

Treatment of Cellulose with Cationic, Nucleophilic Polymers to Enable Reactive Dyeing at Neutral pH Without Electrolyte Addition

Richard S. Blackburn, Stephen M. Burkinshaw

Centre for Technical Textiles, University of Leeds, Leeds LS2 9JT, UK

Received 25 March 2002; revised 15 July 2002; accepted 22 October 2002

ABSTRACT: Reactive dyeing of cotton requires very high concentrations of salt, which pollutes freshwater courses. The dyeing effluent is highly colored as a result of high levels of hydrolysis of the dye, and high volumes of water are used in the wash-off process to remove the hydrolyzed dye in order to achieve the excellent wash-fastness levels expected. A substantive cationic, nucleophilic polymer was applied to cotton as a pretreatment agent prior to dyeing. This enabled salt and alkali to be completely eliminated from the dyeing process, significantly reducing the duration of the dyeing process and requiring less than 50% of the volume of water compared with those of the standard reac-

tive dyeing processes. Dyeings secured using the pretreatment method required one simple washing stage to give wash-fastness values equal to those observed for the standard reactive dyeings that required several wash-off stages. The color strength of the pretreated dyeing was also slightly higher than that of the standard dyeings, and this was attributable to a reduction in dye hydrolysis and hence a higher fixation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1026–1031, 2003

Key words: pretreatment; reactive dye; salt; alkali; water use reduction

INTRODUCTION

Cotton and other cellulosic fabrics are the most widely used textiles in the world, accounting for more than 50% of total consumption. Dyed cotton must have high colorfastness to repeated domestic launderings at 40°C–60°C. The most wash-fast dyes on cotton are “vat dyes” such as indigo, but these are very expensive, require complicated dyeing procedures, and involve the use of strong reducing agents.

Reactive dyes are most commonly employed to achieve dyeings with high wash fastness on cotton. Their high wash fastness arises from the formation of a covalent bond between the reactive group of the dye and nucleophiles in the fiber. Reactive dyes are the only dye type with an increasing market worldwide, comprising 50% of total dye usage.¹ However, reactive dyes on cotton suffer from many disadvantages, particularly pertaining to environmental issues—arguably, reactive dyeing causes the greatest effluent problems for the production and application dye industry.

Reactive dyeing requires very high concentrations of salt (100 g/dm³ is commonplace). Electrolytes are needed in the dyeing process to overcome the long-

range repulsion forces operating between slightly negatively charged fibers and negatively charged dye molecules (as a result of water-solubilizing sulfonic acid groups). Without the addition of salt, the adsorption of dye to fiber will not occur, and with dyes such as reactive dyes, which are very soluble in water, a large amount of salt is required in the dyeing process. The U.S. textile industry uses about 95,000 tonnes of sodium sulfate per year in dyeing processes. Industry officials have said the companies cannot afford to remove all the dissolved salt from wastewater; thus, effluent rich in sodium contaminates freshwater, killing fish and making soil too alkaline to support crops. The freshwater lakes and rivers that have been turned permanently saline by dyeing operations are examples of this.

Another problem with reactive dyeing is an effluent that is highly colored as a result of high levels of hydrolysis of the dye. Between 10% and 40% of the dye applied is hydrolyzed. Hydroxyl anions (OH⁻) in the alkaline solution needed for fixation of dye to fiber are equally reactive with ionized hydroxyl groups in the cellulose (cell-O⁻), which are the nucleophiles for the dye–fiber reaction. The hydrolyzed dye is substantive to the fiber but not permanently fixed, and it must be washed off to give the dyeings their desirable excellent wash fastness. It produces a significant amount of colored effluent, which is undesirable from an aesthetic viewpoint. But more important, the color ab-

Correspondence to: R. S. Blackburn (r.s.blackburn@leeds.ac.uk).

