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Synthesis of Temporarily Solubilized Reactive Disperse Dyes and Their Application to the Polyester/Cotton Blend Fabric

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Abstract: Five temporarily solubilized reactive disperse dyes were synthesized and characterized. They were applied to polyester/cotton blend fabric using one-bath dyeing method without dispersing agent. The dye that has azonaphthalene chromophore seemed to not only be exhausted on polyester but also react with cotton. But other dyes were selectively dyed on polyester and showed limited uptake on cotton. Good levelling as well as moderate to good colour fastness was obtained with the dyes on P/C blend fabric.

Keywords: Temporarily solubilized reactive disperse dyes, Sulfatoethylsulfone, Polyester/cotton blend, One-bath dyeing, Dispersant-free dyeing

Introduction

Reactive disperse dyes have properties of both disperse dyes and reactive dyes. The first reactive disperse dyes are *Procinyl* range of ones, which were introduced by ICI in 1958[1]. They were disperse dyes that carried reactive groups and were intended to combine the favorable properties of disperse and reactive dyes on nylon, namely excellent coverage of substrate irregularities and high wetfastness, respectively. A number of studies[2-5] with reactive disperse dyes have been reported for the application of transfer printing of wool or nylon to improve wetfastness. In addition, the applications to one-bath blend dyeing such as wool/polyester, silk/polyester, silk/nylon and cotton/acrylic with reactive disperse dyes have been studied[6-9].

Temporarily solubilized disperse dyes were first synthesized in 1922[10,11]. These dyes, such as those of the Ionamine ranges, contained *N*-methylsulfonic acid group that gave temporary solubility to the dye molecules. They are hydrolyzed in the dyebath during dyeing to form insoluble species that are adsorbed onto the surface of the hydrophobic fiber, and diffuse into it. In a previous study[12,13], we found that temporarily solubilized disperse dyes containing β-sulfatoethylsulfonyl group can be used for the dispersant-free polyester dyeing. During the dyeing procedure, these water-soluble dyes are hydrolyzed into insoluble vinylsulfone derivatives that have substantivity to the hydrophobic polyester fibre. These dyes have not only temporarily solubilized property but also fiber-reacting ability when the β-sulfatoethylsulfonyl group is converted to reactive vinylsulfone group. Therefore, these dyes can be used as temporarily solubilized reactive disperse dyes. In an earlier study, M. Dohmyou *et al.*[9] applied temporarily solubilized reactive disperse dyes containing β-sulfatoethylsulfonyl group to polyester/silk blends. Burkinshaw and Collins[4] studied similar dyes for improvement of wetfastness in nylon dyeing.

The usual methods of dyeing polyester/cotton (P/C) blends have traditionally involved the use of various two-pass processes that are time-consuming, often cumbersome and thereby expensive to operate. Some efforts for other method of polyester/cotton blends dyeing have been made[14-16]. ICI developed a rapid one-bath method for the dyeing of P/C blends. It consists of dyeing with a selected mixture of disperse and reactive dyes[17]. Modification of cotton component has been attempted for one-bath dyeing of P/C blend with disperse dye alone[18,19]. One-bath dyeing of P/C blend with reactive disperse dyes has been studied by some workers[7,20]. But no studies have been reported about one-bath dyeing of P/C blend with temporarily solubilized reactive disperse dyes.

In this study, some temporarily solubilized azo reactive disperse dyes containing β-sulfatoethylsulfonyl group were synthesized and applied to P/C blend using one-bath dyeing method without dispersing agent. The dyeing behavior of temporarily solubilized reactive disperse dye was investigated by colour yield on either polyester and cotton or P/C blend. Colour fastness as well as levelling properties was also examined.

Experimental

Materials

Aminophenyl-4-(β-sulfatoethylsulfone) (Kyung-In Synthetic Co.) was used as the diazo component. *N*-methylaniline, *N*,*N*-diethylaniline, β-naphthol, 1-naphthylamine were purchased from Aldrich and used as the coupling component. All other chemicals used were of laboratory grade. Eriopon OS (Ciba Specialty Chem., nonionic surfactant) were used for soaping

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agent. Scoured woven polyester/cotton blend (65/35, density 104×54 picks) fabric was obtained from Kabool Textile Co.

