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〈Research Paper〉

Dispersant-free dyeing of acetate with temporarily solubilized azo disperse dyes

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Abstract— Temporarily solubilized azo disperse dyes containing β-sulfatoethylsulfonyl group were applied to acetate fabric and the feasibility of dispersant-free dyeing was investigated. The color yields of the dyes on acetate fabric were found to be dependent on dye bath pH as well as dyeing temperature. The optimum results were obtained at pH 6 and 80℃. The dyes showed good exhaustion and levelling properties. Vinylsulfone derivatives of the dyes were prepared and applied to acetate with dispersant. Dyeing properties of the temporarily solubilized disperse dyes were similar to or better than those of the vinylsulfone dyes. The dyes showed moderate to good fastness properties on acetate.

Keywords: *Temporarily solubilized azo disperse dye, β-sulfatoethylsulfonyl group, Dispersant-free dyeing, Acetate, levelling property*

1. Introduction

When cellulose acetate fibers were first produced by the British Celanese Company in the 1920s, they presented a serious problem to the dyer. Since they were hydrophobic and could not be penetrated by water, they could not be dyed by water-soluble dyes[1]. In 1922, Green and Saunders invented the dyes for cellulose acetate, which had methane-sulfonyl group in their molecular structures. These 'temporarily solubilized' dyes were marketed as the Ionamines, the example given in Scheme 1 being Ionamine Red KA(BDC), C.I. 13040. The Ionamine range of dyes were the intermediate precursor of disperse dyes. They are hydrolyzed in the dye bath during dyeing to form parent, insoluble dye that are adsorbed onto the surface of the hydrophobic acetate fiber, and diffuse into it. However, these dyes were not developed further owing to the difficulty in controlling their rate of hydrolysis. This dye range was superseded in 1920s by ranges of disperse dyes, that were devoid of ionic solubilizing groups[2-4].

After polyester fiber was introduced in 1950s, lots of works about disperse dyes were concentrated on application to polyester instead of acetate fiber. However, acetate and its blend fibers are still widely used such as suits for women, sports wear and socks. Disperse dyeing of hydrophobic fiber such as acetate and PET is usually performed in the presence of dispersants. Dispersants are added to increase solubility of dye and to maintain dispersion stability during dyeing. However, they may cause staining of the fabric. They are also discharged as effluents with the residual dyeing liquor, which increases the COD and BOD values of the effluent [5].

In an effort to overcome some of the environmental problems associated with the use of dispersants, our group prepared temporarily solubilized azo disperse dyes containing β-sulfatoethylsulfonyl group and investigated the feasibility of dispersant-free polyester dyeing[6-7]. The terminal sodium sulfate group of the dye confers on sufficient water solubility at room temperature without the aid of dispersants. During the dyeing procedure,

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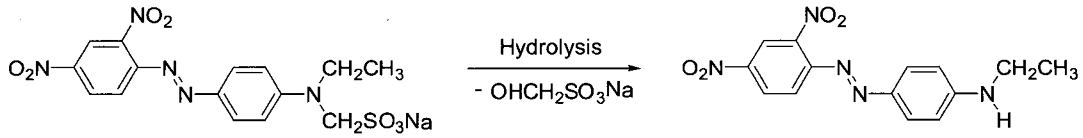
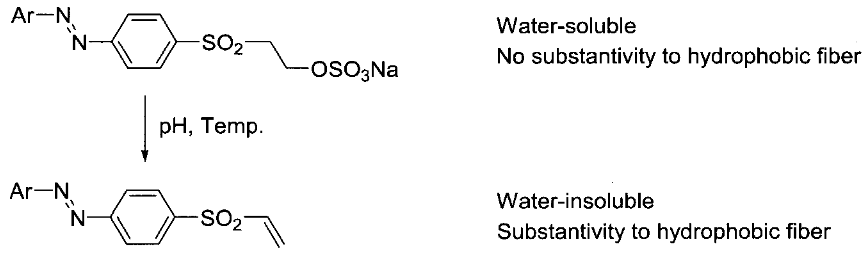


Scheme 1. Structure of Ionamine Red KA and hydrolysis of the dye during dyeing.



