in different structural units of the cellulose. The environment in which the crosslinking reactions occur in fabric finishing is governed by the presence of foreign substances, viz. additives, contaminants, and dyes/colorants, as well as by the amount of moisture present in the fibre at the time of reaction². Braun and Rieker³ observed that a variation in the resin treatment parameters significantly affects the degree of fixation and the shade of the dyed fabric. Extensive studies^{4,5} were carried out on the relationship between selected fabric residues and formaldehyde release. In the present investigation, chemical modification by crosslinking reactions were carried out on direct- and reactive-dyed cotton fabrics using DMDHEU resin. An attempt has been made to correlate the effect of crosslinking on the fastness properties and formaldehyde release of the finished fabric as

well as to study the structural changes brought about by the different dyes present on the modified crosslinked fabric.

2 Materials and Methods

2.1 Fabric

Mill mercerized-bleached poplin having the following specifications was used: count, 39s × 36s; reeds/in, 50; picks/in, 24; and weight, 117 g/m².

2.2 Dyes

Four direct dyes and three reactive dyes were used. The structure and other details of direct dyes are given in Table 1 and the structures of reactive dyes are given in Fig. 1.

2.3 Dyeing Procedure

Dyeing with direct dyes was carried out in an automatic laboratory jigger by exhaust method. The dyeing recipe and dyeing conditions used for direct dyes are as follows:

Dye, X% owf
Sodium sulphate, 10 g/l
Dyeing temperature, 60-95°C
Material-to-liquor ratio, 1:10
Duration of dyeing, 2 h

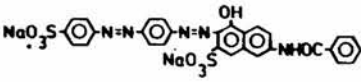
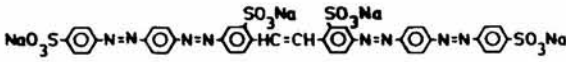
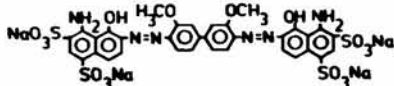
The dyeing techniques, recipes and other conditions for reactive dyes are given in Table 2.

2.4 Finishing

Resin finishing was carried out after padding in

^aPaper presented at the 42nd Southeast/46th Southwest Combined Regional Meeting of the American Chemical Society held at SRRC, New Orleans, during 5-7 December 1990.

Table 1—Structures and other details of direct dyes

Commercial Name	Colour Index	Constitution No.	Molecular Weight	Structure	Solubilising Group	Maximum Affinity at
Atul Direct Brown MR	C.I. Direct Brown 2	22311	627		1	60–80°C
Chlorantin Fast Red 5 B	C.I. Direct Red 81	28160	675		2	60°C
Chlorantin Fast Orange TGLL	C.I. Direct Orange 34	40215	1004		4	80–90°C
Diazol Blue 6 B	C.I. Direct Blue 1	24410	992		4	60–80°C

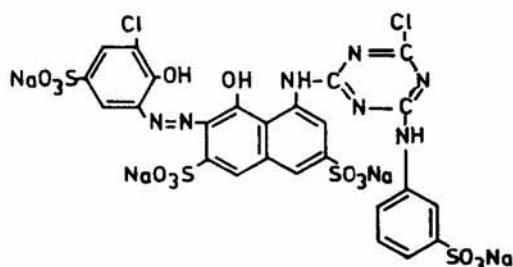
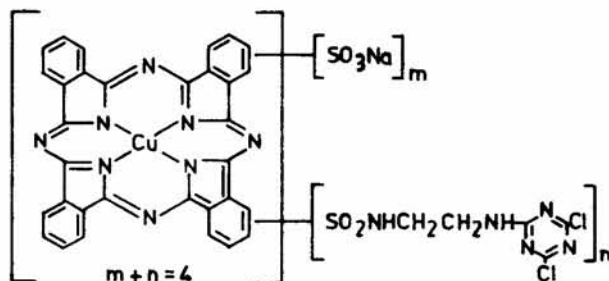
C.I. Reactive Orange 4C.I. Reactive Violet 1C.I. Reactive Blue 140

Fig. 1—Structures of reactive dyes

a Benz vertical/horizontal padding mangle. The following finishing formulations were used:

- 60 g/l Resin + 5 g/l $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.33 g/l NH_4Cl + 20 g/l Aqualine N + 1 g/l Lissapol N
- 90 g/l Resin + 10 g/l $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.66 g/l NH_4Cl + 20 g/l Aqualine N + 1 g/l Lissapol N
- 120 g/l Resin + 15 g/l $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ + 1 g/l NH_4Cl + 20 g/l Aqualine N + 1 g/l Lissapol N

where Aqualine N is a cationic softener; and Lissapol N, a wetting agent.