Instrumentation

Melting points were recorded in capillaries (Electrothermal 9100, Dong-Bo Chem. Co.) and are uncorrected. NMR spectra were recorded in DMSO-d_6 using a Jeol lambda series 300 MHz instrument. Visible spectra were recorded in DMF in 1 cm quartz cells using a HP 8452A spectrophotometer. Mass spectra were recorded in fast atom bombardment ionization mode using Jeol JMS-AX505WA/HP 5890 Series II GC-Mass Spectrometer.

Synthesis of Temporarily Solubilized Reactive Disperse Dye

Aminophenyl-4-(β-sulfatoethylsulfone) (2.81 g, 0.01 mol) was dissolved in 200 m*l* water containing concentrated hydrochloric acid (2.4 m*l*) at room temperature. The solution was cooled to 0-5 °C and sodium nitrite (0.69 g, 0.01 mol) was added. After diazotization was complete excess nitrous acid was removed by adding 10 % sulfamic acid. Coupling component was dissolved in 100 m*l* water containing either 0.5 g sodium hydroxide for β-naphthol or 2 m*l* concentrated hydrochloric acid for the other coupling components. The prepared diazonium salt solution was added into the corresponding coupling component solution and the temperature was maintained between 0 and 5 °C. The whole solution was stirred for 2 h and allowed to reach room temperature. The pH was adjusted between 4 and 5. After 30 g sodium chloride was added to the solution, the precipitate formed was filtered and dried in a vacuum oven at room temperature. To remove excess sodium chloride, 5 g of dried dye was dissolved in 100 m*l* dimethyl formamide (DMF). The solution was filtered and poured into 200 m*l* of dichloromethane. The precipitated dyes 1-4 were filtered and dried.

The dye 5 was prepared from dye 4. Cyanuric chloride (1.84 g, 0.01 mol) was added and dispersed in 30 m*l* water. The aqueous solution of dye 4 (0.01 mol) was added to it. The reaction mixture was stirred for about 5 hrs and pH was kept to be 6 by adding sodium carbonate. The reaction was terminated when the pH of the mixture was not changed any more. The salting-out and purification process were carried out with the same method for dyes 1-4. The structures of the synthesized dyes are shown in Figure 1.

One-bath Dyeing of P/C Blend

Polyester/cotton blends were dyed in an IR dyeing machine (DL6000A, DaeLim Co.) without any dispersing agent using the one-bath dyeing profile as shown in Figure 2. The dyebaths were prepared with temporarily solubilized disperse dyes 1-5 (1 % weight of fibre) and salt and then buffered with pH being 5 or 6 which was optimum for dyeing: at pH 5 with sodium acetate (0.05 M)/acetic acid; at pH 6 with sodium dihydrogen phosphate (0.05 M)/disodium hydrogen phosphate. The substrate was either 4 g of polyester/cotton blend (65/35) fabric or 2.6 g of polyester and 1.4 g of cotton keeping the polyester/cotton weight ratio 65:35. The liquor ratio was 20:1.

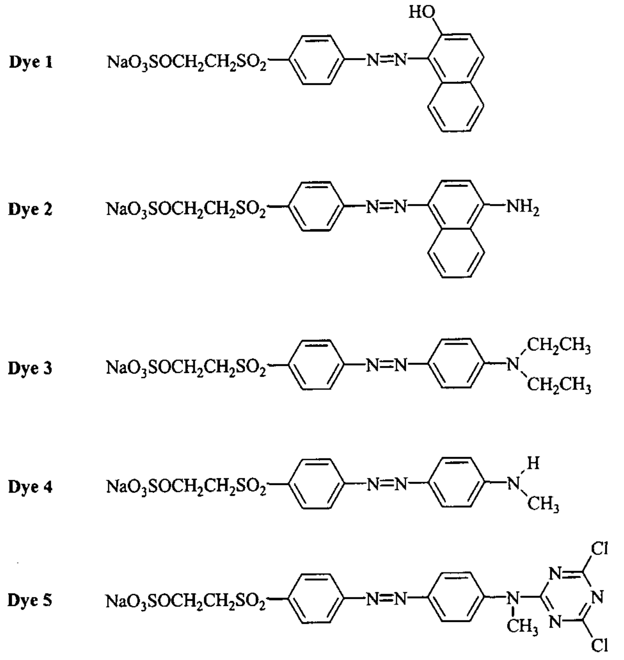


Figure 1. Structures of the temporarily solubilized reactive disperse dyes synthesized in this study.