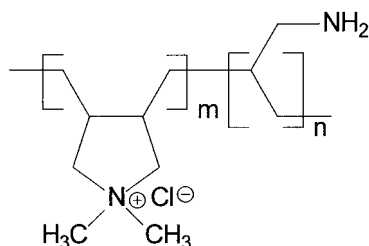


Figure 1 Copolymer of diallyldimethyl ammonium chloride and 3-aminoprop-1-ene.

sorbs sunlight entering the water, and bacteria cannot grow sufficiently to degrade impurities in the water, resulting in lower levels of organisms at the bottom of the food chain.² Dye wastewater also poses a problem because of its potential carcinogenicity and toxicity.³

Arguably, the most important environmental issue is the high volume of water used in the wash-off process to remove the hydrolyzed dye. This is particularly relevant in developing countries where water is at a premium and is relevant to all dyers as it reduces cost and time. Wash-off alone can account for 50% of the total cost of reactive dyeing.⁴

The work described here details the application of pretreatment agents to cotton and their detailed mechanism of operation, by which they enable a more environmentally friendly system of dyeing cotton with reactive dyes.

General structure and operation of pretreatment agents

Previous discussions⁵ of this subject have not covered the detailed structure of the pretreatment agents and their method of operation. It was proposed that the polymer that comprised both areas of cationic charge (for affinity to anionic dye) and also possessed highly reactive nucleophilic sites (for reaction with dye) could be dyed with reactive dye to enable reactive dyeing to be carried out in a more efficient manner, without salt at neutral pH values.

The pretreatment agents used include copolymers of diallyldimethyl-ammonium chloride and 3-aminoprop-1-ene (PT1; Fig. 1) and polymers of 4-vinylpyridine quaternized with 1-amino-2-chloroethane (PT2; Fig. 2). These polymers have a molecular weight in the region of 10,000–30,000 g/mol. Generally, the degree of cationicity is at least 1 cationic center per 500 g/mol, with a maximum of 1 per 150 g/mol. For PT1 the ratio of cationic comonomer (*m*) to nucleophilic comonomer (*n*) is between 1:1 (*m*:*n*) and 1:5. For PT2 the ratio of free pyridine (*m*) to quaternized, nucleophilic pyridinium (*n*) is between 1:3 (*m*:*n*) and 3:1.

Both pretreatment agents are highly substantive to cellulosic fiber; this is through a combination of ion-

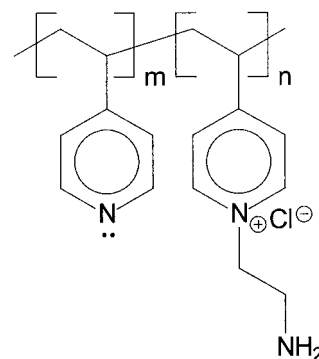


Figure 2 Polymer of 4-vinylpyridine quaternized with 1-amino-2-chloroethane.

ion forces, strong hydrogen bonding, and van der Waals forces. Adsorption of the pretreatment agent into the cotton arises through ion-ion interactions operating between the cationic groups in the agent and the anionic carboxylic acid groups in the substrate,^{6,7} which, because of their relatively low pK_a values, are ionized at the pH values of the application (pH 6–7).

Other forces of interaction between the pretreatment and the fiber vary between polymers. PT1 is substantive to cotton through van der Waals and strong H-bonding forces. Cellulose and diallyldimethyl-ammonium chloride have similar conformational structures, and this would be expected to contribute to strong interactions (Fig. 3). For poly(4-vinylpyridine) quaternary ammonium compounds (PT2), strong H-bonding would be expected to contribute to agent-fiber attraction through so-called Yoshida forces⁸ operating between the electron-deficient hydrogen atom of the hydroxyl groups in the fiber and the π -electron system of the unquaternized pyridine rings in the pretreatment agent. In addition, further ion-dipole interaction may be expected between the positively charged nitrogen atoms of the pyridinium rings and the lone pair of electrons on the oxygen atom of the cellulosic hydroxyl groups (Fig. 4). Once adsorbed, the pretreatment agents are very durable to laundering.

