Single-Step Dyeing and Finishing Treatment of Cotton with 1,2,3,4-Butanetetracarboxylic Acid

HYUNG-MIN CHOI[1,]* MAGESH SRINIVASAN,[1] and NANCY M. MORRIS[2]

[1]Department of Clothing and Textiles, Kansas State University, Manhattan, Kansas 66506; [2]Southern Regional Research Center, ARS, USDA, New Orleans, Louisiana 70179

SYNOPSIS

A single-step dyeing and finishing (SDF) process was developed to eliminate dyeing problems associated with cotton crosslinked by polycarboxylic acid such as 1,2,3,4-butanetetracarboxylic acid (BTCA). This process consisted of several steps: (a) impregnation of the fabric by the bath containing BTCA, dye, and catalyst; (b) drying; and (c) curing at high temperature. Color strength (K/S) and dye fixation of cotton treated by the SDF process were excellent, especially with reactive dyes containing mono- or dichlorotriazinyl compounds and, in some cases, were higher than those of the sample dyed by a conventional batch process without finishing treatment. The presence of dye in the SDF process did not interfere with crosslinking of cotton. We believed that the reaction occurred between carboxyl groups of BTCA and s-triazinyl groups in reactive dyes in the presence of imidazole and other catalyst. FTIR, Raman, and X-ray fluorescence spectroscopies were used to confirm the mechanism of dye fixation. Elemental analysis also supported this mechanism. The SDF process can be an excellent way to dye fabric that also requires crosslinking treatment for smooth drying appearance. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Recent studies have indicated that crosslinking treatment of cellulose using polycarboxylic acids provide a means to produce nonformaldehyde durable press finished cotton.[1-5] Various polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid, and a mixture of maleic acid and itaconic acid were investigated and their advantages and disadvantages in terms of crosslinking efficiency, economy, durability of finish, and strength retention of the treated fabric have been studied.[1,2,5]

Although crosslinking treatment of cotton via etherification with *N*-methylol derivatives or esterification with polycarboxylic acids improved smooth drying appearance of the treated fabric, it renders substantial reduction in dye uptake and fixation. Two reasons could cause this reduction: (a) limited availability of dye sites that are already occupied by finish molecules, and (b) blocking of cellulose hydroxyl groups by crosslinking reaction.[6]

Specifically, the esterification reaction of cellulose with polycarboxylic acids provides large amounts of unreacted free carboxyl groups within the fiber.[1] These free carboxyl groups cause substantial decrease in the affinity of cellulose toward conventional cotton dyes, such as direct dyes and reactive dyes.[7] In many cases, therefore, cotton fabrics are dyed prior to crosslinking treatment.[8] However, crosslinking treatment of dyed cotton often produces undesirable effects, such as fastness problems and shade changes, and these effects are more pronounced in the presence of a reductive catalyst, such as sodium hypophosphite, when the fabrics are dyed with sulfur dyes and some reactive dyes.[2,9]

Many attempts have been made to minimize the problems associated with the dyeing of crosslinked fabrics. Hebeish et al.[6] and Refai and Ibrahim[10] have investigated factors that affect dyeability. Blanchard and Reinhardt[8] have studied the use of hydroxylamines that reacted with *N*-methylol agents on cel-

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* To whom correspondence should be addressed. Present address: Kimberly-Clark Corporation, 2100 Winchester Road, Neenah, WI 54957-0999.

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lulose to produce a crosslinked fabric that had affinity for anionic dyes.

Another approach to solving the dyeing difficulty of crosslinked fabric has been a simultaneous dyeing and finishing process.[11-13] By using this process, dyed fabrics showed excellent color strength (K/S) and fixation. It was believed that nucleophilic groups within the dye molecules reacted with cellulose hydroxyl groups during the crosslinking treatment, resulting in excellent fixation. The number of nucleophilic groups, structure, molecular size, and steric configuration of the dyes were important factors in fixation.[11] In addition, other advantages, such as cost-effectiveness, can be introduced by using this single-step dyeing and finishing process.

Previous studies on the single-step process, however, have been based mainly on the use of *N*-methylol compounds as the crosslinking agent. In the present study, we investigated the single-step dyeing and finishing process of cotton fabrics using polycarboxylic acid as a crosslinking agent and imidazole as a catalyst. This process could overcome dyeing problems in addition to being cost-effective and simple.

EXPERIMENTAL

The fabric used was a desized, scoured, and bleached 100% cotton print cloth weighing approximately 3.1 oz/yd^2 (107 g/m^2). The crosslinking agent used was BTCA (Tokyo Kasei Chemicals) and the catalyst used was imidazole (Aldrich Chemical Co.). Additional catalysts, such as sodium hypophosphite and 2-methylimidazole supplied by Aldrich, were also used for comparison purposes. Triton X-100 (Aldrich) and Cyanaluble TSI (American Cyanamide) were used as a nonionic wetting agent and softener, respectively. Triethanolamine and polyethylene glycol with molecular weight of 600 (PEG-600), both from Aldrich, were used as additives. Dyes supplied by various commercial sources were commercial grade, used without further purification.

Unless otherwise stated, a fabric sample (15 cm × 13 cm) was padded in a solution containing 6.5% owb (on the weight of bath) BTCA, imidazole (one-to-one mole ratio vs. BTCA), 1% owb Cyanaluble TSI, 0.1% owb Triton X-100, 2-3% owf (on the weight of fiber) dye, and, if necessary, additives. The liquor-to-goods ratio was 10 : 1. One dip-and-nip at 200 kPa gave a wet pickup of about 75% using a Werner-Mathis Laboratory Pad Range. The sample was then dried for 5 min at 85°C and cured for 1.5 minutes at 180°C, 190°C, or 200°C. The cured sample was washed through running water and then dried at an ambient condition.

For comparison purposes, some samples were dyed by a conventional batch process. The sample was placed in a bath containing NaCl (17% owb) and distilled water (liquor-to-goods ratio 20 : 1) and agitated for 10 min at 40°C. After the stock dye solution (2% owf) was added, the bath was again agitated for 30 min. Finally, Na_2CO_3 (20% owf) was added to the dyebath to promote reaction and the bath was agitated for another 30 min. The temperature was maintained at 40°C to minimize hydrolysis of the dye molecules.

