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Dye-resist Properties of Hetero-multifunctional Dye-resist Agents in Acid Dyeing of Wool

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Abstract: The dye-resist effect and leveling properties of hetero-mulifunctional dye-resist agents in acid dyeing of wool were investigated. The dye-resist agent with dichlorotriazinyl group achieved better resist effectiveness than those with monochlorotriazinyl group. The resist effectiveness was improved by increasing the number of sulfonate group in dye-resist agents. Also, the resist agents with more sulfonate groups showed better dye-assist effectivness, attributable to the increased electrostatic attraction between dye-resist agents and the cationic dye. However, the leveling properties of dye-resist agents decreased with the number of sulfonate groups in the molecule.

Keywords: Dye-resist, Acid dye, Wool, Dye-resist agent, Leveling property

Introduction

A dye-resist process is one in which the dye uptake is lower or less than that on the untreated substrate, and can be obtained by either physical methods or chemical modification of the substrate which is to be resist printed [1]. An effective dye-resist process has been sought as an alternative to the conventional discharge process used in wool dyeing and printing. Dye-resist agents have shown potential as reserving agents during the union dyeing of wool/nylon or wool/cotton blends. Various chemicals have been designed and studied for imparting dye-resist effects on wool [2-12]. Among them, reactive dye-resist agents are preferred because of their easy handling and application [3].

In previous work, we compared the resist effectiveness and leveling properties of α-bromoacrylamide based and 2,4-dichloro-s-triazine based dye-resist agents for wool [13]. The dichlorotriazine based dye-resist agents showed higher resist effectiveness than their α-bromoacrylamide counterparts. However, the dye-resists based on α-bromoacrylamide achieved better leveling properties than those based on dichlorotriazine.

In this study, the dye-resist effectiveness and leveling property of hetero-multifunctional reactive dye-resist agents in acid dyeing of wool were investigated.

Experimental

Materials

The scoured wool fabrics (plain weave, 102 g/m^2, KS K 0905) were used for dyeing. All the chemicals used in this study were of laboratory-reagent grade. The dyes used in this study are shown in Table 1.

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Synthesis of Dye-resist Agents

The synthesis of hetero-multifunctional reactive dye-resist agents has been described in the previous work [14,15]. The synthesized dye-resist agents DR-1~DR-5 that were used throughout the study were given in Table 2.

Application of Reactive Dye-resist Agents on Wool Fabrics

A 5 g wool sample was pre-treated with each reactive dye-resist agents at various concentrations (1, 2, 4, 8 and 16 % owf) by an exhaustion process using a liquor ratio of 20:1 using a Laboratory IR Dyeing Machine (Ahiba Nuance, Datacolor, Switzerland). The pretreatment bath was composed as follows:

Wetting agent (Albegal FFA, 0.25 g/*l*) as; dye-resist agents (x% o.w.f.); pH 4.5 buer system (acetic acid/sodiumacetate).

The process was started at 40 °C and run for 10 min, during which a pH of 4.5 was established and the dye-resist agents were added. Then the dyebath was raised to the boil over 60 min, held for 60 min at 100 °C and cooled over 10 min to 80 °C. Afterwards, samples were rinsed and dried at room temperature.

Determination of Mass Gain

The degree of fixation of the reactive dye-resist agents examined in this work was assessed as dry mass gains, calculated from oven-dry masses determined before and after the treatment. The wool samples were dried to a constant mass in a circulating oven at 95 °C.

Dyeing of Wool Fabrics

The resist effectiveness of reactive dye-resist agents on wool was evaluated with the dyes **1-6**. These dyes were applied to wool fabric at dye concentrations shown 1/1 standard depth on untreated wool. In order to simulate commercial resist dyeing, competition dyeing method used