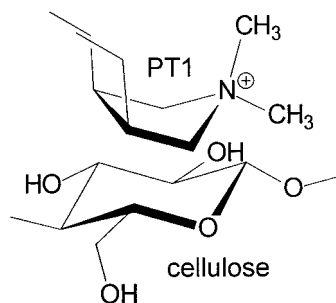


Figure 3 Conformational interaction between cellulose and PT1.

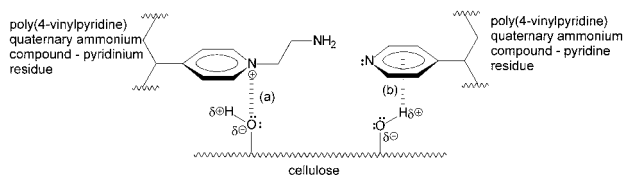


Figure 4 (a) Ion-dipole interactions between cellulose hydroxyl groups and pyridinium residues of the pretreatment polymer and (b) Yoshida H-bonding between cellulose hydroxyl groups and pyridine residues in PT2.

Once the agent has been adsorbed onto the cotton, reactive dyes are introduced. The anionic dye molecules are attracted to the cationic sites in the polymer through ionic association, and the extended π -electron systems of both dye and pretreatment agent have high levels of interaction and association. This enables adsorption of the dye without the need for adding salt at a neutral or slightly acidic pH. Then reaction between the amino-functional nucleophiles in the pretreatment agent and the reactive group in the dye proceeds either via a nucleophilic substitution mechanism (Fig. 5) or a Michael addition to a double bond. As the primary amino nucleophile is highly reactive, fixation will occur at a neutral pH, and hydrolysis of the dye (which ordinarily occurs at pH 11) will be dramatically reduced and potentially the wash-off procedure not required.

EXPERIMENTAL

Materials

Commercial samples of Procion Yellow H-EXL (C. I. Reactive Yellow 138:1),⁹ Procion Brilliant Red H-EGXL (C. I. Reactive Red 231), Procion Blue H-EXL (C. I. Reactive Blue 198), Remazol Yellow RR, Remazol Red RR, Remazol Blue RR, Cibacron Yellow F-3R (C. I. Reactive Orange 91), Cibacron Red F-B (C. I. Reactive Red 184), and Cibacron Blue F-R (C. I. Reactive Blue 182) were used. Procion H-EXL dyes have monochlorotriazinyl reactive groups, Remazol RR dyes have vinylsulfone reactive groups, and Cibacron F dyes have monofluorotriazinyl reactive groups (Cibacron dyes supplied by Ciba). Bleached, scoured, fluorescent brightener-free woven cotton (150 g/m²) was used. Uniqema (Middlesbrough, UK) supplied the pretreatment agent. All other chemicals were of general laboratory grade.

Dyeing by pretreatment method

Cotton samples were pretreated, dyed, and washed off in sealed stainless-steel dye pots of 300 cm³ in capacity and housed in a laboratory-scale Roaches Pyrotec S dyeing machine. The method involves pre-

treating the fabric with 1% omf (on mass of fiber) pretreatment agent using a liquor ratio of 10:1. The temperature was raised from 20°C to 45°C over 15 min and held at 45°C for a further 30 min. The bath was dropped. The pretreated fabric was dyed with each of the nine dyes detailed in Table I at 2% omf concentration using a liquor ratio of 20:1. The pH of the liquor was around 6.5, the pH of tap water, in contrast to a previous study,⁵ which used a phosphate buffer system. The temperature was raised from 20°C to 98°C over 40 min and held at 98°C for a further 60 min. The bath was dropped. The dyed pretreated fabric was washed off with nonionic detergent (1 g/dm³) using a liquor ratio of 20:1. The temperature was raised from 20°C to 98°C over 20 min and held at 98°C for a further 10 min. The bath was dropped and the fabric dried.