Treated fabrics were divided into four pieces. One-fourth of the samples were treated with 0.1% Tanapon X-70 (modified polyglycol ether from Sybron Chemical, Inc.) solution at 100°C for 10 min. Another fourth of the samples was treated with 50/50 (v/v) dimethyl formamide (DMF)/water solution at 100°C for 10 min to assess the extent of fixation.

Some samples were mercerized with sodium hydroxide solution in a tensionless state according to a previous study.[14] Conditioned wrinkle recovery angles (AATCC Test method 66-1990)[15] were evaluated to measure smooth drying appearance of the treated fabric. A Hunter Ultrascan Sphere Spectrophotometer was used to measure the reflectance, and K/S values were calculated automatically according to the Kubelka–Munk equation:

$$K/S = (1 - R)^2/2R$$

where R is the reflectance at the wavelength of maximum absorption.[8] Percent fixation was calculated as the ratio of the K/S value after Tanapon X-70 or DMF/water treatments to the K/S value before these treatments.

Fourier transform infrared (FTIR) spectra were obtained on potassium bromide disks of fabric ground in a Wiley mill to pass a 20-mesh screen.[1] The infrared spectra of the treated fabrics were obtained on a Digilab FTS40 spectrometer (BioRad, Digilab Division, Cambridge, MA) equipped with a deuterated triglycine sulfate detector, a water-cooled source, and a dry air purge (Balston, Inc., Lexington, MA). One hundred scans of each sample were collected at a resolution of 4 cm^{-1}. All of the spectra were transferred through Kermit protocol to an IBM-compatible computer for analysis and plotting by SpectraCalc software (Galactic Industries, Nashua, NH). A 15-point Savitsky–Golay smoothing algorithm was applied to all of the spectra prior to subtraction. If necessary, a two-point baseline correction between 3850 and 1850 cm^{-1} was also applied.

Fourier transform Raman spectra were obtained on a Spex FT R/IR (J-Y/SPex/Instruments SA, Edison, NJ) equipped with a Bomem Michelson interferometer and a 750 M-35 Nd:YAG Laser (Lee Laser Inc., Orlando, FL). Two layers of fabric were placed in the sample holder and 100 scans of each sample at a resolution of 4 cm^{-1} were collected. The Raman spectrum of the dye itself was obtained on a KBr disk prepared for FTIR. The spectra were smoothed using a factor of 12 and were transferred to SpectraCalc through J-Camp for subtraction and plotting.

An energy dispersive X-ray fluorescence spectrometer (Kevex EDX-771, Fisons Instruments, Inc., San Carlos, CA) was used to analyze the presence of residual chlorine in the treated samples. Samples were ground to pass 20-mesh screen, pressed at 20,000 psi for 20 seconds, and analyzed with a potassium secondary target for 100 seconds in a Helium atmosphere at 30 kV and 1.0 ma.

RESULTS AND DISCUSSION

Various Dyes in SDF Process

Cotton fabrics were dyed and crosslinked simultaneously using different classes of dyes, such as direct, acid, disperse, and reactive dyes. Tables I and II show the K/S values of dyed samples and those treated with Tanapon and DMF/water solutions to assess the extent of dye fixation. Uniform dyeing was obtained for all samples. No appreciable difference was observed in color strength of the samples treated at three different temperatures, however the fixation increased substantially at higher curing temperature in each dyestuff.

Better fixation was expected with C.I. (Colour Index)[16] Direct Green 6 than with C.I. Direct Red 81 since the former has good exhaustion property and a larger number of nucleophilic groups (total 3).[16] However, results revealed that C.I. Direct Red 81 showed much greater fixation than that of C.I. Direct Green 6. C.I. Direct Red 81 is smaller than C.I. Direct Green 6 in molecular size. This suggested that in a single-step dyeing and finishing (SDF) process, the size of the molecule could play an important role in determining dye fixation by hindering good penetration of the dyestuff to the vicinity where the reaction took place. Other factors such as steric configuration and high aggregation properties of the dyestuffs could also have contributed to this difference.[12] No advantage was shown with a dye concentration increase to 3% with respect to both color strength and dye fixation (Table I).

Acid dyes generally have no or little affinity towards cellulosic fibers. But in the SDF process, good fixation of the acid dyes was obtained. Especially with C.I. Acid Orange 7, the increase of dye fixation

Table I Color Strength (K/S) Values of Cotton Treated by SDF Process Using BTCA and Different Classes of Dyes[a]

	Cured at 180°C			Cured at 190°C			Cured at 200°C		
Dyes (2% owf)	Initial K/S	A[b]	B[c]	Initial K/S	A	B	Initial K/S	A	B
Direct Green 6	0.93	0.49 (52.9)[d]	0.45 (48.4)	1.74	0.66 (38.3)	0.92 (53.4)	1.70	0.89 (52.2)	1.01 (59.7)
Direct Red 81	9.18	6.81 (74.2)	5.76 (62.7)	11.34	9.85 (86.8)	10.30 (90.8)	10.56	9.69 (91.8)	10.35 (98.0)
Direct Red 81 (3% owf)	10.90	8.03 (73.7)	7.37 (67.6)	11.32	7.77 (68.6)	7.13 (63.0)	10.12	7.27 (71.9)	7.76 (76.7)
Acid Orange 7	2.45	0.61 (24.8)	0.88 (35.9)	2.89	0.83 (28.8)	1.75 (60.5)	2.09	2.02 (69.6)	2.27 (78.2)
Acid Yellow 42	1.43	1.02 (71.0)	1.01 (70.3)	1.43	1.05 (73.6)	1.02 (71.0)	1.50	1.14 (76.1)	1.19 (79.5)
Disperse Blue 3	1.04	0.61 (59.2)	0.54 (52.0)	1.20	0.72 (60.0)	0.72 (59.8)	1.03	0.73 (71.1)	0.79 (77.1)
Disperse Red 5	0.81	0.57 (69.7)	0.46 (56.3)	1.83	1.19 (65.1)	1.27 (69.3)	1.72	1.30 (75.5)	1.30 (75.6)

[a] The treating bath contained 6.5% owb BTCA, imidazole (1 : 1 mole ratio vs. BTCA), 1% owb softener, 0.1% owb wetting agent, and 2% owf dyes. The samples were dried at 85°C for 5 minutes and cured for 1.5 min. [b]Tanapon treated. [c]DMF/water treated. [d]Percent fixation value is shown in parentheses.