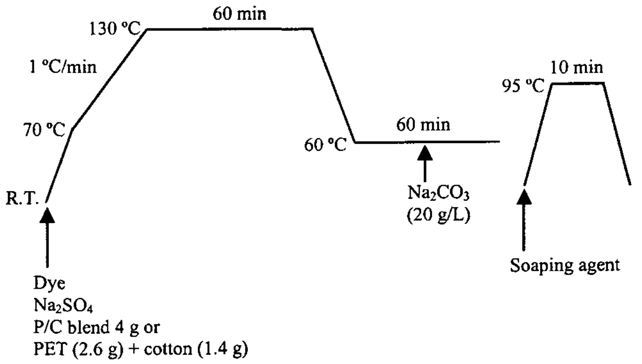


Figure 2. One-bath dyeing profile of P/C blend with temporarily solubilized reactive disperse dyes.

Dyeing was commenced at 70 °C. The dyebath temperature was raised by 1 °C/min to 130 °C, maintained at this temperature for 60 min and cooled to 60 °C. After 30 min at 60 °C, 20 g/*l* of alkali (Na_2CO_3) was added to effect fixation of the dye on cotton and maintained at 60 °C for further 30 min. The dyeings were rinsed and soaped at 95 °C for 10 min with 2 m*l*/*l* of soaping agent.

Fastness Test

The dyed fabrics were subjected to wash (ISO 105:C06

C1S), light (AATCC 16-1998), sublimation (ISO 105:X11) and rubbing (ISO 105:X12) fastness tests after stentering at 180 °C for 60 s. The shade change, together with staining of adjacent fabrics, was rated according to appropriate grey scale.

Levelling

5 points of the dyed sample were chosen arbitrarily and L^*, a^* and b^* values of them were measured by Macbeth coloreye 3000 spectrophotometer. The colour difference between optional two points was calculated using equation (1):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

The levelling properties of the dyes on polyester/cotton blend were evaluated with 10 combination results of the colour differences.

Results and Discussion

Dye Synthesis

Dyes 1-4 were synthesized by common diazo-coupling reaction. Aminophenyl-4-(β-sulfatoethylsulfone) was diazotized using hydrochloric acid and sodium nitrite at 0-5 °C and the diazonium salt was coupled with aniline or naphthalene compounds at pH 4-5 to give temporarily solubilized reactive disperse dyes. Dye 5 was obtained by condensation reaction of dye 4 with cyanuric chloride. The dyes synthesized were characterized using NMR and Mass spectrometry. Yields and characterization data of the dyes are shown in Table 1. In the ^{1}H-NMR spectra of dyes 4 and 5, the peak for the methyl protons attached to the nitrogen atom was found in the different position. Thus the peak of dye 4 was found at 2.48 ppm while that of dye 5 was shown at 3.51 ppm. This may be due to the decrease of the electron density of the methyl protons of dye 5 by the chlorotriazine substituent that is a strong electron-withdrawing group. In the absorption spectra of dyes 3 and 4, dye 3 exhibited higher λ_{max} value than dye 4. This can be explained by considering that diethylamino group is more powerful electron-donating group than methylamino group. Thus in the excited state, the redistribution of electron density is larger for diethylamino group[21].

One-bath Dyeing of Polyester and Cotton Fabrics

Polyester and cotton fabrics were dyed in the same dyebath to investigate the dyeing behavior of each component. Figures 3 and 4 show the colour yields of dyes 1 and 2 on polyester or cotton components respectively from one-bath dyeing at initial pH value of 5 and 6. Dyes 1 and 2 were successfully dyed on polyester component without using dispersing agent. The colour yields of the both dyes on polyester component reached maximum value in the first stage of dyeing at 130 °C for an hour and did not increase in the second dyeing stage. For cotton component, the colour yield of the dye 2 was not increased in the first dyeing stage and then increased after alkali addition in the second dyeing stage at 60 °C. This may be due to the fixation of the reactive disperse dye on cotton in the second stage of dyeing.