2.5 Fastness Tests

Wash fastness of the samples was assessed by ISO 2 test for direct dyes and by ISO 4 test for reactive dyes. Light fastness was assessed by a Xenotest 150.

2.6 Determination of Formaldehyde Release

Formaldehyde release of the finished fabric was evaluated by AATCC-112 (1984) sealed jar method.

2.7 Cuprammonium Dissolution for Detection of Crosslink

Dyed-finished and crosslinked sample (0.1 g) was kept in a stoppered conical flask containing 30 ml cuprammonium hydroxide solution for 20 h at $29 \pm 1^\circ\text{C}$. The content of the flask was filtered through a G-1 crucible and subsequently the residue was treated with HCl (0.1N) for dissolving cuprammonium in the residue and then

Table 2—Dyeing techniques and conditions for reactive dyes

Dyeing technique	Dye bath				
	Sodium chloride g/l	Sodium carbonate g/l	Urea g/l	Sodium bicarbonate g/l	Resist salt g/l
C.I. Reactive Blue 140					
Exhaust technique M:L ratio, 1:5 Total dyeing time, 2 h Exhaustion at 40-50°C followed by fixation at 85-90°C for 1 h	50	10	—	—	—
C.I. Reactive Orange 4					
Pad-batch technique Batching time, 20 h at 30 ± 1°C	—	5	—	15	—
C.I. Reactive Violet 1					
Pad-dry-cure technique Drying at 85-90°C for 5 min Curing at 165°C for 3 min	—	16	150	—	10

rinsed thoroughly with water and dried at 100°C for 4 h.

2.8 Infrared Studies

Infrared (IR) studies on crosslinked fabric were carried out on a Hitachi Model 270-30 IR Spectrophotometer using KBr pellet technique.

2.9 X-ray Studies

X-ray diffraction (XRD) scans of DMDHEU crosslinked fabric samples were obtained using a Philips X-ray Generator (Model PW-1720) with microprocessor-based PW-1710 Textured Goniometer Control.

2.10 Wickability Test

Wicking tests on direct- and reactive-dyed crosslinked fabrics were carried out as per the method reported by Ravichandran *et al.*⁶.

2.11 Moisture Regain

Moisture regain and water imbibition of crosslinked cotton fabrics were determined by the standard methods reported earlier⁷.

2.12 Optical Microscopic Studies

Microscopic studies on crosslinked residue of direct- and reactive-dyed fabrics were carried out using the Ernst Leitz Compound Microscope at ×100 magnification. Samples of Direct Red 81 and Reactive Blue 140 dyed finished residues were treated in cuprammonium solution for 5.5 min and exposed for 2 s to obtain the micrographs.

Table 3—Conditioned WRA of dyed cotton fabrics at various levels of DMDHEU finishing

Sample	Cond. WRA (W + F), deg			
	DMDHEU, g/l	60	90	120
Undyed		265	285	299
Dyed with				
Direct Brown 2	258	280	292	
Direct Red 81	258	270	293	
Direct Orange 34	251	280	296	
Direct Blue 1	258	277	293	
Reactive Blue 140	257	279	295	
Reactive Orange 4	252	257	267	
Reactive Violet 1	252	267	269	

WRA of unfinished white control, 198°

3 Results and Discussion

Crosslinking reactions with resin as well as other agents on cellulose not only improve easy care property but also enhance wet fastness properties. Figs 2 and 3 show the improvement in the wash fastness properties of direct- and reactive-dyed samples respectively. With the increase in the concentration of resin, crosslinking increases and the fastness properties are enhanced from a rating of 1 to 3-4 in the case of direct-dyed fabrics. In the case of reactive-dyed samples, only the Blue 140 dyed and finished sample shows some increase in the fastness rating (2-3 to 4).