Table II Color Strength (K/S) Values of Cotton Treated by SDF Process using BTCA and Various Reactive Dyes

	Cured at 180°C			Cured at 190°C			Cured at 200°C		
Reactive dyes (2% owf)	Initial K/S	A	B	Initial K/S	A	B	Initial K/S	A	B
Reactive Red 8	9.70	7.66 (79.0)	8.32 (85.8)	10.74	9.72 (90.5)	10.04 (93.5)	11.32	10.78 (95.2)	10.51 (92.8)
Reactive Red 4	6.49	5.92 (91.2)	5.91 (91.1)	5.88	5.61 (95.5)	5.69 (96.8)	6.01	5.52 (92.0)	5.54 (92.4)
Reactive Blue 4	1.63	1.23 (75.8)	1.33 (81.6)	1.51	1.31 (86.9)	1.41 (93.0)	1.59	1.45 (91.2)	1.46 (91.6)
Reactive Blue 5	1.42	1.05 (74.2)	1.21 (84.9)	1.38	1.21 (87.6)	1.23 (89.0)	1.35	1.26 (93.0)	1.19 (88.3)
Reactive Red 21	4.86	3.92 (80.6)	4.31 (88.5)	4.98	4.41 (88.5)	4.58 (92.1)	5.57	4.61 (82.9)	4.25 (76.3)
Reactive Yellow 17	3.48	1.84 (52.8)	2.79 (80.0)	3.13	2.84 (90.7)	2.47 (78.9)	3.47	3.09 (89.1)	2.86 (82.4)
Reactive Red 8 (3% owf)	12.57	8.26 (65.7)	9.03 (71.9)	13.04	11.05 (84.7)	11.16 (85.6)	13.33	10.36 (77.7)	11.66 (87.5)

at 200°C curing was substantial. Fabrics dyed using these acid dyes in the absence of BTCA and imidazole catalyst showed 1.6–2.2% dye fixation values with 0.49 (Orange 7) and 0.78 (Yellow 42) color strength. This indicated that some sort of chemical reaction could have occurred between nucleophilic groups of dyestuffs such as —OH and free carboxyl groups of BTCA which did not react with cellulose.

Disperse dyes, being insoluble in water, are unsuitable for dyeing cellulosic fibers; but uniform dyeing and good fixation were obtained when these dyes were incorporated into the SDF process. Nevertheless, color strength of the fabrics dyed with disperse dyes was generally lower than that of the fabrics dyed with acid or direct dyes, due to low solubility of disperse dyes that greatly reduced dye penetration to the reaction site.

Table II shows color strength values of cotton treated by the SDF process using BTCA and various reactive dyes in the presence of imidazole. These reactive dyes show much higher color strength values compared with those of the fabrics dyed with other types of dyes. Increase in curing temperature from 180° to 190°C during the SDF process considerably improved dye fixation but fixation leveled off at 190°C in many cases. An increase in dye concentration to 3% increased color strength values slightly, but fixation values decreased at each temperature, indicating the presence of more surface dyes.

Table III Color Strength (K/S) Values of Dyed Cotton (Unfinished and Previously Finished by Two-Step Process)[a]

				Dyed and Finished Cotton Samples Treated by Two-Step Process								
	Unfinished Sample			Cured at 180°C[b]			Cured at 190°C			Cured at 200°C		
Dyes (2% owf)	Initial K/S	A	B	Initial K/S	A	B	Initial K/S	A	B	Initial K/S	A	B
Reactive Red 8	6.25	1.55 (24.9)	1.27 (20.3)	0.65	0.19 (28.8)	0.22 (33.0)	0.51	0.18 (34.8)	0.24 (47.7)	0.56	0.16 (28.0)	0.19 (33.5)
Reactive Red 4	7.55	6.67 (88.3)	6.72 (89.0)				1.25	0.64 (51.2)	0.68 (54.4)			

[a] The samples were dyed by a conventional batch process. [b] Curing temperatures for a separate finishing process with BTCA.

Table IV Conditioned Wrinkle Recovery Angle (WRA) of Cotton Treated by SDF Technique

	Cured at 180°C		Cured at 190°C	Cured at 200°C
Dyes (2% owf)	Initial WRA	DMF/Water Treated	Initial WRA	Initial WRA
Undyed	280	—	284	292
Reactive Red 81	286	273	295	289
Reactive Red 8	282	272	293	293

We also dyed the unfinished fabric and the fabric separately, finished by BTCA and imidazole at different curing temperatures, to compare with the fabric treated by the SDF process. When the comparison was made between the SDF-treated fabric and the unfinished fabric in Tables II and III, the unfinished fabric showed considerably low color strength and dye fixation in the case of C.I. Reactive Red 8. With C.I. Reactive Red 4 the difference in color strength and dye fixation between the two fabrics was small. On the other hand, the previously finished cotton fabric, in a separate step, resulted in remarkable reduction in color strength as well as in dye fixation. These decreases occurred at all curing temperatures, suggesting that even at the temperature of 180°C the BTCA-finished fabric lost most of its affinity toward conventional cotton dyes, such as reactive dyes. This was due to the blocking of cellulose hydroxyl groups by crosslinking reaction and the repulsive force coming from free carboxyl groups. These results clearly indicate that with the SDF process, dyeing problems encountered with the fabric finished with polycarboxylic acids such as BTCA can be eliminated or at least substantially minimized.