Dyeing by standard method

For comparison purposes, standard dyeings were carried out on cotton that had not been pretreated following the dye manufacturer's recommendations, for Remazol RR reactive dyes,¹⁰ Procion H-EXL reactive dyes,¹¹ and Cibacron F reactive dyes.¹² The details of the chemicals, water, and time involved in the process are detailed in Table II.

Wash fastness testing

Samples were subjected to the ISO 105:C06/C2S wash test (60°C) using SDC multifiber as adjacent fabric.¹³

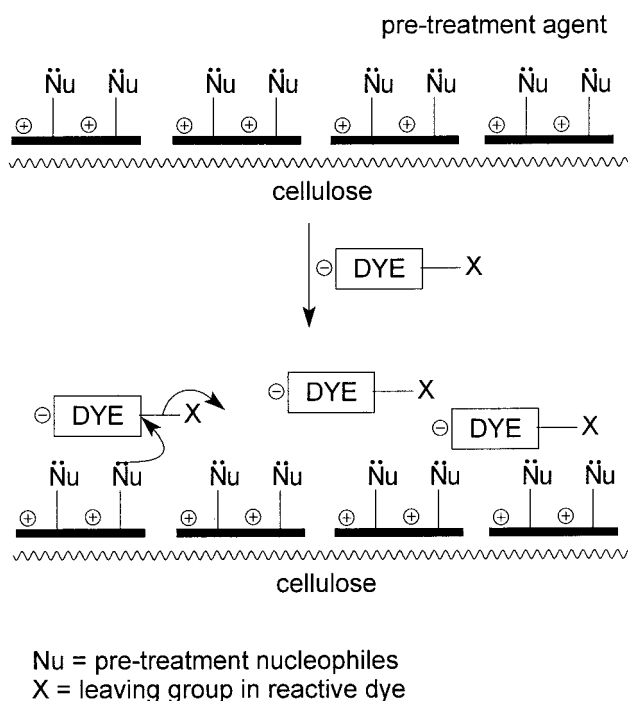


Figure 5 Pretreatment of cotton and dyeing with reactive dyes via nucleophilic substitution.

TABLE I
K/S Values and Wash Fastness Gray-Scale Ratings of Standard Reactive Dyeings and Pretreated Reactive Dyeings on Cotton Following ISO 105:C06/C2S Wash Tests

Dye	Standard/PT	K/S	Washes	S	D	C	N	P	A	W
Remazol yellow RR	Standard	3.75	1	5	5	5	5	5	5	5
			5	4/5	5	4/5	5	5	5	
			5	4/5	5	4/5	5	5	5	
Remazol red RR	Standard	8.41	1	4/5	5	5	5	5	5	5
			5	4	5	4	4/5	5	5	5
			5	4/5	5	4/5	5	5	5	
Remazol blue RR	Standard	6.61	1	4/5	5	5	5	5	5	5
			5	4	5	4	4/5	5	5	5
			5	4/5	5	5	5	5	5	
Procion yellow H-EXL	Standard	10.01	1	5	5	5	5	5	5	5
			5	4/5	5	4/5	4/5	5	5	5
			5	4/5	5	4/5	5	5	5	
Procion brilliant red H-EGXL	Standard	8.32	1	5	5	5	5	5	5	5
			5	4/5	5	4/5	5	5	5	5
			5	4/5	5	4/5	5	5	5	
Procion blue H-EXL	Standard	6.26	1	5	5	5	5	5	5	5
			5	4/5	5	4/5	4/5	5	5	5
			5	4/5	5	4/5	5	5	5	
Cibacron yellow F-3R	Standard	5.23	1	5	5	5	5	5	5	5
			5	4/5	5	4/5	5	5	5	5
			5	4/5	5	4/5	5	5	5	
Cibacron red F-B	Standard	5.35	1	5	5	5	5	5	5	5
			5	4/5	5	4/5	5	5	5	5
			5	4/5	5	4/5	5	5	5	
Cibacron blue F-R	Standard	4.36	1	5	5	5	5	5	5	5
			5	4/5	5	4/5	5	5	5	5
			5	4/5	5	4/5	5	5	5	

Gray-scale ratings from 5 to 1 for S, shade change and staining, to D, diacetate; C, cotton; N, nylon; P, polyester; A, acrylic; W, wool.