Conditioned WRA of cotton dyed with four direct dyes and three reactive dyes and subsequently finished with various concentrations of

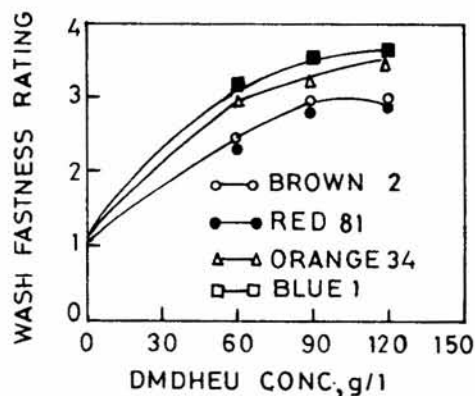


Fig. 2—Correlation of wash fastness of direct-dyed cotton with concentration of crosslinking agent

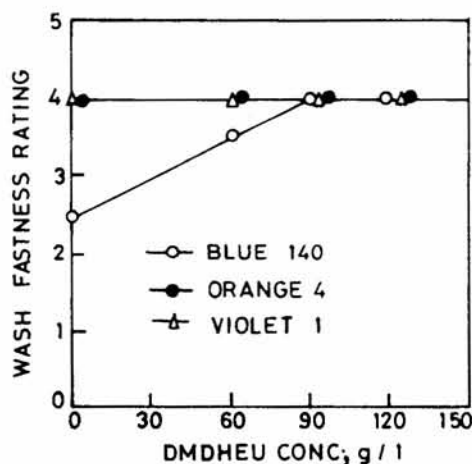


Fig. 3—Correlation of wash fastness of reactive-dyed cotton with concentration of crosslinking agent

DMDHEU resin (60, 90 and 120 g/l) are shown in Table 3. It is observed that the conditioned WRA increases progressively for both types of dye with increase in resin concentration. It is further observed that all the direct-dyed samples show more or less same values at a particular resin concentration while among the reactive-dyed samples, Blue 140 dyed sample shows higher WRA as compared to the other two samples.

Formaldehyde release from the crosslinked fabric increases with the increase in resin concentration. As the fabric acidity or alkalinity influences the formaldehyde release from the finished fabric, the same is tested and adjusted if necessary to make it neutral before finishing with sodium bicarbonate and dil. acetic acid respectively. Figs 4 and 5 show the data on formaldehyde release from direct- and reactive-dyed and DMDHEU-finished fabrics respectively. It is observed that at the same level of resin concentration and catalyst, formaldehyde release varies from dye to dye as well as with the type of dye