Scheme 2. Conversion of β-sulfatoethylsulfonyl group into vinylsulfone group of the temporarily solubilized disperse dyes.

the soluble dye is gradually converted to insoluble form as the β-sulfatoethylsulfonyl group is hydrolyzed into vinylsulfone group through β-elimination reaction(Scheme 2). Then the water-insoluble form of the dye having substantivity to hydrophobic polyester fiber can be adsorbed onto polyester. The temporarily solubilized disperse dyes were successfully dyed on polyester without using dispersants and they exhibited moderate to good fastness properties.

Recently, our group has attempted to synthesize the temporarily solubilized disperse dyes which have more variety of color range. Thus, a series of dyes of azopyridone[8] and azoindole[9] derivatives for the yellow color and aminoazobenzene[10] for orange, red and purple color shade were reported.

Thus, several works about dyeing properties of the temporarily solubilized disperse dyes containing β-sulfatoethylsulfonyl group on polyester and its blend have been reported. However, application of the dyes to acetate fiber has not been studied yet. Although polyester and acetate fibers are both hydrophobic and fiber structures, the dyeing properties are quite different from each other. For example, disperse dyes suitable for relatively open structured acetate are often found unsuitable for the much more hydrophobic polyester. In this study, dispersant-free dyeing of the temporarily solubilized dyes on acetate fabric was investigated. The effect of dye bath pH or dyeing temperature on color yield was studied. In order to compare dyeing properties of the dyes to those of vinylsulfone dyes, vinylfulfone derivatives were prepared and applied to acetate fabric using dispersant. Color fastness and levelling properties of the dyes have also been examined.

2. Experimental

2.1. Materials

Scoured, woven acetate fabric(148×74 tpi, 187 g/yd) was obtained from SK Chemical Co. Temporarily solubilized disperse dyes 1-3 were prepared as described in previous papers[8, 10]. The structures and spectral data of the dyes are shown in Fig. 1 and Table 1.

2.2. Dispersant-free dyeing of acetate

Acetate fabric was dyed in an Ahiba dyeing machine at a liquor ratio of 20:1. The dye baths were prepared with the dyes 1-3 without using any dispersants and buffered as follows: at pH 5 with sodium acetate(0.05M)/acetic acid, at pH 6, 7 and 8 with sodium dihydrogen phosphate(0.05 M)/disodium hydrogen phosphate and at pH 9 with sodium dihydrogen phsphate(0.05 M)/trisodium phosphate.

Dyeing was performed at 50 ℃. The dyebath temperature was raised at a rate of 1℃/min to 88 or 98℃, maintained at these temperatures for 60 min and then rapidly cooled to room temperature. The dyeings were rinsed and then reduction cleared in an aqueous solution of 2g/l sodium hydroxide and 2g/l sodium hydrosulfite at 70 or 80℃ for 20 min.

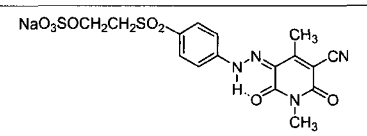
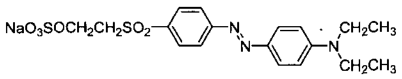
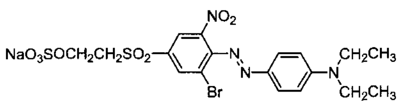
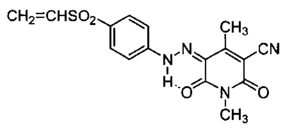
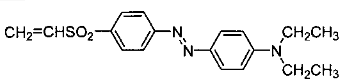
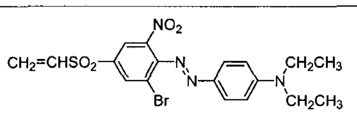
Dye	Structure
1	
2	
3	
4	
5	
6	

Fig. 1. Chemical structures of dyes used in this study.

Table 1. Spectral data of temporarily solubilized azo disperse dyes

Dye	λ_{max} [a] (nm)	ε_{max} [a] (l mol^{-1} cm^{-1})
1	430	40,200
2	464	30,000
3	508	30,800

[a] measured in DMF

The color parameters of the dyed fabrics were determined on a Macbeth coloreye 3000 spectrophotometer, under illuminant D65 using the 10° standard observer with specular component excluded and UV component included.