Table 1. Dyes used in this study

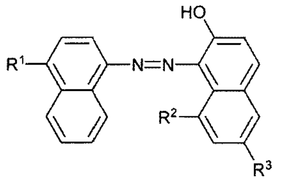
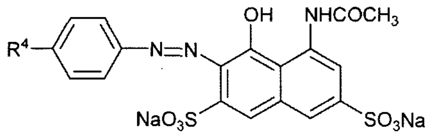
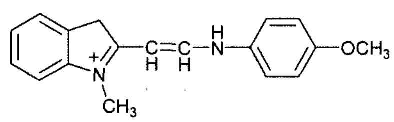
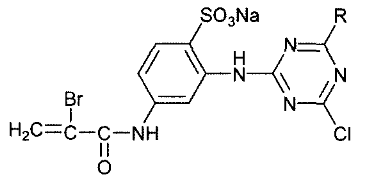
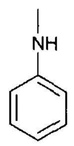
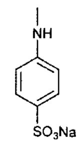
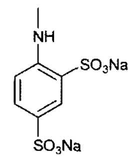
Group	Chemical structures	Dye	Substituents/Generic name
I		1	$R^1 = SO_3Na$, $R^2 = H$, $R^3 = H$ C.I. Acid Red 88
		2	$R^1 = H$, $R^2 = SO_3Na$, $R^3 = SO_3Na$ C.I. Acid Red 44
		3	$R^1 = SO_3Na$ $R^2 = SO_3Na$, $R^3 = SO_3Na$ C.I. Acid Red 18
II		4	$R^4 = H$ C.I. Acid Red 1
		5	$R^4 = C_{12}H_{25}$ C.I. Acid Red 138
III		6	C.I. Basic Yellow 13

Table 2. Reactive dye-resist agents used in this study



Dye-resist agents	DR-1	DR-2	DR-3	DR-4	DR-5
R	-Cl	$-NH-(CH_2)_{11}-CH_3$			

by Bell *et al.* [5] was carried out with a 3:1 (w/w) ratio of untreated to treated wool, using a liquor ratio of 20:1. The process was started at 40 and run for 10 min, during which a pH of 4.5 was stabilized and the acid dyes were added. The dyebath was composed as follows:

Wetting agent (Albegal FFA, 0.25 g/*l*); glauber's salt (5 % o.m.f.); dye.

Then the dyebath was raised to 100 °C over 50 min, held for 60 min and cooled over 10 min to 80 °C. The samples were rinsed and dried at room temperature.

Determination of Migration Index (MI) of Acid Dyes

The procedure used for the measurement of migration index of a reactive dye is described in a previous report by Rashid *et al.* [15]. Each dye was applied at the concentration for 1/1 standard depth to wool samples under the same condition described earlier. Wool samples (of weight 2.5 g each) and two baths were used as follows:

- the dyebath containing dye, auxiliaries and water plus two fabric samples (marked D1 and D2)
- the blank bath containing auxiliaries and water plus two fabric samples (marked B1 and B2).

After the two baths were dyed together, sample D2 from the dyebath was exchanged with sample B2 from the blank bath, excess liquor being squeezed during the transfer. Sample B2 was rolled inside sample D1 before being returned to the dyebath. In a similar manner, sample B1 was rolled inside sample D2 before being returned to the blank bath. The same dyeing process was repeated under the same dyeing condition in order to allow migration to occur in the balk bath. The fabric samples were then removed washed and dried.

The K/S values of dyed samples and migrated samples were measured using a spectrophotometer (Color-Eye 3000, Macbeth, standard light D65, 10° standard observer, specular component included) interfaced with a personal computer.

The migration index (MI) was calculated according to equation (1):

$$\text{MI}(\%) = \frac{(K/S)_{migrated}}{(K/S)_{dyed}} \times 100 \qquad (1)$$

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

K: Absorption coefficient

S: Scattering coefficient

R: Reflectance

$(K/S)_{migrated}$: K/S values migrated samples

$(K/S)_{dyed}$: K/S values of dyed samples

If the visual color yields of fabrics B1 and D2 were the same, then complete color redistribution would have occurred and the migration index would be 100 %.

Evaluation of Dye-resist Effect

The extent of resist effectiveness was quantied by using the following equation with K/S values of the dyed fabric obtained on a spectrophotometer at the wavelength of maximum absorption. The percentage resist was then calculated by using equation (2) [5]:

$$\%\,\text{Resist} = \frac{(K/S)_{untreated} - (K/S)_{treated}}{(K/S)_{untreated}} \times 100 \qquad (2)$$

where, $(K/S)_{treated}$: K/S values of dye-resist treated samples

$(K/S)_{untreated}$: K/S values of untreated samples

Leveling Test of Reactive Dye-resist Agents

A pretreatment bath containing appropriate auxiliaries and each reactive dye-resist agents at the concentration to obtain 80 % dye-resist effectiveness was prepared. A 2.5 g wool sample was treated from the start to 70 °C, then, another 2.5 g sample was put in the same bath and treated together for 60 min at 100 °C as described earlier. The treated samples were dyed and their resist effectiveness of each sample was evaluated. The less the difference of %resist between sample treated from 40 °C and sample treated from 70 °C, the better leveling property.