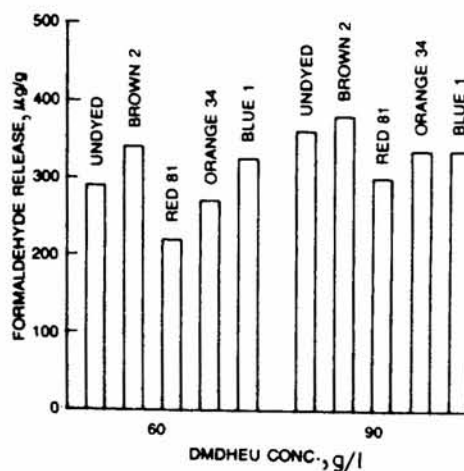


Fig. 4—Effect of resin finishing on formaldehyde release of direct-dyed cotton

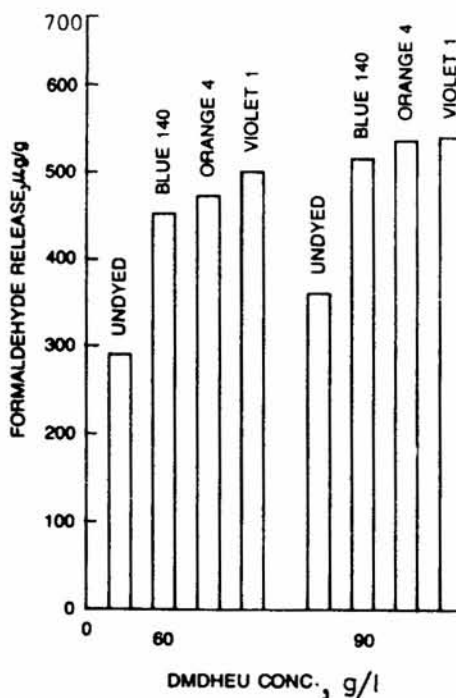


Fig. 5—Effect of resin finishing on formaldehyde release of reactive-dyed cotton

(Fig. 6). It has been reported³ that the varying formaldehyde levels are obtained in presence of different dyes and possibly there exists a correlation between formaldehyde release and dye. In the present investigation, among the direct-dyed fabrics, Brown 2 dyed fabric shows the highest value and Red 81 dyed fabric, the lowest. Among the reactive-dyed fabrics, Violet 1 dyed fabric shows the maximum formaldehyde release and Blue 140 dyed fabric, the lowest. This indicates that the formaldehyde release is, to some extent, dye specific.

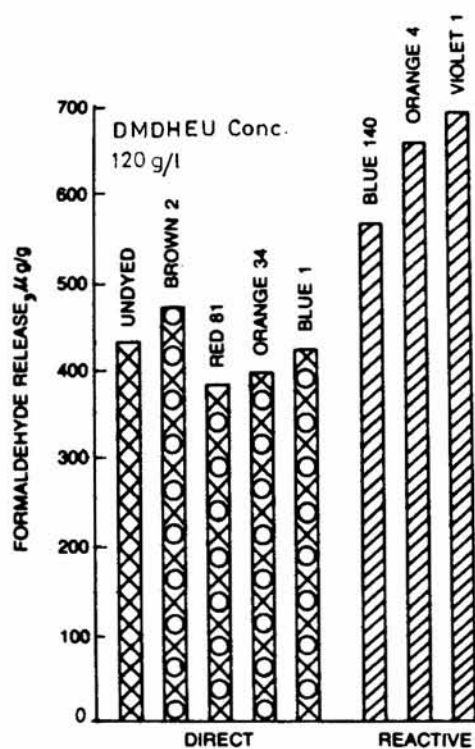


Fig. 6—Comparative values of formaldehyde release from direct- and reactive-dyed cotton

Table 4—Comparative data on nitrogen content and conditioned WRA of dyed samples finished with 120 g/l DMDHEU

Sample	Nitrogen content for unfinished %	Nitrogen % (owf)	Cond. WRA (W + F) deg
Untreated undyed control	0.04	—	198
Untreated undyed	—	0.81	299
Dyed with			
Direct Brown 2	0.07	0.84	292
Direct Red 81	0.10	0.84	293
Direct Orange 34	0.16	1.02	296
Direct Blue 1	0.03	0.78	293
Reactive Blue 140	0.09	0.97	295
Reactive Orange 4	0.14	0.65	267
Reactive Violet 1	0.14	0.68	269

Table 4 shows the nitrogen content and conditioned WRA of direct- and reactive-dyed finished fabrics. Data on nitrogen content reveal that fixation of nitrogen is more in direct-dyed sample than in reactive-dyed samples except in Blue 140 dyed sample which shows higher WRA also. However, the higher value of nitrogen content on

direct-dyed finished fabric may not indicate more crosslinking.

Direct dyes are held inside the fibre by van der Waals' forces or hydrogen bonding. After reaction with DMDHEU, the free amino or hydroxyl group of the direct dye may react with one end of the bifunctional resin while the other end forms ether linkage with cellulose. The direct-dyed samples when soaped under mild condition showed no bleeding. It may be noted that although Direct Orange 34 does not possess any OH or NH₂ group, due to its planar and linear structure this dye tends to form dimer or higher aggregates, thus becoming insolubilized inside the fibre structure and improving wash fastness properties. This shows that the dye which has reacted with the resin is anchored or entangled mechanically inside the cellulose network, thereby improving wash fastness and the wrinkle recovery angles also. Further studies on the extraction with 25% aqueous pyridine of the direct-dyed and dyed-finished samples showed that significant reduction in bleeding could be achieved after resin finishing. The optical densities of the extracts for Direct Brown 2, Red 81, Orange 34 and Blue 1 at the unfinished stage were 3.81, 3.81, 3.74 and 2.04 respectively whereas the values for finished samples were 1.38, 2.42, 0.07 and 1.04 respectively.