Table 1. Yields and characterization data of the dyes 1-5

Dye	Yield (%)	m.p. (°C)	$\lambda_{max}$$^{a)}$ (nm)	Mass (m/z)	^{1}H-NMR$^{b)}$ (δ, ppm)
1	90	274-276	486	459 (MH$^+$)	3.64-3.68 (2H, t, CH_2SO_2) 3.95-3.98 (2H, t, NaO_3SOCH_2) 6.52-8.49 (10H, m, aromatic protons)
2	95	221-223	500	458 (MH$^+$)	3.65-3.68 (2H, t, CH_2SO_2) 3.96-3.99 (2H, t, NaO_3SOCH_2) 7.05-8.76 (10H, m, aromatic protons)
3	51	204-206	464	464 (MH$^+$)	1.18-1.20 (6H, t, two CH_3) 3.44-3.49 (4H, q, two NCH_2) 3.67-3.70 (2H, t, CH_2SO_2) 3.95-3.98 (2H, t, NaO_3SOCH_2) 6.85-8.02 (8H, m, aromatic protons)
4	94	237-239	440	422 (MH$^+$)	2.48 (3H, s, NCH_3) 3.62-3.66 (2H, t, CH_2SO_2) 3.97-4.04 (2H, t, NaO_3SOCH_2) 6.72-8.14 (8H, m, aromatic protons)
5	82	284-286	440	469 (MH$^+$)	3.51 (3H, s, NCH_3) 3.71-3.76 (2H, t, CH_2SO_2) 3.98-4.02 (2H, t, NaO_3SOCH_2) 7.70-8.18 (8H, m, aromatic protons)

$^{a)}$measured in DMF.
$^{b)}$measured in DMSO-d_6.

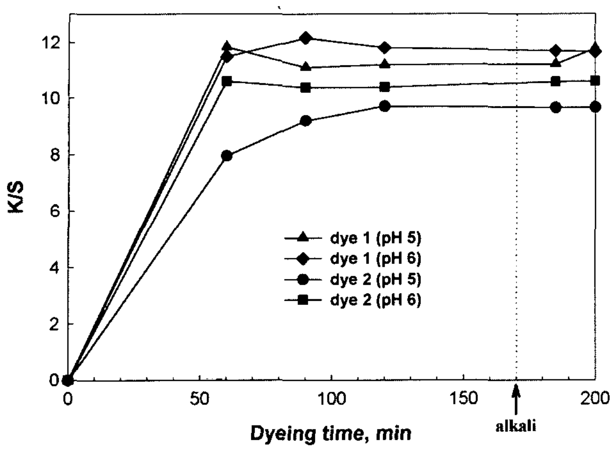


Figure 3. Colour yields of dyes 1-2 on polyester component from one bath dyeing of polyester and cotton (1 % owf, pH 5 or 6, liquor ratio 20:1).

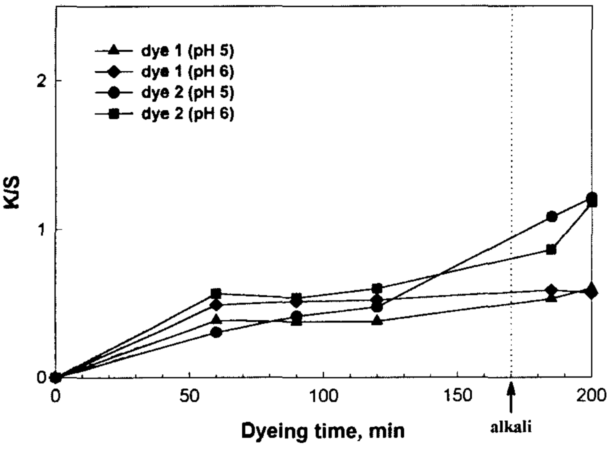
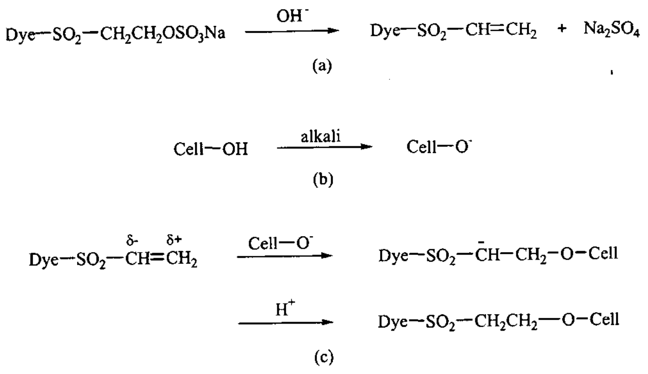