The objective of the SDF process was to dye cotton as well as to increase its smooth drying appearance. Therefore, conditioned wrinkle recovery angles (WRAs) of the SDF-treated samples were evaluated as shown in Table IV. Addition of reactive dyes in

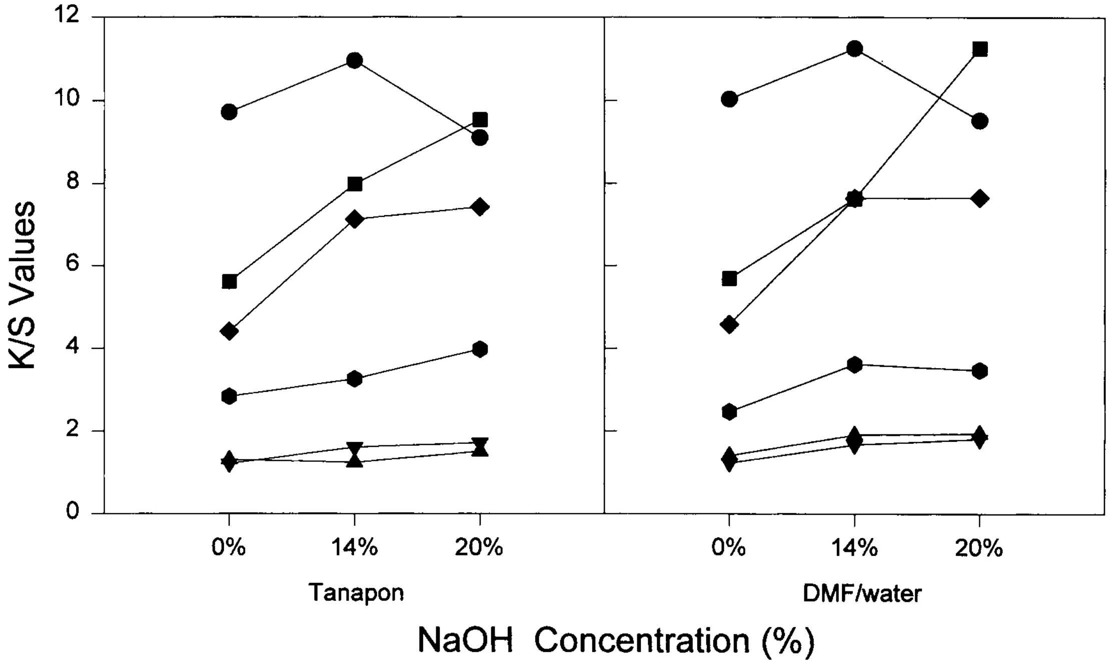


Figure 1 Effect of mercerization on color strength of cotton dyed with reactive dyes (cured at 190°C for 1.5 min). (●) C.I. Reactive Red 8; (■) C.I. Reactive Red 4; (▲) C.I. Reactive Blue 4; (▼) C.I. Reactive Blue 5; (◆) C.I. Reactive Red 21; (●) C.I. Reactive Yellow 17.

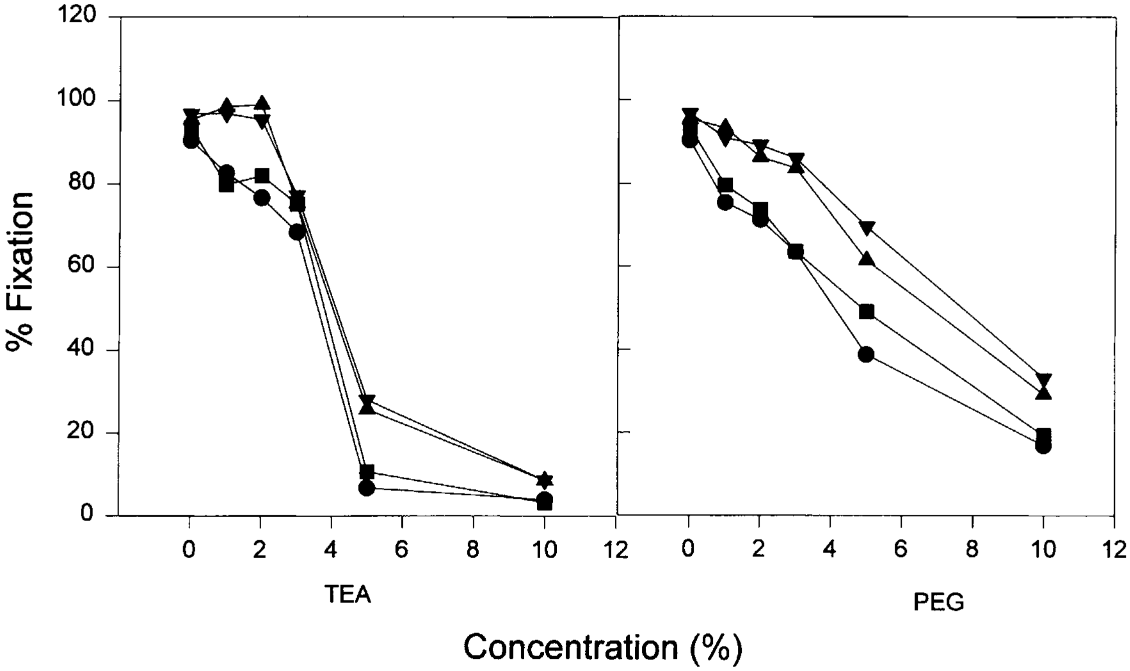


Figure 2 Effect of bath additives on reactive dye fixation of cotton. (●) C.I. Reactive Red 8 and Tanapon-treated; (■) C.I. Reactive Red 8 and DMF/water-treated; (▲) C.I. Reactive Red 4 and Tanapon-treated; (▼) C.I. Reactive Red 4 and DMF/water-treated.

the SDF process did not reduce WRA values of the treated fabric, suggesting little or no hindering of crosslinking reaction in the presence of dyes. After extraction with DMF/water treatment, a slight reduction was observed in WRA values. In addition, there was an increase in WRA values at higher curing temperatures, which was in accordance with the greater fixation of dyes at higher temperatures.

Effect of Mercerization

Cotton samples submercerized (14%) and mercerized (20%) according to a previous study[14] were dyed and finished by the SDF process using reactive dyes. From Figure 1 it can be concluded that the color strength of dyed submercerized and mercerized samples was generally higher than that of the unmercerized samples. Also the fully mercerized samples (20%) showed higher color strength than the submercerized samples (14%). It is well known that the mercerization brings about increased accessibility and decreased molecular orientation of the cellulose, and high reactivity towards finishes and dyes.[6] Contrarily, in many cases mercerization of the cotton tended to decrease dye fixation (not shown). This could be due to the opened structures of the mercerized cotton resulting in free absorption and desorption of dyes within the molecules.

In general, improvement of color strength by mercerization was greater with a dye having larger molecular weight, such as C.I. Reactive Red 4, than that of smaller dye, such as C.I. Reactive Red 8. Increased pore size in cotton due to mercerization could facilitate the entry of larger molecules into interfibrillar spaces, resulting in increased color strength.