Table 5 shows the data on detection of crosslinks in direct- and reactive-dyed cotton. The dyed fabrics were crosslinked with DMDHEU (120 g/l) alongwith the mixed catalyst and the dissolution of the finished samples in cuprammonium solution was studied. Considerably higher flow time for reactive-dyed samples before finishing suggests that the covalent bond formed between the triazinyl group and cellulose imparts marginal crosslinking. Reactive-dyed samples after resin finishing become completely insoluble. The flow time for direct-dyed samples also increases and Brown 2 dyed samples became insoluble. As the fluidity could not be measured, the crosslinked samples were treated with cuprammonium hydroxide solution for 20 h and then filtered through a G1 crucible. The details are given in the experimental methods.

Taking undyed finished control fabric as 100%, it is observed from Table 5 that the reactive-dyed finished fabrics have more residue as compared to the direct-dyed finished samples, possibly due to more crosslinking in the former as compared to the latter. However, moisture regain and water imbibition values are higher for reactive-dyed crosslinked samples as compared to that for the

Table 5—Detection of crosslinks in direct-dyed and reactive-dyed cotton by dissolution in cuprammonium solution

Sample	Nitrogen fixed due to resin only %	Cond. WRA of finished samples deg	Flow time, s		Fluidity, s		Residue of crosslinked samples %
			Unfinished sample	Finished sample	Unfinished sample	Finished sample	
White Control	0.56	299	436	Insoluble	3.66	Insoluble	100
Dyed with							
Direct Brown 2	0.66	290	358	Insoluble	4.10	Insoluble	78
Direct Red 81	0.55	277	389	659	2.71	2.51	88
Direct Orange 34	0.61	270	554	565	2.65	2.68	85
Direct Blue 1	0.90	290	512	1800	2.98	Insoluble	84
Reactive Blue 140	0.95	295	Insoluble	Insoluble	Insoluble	Insoluble	95
Reactive Orange 4	0.59	267	719	Insoluble	2.12	Insoluble	91
Reactive Violet 1	0.60	269	Insoluble	Insoluble	Insoluble	Insoluble	95

direct-dyed crosslinked samples (Table 6). The water imbibition values in Table 6 are of DMDHEU-finished samples. Therefore, these values are much lower than that of unfinished control⁸. It is interesting to note that although there is more crosslinking in the reactive-dyed samples, the moisture content and water imbibition are still higher as compared to those of direct-dyed finished samples. The hydroxyl groups of cellulose which did not react with reactive dye or resin are still available for H-bonding with the water molecule. Further, the spatial arrangement of the reactive dyes inside the amorphous region of cellulose possibly forms a network structure having more accessible regions. On the other hand, direct dyes are absorbed inside the fibre structure at the accessible regions and due to the penetration of resin, the crosslinked structure is modified in such a way that the structure becomes more compact. The hydroxyl groups of cellulose responsible for H-bonding with water molecules are now weakly bonded with the direct dyes, thus making the direct-dyed finished fabric less hydrophilic.

3.1 Microscopic Studies on Crosslinked Samples

The crosslinked residues were examined under microscope after treating with cuprammonium solution and the treated cellulose structures of direct- and reactive-dyed cotton are shown in the micrographs (Fig. 7).

Direct Red 81 dyed-finished residue on treatment with cuprammonium hydroxide solution swelled into a balloon shaped structure (Fig. 7A), indicating very less amount of crosslinking in this structure⁹. On the other hand, the structure of reactive Blue 140 dyed-finished residue was not much affected on cuprammonium treatment due

Table 6—Moisture regain and water imbibition of poplin dyed with direct and reactive dyes and finished with 120 g/l DMDHEU

Sample	Moisture regain %	Water imbibition %
Undyed finished	5.60	7.89
Dyed with		
Direct Brown 2	5.30	7.10
Direct Red 81	5.30	7.80
Direct Orange 34	5.40	7.30
Direct Blue 1	5.40	7.00
Reactive Blue 140	6.00	11.00
Reactive Orange 4	6.00	11.40
Reactive Violet 1	6.00	9.50

Table 7—X-ray diffraction data on various untreated and treated cotton samples

Sample	Ratio of 10 $\bar{1}$ and 002 peaks	Half width of 002 peak, deg
Undyed		
Control	0.11	1.7
Control alkali-treated	0.50	3.3
Finished	0.12	1.8
Finished, alkali-treated	0.36	2.5
Direct Red 81 Dyed		
Control	0.12	1.7
Control alkali-treated	0.49	3.5
Finished	0.11	1.7
Finished, alkali-treated	0.45	3.1
Reactive Blue 140 Dyed		
Control	0.10	1.5
Control alkali-treated	0.42	3.1
Finished	0.12	1.5
Finished, alkali-treated	0.37	2.5