Results and Discussion

Dye-resist Effect

For dye group I (dyes 1-3), a series of acid dyes having dierent numbers of sulfonate groups were selected. The resist effectiveness of dye-resists against dyes 1-3 is shown in Figure 1. As the mass gain of dye-resist agent increases, resist effect to reactive dyeing is obtained since the pretreatment of wool with dye-resist agents containing hetero-multifunctional group restricts the exhaustion of acid dyes on wool, due to their prior occupation of dyeing site of wool

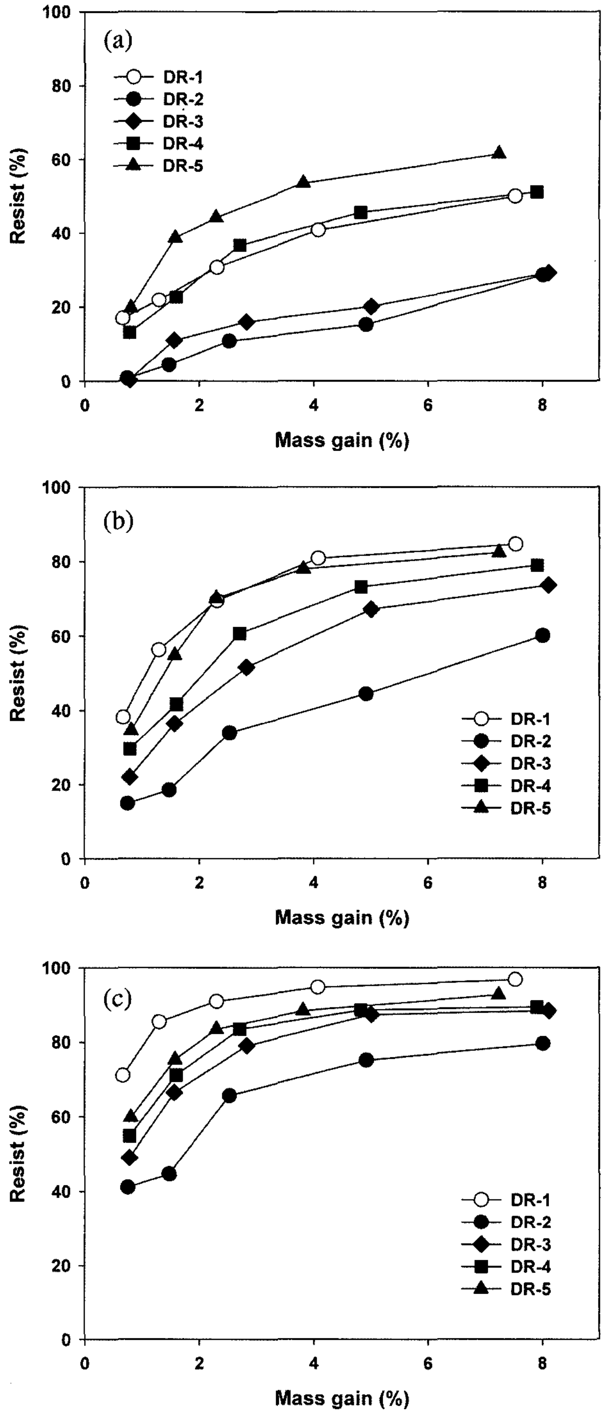


Figure 1. Resist efficiency against dye group I on wool treated with various hetero-multifunctional reactive dye-resist agents. (a) dye 1 (C.I. Acid Red 88), (b) dye 2 (C.I. Acid Red 44), (c) dye 3 (C.I. Acid Red 18).