Influence of Additives

The effect of additives such as triethanolamine (TEA) and polyethyleneglycol (PEG) was also studied. It was claimed that TEA and PEG reacted with the BTCA crosslinking agent to produce fabric that had an affinity for anionic dyes, such as reactive dyes, direct dyes, etc.[8] The dye fixation decreased consistently with increase in additive concentration, as shown in Figure 2. The decrease in fixation was more noticeable at higher concentration levels. The same trend was shown with the K/S values (not shown). At higher concentration levels, the decrease in fixation was more pronounced in the case of TEA compared with PEG. The decrease in fixation was due to a competing reaction between nucleophilic groups of the additive and the dye to react with free carboxylic groups of BTCA. Also, due to its basic nature, TEA increased the pH of the SDF bath at

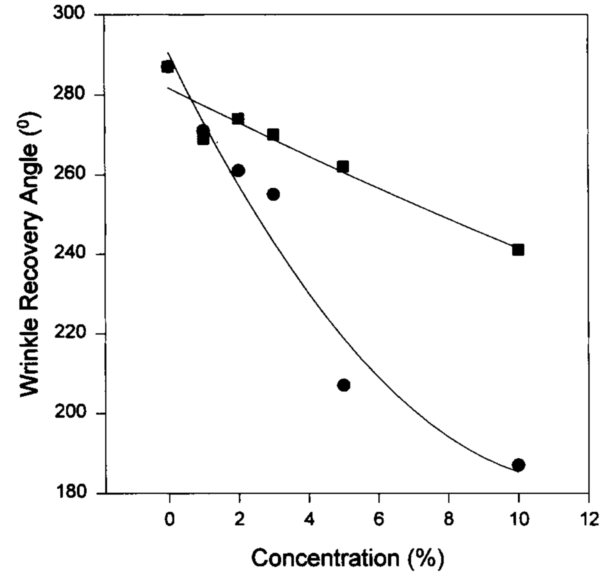


Figure 3 Effect of bath additives on conditioned wrinkle recovery angle of cotton. Samples were cured at 190°C for 2 min. (●) TEA; (■) PEG.

high concentration, which further hindered the esterification reaction. In addition, it was observed that at higher concentration PEG tended to form a surface coating which might further hinder the dye diffusion.

The influence of the additives on WRA values is shown in Figure 3. There was a drastic decrease in WRA of the samples treated with TEA at high concentration levels. This further confirmed that high concentration of TEA hindered the crosslinking reaction as well as dye fixation. In the case of PEG, although the effect was not as pronounced as that of TEA, substantial decrease in WRA was observed.

Cotton samples were separately finished by BTCA along with 2% additives and then dyed. In Tables III and V, results show that at 2% the presence of additive in the finish bath only slightly increased K/S and dye fixation of cotton, compared with cotton dyed by the two-step process without involving additives. Although high K/S values might be obtained at high concentration of additives in the finish bath, this could decrease the fixation.

Mechanism of Dye Fixation

Crosslinking of cotton using BTCA was obtained through esterification reaction between BTCA and cellulose in the presence of an imidazole catalyst. A similar chemical reaction was expected to take place between nucleophilic groups of the dyes and free carboxyl groups of BTCA, which consequently resulted in a high level of dye fixation.

To analyze the reaction mechanism between the dye, BTCA, and cellulose, samples were dyed and finished without imidazole. The dye fixation was considerably low (i.e., about 18–64%) in the absence of imidazole as shown in Table VI, indicating the low extent of the reaction. In addition, cotton treated without BTCA had even lower dye fixation, ranging from 7.8% to 14.2%. Even in the absence of BTCA, a basicity of imidazole was not high enough to induce a nucleophilic substitution reaction between the *s*-triazinyl chloride and the hydroxyl groups of cellulose. This was represented by remarkably low dye fixation and K/S.

We also examined the presence of any chemical reaction between dye and cellulose by the action of imidazole at low pH values without involving BTCA. This was based on the assumption that BTCA acted as an acid catalyst. The pH of baths prepared by imidazole and dye in the absence of BTCA was adjusted to 3.1 and 1.8 (similar to the bath pH with BTCA) by using acetic acid and sulfuric acid, respectively. Both cases showed little or no dye fixation. These results continuously confirmed that a

Table V Color Strength (K/S) Values of Cotton Treated by Two-Step Process (Finished along with 2% Additives and then Dyed)[a]

Reactive dyes (2% owf)	Triethanolamine			Polyethyleneglycol		
	Initial K/S	A	B	Initial K/S	A	B
Reactive Red 8	0.67	0.23	0.29	0.76	0.23	0.39
		(34.3)	(43.3)		(30.3)	(51.3)
Reactive Red 4	1.69	0.93	0.91	81.64	1.51	0.88
		(55.0)	(53.8)		(92.1)	(53.7)

[a] The fabric was first finished by the treating bath containing 6.5% owb BTCA, imidazole (1 : 1 mole ratio vs. BTCA), 2% owb additive, 1% owb softener, and 0.1% owb wetting agent, dried at 85°C for 5 mins, and cured at 190°C for 1.5 min. The sample was then dyed with 2% owf reactive dyes by a batch method.

Table VI Effect of Various Components in SDF Process on the Fixation of Reactive Dyes[a]

	C. I. Reactive Red 8			C. I. Reactive Red 4		
Bath Component	Initial K/S	A	B	Initial K/S	A	B
BTCA + Imidazole	10.74	9.71 (90.5)	10.04 (93.5)	5.88	5.61 (95.5)	5.69 (96.8)
BTCA + 2-methyl imidazole	7.23	6.05 (83.7)	6.42 (88.8)	—	—	—
BTCA + sodium hypophosphite	7.67	7.83 (100.0)	6.52 (85.0)	—	—	—
BTCA	4.62	1.40 (30.3)	1.36 (29.4)	2.36	1.51 (64.0)	1.31 (18.0)
Imidazole	3.57	0.44 (12.3)	0.28 (7.8)	2.12	0.30 (14.2)	0.20 (9.4)
Imidazole at pH = 3.1[b]	3.20	0.50 (15.6)	0.30 (9.4)	—	—	—
Imidazole at pH = 1.8[b]	6.59	0.48 (7.3)	0.34 (5.2)	5.48	0.54 (9.9)	0.37 (6.8)

[a] The treating bath contained 6.5% BTCA (as needed), catalyst (1 : 1 mole ratio, as needed), 1% softener, 0.1% wetting agent, and 2% owf dyes, dried at 85°C for 5 min, and cured at 190°C for 1.5 mins. [b] The bath pH was controlled by acetic acid to 3.1 and by sulfuric acid to 1.8.

synergistical chemical interaction had occurred between the dye, BTCA, and cellulose molecules in the presence of imidazole.