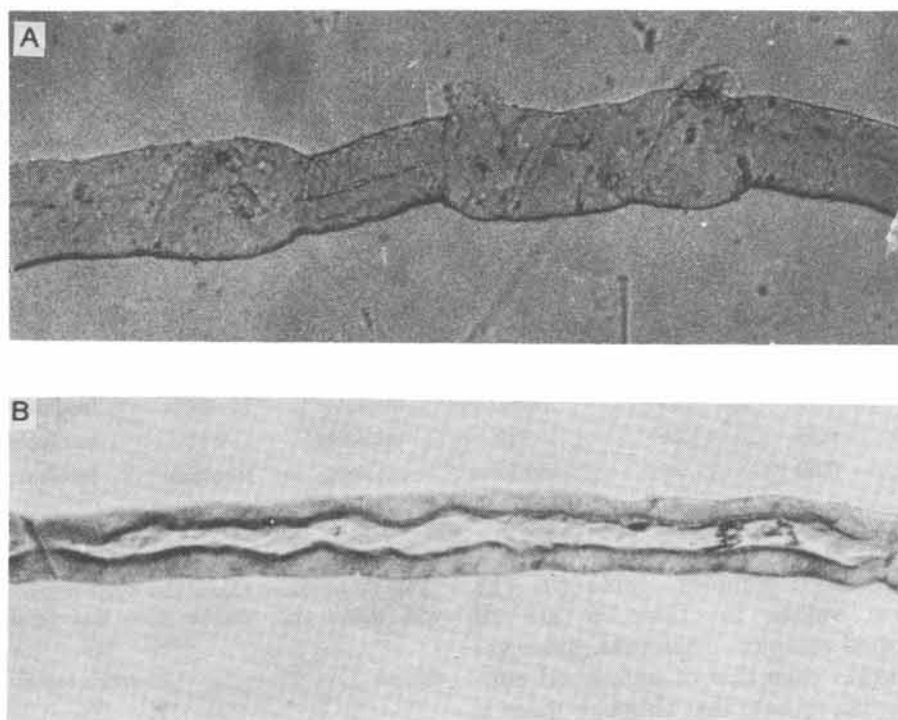


Fig. 7—Optical micrographs of dyed finished cotton treated with 0.5% cuprammonium hydroxide solution: **A**—Direct Red 81 dyed sample showing enormous swelling with constructions in between them, and **B**—Reactive Blue 140 dyed sample showing very little swelling, indicating moderate crosslinking

to the higher crosslinks already present (Fig. 7B). Studies on the wickability of the dyed-finished fabric showed that the reactive-dyed samples have more accessible regions (Fig. 8). These observations are in conformity with the results on moisture regain and water imbibition.

3.2 IR Studies

The IR spectra of the control and finished samples are shown in Fig. 9. In the case of undyed resin-finished and reactive-dyed finished samples, an additional band at 1720 cm^{-1} indicates the crosslinking of resin with cellulose¹⁰. In the case of direct-dyed finished samples, a weak band indicates only very less crosslinks which goes hand in hand with the microscopic investigations.

3.3 XRD Studies

When the cotton cellulose is swollen in alkali the lattice undergoes transformation from cellulose I to II. The fraction of cellulose II in the sample is indicated by the relative intensities of $10\bar{1}$ and 002 peaks of cellulose II and also broadening of 002 peak in XRD scan¹¹. When some restrictions are imposed upon the structure in any form, and in this case by covalent lateral linkages, the transformation will be incomplete. Therefore,

