Possibilities of Polymer-Aided Dyeing of Cotton Fabric with Reactive Dyes at Neutral pH

B. J. Agarwal, S. D. Bhattacharya

Department of Textile Chemistry, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara 390 001, Gujarat, India

ABSTRACT: Water-soluble polymers have versatile application, viz., water-soluble polyacrylates have been widely used in the reactive dyeing of cellulosic fibers and the related soaping as an important component of the leveling and washing agent. In this article, one such water-soluble polymer, polyacrylic acid has been synthesized, characterized, and applied in conjunction with various types of reactive dyes, namely triazinyl, vinyl sulfone, high exhaustion, and bifunctional reactive dyes, along with crosslinking agents, namely glycerol 1,3-dichlorohydrin and hexamethylene tetramine-hydroquinone, respectively. One of the crosslinking agents (the former one) has been synthesized in the laboratory. Crosslinking agent is necessary to adhere the dye molecule onto the cellulose macromolecule. Different process sequences have been formulated and explored for dyeing purpose. All such dyeings were carried out at neutral pH. The dyed samples were assessed through color strength in terms of K/S values and their fastness properties were assessed by standard methods. All such dyeings were compared with conventional dyed samples. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1257–1269, 2010

Key words: dyes/pigments; water-soluble polymer; crosslinking; modification; reactive processing

INTRODUCTION

For the dyeing of cotton substrates, the most widely used dyes are reactive dyes because of their acceptable price, brilliancy of shades, good tinctorial value, reasonably good fastness properties, etc. Cotton fabric dyed with reactive dyes suffers from several drawbacks—one of which is environmental hazards due to the utilization of very high concentrations of exhausting agent, viz., sodium chloride or sodium sulfate (up to 100 gpl) as well as alkali (up to 20 gpl) in its dyeing process. Together with this, commercial reactive dyes give only 65–70% exhaustion of the dyebath liquor. Removal of the unfixed dye from the substrate is time-consuming, energy intensive, and requires expensive washing-off procedures.

Unfixed reactive dye and/or hydrolyzed dye along with alkali used for fixation may also pose an environmental hazard because the hydrolyzed dye will pass in the effluent thereby increasing the pollution load. Certain reactive dyes, like mono- and dichlorotriazine, or flourotriazine type of reactive dyes may cause the passage of organo-halogen in the discharge effluent, which may by-pass the permissible discharge limit fixed by certain countries.

The achievement of high-dye fixation in a nonpolluting dyeing procedure would be of great benefit. This can be attained either by the modification of the dyeing procedure or the substrate itself, or by the development of dyes with high fixation yields.

Treatment of cotton with various chemicals prior to its dyeing has been reported in literature to improve its dyeability with reactive dyes.[1–4] Dyeing of such pretreated fabric was followed by treatment with an alkali for the fixation of these dyes. Other approaches have been reported[5–11] where some chemicals have been devised, namely Glytac A, etc., for improving the dyeability of cotton with reactive dyes, which is due to increased dyebath exhaustion. In all these cases, alkaline conditions have been used for dyeing. In spite of extensive search, very little information has been received for dyeing cotton with reactive dyes at neutral pH. Burkinshaw et al.[12,13] recently reported a method of dyeing cotton using Hercosett resin pretreatments, thereby improving the substantivity and reactivity of cotton. This facilitates dyeing process at neutral pH but lowers the light fastness. Thus, it would be a great achievement if reactive dyes can be applied to cotton without utilization of any alkali or salt in the dyebath. In this article, an attempt has been made to study the modification of cotton material to perform reactive dyeing even at neutral pH conditions, i.e., without utilizing salt, alkali, or any other chemical in the dyebath. For this purpose, a pretreatment with a highly reactive water-soluble polymer has been suggested. One

such polymer is polyacrylic acid (PAA), whose polyanion, polyacrylate (PAC) is one of the most commonly used polyelectrolyte on industrial scale.[14] Poly(acrylic acid) as well as PAC are nontoxic and environmentally benign, but are not biodegradable. Water interacts strongly with such polyanions, such as PAC, via hydrogen bonding to the anionic groups aiding in the dissolution of the polymer.[15] On neutralization with a suitable base, the carboxylate group ionizes, and mutual ionic repulsion between these groups causes the molecule to adopt a greatly expanded configuration.[16,17] PAC can be crosslinked by using a multifunctional vinyl monomer. Many crosslinking agents, such as trimethylolpropanetriacrylate, etc., are used in commercial processes and have also been reported in the literature.[18]

MATERIALS AND EXPERIMENTAL PROCEDURES

Materials

Cotton fabric (poplin, 78 g/m^2) with 54 ends/inch and 44 picks/inch was used for this study. The fabric was scoured with 5 gpl nonionic detergent (Lissapol N) and 5 gpl soda ash at boil for 90 min. After proper washing, the scoured fabric was then bleached with sodium hypochlorite (5 gpl of available chlorine) using pH 10 at room temperature for 1 h and subsequently washed thoroughly till it became neutral.

Acrylic acid monomer (A.R. grade) was used for the present investigation. Two crosslinking agents, namely glycerol 1,3-dichlorohydrin (C_A) and hexamethylene tetramine-hydroquinone (HMTA-HQ) (C_B) utilized were based on non-nitrogenous and nitrogenous type products, respectively. The former crosslinking agent, glycerol 1,3-dichlorohydrin has been synthesized in the laboratory. For the synthesis, epichlorohydrin (mol. wt. 92.53 and purity 98%) and other chemicals used were of laboratory grade. The second crosslinking agent, i.e., HMTA-HQ used was of analytical reagent grade and was procured from the market. Various commercial reactive dyes used for the work are represented in Table I.

Experimental methods

Polymer preparation

PAA was synthesized from its monomer acrylic acid by standard polymerization process.[19] The polymer thus formed was with viscosity average molecular weight of 3,416 (intrinsic viscosity, η = 0.712) and 16.29% solid content.

Preparation of glycerol 1,3-dichlorohydrin

Glycerol 1,3-dichlorohydrin was prepared by interaction of epichlorohydrin and hydrochloric acid. Epi-

TABLE I
Various Reactive Dyes Used

Dye	CI reactive
Dichlorotriazine (DCT) dye	
Procion Brilliant Red M5B (D I)	Red 2
Monochlorotriazine (MCT) dye	
Procion Brilliant Red H7B (D II)	Red 141
Procion Brilliant Yellow H7G (D III)	–
Vinyl sulphone (VS) dye	
Remazol Brilliant Violet 5R (D IV)	Violet 5
High exhaustion (HE) reactive dye	
Procion Red HE-3B (D V)	Red 120
Bifunctional (ME) reactive dye	
Benzofix Orange ME 2RL (D VI)	–

chlorohydrin was gradually added to a mixture of one part of concentrated hydrochloric acid and three parts of 13% by weight sodium chloride solution at 30°C over a period of 2 h.[20]

Pretreatment

In the trial experimental work, cotton fabric was treated with PAA (5 gpl) and crosslinking agent (3 gpl) and then immediately padded (to minimize the reaction between PAA and the individual crosslinking agent) by 2-dip-2-nip technique (using 65% expression). After padding, the fabric was dried at an ambient temperature and cured at 150°C for 5 min. The curing conditions were so chosen as these are commercially practiced in textile mills. The pretreated sample was rinsed with water and dried. The mass add-on of the PAA-C_A treated sample was found to be 8.8% and that of PAA-C_B treated sample was 12.1%.