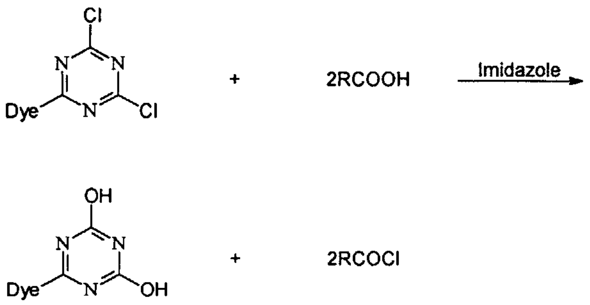
Other catalysts, such as 2-methylimidazole and sodium hypophosphite, also resulted in good fixation of dyes (Table VI). This tended to suggest that any catalysts which can enhance esterification reaction between BTCA and cellulose could improve dye fixation on cotton in the SDF process. However, with sodium hypophosphite the fabric dyed by C.I. Reactive Red 8 substantially changed its shade due to the reductive nature of the catalyst.

The fixation of the reactive dyes (mono- and dichloro *s*-triazinyl dyes) was exceptional when compared with that of dyes from other classes. A possible mechanism can be proposed to explain this superior fixation. It is known that cyanuric chloride reacts with carboxylic acid in the presence of a catalyst such as amine to form acylchloride and cyanuric acid.[17] Similarly, as shown in Scheme 1, dichloro or monochloro *s*-triazinyl dyes could react with BTCA in the presence of imidazole or other similar catalysts to form acid chloride and hydroxy-substituted triazinyl dye.

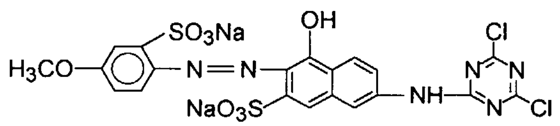
As a result of this reaction the number of nucleophilic groups in the dye was increased by one or two, depending upon whether the dye was mono- or di-chloro triazinyl dye. So the larger the number of nucleophilic groups, the greater the probability of the dye reacting with the free carboxylic acid groups, and the better the fixation of the dye.

FTIR and Raman Spectroscopic Analyses

Fourier transform infrared (FTIR) and Raman spectroscopic analyses were carried out to confirm some of the assumptions proposed earlier. When C.I. Reactive Red 8, whose chemical structure is illus-



C.I. Reactive Red 8



Scheme 1

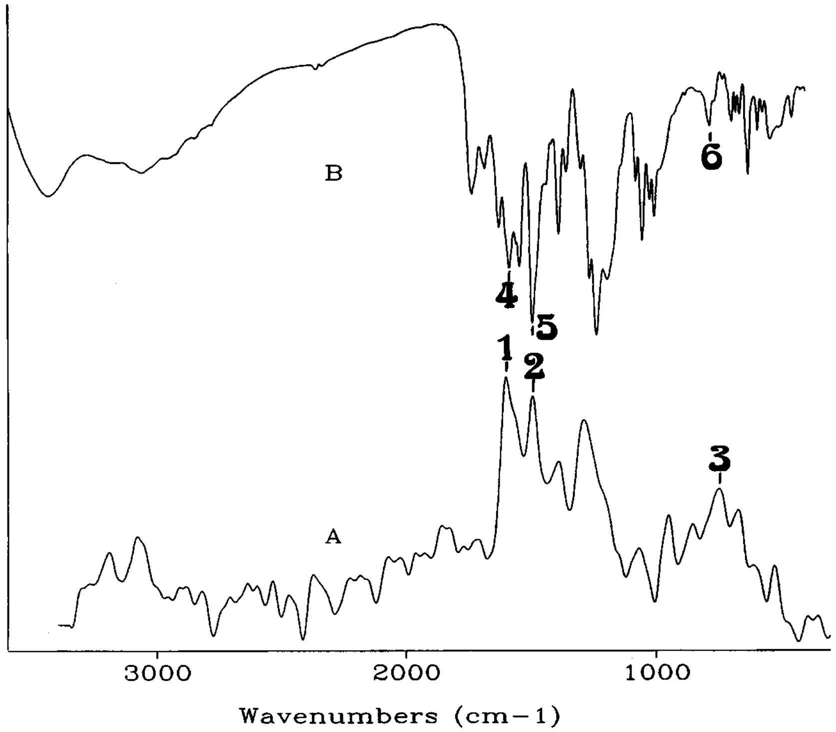


Figure 4 FTIR and Raman spectra of C.I. Reactive Red 8. A: FT Raman spectrum [peak 1: 1593 cm^{-1}, peak 2: 1492 cm^{-1}, peak 3: 747 cm^{-1}]; B: FTIR spectrum [peak 4: 1585 cm^{-1}, peak 5: 1493 cm^{-1}, peak 6: 783 cm^{-1}].