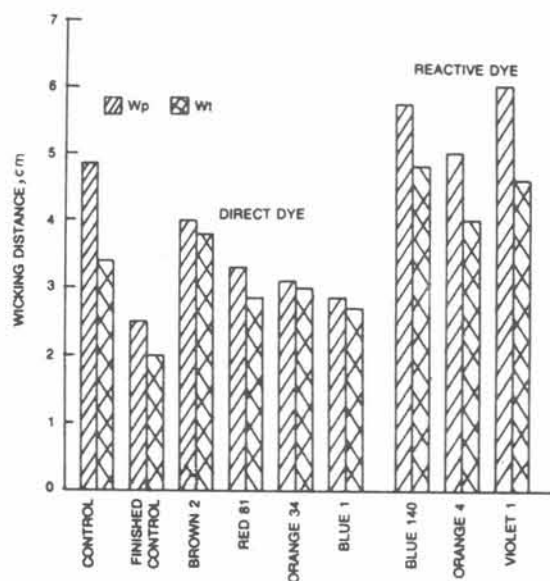


Fig. 8—Wicking distance of direct- and reactive-dyed samples finished with DMDHEU (120 g/l)

in the present study, the restriction imposed upon lattice conversion was assessed by taking X-ray diffraction scans of various samples treated with 20% alkali for 10 min at 20°C and subsequently

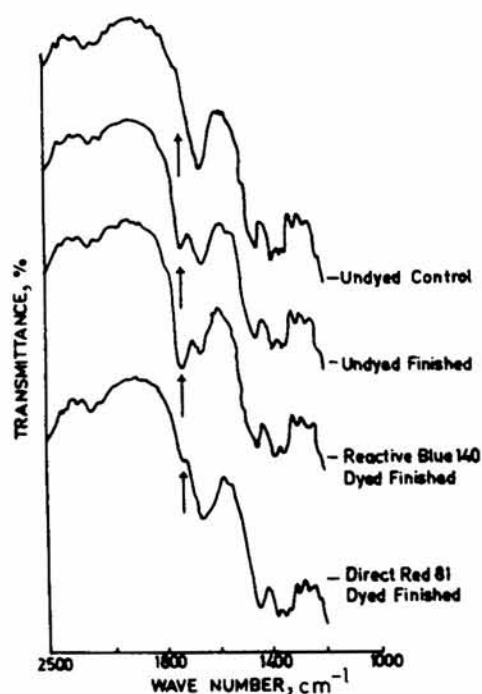


Fig. 9—Infrared spectra of control and finished cotton samples

measuring the relative intensities of 101 and 002 peaks as well as the half width of the 002 peak in the cellulose diagram. The XRD scans of various samples are shown in Figs 10 and 11 and the XRD data are given in Table 7.

In the case of undyed control sample, since there is no restriction due to covalent bonds resulting from crosslinks, conversion of cellulose I to II is maximum on swelling, as indicated by the relative intensities of 101 and 002 peaks and also the maximum broadening of the peaks. Undyed finished and reactive-dyed finished samples, however, show much less conversion of the cellulose I to II as well as the less broadening of 002 peak as compared to the control, due to the restrictions imposed by covalent crosslinking.

On the other hand, for the direct-dyed finished sample, on swelling, cellulose I to II conversion and the half width of 002 peak are more. This implies that in the case of direct-dyed finished samples only a limited restriction due to covalent linkages is present, probably most of the covalent bonds are formed by resin with direct dye and not with cellulose hydroxyl groups. Hence, on swelling, cellulose I and II conversion is more in

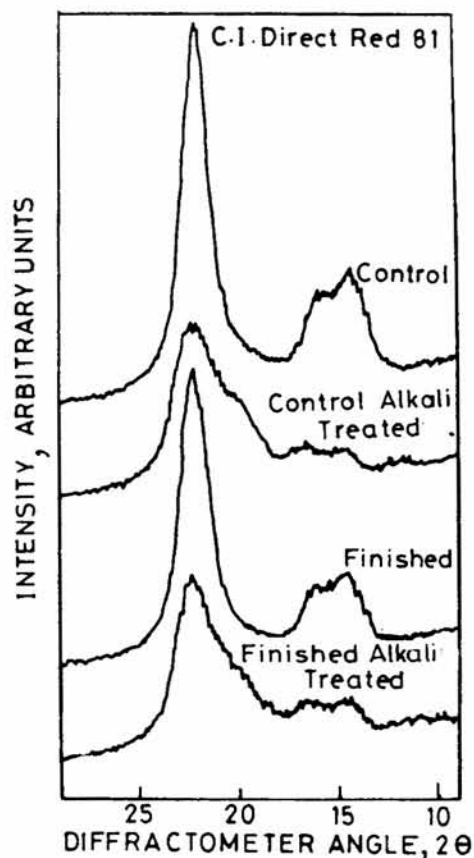


Fig. 10—XRD scan of cotton dyed with Direct Red 81 and finished with DMDHEU resin