The concentrations of PAA and each individual crosslinking agent C_A and C_B were optimized followed by the assessment of their dyeability (K/S values) with five of six commercial reactive dyes mentioned in Table I.

The dyeing of these dyes has been performed by exhaust process (for 90 min at boil for MCT, VS, and HE dyes and at 50°C DCT and ME dyes) and pad-dry-cure (at 150°C/5 min for MCT, VS, and HE dyes and at 150°C/1 min for DCT and ME dyes) process. The pH of the dyebath was 7.0 ± 0.1 as no alkali/salt was used. After dyeing, the dyed sample was washed, soaped with a nonionic detergent, Lissapol N (2 gpl) and soda ash (1 gpl) at 60°C for 30 min using a liquor ratio of 30 : 1, followed by thorough rinsing and drying.

Dyeing procedures

After optimization, dyeing was performed with exhaust as well as pad-dry-cure methods at different depth of shades, viz., 0.5, 1, 2, 3, and 5%, respectively. Subsequently, different process sequences

have been formulated and six commercial reactive dyes containing various reactive systems were applied on pretreated samples at 2% shade. Various dyeing sequences adopted were as follows:

S I: Exhaust dyeing

Pretreated sample was dyed for 90 min at boil (for MCT, VS, and HE dyes) and at 50°C (for DCT and ME dyes).

S II: Pretreatment followed by pad-dry-cure dyeing

Pretreated sample was padded with requisite amount of dye solution using 2-dip-2-nip technique (65% expression), dried and cured.

S III: Simultaneous dyeing

Sample was padded with optimum concentration of PAA and crosslinking agent along with the reactive dye, dried and cured.

C_{ex}: Conventional exhaust dyeing

Parent (untreated) sample was dyed for 1 h using 20 gpl glauber's salt (for exhaustion) and 5 gpl soda ash (for fixation). The dyeing temperatures for individual dyes are: room temperature for DCT and ME dyes; 60°C for VS dyes; 70°C for MCT dyes; and 80°C for HE dyes.[21]

C_{pdc}: Conventional pad-dry-cure dyeing

Parent (untreated) sample was padded with requisite amount of dye solution using 2-dip-2-nip technique, dried and cured.[21] For sequences S II, S III, and C_{pdc}, the curing conditions chosen were 150°C/5 min for MCT, VS, and HE dyes and 150°C/1 min for DCT and ME dyes, while the washing and soaping procedures were kept same as mentioned earlier. Various dyeings were also compared with conventionally dyed samples.

Testing and analysis

Mechanical properties

Tensile properties, namely breaking strength and elongation at break, of the treated and untreated samples were determined on the Instron 1121 tensile tester. An average of 10 readings was taken.

Determination of nitrogen content

Nitrogen content of the treated and untreated samples was determined on C, H, and N Analyzer (Perkin Elmer Model 240 Elemental Analyzer).

Infrared analysis

The Infrared (IR) analysis of both treated and untreated cotton was carried out on IS 460 SHI-MADZU Spectrometer, using the diffuse reflectance accessory; this device collects reflected radiations that have penetrated the fabric, at the same time ignoring specular or nonabsorbed radiation. Using the computing power of the instrument, it is possible to store and subsequently substrate spectra, thus giving accurate information as to the state of chemical modification of cotton.

Evaluation of color strength

The dyeing performance of various dyed samples was assessed on Data Spectraflash SF 600 Spectrophotometer by measuring the relative color strength (K/S value) spectrophotometrically. These values are computer calculated from reflectance data according to Kubelka–Munk equation.[22]

Assessment of fastness properties[23]

Wash fastness was evaluated according to ISO Standard Test No.3 on Launder-o-meter; light fastness on Fade-o-meter using carbon-arc continuous illumination (BS 1006: 1987) and rub fastness (both dry as well as wet) on Crockmeter (BS 1006: No.X12; 1978).

Determination of wrinkle resistance

Wrinkle resistance (crease recovery) of the untreated and treated samples was measured on crease recovery tester (Model: Sasmira) using standard method.[23]

RESULTS AND DISCUSSION

Optimization of concentration of the PAA

Cotton fabric treated with PAA and individual crosslinking agent was dyed with reactive dyes (CI Reactive Red 141 and CI Reactive Red 2) without using alkali/salt, i.e., at neutral pH (7.0 ± 0.1). Uniform dyeings were obtained. Therefore, the concentrations of PAA and crosslinking agents were optimized. This was carried out by using various concentrations of PAA (5, 10, 15, 20, and 25 gpl) and crosslinking agent (3, 5, 7, 10, and 15 gpl) for both exhaust as well as pad-dry-cure dyeing methods. Optimized concentrations of these three pretreatment liquor constituents were found out individually by assessing the dyeing performance in terms of K/S values of the respective sample as mentioned in Table II. From Table II, it can be visualized that in case of Procion (chloro-s-triazinyl) dyes applied by

TABLE II
Role of Polymer Concentration on Color Strength Value of Dyed Cotton

| | K/S values for | | | | | | | | | |
| | Conc. of PAA (gpl) Conc. of C_A[a] = 5 gpl | | | | | Conc. of PAA (gpl) Conc. of C_B[b] = 5 gpl | | | | |
Dye	5	10	15	20	25	5	10	15	20	25
D I	4.26	5.06	5.36	5.21	4.89	6.24	6.95	6.92	6.83	6.80
D II	2.63	2.95	3.02	2.89	2.86	3.56	4.12	3.89	3.63	3.68
D IV	3.12	3.45	3.96	3.83	3.85	4.54	4.59	4.84	4.63	4.22
D V	9.86	9.82	9.63	9.21	9.39	10.69	10.23	10.20	10.12	9.99
D VI	6.92	6.84	6.79	6.62	6.56	7.56	7.23	7.33	7.10	6.86

Process: Pretreatment: Fabric padded with different concentrations (5–25 gpl) of PAA along with 5 gpl concentration of crosslinking agent, dried, cured, washed, and dried. Dyeing: The pretreated fabric dyed with 2% reactive dye by exhaustion process without using any auxiliary in the dye bath.
[a] C_A: Glycerol 1,3-dichlorohydrin.
[b] C_B: Hexamethylene tetramine-hydroquinone.

the exhaustion process, maximum color strength values have been obtained with 15 gpl concentration of PAA in the presence of C_A crosslinking agent and with 10 gpl concentration of PAA in the presence of C_B crosslinking agent for both cold and hot brands of Procion reactive dyes. For instance, in case of the sample pretreated with PAA and C_A combinations, the K/S values of 5.36 and 3.02 have been observed with Procion Brilliant Red M5B (DCT) and Procion Brilliant Red H7B (MCT) dyes, respectively. It may be noted that after these respective concentrations of PAA in the treatment liquor in the presence of the said crosslinking agents, the dyed samples does not show much variation in the color strength value. The vinyl sulfone reactive dye, Remazol Brilliant Violet 5R, gives optimum dyeing performance with 15 gpl concentration of PAA, irrespective of the crosslinking agents used for the purpose of optimization. However, when the bifunctional (HE and ME) brand of dyes are applied by the exhaustion process on the pretreated samples, the optimum concentration of PAA in the treatment liquor gives a comparatively better dyeing results at only 5 gpl concentration of PAA with both crosslinking agents used.