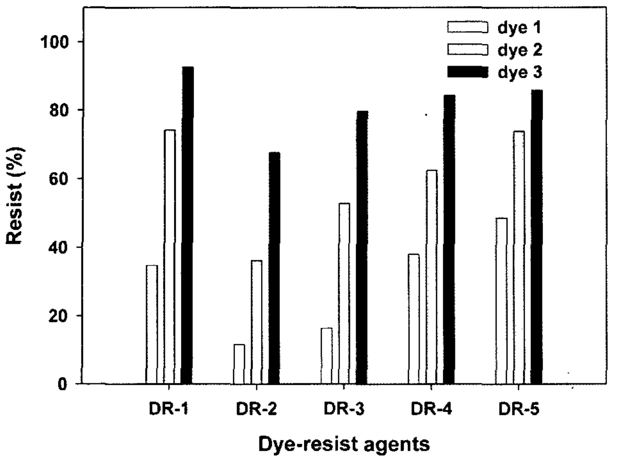


Figure 2. Resist effectiveness of dye-resist treated wool against reactive dyes 1-3 at 3.0 % mass gain.

and electrostatic repulsion with anionic groups of acid dyes.

In a previous study [13], negative resist effect (assist effect) of α-bromoacrylamide based dye-resist agents at lower mass gains in acid dyeing of wool was obtained since the dye-assist effect due to the wool damage during the wool treatment is greater than the resist effect at low mass gain. However, in this study, dye-assist effect was not dominant compared with dye-resist effect at lower mass gains. This result demonstrates that dye-resist effect of hetero-multifunctional dye-resist agents used in this study is greater than monofunctional ones. Therefore, the dye-resist effect is more dominant than dye-assist effect by wool damage in high temperature, irrespective of the mass gain.

Figure 2 shows the resist effectiveness of wool treated with each resist agent to dye group I at 3 % mass gain. Generally, dichlorotriazine based resist agents have better resist effect than α-bromoacrylamide based ones. It is known that dichlorotriazinyl group is more reactive than monochlorotriazin group and can react with wool ber bifunctionally. Therefore it is presumed that dichlorotriazine based agents will deactivate the dye binding sites on ber surface more effectively than monochlorotriazine derivatives, resulting better resist effectiveness [13].

As expected dye-resist agent DR-1 having dichlorotriazinyl group showed better resist effectiveness than dye-resist agent DR-2 having monochlorotriazinyl group since more reactive dichlorotriazinyl group can deactivate the more dyeing sites compared with monochlorotriazinyl group. Also, when compare the resist effectiveness of dye-resist agents having same reactive groups (DR-2, DR-3, DR-4 and DR-5), the resist agents with more sulfonate groups showed better resist effectivness due to the increased electrostatic repulsion between dye-resist agents and dyes (DR-2 < DR-3 < DR-4 < DR-5). In the case of dye-resist DR-2, having hydrophobic aliphatic chains and no sulfonate group in cyanuric chloride ring, showed the lowest dye-resist effectivenss.

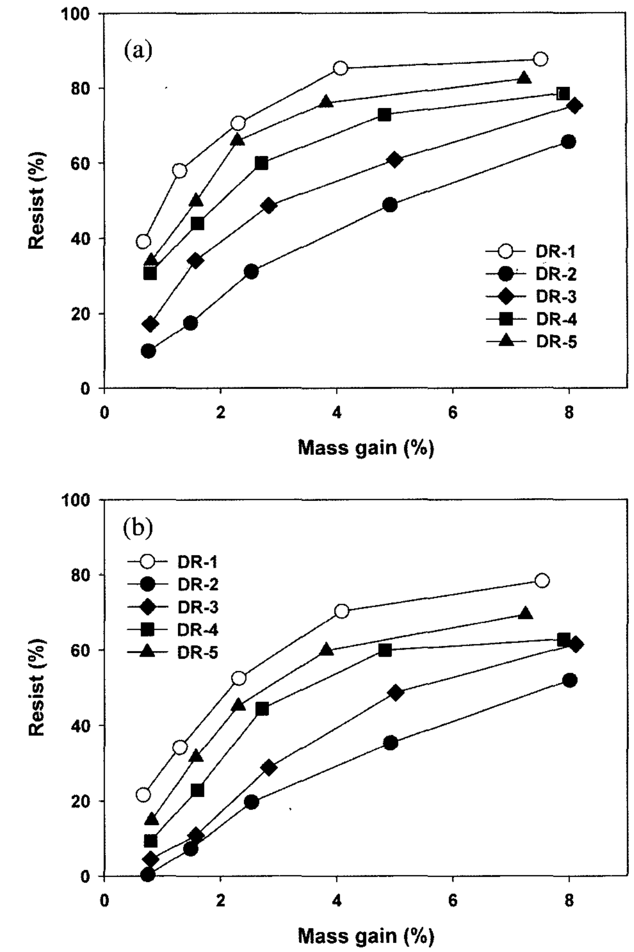


Figure 3. Resist efficiency against dye group II on wool treated with various hetero-multifunctional reactive dye-resist agents (a) dye 4 (C.I. Acid Red 1), (b) dye 5 (C.I. Acid Red 138).