2.3. Preparation of vinylsulfone dyes 4-6 and dyeing

Three grams of dye 1 was dissolved in water(300 ml) and about 10 g of sodium carbonate was added into the solution with pH adjusted to 11. The solution was stirred for 3 hrs and the precipitated dye(dye 4) was filtered and dried. Dyes 5 and 6 were obtained from dyes 2 and 3 respectively in a similar manner (Scheme 3). The structures of dyes 4-6 are shown in Table 1.

One gram of dyes 4, 5 or 6 was added to the mixture of dispersant (1.33 g), wetting agent(1 ml/l) and water(100 ml). The pH of the mixture was adjusted to 4-4.5 using sodium acetate and acetic acid and then 480 g of glass bead was added. After milling around a week, the dye dispersion was directly used as dyeing liquor. Acetate fabric was dyed with the dyeing liquor from dyes 4-6 at 98℃ for 60 min with a similar procedure to that for dyes 1-3 except that 1 g/l of dispersant was added to the dye bath.

2.4. Exhaustion and levelling properties of dyes

The exhaustion of dye on the acetate fabric was measured by dye bath residue method. Before and after dyeing, five milliliters of dye bath was extracted and mixed with pyridine(15 ml) and then the absorbance of the solution was determined using a HP 8452A UV/VIS spectrophotometer. The percentage exhaustion was calculated using Equation 1:

$$\text{Exhaustion}\ (\%) = (C_0 - C_t)/C_0 \times 100 \qquad (1)$$

where C_t is the amount of dye in the residual dyebath at time t and C_0 is the amount of dye in the initial dyebath.

Five locations on the dyed fabric were arbitrarily chosen and L^*, a^* and b^* values were measured by spectrophotometer. The CIEL*a*b* color difference between any two points was calculated[11]. The levelling properties of the dyes on acetate fabric were assessed using the mean of 10 such color difference results.

2.5. Fastness test

The dyed fabrics were subjected to wash (ISO 105-C06/C2S:1994), light(AATCC Test Method 16A-1998), rubbing(ISO 105-X12:2001) and perspiration

$$\text{Dye}-SO_2CH_2CH_2OSO_3Na \xrightarrow[\text{pH 11}]{Na_2CO_3} \text{Dye}-SO_2CH{=}CH_2$$

Scheme 3. Synthesis of dyes of vinylsulfone derivatives (dyes 4-6) from dyes 1-3.

(ISO 105-E04:2001) fastness tests after heat setting at 170 ℃ for 60 sec. The shade change, together with staining of adjacent fabrics, was assessed according to appropriate SDC grey scale.

3. Results and Discussion

3.1. Dyeing properties

As shown in previous studies[6, 7], pH condition and dyeing temperature are crucial factors for application of temporarily solubilized disperse dyes because the above mentioned factors are directly related to the conversion rate of soluble β-sulfatoethylsulfone form into insoluble vinylsulfone form. Therefore, it is important to investigate the effect of pH condition and dyeing temperature on the color yield of acetate fabric. Fig.s 2-4 show the color yields of dyes 1-3 on acetate fabric at various pH values and at 88 or 98 ℃ dyeing temperature. As expected, the color yields were highly dependent upon dyeing pH as well as dyeing temperature.

In Fig. 2, a good color yield was obtained at pH 6 irrespective of dyeing temperature studied. At pH 5, dyeing rate was slow and color yield was lower than that at pH 6, which is due to the low conversion rate of the soluble dye into the insoluble vinylsulfone form. In a previous paper, color yield of dye 1 on polyester fabric was quite good at pH 5[8]. This can be explained by considering that polyester was dyed at 130℃ while acetate in this study was dyed at 88 and 98℃. Thus pH 5 is a good condition for high temperature dyeing but could be less effective at low temperatures. Color yields at over pH 7 were unsatisfactory, which can be attributed to the rapid conversion of dye causing a collapse in the dyebath dispersion stability. The dyed fabric at pH 8 and 9 also showed unlevelness. In case of dyeing temperature, 98 ℃ was better because, at pH 6, dyeing was equilibrated earlier at 98 ℃ than at 88 ℃.

This can be explained that, at higher temperature, the activation energy of dyeing decreases, which makes the dye diffuse into the acetate fiber more easily. Fig. 3 shows that dyeing behavior of dye 2 on acetate is similar to that of dye 1.