From Table II, it can be seen that the high-exhaust type of bifunctional reactive dyes, i.e., HE and ME dyes give a comparatively better dyeing performance on the pretreated samples. For both these dyes, the pretreatment procedure utilizes a comparatively lower concentration of PAA solution than chloro-s-triazinyl (MCT and DCT) and vinyl sulfone (VS) reactive dyes. The polymer concentration required for pretreatment is only 5 gpl with bifunctional reactive dyes, whereas the pretreatment liquor requires 10–15 gpl of PAA concentration with monofunctional hot brand and cold brand reactive dyes (MCT, DCT, and VS dyes) to obtain maximum color yield.

Various grades of PAA polymer, having variation in the viscosity, were prepared for the trial purpose.

The intrinsic viscosity of all these preparations of PAA was determined by the viscosity measurement method using Ostwald's Viscometer. The results are represented as follows:

PAA	Intrinsic viscosity (η)	Viscosity average molecular weight (η_{av})
Grade 1	0.589	1,680
Grade 2	0.656	2,198
Grade 3	0.712	3,416
Grade 4	0.852	5,213
Grade 5	1.219	8,456

Dyeing with reactive dyes was carried out with various grades of PAA (15 gpl) along with crosslinking agent (both separately, 5 gpl) by usual pad-dry-cure method and it was found that the color yield offered by the sample of Grade 3 (i.e., η = 0.712) was probably suitable for satisfying all necessary conditions for dyeing. Beyond this value of η, i.e., for Grades 4 and 5, the color yield was not uniform and some other practical problems, associated with agglomeration, channeling, etc., of the polymer at the elevated (i.e., curing) temperature, were also observed. This results in uneven and patchy dyeing. This is also related to the dye structure and its molecular weight. Details of this need further extensive work, which is not included in this article. Above the Grade 3, the color yield was less because of shear thinning effect of the polymer at the elevated temperature during curing, which restricted the contacts of the polymer (PAA), crosslinking agent and the reactive dye.

The optimum concentration of PAA was also determined by dyeing the pretreated samples using pad-dry-cure process. All the dyes applied by the pad-dry-cure process give the maximum color yield on those pretreated samples, which utilized the polymer concentration in the range of 10–20 gpl, as could be

TABLE III
Role of Polymer Concentration on Color Strength Value of Dyed Cotton

	K/S values for									
	Conc. of PAA (gpl) Conc. of C_A[a] = 5 gpl					Conc. of PAA (gpl) Conc. of C_B[b] = 5 gpl				
Dye	5	10	15	20	25	5	10	15	20	25
D I	9.26	9.86	9.79	9.80	9.21	10.25	10.82	10.79	10.70	10.22
D II	8.96	8.84	9.12	9.02	8.96	9.21	9.63	9.57	9.26	8.21
D IV	11.33	11.72	12.15	11.86	11.80	12.62	13.21	12.75	11.21	11.39
D V	5.32	5.46	5.89	6.36	6.33	5.86	6.26	6.95	6.75	6.68
D VI	5.11	5.28	5.30	5.86	5.80	5.23	5.95	6.35	5.75	5.08

Process: Pretreatment: Fabric padded with different concentrations (5–25 gpl) of PAA along with 5 gpl concentration of crosslinking agent, dried, cured, washed, and dried. Dyeing: The pretreated fabric padded with 20 gpl reactive dye liquor, dried, and cured.
[a] C_A: Glycerol 1,3-dichlorohydrin.
[b] C_B: Hexamethylene tetramine-hydroquinone.

visualized from Table III. The cold brand dichloro triazinyl reactive dye, Procion Brilliant Red M5B, gives maximum color on the sample, which has been pretreated with 10 gpl PAA, irrespective of the crosslinking agent used in the pretreatment bath. On the other hand, the hot brand monochloro triazinyl (Procion Brilliant Red H7B) as well as vinyl sulfone (Remazol Brilliant Violet 5R) reactive dyes show higher K/S values for the samples, which are pretreated with 15 gpl PAA for C_A crosslinking agent and with 10 gpl PAA for C_B crosslinking agent during pretreatment.

On the other hand, in case of bifunctional dyes, HE (Procion Red HE-3B) and ME (Benzafix Orange ME 2RL), the concentration of PAA utilized in the pretreatment bath was slightly higher (15 and 20 gpl), as indicated in the table. This is obvious because these dyes are particularly suitable for exhaustion process and are seldom applied by the pad-dry-cure process in the industry. This may be the probable reason for such behavior in the dyeing of these dyes on the pretreated sample.

From the above two tables, it may be postulated that the amount of polymer required in the pretreatment liquor is comparatively less when the subsequent dyeing has been done by the exhaustion method (5–15 gpl) rather than the pad-dry-cure method (15–20 gpl). This may be due to the longer dyeing time in the exhaustion process, whereby even the lower concentration of the fixed polymer assists the fixation of the reactive dye during the neutral dyeing process.

Optimization of concentration of the crosslinking agent

In the secondary part of the optimization study, the concentration of the crosslinking agents (C_A and C_B) is being optimized by keeping the polymer concentration constant (as optimized for each individual crosslinking agent and the reactive dye in the previous section) in the pretreatment liquor.

The color strength (K/S) value of the samples dyed by exhaustion process on the samples pretreated with optimum concentration of PAA and varying concentration of crosslinking agents is given in Table IV. When pretreatment is followed by dyeing using exhaustion method, it can be observed that with all

TABLE IV
Role of Crosslinking Agent Concentration on Color Strength Value of Dyed Cotton

	K/S values for									
	Conc. of C_A[a] (gpl) PAA conc. = Optimum (gpl)					Conc. of C_B[b] (gpl) PAA conc. = Optimum (gpl)				
Dye	3	5	7	10	15	3	5	7	10	15
D I	3.86	4.21	3.72	3.65	3.60	5.16	5.26	5.20	5.03	4.98
D II	2.89	3.12	2.65	2.31	2.30	3.15	3.86	3.80	3.75	3.28
D IV	3.86	3.96	4.06	3.85	3.80	4.21	4.81	4.65	4.28	4.30
D V	9.98	10.06	9.56	9.23	9.63	11.63	1126	11.15	11.20	11.23
D VI	5.98	6.15	6.05	5.86	5.73	7.23	7.02	6.98	6.89	6.83

Process: Pretreatment: Fabric padded with different concentrations (5–25 gpl) of PAA along with 5 gpl concentration of crosslinking agent, dried, cured, washed, and dried. Dyeing: The pretreated fabric dyed with 2% reactive dye by exhaustion process without using any auxiliary in the dye bath.
[a] C_A: Glycerol 1,3-dichlorohydrin.
[b] C_B: Hexamethylene tetramine-hydroquinone.