Figure 4. Colour yields of dyes 1-2 on cotton component from one bath dyeing of polyester and cotton (1 % owf, pH 5 and 6, liquor ratio 20:1).



Scheme 1. Reaction of temporaily solubilized reactive disperse dye with cotton. (a) conversion of β-sulfatoethylsulfonyl form into reactive vinylsulfone form, (b) formation of cellulosate anion by alkali-addition, (c) nucleophilic addition of the dye with cellulosate anion.

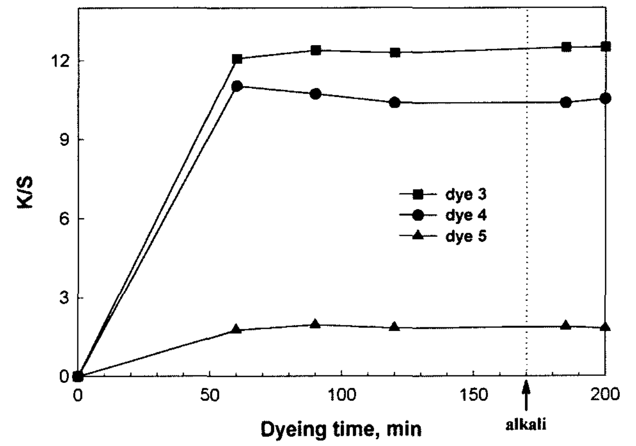


Figure 5. Colour yields of dyes 3-5 on polyester component from one bath dyeing of polyester and cotton (1% owf, pH 6, liquor ratio 20:1).

According to the result from previous study[12], at the end of the first dyeing stage, the β-sulfatoethylsulfonyl group of the dye will be hydrolyzed and most of the dye will exist as a reactive vinylsulfone form. When alkali was added into the dyebath in the second dyeing stage, the cellulose of the cotton fabric should be changed into cellulosate anion. Then the reactive vinylsulfone group of the dye would react and form covalent bonding with cotton as shown in Scheme 1 resulting in the increase of colour yield. The more desirable result was obtained when the initial pH was 5.

In the case of dye 1, the colour yield was not increased as much as that of dye 2 after alkali was added in the second dyeing stage. This suggests that only a few number of the dye 1 react with cotton fiber.

Figures 5 and 6 show the colour yields of dyes 3, 4, and 5 on polyester or cotton components respectively from one-bath dyeing at initial pH value of 6. The results for dyes 3 and 4 were the same trend with that of dye 1. Thus the dyes 3 and 4 were successfully dyed on polyester without using dispersing agent, but the dye uptake on cotton component was very low and the colour yields were not much increased after alkali-addition in the second dyeing stage. This may be due to the low affinity of dyes 3 and 4 to cotton owing to their small size of dye molecule.

The colour yields of dyes 1-4 on polyester component were higher than those on cotton component. Change of dye structure such as introducing more polar and hydrophilic group or increasing the size of the dye seems to be needed for the dye to get more affinity to cotton.