The samples were washed five times using the same piece of multifiber strip for each washing. After washing, the samples were visually assessed using gray scales according to the ISO 105:A02 and ISO 105:A03 test protocols¹³ to determine the degree of wash down

and cross staining, respectively. The gray scale ranges from 5, for no shade change (or no stain on the adjacent fibers), to 1, for a severe shade change (or staining), with half points (between 4 and 5, 3 and 4, 2 and 3, 1 and 2) in between.

TABLE II
Comparison of Different Systems Employed

Procedure	Wash-off stages	Time (min)	Water (ℓ /kg fabric)	NaCl (g/kg fabric)	Na ₂ SO ₄ (g/kg fabric)	Na ₂ CO ₃ (g/kg fabric)	Other chemicals (g/kg fabric)
Remazol RR	6	355	145	0	1250	500	acetic acid (60), detergent (20)
Procion H-EXL	4	365	105	1625	0	500	detergent (20)
Cibacron F	5	295	125	0	1500	500	acetic acid (60), detergent (20)
Pretreatment	1	195	50	0	0	0	pretreatment (10), detergent (20)

Color measurement

The samples were measured using an Image Master™ color spectrophotometer attached to a personal computer. From the reflectance values at the λ_{\max} of the dyeings (R), the color strength (K/S) of the sample was calculated using the Kubelka–Munk equation.¹⁴

$$K/S = \frac{(1 - R)^2}{2R} \quad (1)$$

RESULTS AND DISCUSSION

Table I shows the color strength (K/S) values of the dyeings. It was observed that the K/S values secured using the pretreatment method were higher for all dyes used than for standard dyeings. The application of neutral pH on dyeing processes minimizes any hydrolysis of the dye; hence, nearly all the dye that is applied fixes to the fiber, potentially reducing the cost, as less dye must be applied to achieve a standard shade, and reducing the concentration of dye in the effluent. In a standard situation, if 40% of the dye applied is hydrolyzed, then the maximum dye fixation that could be expected from a 2% omf application would be 1.2% omf, whereas with the pretreatment system a 2% omf application could theoretically yield a 2% omf dyeing, that is, 100% fixation. Indeed, Table I shows that in every case the color strength (K/S) for each dye applied was higher on the pretreated substrate than on the standard cotton fabric. It is suggested that higher K/S values are a direct result of reduced dye hydrolysis and hence higher fixation levels for the dyeings obtained using the pretreatment method.

Table I also shows the wash fastness results for the standard and pretreated dyeings. It was observed after one wash that all the dyeings produced using the various processes displayed excellent wash fastness, from which it was concluded that the pretreatment process secured dyeings for which the dye was adequately fixed. A lack of staining of adjacent fabric, particularly in the first wash, indicated that extensive wash-off of unfixed dye was not required with the pretreatment method. After five washes the wash fastness of the dyeings using the pretreatment method was slightly superior to those secured with the conventional systems.

It is suggested that for conventionally dyed cotton, a small amount of initial dye–fiber bond cleavage occurs as a result of the long wash-off stages. It is known that the dye–fiber bond formed using vinyl-sulfone reactive dyes on cotton is more alkali-sensitive than that derived from monohalotriazine dyes,¹⁵ and this would explain the Remazol RR dyeings having slightly inferior wash fastness than the Procion H-EXL

and Cibacron F dyeings. The cotton adjacent picks up the small amount of loose color that is generated, the stain becoming quite noticeable after five washes; in addition, the color strength of the dyeing is reduced. With the pretreatment method, the long wash-off method is negated, thus slightly reducing the cumulative dye–fiber bond cleavage.