TABLE V
Role of Crosslinking Agent Concentration on Color Strength Value of Dyed Cotton

	K/S values for									
	Conc. of C_A[a] (gpl) PAA conc. = Optimum (gpl)					Conc. of C_B[b] (gpl) PAA conc. = Optimum (gpl)				
Dye	3	5	7	10	15	3	5	7	10	15
D I	7.86	8.56	8.23	8.01	8.10	10.54	10.21	9.85	9.72	9.11
D II	6.73	7.12	7.89	7.66	7.54	9.64	9.52	9.19	8.76	8.95
D IV	9.28	9.22	9.15	8.92	8.86	11.98	11.63	11.26	10.54	10.12
D V	5.12	5.23	4.86	4.80	4.35	6.74	6.26	6.11	5.86	5.45
D VI	4.26	4.86	4.32	4.30	4.11	5.64	5.23	5.02	4.79	4.23

Process: Pretreatment: Fabric padded with different concentrations (5–25 gpl) of PAA along with 5 gpl concentration of crosslinking agent, dried, cured, washed, and dried. Dyeing: The pretreated fabric padded with 20 gpl reactive dye liquor, dried, and cured.
[a] C_A: Glycerol 1,3-dichlorohydrin.
[b] C_B: Hexamethylene tetramine-hydroquinone.

the three monofunctional dyes used for the study, the color strength value does not change much beyond 5 gpl concentration (with one exception) with both the crosslinking agents used. Thus, for all practical purposes, the 5 gpl concentration of C_A and C_B crosslinking agents has been considered to be optimum for the pretreatment. However, for the bifunctional reactive dyes of HE and ME types, it has been found that both the dyes give the optimum concentration of the crosslinking agent as 3 gpl except for one combination, where HE brand of dye correspondingly gives a slightly better color strength (K/S), viz., 10.06 for the samples pretreated with PAA in the presence of C_A crosslinking agent for 5 gpl concentration. The respective values for 3 gpl concentration of this agent are found to be 9.98. Thus, although the optimum concentration of C_A agent is found to be 5 gpl, but as the difference in the color strength values between 3 and 5 gpl concentrations of these crosslinking agents, for this particular dye, is only 0.79%, so here also for all practical purposes as well as from economical aspects, the 3 gpl concentration of the C_A agent is considered as optimum for the further part of the study.

Similarly, the pad-dry-cure process has also been used for dyeing the pretreated samples, where the optimum concentration of PAA is utilized as determined in the earlier part of this study (from the Table II) and the concentration of crosslinking agents, C_A and C_B are being varied. The color strength (K/S) values of the dyed samples are mentioned in Table V. The C_A crosslinking agent did not follow any usual trend with various reactive dyes. With MCT reactive dye, its concentration rises up to 7 gpl to give maximum color strength (7.89), whereas for DCT as well as HE and ME dyes, 5 gpl of this crosslinking agent is used in this bath. The K/S values, corresponding for optimum concentration of C_A agent, are 8.56 for DCT reactive dye and 5.23 and 4.86 for HE and ME type of reactive dyes, respec-

tively. For VS (Remazol) dye, its concentration utilized in the treatment bath is only 3 gpl corresponding to maximum color yield (9.28), but as such there is not much variation for higher concentration of C_A. The K/S values are 9.22 and 9.15, respectively, at 3 gpl and 7 gpl concentrations of C_A agent.

The C_B type of crosslinking agent has given better performance between the two crosslinkers used for the present study. Only 3 gpl concentration of this particular agent is used to give maximum color strength value, irrespective of the dye used for the application. For instance, the K/S value for DCT and VS reactive dyes are 10.54 and 11.98, respectively, at 3 gpl concentration of C_B agent. Further increase in the concentration of this agent decreases the color strength value.

During the pretreatment of cotton material with various concentrations of polymer and crosslinking agents, it has been observed that there is no yellowing of the fabric due to such pretreatment. Thus, the partial crosslinking of PAA with cellulose substrate, in presence of crosslinking agent does not hamper the whiteness of the fabric even at higher temperature during the curing stage.

The feel of the fabric is also not affected even at higher concentrations of PAA and crosslinking agents. The fabric surface remains smooth and soft after the treatment and even before washing. After washing and soaping procedures, the fabric surface becomes much smoother than even the original (untreated) cotton substrate. Thus, the pretreatment imparts softness and suppleness to the cotton substrates, which may be considered as an additional benefit of such treatment in the neutral dyeing of reactive dyes.
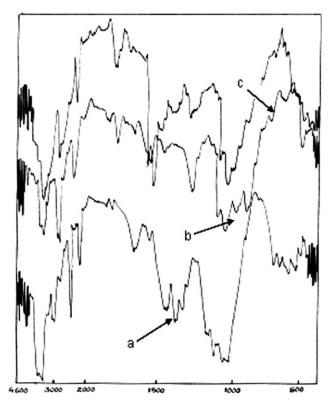
The notable changes incurred in the cellulosic substrate due to such treatment were investigated through nitrogen content determination and tensile properties of the pretreated sample.

The nitrogen content value of only PAA treated (15 gpl/pad-dry-cure process) sample was 0.185% and those treated along with crosslinking agent C_A or C_B (50

gpl) sample were 0.238 and 0.886%, respectively. This higher value of nitrogen content, particularly in case of PAA and crosslinking agent C_B treated sample manifests the possibility of crosslinking reaction being taken place with the cellulose substrate.

The solution study of the PAA solution in the presence of individual crosslinking agent and the reactive dye (DCT) solution has been visualized. For this purpose, 0.01% solution of the reactive dye was prepared with optimum concentrations of PAA and C_A/C_B agent and the resulting solution was cured at 150°C for 1 min, as well as after varying intervals of time, viz., immediately (5 min), 3, 6, 24, 48, 72 h, etc. The reflectance values of these solutions were determined using UV-spectrophotometer (λ_{max}, 660 nm) and the values were compared with uncured sample for the same period of time. It has been observed that the admixture of PAA, C_A and the DCT reactive dye was much more stable compared with the admixture of PAA, C_B and the DCT reactive dye. The solution of PAA, C_B and the reactive dye became pale after 48 h. This may be due to the greater crosslinking capability of C_B agent, which may have lead to the discoloration of the dye solution in its presence. On the other hand, the prepared admixture of PAA, C_A and the DCT reactive dye shows stability up to 96 h, after which the depth of the color of the solution became lighter gradually. After 120 h, the solution became completely colorless. This observation significantly shows that the amino groups present in the HMTA-HQ (C_B) crosslinking agent might have destroyed the chromophoric group present in the reactive dye during storage and subsequent curing.

The sample pretreated with PAA and crosslinking agent C_A (at optimized concentration) showed 11.3 kg breaking strength and 12.5% elongation at break. The respective values for PAA and crosslinking agent C_B treated sample (at optimized concentration) are 10.2 kg and 11.8% when compared with 12.25 kg and 11.5% breaking strength and elongation at break, respectively, for untreated sample. The decrease in breaking strength, viz., 10.3% (in case of crosslinking agent C_A) and 16.8% (in case of crosslinking agent C_B) is also an indicative of crosslinking reaction being taking place.