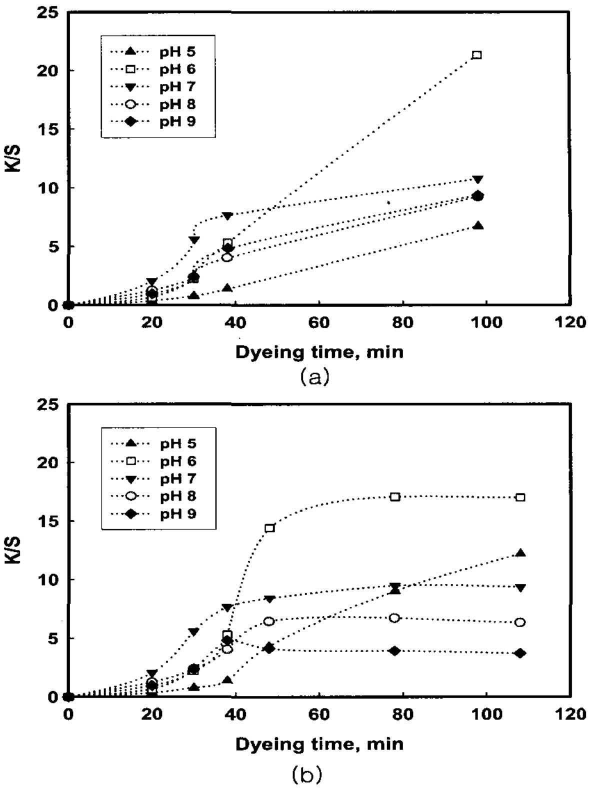


Fig. 2. The effect of pH and dyeing temperature on color yield of dye 1(1% owf) on acetate fabric dyed at (a) 88 ℃ and (b) 98 ℃.

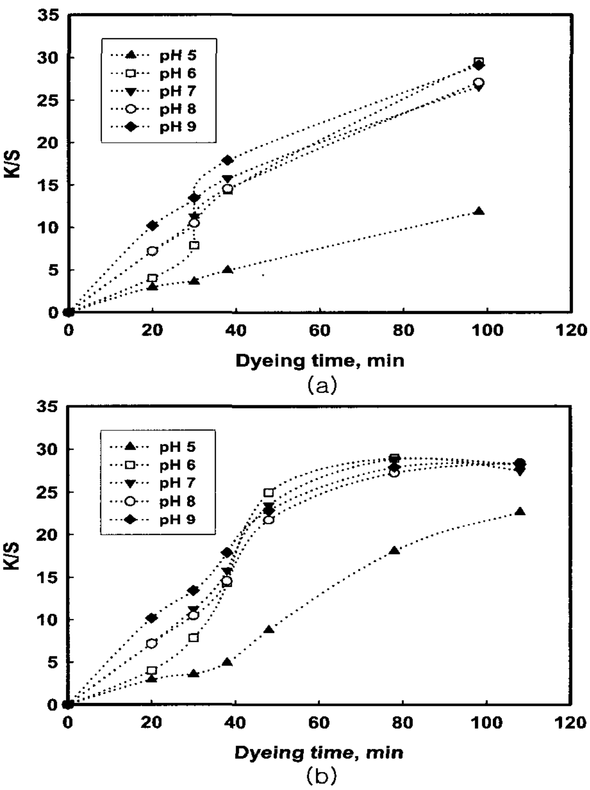
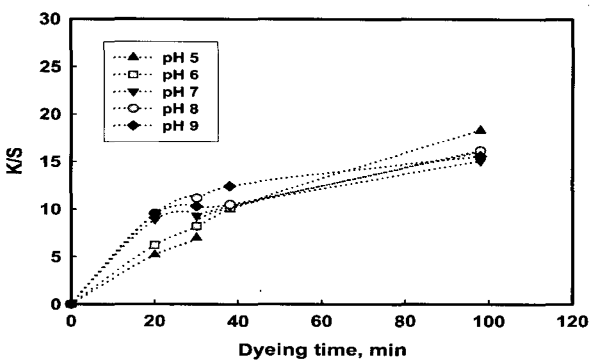
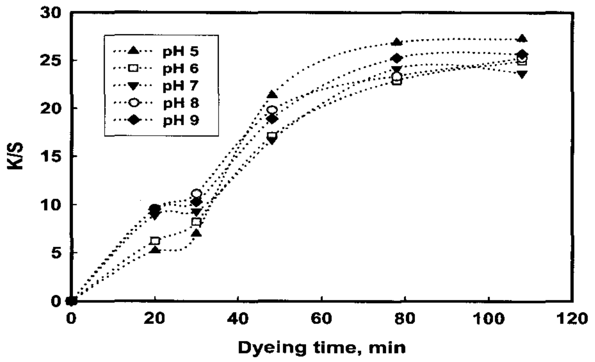