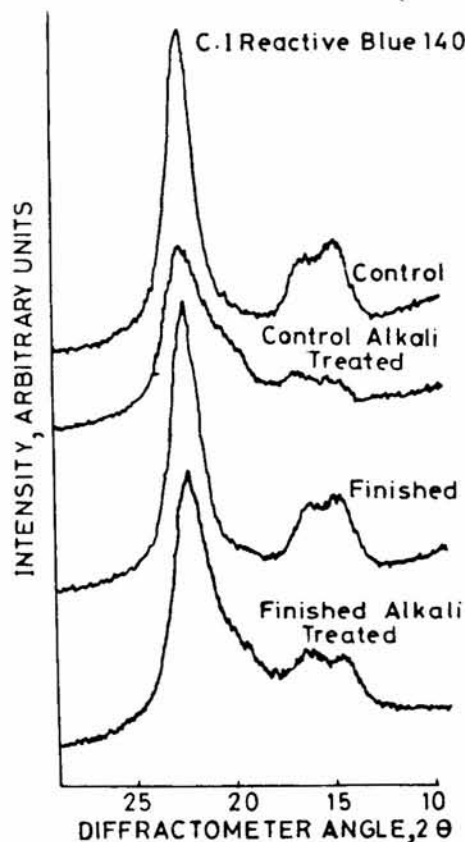


Fig. 11—XRD scan of cotton dyed with Reactive Blue 140 and finished with DMDHEU resin

the case of direct-dyed finished samples as compared to that in reactive-dyed finished samples. XRD studies also show that the crosslinking behaviour in direct-dyed and reactive-dyed samples are different.

4 Conclusions

Chemical modification of cotton through crosslinking reaction with DMDHEU resin improves the wash fastness properties of direct-dyed cotton significantly as compared to that of the reactive-dyed finished fabrics. Presence of different classes of dye as well as their structures play important role during crosslinking reactions.

The values of WRA are more or less same for direct- and reactive-dyed samples at the finished stage. More crosslinking takes place in the reactive-dyed samples as compared to that in the direct-dyed ones.

Formaldehyde release from the finished fabric is lower in the case of direct-dyed cotton as compared to that in reactive-dyed cotton.

Crosslinked lamellae seem to be different for cotton samples dyed with direct and reactive dyes. The resin probably reacts preferentially with the functional groups present in the direct dyes studied rather than with the hydroxyl groups of cellulose.

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References

- 1 Beck Keith R, Springer Karen, Wood Karl & Wusik Martin, *Text Chem Color*, 20(3) (1988) 35.
- 2 Giuliano C T, *Crosslinking of cellulose, functional finishes*, Part A (Marcel Dekker Inc), 1983, 6.
- 3 Braun W & Rieker J, *Melliand Textilber (Eng)*, 11 (1982) 796.
- 4 Andrews B K & Reinhardt R M, *Text Res J*, 52 (1982) 123.
- 5 *The relationship between selected fabric residues and formaldehyde release*, *Text Chem Color*, 14(12) (1982) 249.
- 6 Ravichandran V, Wilde M, Gadoury D R, Lemley A T & Obendorf S K, *Some observations on the effect of selected dye carriers on poly(ethylene terephthalate)*, *Book of Papers, 1986 International Conference and Exhibition*, (American Association of Textile Chemists and Colorists, N.C., USA), 1986, 107-110.
- 7 Reeves W A, Perkins R M & Chance L H, *Text Res J*, 30 (1960) 179.
- 8 Varghese J, Patel S K, Doshi B A & Mistry P R, *Indian J Text Res*, 12 (1987) 173.
- 9 deGrug I V, Carra J H & Goynes W R, *The fine structure of cotton* (Marcel Dekker Inc, New York) 1973, 46-49.
- 10 *Instrumental analysis of cotton cellulose and modified cotton cellulose*, edited by Robert T O' Conner (Merck Dekker, Inc., New York), 1972, 433.
- 11 Manjunath B R, Venkataraman A, *Indian J Text Res*, 5 (6) (1980) 29.