Infrared analysis of the treated and untreated cotton has been performed on IR 460 Shimadzu Spectrometer using diffuse reflectance accessory and their respective spectra are demonstrated in Figure 1. Various absorption bands occur at $\sim$ 3300–3400 cm^{-1}, 1640–1660 cm^{-1}, 1420 cm^{-1}, 1380 cm^{-1}, 1000–1210 cm^{-1}, 620–680 cm^{-1}, and 540 cm^{-1} corresponding to hydrogen bonded —OH stretching vibrations, —CH stretching vibrations, absorbed water vibrations, —C—O symmetric stretching, CH bending, asymmetric bridge —C—O—C stretching, OH out of the plane bending, respectively. Samples treated with PAA and HMTA-HQ (C_B) gives an absorption bands at 3370–3390 cm^{-1} corresponding to —NH stretching and a strong absorption band at 1510–1550

Figure 1 Infrared spectra of (a) untreated cotton fabric, (b) cotton fabric treated with PAA and C_A (glycerol 1,3-dichlorohydrin), and (c) cotton fabric treated with PAA and C_B (hexamethylene tetramine-hydroquinone).

cm^{-1}, which is responsible for N—H stretching due to C_B crosslinking agent. One of the common observation with the IR spectra of all the treated sample is the strong IR absorption band at 1720–1750 cm^{-1}, corresponding to the carbonyl stretching absorption and is responsible for C=O stretching due to the carboxylic group present in the PAA polymer. This common feature, observed for the pretreated samples, manifests the crosslinking of the PAA polymer with the cotton substrate in the presence of C_A/C_B agents.

Dyeing performance of various crosslinking agents at different concentrations of reactive dye in bath

The optimized concentrations of PAA and the two crosslinking agent have been used to study their various dyeing behavior at neutral pH. It has been observed that pretreated fabric offered very good dyeing with pad-dry-cure dyeing technique when compared with exhaust dyeing. Therefore, cotton fabric was subsequently dyed by these two dyeing processes at different depth of shades with five reactive dyes, one each of MCT, DCT, VS, HE, and ME brand of dyes. The results are represented in Tables VI and VII. It can be seen that satisfactory dyeing is achieved on pretreated samples at all levels of dyeing. The dye uptake increases with the increase in

TABLE VI
Color Strength (in Terms of K/S) Values for Cotton Fabric Dyed with Different Percent Shades Using Reactive Dyes by Exhaustion Dyeing Process

| Dye | Conc. of the dye (%) | K/S values for | | |
		A	B	C
D I	0.5	2.39	1.62 (−32.21)	2.02 (−15.48)
Procion	1.0	4.28	2.98 (−30.37)	3.68 (−14.01)
Brilliant	2.0	6.92	5.28 (−23.69)	6.89 (−0.43)
Red M5B	3.0	8.56	6.86 (−19.86)	7.98 (−6.77)
(DCT)	5.0	10.98	7.69 (−29.96)	10.32 (−6.01)
D III	0.5	1.14	0.96 (−15.78)	1.42 (+24.56)
Procion	1.0	2.32	1.45 (−37.50)	2.06 (−11.20)
Brilliant	2.0	4.19	2.12 (−49.40)	3.23 (−22.91)
Yellow	3.0	6.28	4.02 (−35.98)	5.23 (−16.72)
H7G				
(MCT)	5.0	8.56	7.23 (−15.53)	8.21 (−4.08)
D IV	0.5	2.86	1.84 (−35.66)	2.45 (−14.33)
Remazol	1.0	4.65	2.96 (−36.34)	3.64 (−21.72)
Brilliant	2.0	6.32	3.84 (−39.24)	4.80 (−24.05)
Violet 5R	3.0	8.48	5.44 (−36.29)	7.59 (−10.49)
(VS)	5.0	11.63	9.98 (−14.18)	11.59 (−0.34)
D V	0.5	5.86	4.02 (−31.39)	5.45 (−6.99)
Procion	1.0	7.95	6.24 (−21.51)	7.41 (−6.79)
Red	2.0	11.26	9.79 (−13.05)	10.63 (−5.59)
HE−3B	3.0	15.93	12.63 (−21.71)	14.98 (−5.96)
(HE)	5.0	20.08	17.26 (−14.04)	19.93 (−0.74)
D VI	0.5	3.11	1.98 (−36.33)	2.88 (−7.39)
Benzafix	1.0	5.26	3.86 (−26.61)	4.95 (−5.89)
Orange	2.0	8.29	6.25 (−24.60)	7.63 (−7.96)
ME 2RL	3.0	11.62	9.88 (−14.97)	11.45 (−1.46)
(ME)	5.0	16.29	11.45 (−18.90)	15.59 (−2.08)

The values in parentheses indicate percentage loss in color strength with respect to conventional dyeing. A: Conventional exhaust dyeing at boil for 90 min using 20 gpl Glauber's salt and 5 gpl soda ash in the dye bath. B: Samples pretreated with optimum concentration of PAA and C_A and subsequently dyed under neutral pH at boil for 90 min. C: Samples pretreated with optimum concentration of PAA and C_B and subsequently dyed under neutral pH at boil for 90 min.
C_A: Glycerol 1,3-dichlorohydrin.
C_B: Hexamethylene tetramine-hydroquinone.

the concentration of the dye in the dyebath. HE and ME brand of dyes performed well for the exhaustion process, whereas VS-based dye gave best dyeing performance with pad-dry-cure dyeing process. This is in good agreement with the observations reported in literature.[23]

Possibilities of reaction mechanisms with polymer-aided neutral dyeing of reactive dyes

PAA is a highly reactive water-soluble polymer, which is synthesized by the polymerization of acrylic acid. This study deals with the possibilities of structural and chemical modification of cotton cellulose with such reactive polymer in the presence of suitable crosslinking agent of varied structure. The pretreatment has been carried out by padding the cotton fab-

ric with optimum concentrations of PAA and individual crosslinking agent, followed by drying at an ambient temperature and curing at 150°C for 5 min. This pretreatment is subsequently followed by dyeing with various classes of reactive dyes, containing different reactive groups as well as reactivity, by exhaustion and pad-dry-cure dyeing techniques. Because of such pretreatment and subsequent dyeing, various possibilities of reactions are likely to occur. These are:

- Possibility of reaction and partial crosslinking of PAA with the crosslinking agent, due to the utilization of these agents in the treatment liquors, resulting in the formation of a condensate product of PAA and the crosslinking agent.
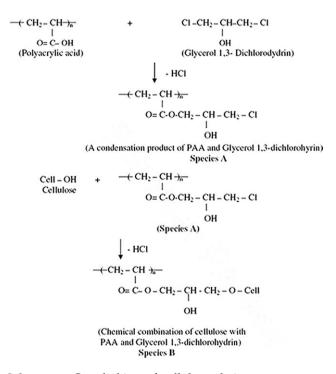- Possibility of partial crosslinking of the polymer (PAA) with cellulose in the presence of