A summary of the differences in the dyeing processes used is given in Table II. It was observed that the pretreatment method vastly reduced the total time of the dyeing operation. The amount of water used is calculated using eq. (2) by a summation of the water used in each separate process, where the liquor ratio (LR) is given as a ratio of liquor to fiber, for example, a 25:1 liquor ratio is 25 L of water per kilogram of fiber used. Each of the standard reactive dyeing processes used more than 100 L of water per kilogram of fabric dyed, with most of the water consumed in the wash-off processes; however, the pretreatment method consumed less than half the volume, with a water concentration of only 50 L/kg of fabric used.

Volume water used (L/kg fibre)

$$= LR \text{ (dyeing)} + LR \text{ (pre-treatment)} \\ + LR \text{ (washoff 1)} + LR \text{ (washoff 2)} + \dots \quad (2)$$

A high amount of salt (up to 1.6 kg per kilogram of fabric dyed) and alkali (0.5 kg Na_2CO_3 /kg of fabric) was consumed in the standard reactive dyeing processes, but by employing the pretreatment method, both salt and alkali were completely eliminated from the dyeing process.

Considering the other chemicals used in the dyeing processes, the pretreatment agent was applied in relatively low concentration, and it is suggested that it would have high exhaustion values; hence, its presence in the effluent would be expected in extremely low concentrations. In addition, the agent is polymeric and as such poses minimal environmental impact.

CONCLUSIONS

Application of a cationic, nucleophilic polymer to cotton prior to dyeing enabled the application of reactive dyes at neutral pH without salt. The neutral pH of application enabled maximum fixation of the dye to the fiber as hydrolysis of the dye was minimized. This was manifest as deeper dyeings that required minimal wash-off to achieve the excellent wash fastness expected from reactive dyes on cotton. Minimal wash-off enabled saving more than 50% of the total volume of water applied, and the whole dyeing process could be carried out in significantly less time. These benefits would provide a significant cost saving; but more important, they would provide a system that would

be much more environmentally friendly than traditional reactive dyeing operations.

The authors thank Uniqema for its work in the development of the pretreatment agents and the associated application methods. This pretreatment system is patent protected by the University of Leeds and Uniqema. Figure 5 and minor parts of the Results and Discussion section are reproduced by permission of the Royal Society of Chemistry.

References

1. Phillips, D. A. S. *J Soc Dyers & Colourists*, 1996, 112, 183.
2. Papic, S.; Koprivanac, N.; Metes, A. *Environ Tech* 2000, 21, 97.
3. Strickland, A. F.; Perkins, W. S. *Textile Chemist & Colorist* 1995, 27, 11.
4. Shore, J. In *Cellulosics Dyeing*; Shore, J., Ed.; Society of Dyers & Colourists: Bradford, 1995.
5. Blackburn, R. S.; Burkinshaw, S. M. *Green Chemistry* 2002, 4, 47.
6. *Textile Chemistry*; Peters, R. H. ed.; Elsevier: Amsterdam, The Netherlands, 1975; Vol. III.
7. Nevell, T. P. In *The Dyeing of Cellulosic Fibres*; Preston, C., Ed.; Dyers Company Publications Trust: Bradford, UK, 1986.
8. Yoshida, Z.; Osawa, F.; Oda, R. *J Phys Chem* 1964, 68, 2895.
9. *Colour Index International [on CD-ROM]*; Society of Dyers and Colourists: Bradford, UK, 1999.
10. Remazol Automet, pattern card, DF 1004 E, 1987.
11. Procion H-EXL, pattern card, PL 284.
12. Cibacron F, pattern card, 3170-N.
13. *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather*, 5th ed.; Amendment No. 1; Society of Dyers and Colourists: Bradford, UK, 1992.
14. McDonald, R. *Industrial Pass/Fail Colour Matching*. *J Soc Dyers & Colourists*, 1980, 96, 486.
15. Benz, J. *J Soc Dyers & Colourists*, 1961, 77, 734.