Dye 5 exhibited very low colour yield on both polyester and cotton component. The low colour yield on polyester may be explained by considering that the dye molecule was too bulky and big to diffuse into the polyester fiber. We expected that dye 5 would exhibit good dye uptake on cotton

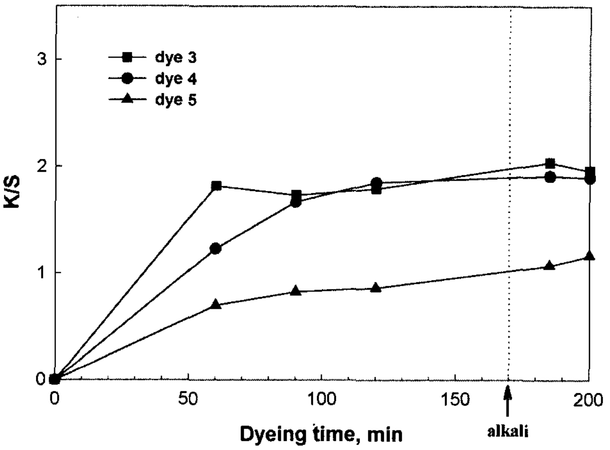


Figure 6. Colour yields of dyes 3-5 on cotton component from one bath dyeing of polyester and cotton (1 % owf, pH 6, liquor ratio 20:1).

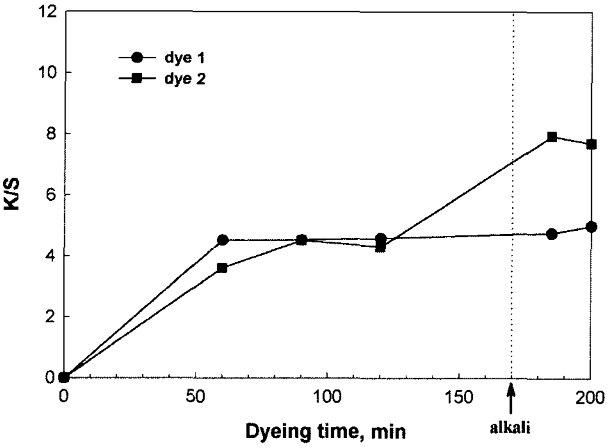


Figure 7. Colour yields of dyes 1-2 on polyester/cotton (65/35) blend fabric (1 % owf, pH 5, liquor ratio 20:1).

because it has two reactive groups of vinylsulfone and chlorotriazine. But the result showed that the colour yield on cotton was even lower than that of dye 4. This may be attributed to the low hydrophilicity as well as low substantivity of dye 5 to cotton possibly because introducing the bulky chlorotriazine group broke the planarity of the dye.

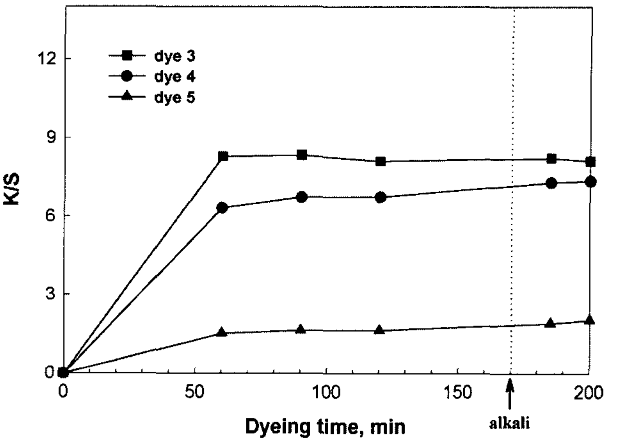


Figure 8. Colour yields of dyes 3-5 on polyester/cotton (65/35) blend fabric (1 % owf, pH 6, liquor ratio 20:1).

One-bath Dyeing of Polyester/Cotton (65/35) Blend Fabric

Figure 7 shows the colour yields of dyes 1 and 2 on polyester/cotton (65/35) blend fabric by one-bath dyeing method with the initial pH being 5 and without using dispersing agent. The colour yield of dye 2 was increased to a certain degree showing maximum value during the first stage of dyeing and increased again after alkali-addition in the second dyeing stage. This indicates that dye 2 should act as a reactive disperse dye and not only be exhausted to polyester part but also react with cotton part of the P/C blend fabric. The colour yield of dye 1 was increased during the first dyeing stage and not increased in the second stage implying that it did not react with cotton part. Figure 8 shows the colour yields of dyes 3, 4, and 5 on polyester/cotton (65/35) blend fabric with the initial pH being 6. Dyes 3 and 4 showed good colour yield on P/C blend but most of the dye seemed to be exhausted on polyester part of the P/C blend fabric like dye 1. Dye 5 exhibited low colour yield on P/C blend as expected from the dyeing result of polyester and cotton.