TABLE VII
Color Strength (in Terms of K/S) Values for Cotton Fabric Dyed with Different Percent Shades Using Reactive Dyes by Pad-Dry-Cure Dyeing Process

| Dye | Conc. of the dye (%) | K/S values for | | |
		A	B	C
D I	5	7.20	4.12 (−42.77)	5.32 (−26.11)
Procion	10	9.25	5.95 (−35.67)	6.86 (−25.83)
Brilliant	20	14.32	9.75 (−31.91)	10.64 (−25.69)
Red M5B	30	21.15	17.98 (−14.98)	20.26 (−4.21)
(DCT)	50	28.32	23.35 (−17.59)	26.95 (−4.83)
D III	5	3.86	2.84 (−26.42)	3.45 (−10.62)
Procion	10	5.61	4.12 (−26.56)	5.21 (−7.13)
Brilliant	20	7.22	5.42 (−24.93)	7.18 (−0.55)
Yellow	30	9.89	8.22 (−16.88)	9.48 (−4.14)
H7G				
(MCT)	50	12.12	9.89 (−18.39)	11.65 (−3.87)
D IV	5	6.11	4.29 (−29.78)	5.88 (−3.76)
Remazol	10	9.52	7.58 (−20.37)	8.49 (−10.82)
Brilliant	20	12.25	11.54 (−5.79)	12.32 (+0.57)
Violet 5R	30	15.56	14.23 (−8.54)	15.65 (+0.57)
(VS)	50	20.63	18.45 (−10.56)	20.11 (−2.52)
D V	5	3.86	2.44 (−36.78)	3.45 (−10.62)
Procion	10	5.19	3.98 (−23.31)	5.11 (−1.54)
Red	20	7.62	6.01 (−21.41)	6.86 (−9.97)
HE-3B	30	9.15	8.06 (−11.91)	9.11 (−0.43)
(HE)	50	12.25	10.49 (−14.36)	11.98 (−2.20)
D VI	5	2.95	1.96 (−33.55)	2.88 (−2.37)
Benzafix	10	4.86	3.48 (−28.39)	4.63 (−4.73)
Orange	20	6.65	5.88 (−11.57)	6.15 (−7.52)
ME 2RL	30	8.32	7.11 (−14.54)	8.02 (−3.60)
(ME)	50	12.15	11.66 (−4.03)	11.98 (−1.39)

The values in parentheses indicate percentage gain/loss in color strength with respect to conventional dyeing. A: Conventional pad-dry-cure dyeing process using 20 gpl soda ash in each bath. Curing done at 150°C for 5 min. B: Samples pretreated with optimum concentration of PAA and C_A and subsequently dyed by pad-dry-cure process under neutral conditions. C: Samples pretreated with optimum concentration of PAA and C_B and subsequently dyed by pad-dry-cure process under neutral conditions.
C_A: Glycerol 1,3-dichlorohydrin.
C_B: Hexamethylene tetramine-hydroquinone.

Scheme 1 Crosslinking of cellulose chains on treatment with PAA–glycerol 1,3-dichlorohydrin condensate product.

crosslinking agent, during the curing stage of pretreatment, leading to the structural and chemical modification of cotton.

- Possibility of further combination of the chemically modified cellulose with the reactive group of the reactive dyes, thereby forming a covalent bond between the dye and the modified cotton substrate and facilitating the fixation of the dye on the fiber.

The reaction mechanism will specify the manner in which cellulose combines with PAA along with crosslinking agent and signifies the possibility of further dyeing with the reactive dyes. The suggested dyeing schemes illustrate the manner in which the covalent bond formation takes place between reactive dye and the modified cotton substrate. The crosslinking agents of varied nature and structure have been selected so as to have a better understanding of the reaction mechanism.

Since five of the six dyes used for this work contain at least one chloro-s-triazine group in their molecular structure, the dyeing scheme has been illustrated with the help of monochlorotriazine (MCT) dye. For vinyl sulfone type of reactive dye, a similar type of addition reaction mechanism can be utilized for the formation of covalent bond between the dye and the fiber. For MCT type of reactive dyes, formation of covalent bond via substitution reaction mechanism has been explained in the following reaction schemes.

Polymer-aided neutral dyeing of modified cotton with PAA and glycerol 1,3-dichlorohydrin

Pretreatment mechanism

The interaction of PAA with the crosslinking agent, glycerol 1,3-dichlorohydrin liberates hydrochloric acid during the curing stage. The condensation product thus produced gets attached with the cellulose molecule with further liberation of hydrochloric acid. The crosslinking agent subsequently helps to bring about partial crosslinking of cellulose with PAA. The reactions occurring during the curing stage may be represented as shown in Scheme 1.
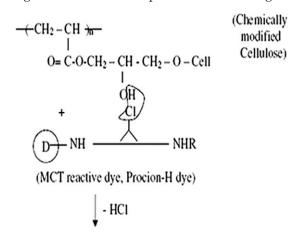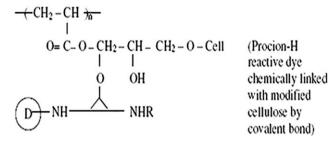
Dyeing mechanism

The above chemically modified cellulosic material contains a free hydroxyl group, which can substitute the chlorine atom present in triazinyl dyes (MCT, DCT, HE, and ME dyes). Thus, the reactive dye can chemically combine and form a covalent bond with the chemically modified cellulosic material. The reaction taking place during dyeing of such dyes on chemically modified cellulose can be represented as shown in Scheme 2.

Polymer-aided neutral dyeing of modified cotton with PAA and HMTA-HQ
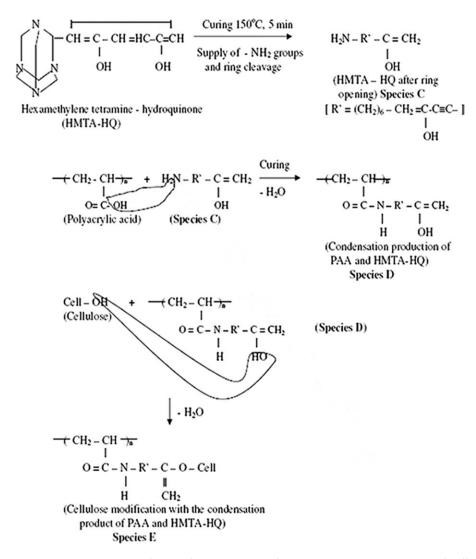
Pretreatment mechanism

During the curing condition, HMTA-HQ ring opening occurs, which provides amino groups in

Scheme 2 Covalent bond formation between MCT reactive dye and crosslinked cellulosic product.
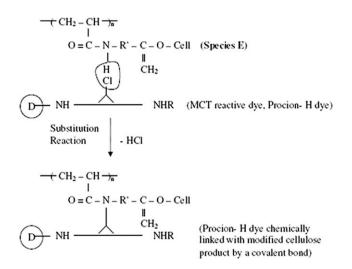
Scheme 3 Various reactions occurring during the curing stage between PAA, HMTA-HQ, and cellulose molecule.

abundance to PAA and a complex condensation product is formed with an elimination of water molecule during curing. The various reactions take place during the curing stage are mentioned in Scheme 3.