Fig. 3. The effect of pH and dyeing temperature on color yield of dye 2 (1% owf) on acetate fabric dyed at (a) 88 ℃ and (b) 98 ℃.



(a)



(b)

Fig. 4. The effect of pH and dyeing temperature on color yield of dye 3 (1% owf) on acetate fabric dyed at (a) 88 ℃ and (b) 98 ℃.

Thus color yield at pH 5 was lower than those at the other pH values because of low conversion rate of dye. At pH 6 and over, all the color yields were high but dyeing curve at pH 6 seemed to be the best and similar to that for the polyester fabric at optimum dyeing condition. Color yield of dye 3 on acetate was not highly dependent on pH values as shown in Fig. 4. Thus, color yields were generally good even at pH 5. This result means that conversion rate of dye 3 from soluble dye into insoluble form is not too low at pH 5 and less sensitive to pH values when compared to that of dye 1 or 2. Higher color yield was obtained for 98 ℃ than 88 ℃ dyeing temperature . From the above results, 98 ℃ and pH 6 were chosen as the optimum dyeing condition of the dyes 1-3 for acetate.

Exhaustion of dye on polyester is usually measured by DMF extraction method. However, the method cannot be applied to the dye containing pyridone moiety such as dyes 1 and 4 because of the degradation of dye during DMF extraction.

Therefore, in this study, the percentage exhaustion of the dye on acetate was determined by dye bath residue method. In order to prepare clear solution of dye bath, small part of dye bath was extracted and mixed with pyridine to make 25% pyridine solution. And then the absorbance of the solution was measured and exhaustion was calculated. The percent exhaustion values of the dyes 1-3 on acetate fabric at various pH values are shown in Table 2. The effect of pH condition on exhaustion was similar to that on color yield. The maximum exhaustion values of the dyes were over 96.9%.

Fig. 5 shows the build-up of the dyes at optimum dyeing condition. Dyes 2 and 3 exhibited good build-up on acetate although color strength of the dye 1 reached saturation at 1% owf.

In order to compare the dyeing properties of the temporarily solubilized disperse dyes containing β-sulfatoethylsulfonyl group with those of vinylsulfone dyes, vinylfulfone derivatives or dyes 4-6 were prepared by hydrolyzing the dyes 1-3. When dyes 4-6 were applied to acetate fabric, dispersant was added to the dye bath as the vinylsulfone dyes were not soluble in water. Table 3 shows final color yield and percent exhaustion values of the dyes 4-6 on acetate fabric. K/S value of the acetate fabric dyed with the vinylsulfone dyes 4-6 using dispersant was

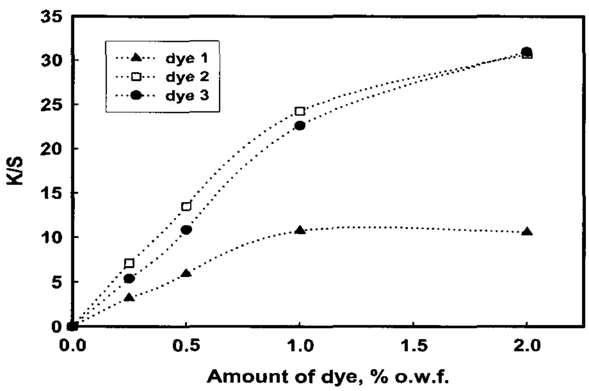


Fig. 5. Build-up properties of dyes 1-3 on acetate fabric (dyed at 98 ℃ for 60 min at pH 6).