Temporarily solubilized disperse dyes in this study showed good levelling property on P/C blend. Table 2 shows the 10 combination results of the colour differences among 5 points of each P/C blend fabric dyed. All the dyed fabrics showed very small colour differences implying that they exhibited good levelling.

Table 2. Colour differences among 5 points of each P/C blend fabric

Dye	Colour difference										
	1	2	3	4	5	6	7	8	9	10	Avg.
1	0.32	0.36	0.23	0.41	0.07	0.50	0.37	0.56	0.34	0.62	0.38
2	0.17	0.26	0.10	0.61	0.39	0.20	0.58	0.25	0.81	0.57	0.39
3	0.70	0.37	0.35	0.68	0.38	0.58	0.22	0.22	0.45	0.65	0.46
4	0.39	0.76	0.17	0.14	0.41	0.49	0.42	0.82	0.82	0.30	0.47
5	0.26	0.17	0.21	0.17	0.40	0.47	0.38	0.17	0.27	0.17	0.27

Table 3. The washfastness of dyes 1-5 on polyester/cotton (65/35) blend fabric (ISO 105:C06 C1S, 1 % o.w.f., heatsetting 180 °C, 60s)

Dye	Change	Staining					
		Acetate	Cotton	Nylon	Polyester	Acryl	Wool
1	5	4/5	5	3/4	5	5	4
2	4	4/5	5	3/4	5	5	3
3	5	4	5	3/4	5	5	3/4
4	5	4	5	3/4	5	5	3/4
5	5	5	5	4/5	5	5	4/5

Table 4. The light (AATCC 16-1998), rubbing (ISO 105:X12) and sublimation (ISO 105:X11) fastness of dyes 1-5 on polyester/cotton (65/35) blend fabric (1 % o.w.f., heatsetting 180 °C, 60s)

Dye	Light	Rubbing		Sublimation		
		Staining		Change	Staining	
		Dry	Wet		Polyester	Cotton
1	3/4	5	4/5	4/5	4	4
2	1	5	4/5	4/5	4/5	4/5
3	3/4	4/5	3/4	4/5	4	4
4	4	4/5	4	4/5	4	4
5	4	5	4	4/5	4/5	4/5

Fastness Properties

Table 3 shows the result of wash fastness of dyes 1-5 on polyester/cotton (65/35) blend fabric. The dyes showed moderate to good wash fastness. They suffered from some staining to acetate, nylon and wool. The staining or colour change seems to be due to polyester part rather than cotton part of the blend fabric. Table 4 shows the results of light, rubbing and sublimation fastness. The rubbing and sublimation fastness of dyes 1-5 were moderate to good. The lightfastness of dyes 1, 3, 4, and 5 was moderate whereas that of dye 2 was very poor of grade 1. From experimental data, it is usually accepted that the lower the basicity of the amino nitrogen atom in the dye molecule, the greater the light fastness of the azo dye[22]. Dye 2 has free amino group of high basicity and this group seems to cause the poor level of lightfastness of the dye.

Conclusions

Temporarily solubilized reactive disperse dyes containing β-sulfatoethylsulfonyl group were synthesized and the feasibility of one-bath dyeing of polyester/cotton blend fabric was examined. The dyes were synthesized by common diazo-coupling reaction. Polyester/cotton blend could be dyed with synthesized dyes using one-bath dyeing method without dispersing agent. The result of colour yield data of dye 2 suggested that the dye should be exhausted to polyester part of P/C blend in the first dyeing stage at 130 °C and then react with cotton part after alkali was added to the dyebath in the second dyeing stage at 60 °C. In the case of dyes 1, 3, 4, and 5, most of the dye seemed to be exhausted on polyester part of the P/C blend fabric and very small amount of the dye on cotton part. Temporarily solubilized reactive disperse dyes exhibited good leveling property on P/C blend and overall fastness of the dyes was moderate to good with a few exceptions.

Acknowledgement

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