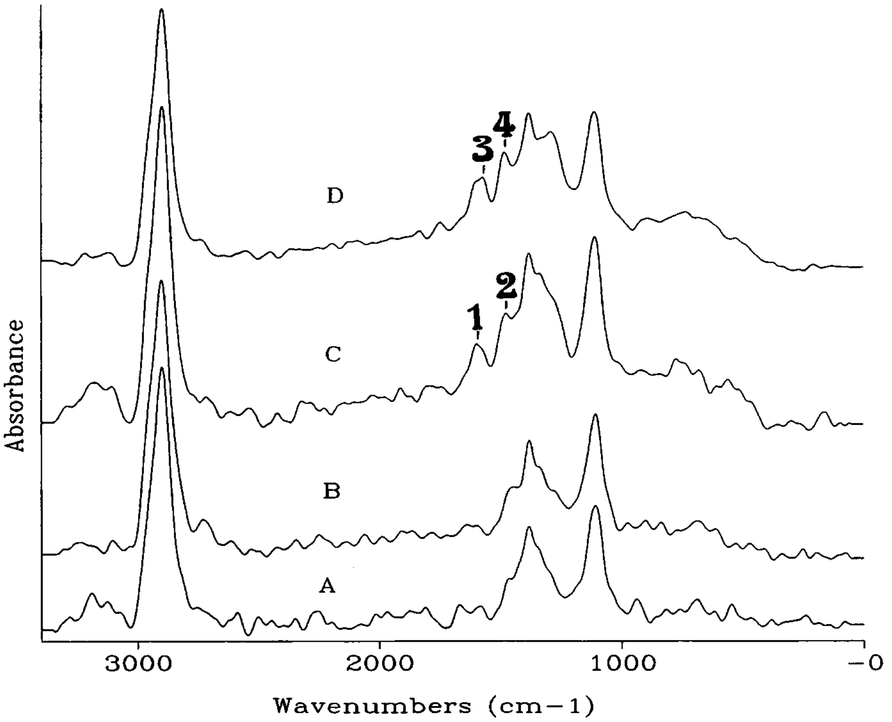


Figure 5 FT Raman spectra of various cotton samples. A: untreated cotton; B: BTCA-finished cotton; C: dyed cotton with C.I. Reactive Red 8 [peak 1: 1589 cm^{-1}, peak 2: 1474 cm^{-1}]; D: dyed and finished cotton by the SDF process [peak 3: 1579 cm^{-1}, peak 4: 1479 cm^{-1}].

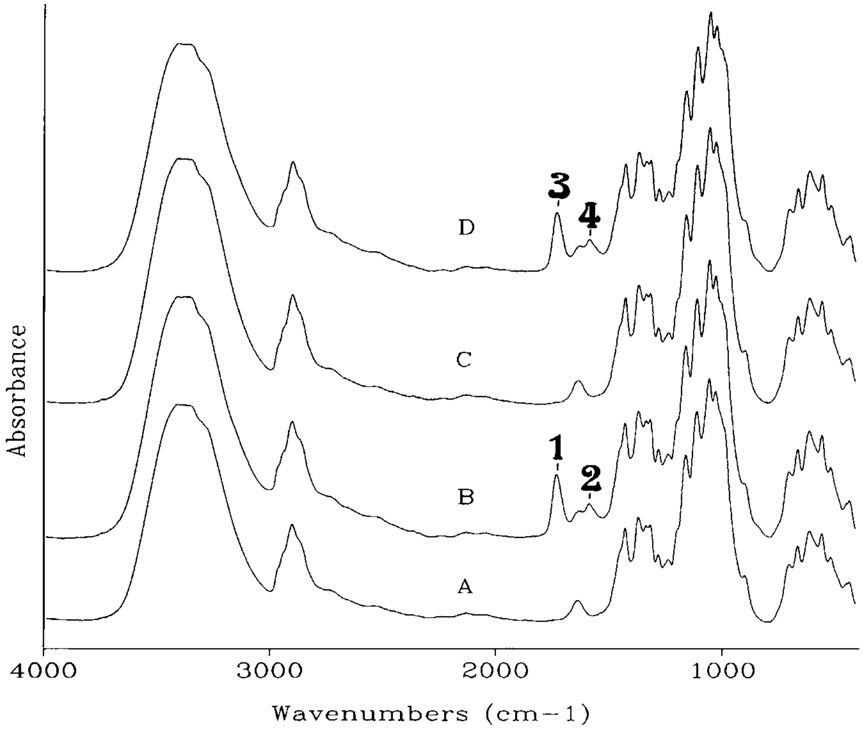


Figure 6 FTIR spectra of various cotton samples. A: untreated cotton; B: BTCA-finished cotton [peak 1: 1732 cm^{-1}, peak 2: 1587 cm^{-1}; C: dyed cotton with C.I. Reactive Red 8; D: dyed and finished cotton by the SDF process [peak 3: 1732 cm^{-1}, peak 4: 1587 cm^{-1}].

trated below, was analyzed by FT Raman spectroscopy, characteristic peaks are shown at 1593 cm^{-1} for —C=C—, 1492 cm^{-1} for —C=N— in *s*-triazinyl ring, and 747 cm^{-1} for —C—Cl (Fig. 4A). When the same dyestuff was analyzed by FTIR, similar results were obtained and peaks were shown at 1585 cm^{-1}, 1493 cm^{-1}, and 783 cm^{-1} for —C=C—, —C=N—, and —C—Cl, respectively (Fig. 4B).

Three cotton samples were finished by BTCA, dyed by C.I. Reactive Red 8, and finished and dyed. Their spectra, along with those of untreated control fabric are shown in Figure 5 for Raman and Figure 6 for FTIR spectroscopies. Once the BTCA-finished cotton was analyzed by Raman spectroscopy, no characteristic carbonyl peak for ester and free carboxyl groups was observed in the spectrum (Fig. 5B). On the other hand, in the Raman spectrum of the dyed fabric the peak was exhibited at 1589 cm^{-1} (peak 1), probably due to —C=C— group of aromatic ring structures in the reactive dye molecule, as shown in Figure 5C. The same peak was shifted to a slightly lower wave number (1579 cm^{-1}) in the case of BTCA-finished and dyed fabric (Fig. 5D). In addition, the dyed sample (Fig. 5C) and the finished and dyed sample (Fig. 5D) exhibited 1474 cm^{-1} and 1479 cm^{-1}, respectively, for —C=N— groups in the s-triazinyl ring structure, indicating the presence of dyes. The peak at 747 cm^{-1} for —C—Cl which was shown in the pure dye disappeared in both the dyed fabric and the finished and dyed fabric. This suggested that the reaction could have occurred through the s-triazinyl group, as proposed above.

Contrarily, in FTIR spectra both the finished (Fig. 6B) and the finished and dyed (Fig. 6D) samples show strong carbonyl peaks at 1732 cm^{-1} for ester/carboxylic acid and 1587 cm^{-1} for carboxylate group in BTCA (Fig. 6). Further analyses were carried out with these two spectra (Figs. 6B and 6D) by normalizing with the spectrum of the untreated sample (Fig. 6A); the results are shown in Figure 7. The only difference between the two spectra was observed at 1485 cm^{-1} due to the —C=N— group in the *s*-triazinyl ring structure. This indicated the presence of dye molecules in the dyed and finished sample, but did not tell whether the reaction had occurred in the *s*-triazinyl ring structure.