Table 2. Percent exhaustion values of dyes 1-3 (1% owf) on acetate fabric(dyed at 98 ℃ for 60 min)

Dye	Dyeing pH				
	5	6	7	8	9
1	76.7	93.9	80.8	81.8	96.9
2	80.6	99.4	99.5	98.4	99.3
3	96.9	87.8	90.5	97.2	96.9

Table 3. Color yield (K/S)· and percent exhaustion values of dyes 4-6 (1% owf) on acetate fabric (dyed at 98℃ for 60min with pH 4.5)

Dye	K/S	Exhaustion (%)
4	8.6	49.1
5	29.8	87.7
6	26.0	62.6

similar to that with the corresponding β-sulfatoethylsulfone dyes 1-3 without using dispersant. The dyes 4-6 showed lower percent exhaustion values than the dyes 1-3. From the results, it can be said that the dyeing properties of the temporarily solubilized disperse dyes are similar to or better than those of the vinylsulfone dyes.

All the dyes showed good levelling on the acetate fabric. Table 4 gives the average of 10 results for the color differences at five random locations of the dyed acetate fabric. All the dyes showed small color differences between locations, suggesting that levelling was good.

3.2. Fastness properties

All the dyeings for the fastness tests were carried out with 1% owf at pH 6. Table 5 shows the results of the wash fastness tests for dyes 1-3 on acetate and dye 1 showed good to excellent wash fastness whiledye 2 and 3 showed moderate for the staining on acetate, nylon and wool and good on the other

Table 5. The wash fastness of dyes 1-3 (1% owf) on acetate fabric

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

Table 6. The light and rubbing fastness of dyes 1-3 (1% owf) on acetate fabric

Dye	Light	Rubbing-staining	
		Dry	Wet
1	5	4/5	4/5
2	5	3	3/4
3	3/4	3	3

adjacent fabrics. Table 6 gives the results of the light and rubbing fastness tests. The lightfastness of dye 1 and 2 are good while dye 3 showed moderate fastness. Dye 3 contains bromo or methoxy group in its structure and these bulky groups seem to prevent the dye molecules from aggregating to each other in the fabric, which could result low lightfastness.

Rubbing fastness was moderate to good. The results of the perspiration fastness tests are summarized in Table 7 and showed good to excellent with a few exceptions.

Table 4. Color differences between five points of acetate fabric

Dye	Color differences										
	1	2	3	4	5	6	7	8	9	10	Avg.
1	0.49	0.13	0.24	0.83	0.46	0.46	1.25	0.12	0.81	0.81	0.56
2	0.34	0.55	0.16	0.95	0.49	0.22	0.71	0.45	1.02	0.82	0.57
3	0.14	0.46	0.26	0.49	0.34	0.29	0.38	0.61	0.11	0.67	0.37
4	0.97	1.17	1.45	0.61	0.33	0.66	0.87	0.35	0.91	1.14	0.85
5	0.44	0.24	0.11	0.25	0.60	0.38	0.37	0.29	0.46	0.29	0.34
6	0.53	0.18	0.16	0.31	0.35	0.65	0.25	0.31	0.17	0.47	0.34

Table 7. The perspiration fastness of dyes 1-3 (1% owf) on acetate fabric

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

4. Conclusions

Dispersant-free dyeing and fastness properties of temporarily solubilized azo disperse dyes containing β-sulfatoethylsulfonyl group were examined.

Acetate fabrics were successfully dyed with the dyes without using any dispersant. The color yields of the dyes on acetate were dependent upon dyeing pH. The optimum result was obtained at pH 6. Dyeing at 98℃ was equilibrated earlier than at 88 ℃. Exhaustion of the dyes was determined by preparing pyridine aqueous solution from the dyebath extract and maximum exhaustion values of the dyes 1-3 were over 96%. Color yield and exhaustion values of the temporarily solubilized disperse dyes were similar to or higher than those of vinylsulfone derivatives with dispersant. The dyes 2 and 3 showed good build-up and all the dyes exhibited good levelling properties. The dyes exhibited moderate to good wash, light and rubbing fastness and perspiration fastness results were good to excellent.

It is expected that dyehouse effluent from acetate dyeing with the temporarily solubilized azo disperse dyes should be cleaner than that from conventional disperse dyeing. It is also expected that these eco-friendly dyes can be applied to not only acetate itself but also to its blend or union fabric such as polyester/acetate and acetate/nylon.

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