Dyeing mechanism

The presence of —NH— group in the molecular chain of the above-modified cellulose allows easy substitution of the chlorine atom from all the triazinyl based reactive dyes. The reaction mechanism of dyeing involving substitution reaction is well illustrated with a MCT type of reactive dye in Scheme 4.

It can be easily visualized through the reaction schemes that there is a possibility of covalent bond formation between the reactive dye and cotton modified chemically with PAA in the presence of several crosslinking agents. The crosslinking agents utilized for the study are capable of providing some

Scheme 4 Covalent bond formation between the MCT reactive dye and chemically modified cellulose substrate.

TABLE VIII
Color Strength (in Terms of K/S values) of the Cotton Fabric Dyed with Various Reactive Dyes for 2% Shade

	K/S values for							
	Conventional		Exhaust dyeing		Pad-dry-cure dyeing			
					PAA + C_A[a]		PAA + C_B[b]	
Dye	Exhaust dyeing	Pad-dry-cure dyeing	PAA + C_A[a]	PAA + C_B[b]	Two step	One step	Two step	One step
D I (DCT)	6.92	14.32	5.15 (−25.57)	6.90 (−0.29)	9.89 (−30.93)	11.21 (−21.71)	10.69 (−25.35)	15.96 (+11.45)
D II (MCT)	5.26	10.15	4.02 (−23.57)	4.96 (−5.70)	9.23 (−9.06)	9.72 (−4.23)	9.82 (−3.25)	10.56 (+4.04)
D III (MCT)	4.19	7.22	2.26 (−46.06)	3.28 (−21.71)	5.49 (−25.00)	6.23 (−14.89)	7.25 (−0.95)	8.29 (+13.25)
D IV (VS)	6.32	12.25	3.96 (−37.34)	4.85 (−23.26)	11.58 (−5.47)	12.02 (−1.87)	12.39 (+1.14)	12.96 (+5.79)
D V (HE)	11.26	7.62	9.82 (−12.79)	10.72 (−4.79)	6.31 (−17.73)	6.42 (−16.29)	7.21 (−5.99)	7.95 (+3.65)
D VI (ME)	8.29	6.65	6.36 (−23.28)	7.69 (−7.23)	5.95 (−22.42)	6.45 (−3.44)	6.23 (−6.73)	7.26 (+8.68)

The values in parentheses indicates percent loss in color strength with respect to conventional dyeing.
[a] C_A: Glycerol 1,3-dichlorohydrin.
[b] C_B: Hexamethylene tetramine-hydroquinone.

groups to the modified cellulosic structure, which can form a covalent bond with the reactive dye. This has been further confirmed by treating the dyed sample with pyridine (100%) as well as its mixture with water (50 : 50). Since no dye strips from the dyed fabric, it must have definitely attached with the fiber through covalent bonding.

Neutral dyeing of reactive dyes by various dyeing sequences and their comparison

An attempt has been made in the present investigation to commercialize this neutral dyeing of reactive dyes on cotton. For this, six commercial reactive dyes, comprising of MCT, DCT, VS, bis-MCT (HE), and bifunctional (ME) groups were dyed by different dyeing sequences as mentioned earlier. The results are mentioned in Tables VIII. Such dyeings were also compared with conventionally dyed sample. No clear trend is observed from the results. The nature of the dye and the dyeing process utilized also influence the dyeing performances.

It can be observed that in case of MCT, DCT, and VS dyes, the color strength of treated sample, dyed by either S I or S II, are only slightly lower in comparison with the respective conventionally dyed samples. This is due to slight lower fixation of the dye in the absence of alkali in S I and S II sequences. However, sample dyed by S III sequence gave better dyeing performance (color strength enhanced up to 11 and 13% with D I and D III dyes, respectively, for PAA and crosslinking agent C_B, and by 1% to 10% with various other reactive dyes) over conventionally dyed samples. The overall dyeing performance of these three dyeing sequences with MCT, DCT, and VS reactive dyes is as follows: S III > S II > S I.

On the other hand, a reverse trend is observed with high exhaust (bis-monochlorotriazine/HE type) and bifunctional (ME type) reactive dyes for obvious reasons, owing to their high reactivity as well as the nature of the dye. With these dyes, the observed dyeing performance is as follows: S I > S III > S II.

The reason for such behavior may be attributed to the fact that in S III sequence, the dye molecule and crosslinking agent molecule compete with each other to combine with either cellulosic hydroxyl group or with the groups on the polymeric chain. The reactive dye is capable of combining with hydroxyl group of cellulose via covalent bond formation, which varies from dye to dye depending on their reactivity. The unfixed reactive dye molecules are also linked with the polymeric chain at the curing stage. This results in increased color strength during S III sequence.

Some of the results from the above two tables may be illustrated as follows:

- When simultaneous pretreatment and dyeing process is conducted by pad-dry-cure application technique, with a combination of PAA and C_B (for pretreatment) and Procion Brilliant Red M5B dye (for dyeing), a K/S value of 15.96 is observed, which is 11.45% higher than the corresponding K/S value for conventionally dyed sample (K/S = 14.32).
- Remazol Brilliant Violet 5R dye shows an increase of 1.14 and 5.79% in the color values for the samples pretreated with PAA and C_B combination. The K/S values for samples dyed by conventional dyeing is 12.25 and those for samples dyed by neutral pad-dry-cure two-step dyeing and simultaneous one-step dyeing are 12.39 and 12.96 respectively.
- Procion Brilliant Yellow H7G dye exhibits the color strength value of 8.29 for simultaneous treatment and neutral dyeing by pad-dry-cure method, which is higher by 4.01%

TABLE IX
Fastness Properties of Cotton Fabric Dyed with Various Reactive Dyes Using Exhaust Dyeing Method

					Fastness grades for							
	Conventional dyeing				Polymer-aided neutral aided							
					PAA + C_A[a]				PAA + C_B[b]			
			R				R				R	
Dye	W	L	Dry	Wet	W	L	Dry	Wet	W	L	Dry	Wet
D I	5	8	5	4–5	5	7–8	5	5	5	8	5	5
D II	5	8	5	4–5	5	8	5	5	5	7–8	5	5
D III	5	7	4	4–5	4–5	7–8	4–5	4	5	7–8	5	4–5
D IV	5	8	5	5	5	8	5	5	5	7–8	5	5
D V	5	7	5	4–5	5	8	5	4–5	5	8	5	5
D VI	5	8	5	4–5	5	7–8	4–5	4	5	8	4–5	5

W, wash fastness; L, light fastness; R, rub fastness.
[a] C_A: Glycerol 1,3-dichlorohydrin.
[b] C_B: Hexamethylene tetramine-hydroquinone.

compared with conventionally dyed sample ($K/S = 7.22$) for PAA and C_B agent combination during pretreatment.

Effect of neutral dyeing on the fastness properties of dyed cotton

The fastness properties of all such dyed sample are quite satisfactory and comparable with conventionally dyed sample (Tables IX and X). However, in polymer-aided exhaust dyeing process (S I), there is slight impairment in the light fastness for some of the dyes, particularly DCT dyes.

Effect of neutral dyeing on the crease recovery of dyed cotton

Improved wrinkle recovery is expected due to occurrence of crosslinking reactions as manifested earlier.