Results illustrated in Figure 7 show that there was considerable difference between two differential spectra in Figure 7A [the spectrum of the dyed sample (6C)—the spectrum of the untreated cotton (6A)] and Figure 7B [{the spectrum of the dyed and fin-

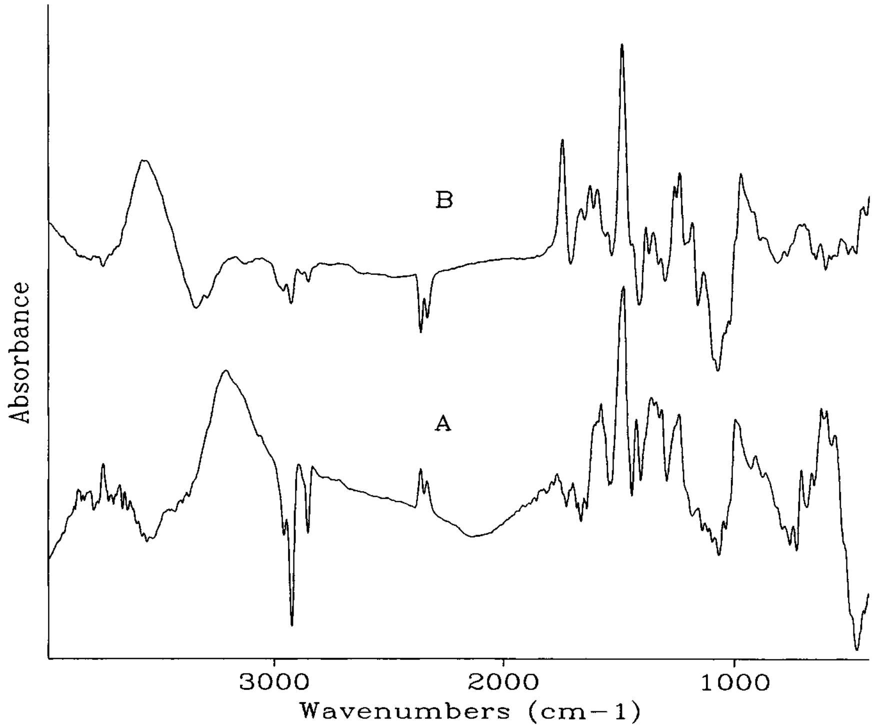


Figure 7 Differential FTIR spectra of cotton samples. A: dyed cotton with C.I. Reactive Red 8 (6C)—untreated cotton (6A); B: {dyed and finished cotton by the SDF process (6D)—untreated cotton (6A)}—{BTCA-finished cotton (6B)—untreated cotton (6A)}.

ished sample (6D)—6A}—{the spectrum of the BTCA-finished sample (6B)—6A}]. This difference suggested that the reaction mechanisms of dye fixation between the sample dyed by a conventional batch dyeing process and the sample dyed by the SDF process could be different.

Elemental analyses were also carried out to determine whether the fabrics had any chlorine content after the treatment. It was found that all three samples (the fabrics finished by BTCA and imidazole, dyed by C.I. Reactive Red 8, and finished and dyed by the SDF process) contained less than 0.5% of total chlorine. Due to the limitations of the experiment, we were not able to distinguish total chlorine below this level.

Table VII X-ray Fluorescence Spectroscopic Analyses of Cotton

Sample	Chlorine level
Untreated control	23.34 ppm
BTCA-finished	47.34 ppm
Dyed by C.I. Reactive Red 8	144.85 ppm
Dyed and finished by the SDF process	38.54 ppm
C.I. Reactive Red 8	7.78%

X-ray fluorescence spectroscopy was also used to confirm the presence of residual chlorine. As shown in Table VII, untreated control, BTCA-finished, and dyed and finished samples contained extremely low levels of chlorine. The sample dyed by C.I. Reactive Red 8 showed a slightly higher level of chlorine sample than that of the sample dyed and finished by the SDF process. This confirmed the previous hypothesis that the fixation of dyes within the SDF technique had occurred through *s*-triazinyl ring structures.

CONCLUSIONS

To solve dyeing problems commonly encountered with cotton crosslinked with polycarboxylic acid such as BTCA, we examined a single-step dyeing and finishing (SDF) process. The fabric was impregnated by a bath containing a crosslinking agent (BTCA), dye, and catalyst; dried; and then cured at 180°C or above for 2 min. Use of other dyes such as direct, acid, and disperse dyes was feasible, but excellent color strength and dye fixation were obtained, especially with various reactive dyes. The advantage of the SDF process over the sample finished and dyed in two separate steps was clearly demonstrated. In some cases, the SDF process resulted in higher color strength and dye fixation values than those of the dyed sample that had not been finished.

Mercerization of the cotton increased color strength of the sample dyed with reactive dyes in the SDF process. NaOH concentration also affected the color strength of the SDF-treated sample, resulting in greater color strength with 20% NaOH-treated samples. However, the same treatment was generally detrimental to the percent fixation of dyes, probably due to easy absorption and desorption of dyes.

Increased concentrations of bath additives such as triethanolamine (TEA) and polyethyleneglycol (PEG) considerably decreased color strength and dye fixation values, due to the competing reactions. The effect of TEA was more substantial in decreasing color strength and dye fixation compared with those of PEG, presumably due to greater effects on bath pH.

The mechanism of dye fixation in cotton was investigated by treating the fabrics with different sets of components. In the absence of BTCA or imidazole (or other esterification catalysts such as 2-methylimidazole or sodium hypophosphite), the color strength and dye fixation were remarkably low, indicating an absence of dye reaction in such a system. This substantiated the fact that there was a synergistic effect between dye molecule, BTCA, and imidazole.

Instrumental analyses by FTIR and Raman spectroscopies indicated that the reaction between BTCA and dye molecule had occurred in the *s*-triazinyl ring structures, presumably by the formation of hydroxy-substituted triazinyl dye and acid chloride. This reaction consequently enhanced the reactivity of dyes towards BTCA. Elemental analysis and X-ray fluorescence spectroscopy revealing the absence of chlorine in the fabric treated by the SDF process also substantiated the mechanism.

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