The dry crease recovery angle (DCRA) values of the polymer-aided dyed samples were 103° (S I), 105° (S II), and 99° (S III) for glycerol 1,3-dichlorohydrin (C_A) crosslinking agent and 101° (S I), 102° (S II), and 100° (S III) for HMTA-HQ (C_B) crosslinking agent, while that of bleached (untreated) and treated (undyed) samples were 65° and 79°, respectively. The DCRA for conventionally dyed sample were 85° (exhaust dyeing) and 87° (pad-dry-cure), respectively. Therefore, the polymer-aided dyed samples indicate an improvement in the wrinkle recovery for obvious reasons. In sequence S III, the extent of crosslinking is restricted because of the process involved, thereby offering comparatively low DCRA values.

CONCLUSIONS

Cotton fabric was pretreated with PAA and crosslinked with either C_A or C_B crosslinking agents by pad-dry-cure (at 150°C for 5 min) technique. The

TABLE X
Fastness Properties of Cotton Fabric Dyed with Various Reactive Dyes Using Pad-Dry Cure Dyeing Method

									Fastness grades for											
					PAA + C_A[a]								PAA + C_B[b]							
	Conventional				Two-Step Process				One-Step Process				Two-Step Process				One-Step Process			
			R				R				R				R				R	
Dye	W	L	Dry	Wet	W	L	Dry	Wet	W	L	Dry	Wet	W	L	Dry	Wet	W	L	Dry	Wet
D I	5	8	5	5	5	8	5	5	5	8	5	5	5	8	5	5	5	8	5	5
D II	5	8	5	4–5	5	8	5	4–5	5	8	5	4–5	4–5	8	5	4	5	8	5	5
D III	5	7	4–5	4	4–5	7–8	4–5	4	5	7	4–5	4–5	4–5	7	5	4	5	8	4–5	5
D IV	5	7–8	5	5	5	7–8	4–5	4	5	8	5	5	4–5	7–8	5	5	5	7–8	4–5	5
D V	5	8	5	5	5	7–8	5	5	5	8	5	5	5	8	5	5	5	8	5	5
D VI	5	8	5	5	5	8	5	5	5	8	5	5	5	8	5	5	5	8	5	5

W, wash fastness; L, light fastness; R, rub fastness.
[a] C_A: Glycerol 1,3-dichlorohydrin.
[b] C_B: Hexamethylene tetramine-hydroquinone.

optimum concentration for PAA was found to be 10 gpl (for exhaust dyeing) and 15 gpl (for pad-dry-cure dyeing) and that for C_A crosslinking agent was 5 gpl (for either dyeing method) and for C_B crosslinking agent were 3 and 5 gpl, respectively, for exhaust and pad-dry-cure dyeing techniques, respectively. The related changes indicate crosslinking reaction through higher nitrogen content (0.238% with C_A crosslinking agent and 0.886% with C_B crosslinking agent), and decrease in tensile strength by 10.3 and 16.8% with C_A and C_B crosslinking agents, respectively.

Such pretreated and partially crosslinked cotton fabric can successfully be dyed with various types of reactive dyes by different process sequences. The color strength of all the dyed samples was adequate and quite comparable with conventionally dyed samples. Among the two catalysts studied, extensively HMTA-HQ (C_B) crosslinking agent offered better performance compared to glycerol 1,3-dichlorohydrin (C_A) crosslinking agent. However, the C_A agent, in the presence of PAA polymer and the reactive dye, has offered color stability of up to 120 h in the aqueous state when compared with 48 h in case of C_B agent in an aqueous medium along with PAA polymer and the reactive dye. In case of simultaneous dyeing (SIII), the dye-uptake was about 1–13% (in case of DCT, VS, and ME dyes) and up to 4% (in case of MCT and HE dyes) higher with respect to their conventionally dyed samples. The plausible dyeing mechanism revealed covalent bond formation, as depicted in the Schemes 2 and 4. Very good, all round fastness properties were observed with all the dyed fabrics. The dyed fabric also exhibited very encouraging wrinkle recovery, which may replace even the subsequent wash-n-wear treatment. The fabric so dyed did not utilize any salt or alkali during dyeing. So polymer-aided neutral dyeing of cotton may be considered as safe dyeing technique for cotton textiles since the utilization of alkali/salt during dyeing has been completely eliminated.

References

1. Soignet, D.; Berni, G.; Benerilo, R. Text Res J 1966, 36, 978.
2. Hebeish, A.; El-Rafie, M. H. Am Dyest Rep 1990, 79, 34.
3. Hamza, H. M.; El-Nabas, H. M. J Soc Dyers Colour 1991, 107, 144.
4. Evans, G. E.; Shore, J.; Stead, C. V. J Soc Dyers Colour 1984, 100, 304.
5. Bhattacharya, N.; Mistry, P. R. Am Dyest Rep 1990, 79, 24.
6. Lewis, D. M.; Lei, X. P. Text Chem Color 1989, 21, 23.
7. Abou-Shousha, M. H. Am Dyest Rep 1988, 77, 32.
8. Lewis, D. M.; Lei, X. P. J Soc Dyers Colour 1991, 107, 102.
9. Harper, R. J. Text Chem Color 1988, 20, 25.
10. Sekamoto, M. J Appl Polym Sci 1973, 17, 283.
11. Vigo, T. L.; Blanchard, E. J. Text Chem Color 1987, 19, 19.
12. Burkinshaw, S. M.; Lei, X. P.; Lewis, D. M. J Soc Dyers Colour 1989, 105, 391.
13. Burkinshaw, S. M.; Lei, X. P.; Lewis, D. M. J Soc Dyers Colour 1990, 106, 307.
14. Low, K. C.; Atencio, A. M.; Meah, A. R.; Anderson, D. E.; Batzel, D. A.; Vallino, B.; Rico, B.; Ross, R. J.; Harms, D.; Spurrier, E.; Below, F. In Presidential Green Chemistry Challenge Awards Program, 1996.
15. Lochhead, R. V.; Davidson, J. A.; Thomas, G. M. In Polymers in Aqueous Media; Glass, J. E., Ed.; American Chemical Society: Washington, DC, 1989.
16. Carbopol Water Soluble Resins, Technical Bulletin GC—67; BF Goodrich Company: Cleveland, OH, 1986.
17. Rice, C. A.; Nagasawa, M. Polyelectrolyte Solutions; Academic: New York, 1961.
18. Bucholz, F. L. J Chem Ed 1996, 73, 512.
19. Huang, M.-Y.; Wu, R.; Jiang, L.-R. J Polym Bull 1983, 9, 5.
20. Peter, R. H. Textile Chemistry—The Physical Chemistry of Dyeing, Vol. 3; Elsevier: Amsterdam, Oxford, New York, 1975.
21. Trotman, E. R. Dyeing and Chemical Technology of Textile Fibres, 5th ed.; Charles Griffin and Company, Ltd: London and High Wycombe, 1975; p 540.
22. Billmeyer, F. W., Jr.; Saltzman, M. Principles of Color Technology, 2nd ed.; Wiley: New York, 1981; p 140.
23. Booth, J. E. Principles of Textile Testing; Butterworth Scientific Publishers: London, 1987.