A dye-resist effect can be achieved when the interaction between dye and ber is eciently prevented. This may be achieved in three dierent ways:

- electrostatic repulsion between dye molecules and wool ber
- hindrance of dye diusion into wool ber
- deactivation of reactive dye binding sites

The resist effectiveness of the five reactive dye-resist agents varies greatly with the types of acid dyes used. An increase in the number of ionic groups in acid dyes leads to better electrostatic repulsion of reactive resist-treated wool and thus improves the resist effectiveness (dye 1 < dye 2 < dye 3). Dye 1 (C.I. Acid Red 88, the monosulfonate dye) is poorly resisted since the ionic repulsion between the dye anions and the sulfonate groups of dye-resists is weak, compared to the hydrophobic forces responsible for dye uptake on wool. Dye 3 (C.I. Acid Red 18, the trisulfonate dye) is strongly resisted due to the stronger ionic repulsion between dye anions of higher charge and dye-resist-treated wool.

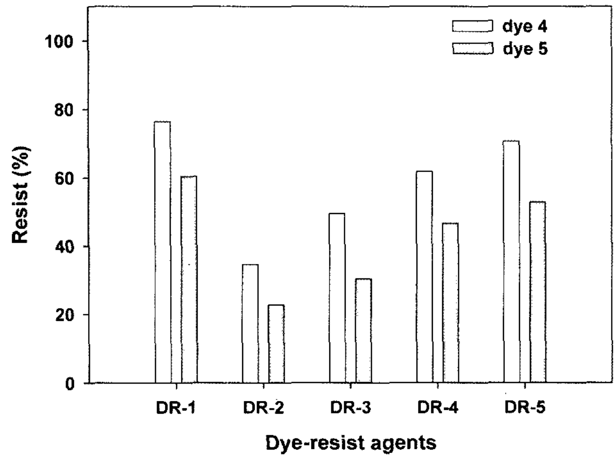


Figure 4. Resist effectiveness of dye-resist treated wool against reactive dyes 4 and 5 at 3.0 % mass gain.

For dye group II (dyes 4 and 5), a series of acid dyes having dierent hydrophobicity were selected. The resist effectiveness of dye-resists against dyes 4 and 5 is shown in Figure 3. The similar results with dye group I were observed: the resist agents with more sulfonate groups or less reactive group showed better resist (DR-2 < DR-3 < DR-4 < DR-5 < DR-1).

In Figure 4, the resist effectiveness of wool treated with each resist agent to dye group 2 at 3 % mass gain was compared. The more hydrophobic dye 5, due to the greater anity for wool, showed lower resist effectiveness than less hydrophobic dye 4.

Zollinger has stated that four types of interactions must be considered between acid dyes and wool, namely [16]:

- electrostatic forces
- van der Waals forces
- hydrogen bonds
- hydrophobic interactions

The migration indexes of acid dyes used in this study are shown in Table 3. Dye 5 containing hydrophobic aliphatic chain (dodecyl group) showed the lowest migration index (3 %) among the acid dyes used in this study. This result demonstrates that the hydrophobic interaction between dye 5 and wool fiber inhibited the dye migration on the wool fiber.

These same interactions are responsible for the low migration property of dye-resist agent DR-2 containing dodecyl group : the poor migration property lowers the cross-linking ability and resist property due to their less prior occupation of dye binding sites, although it has two reactive groups. The low migration property of DR-2 was verified by urea/bisulfite solution test in previous study [15].

Table 3. Migration indexes of acid dyes used in this study

Dyes		K/S		MI
		Dyed	Undyed	(%)
Group I	Dye-1	10.78	7.83	73 %
	Dye-2	10.33	7.25	70 %
	Dye-3	13.34	5.48	41 %
Group II	Dye-4	14.07	10.84	77 %
	Dye-5	19.93	0.49	3 %

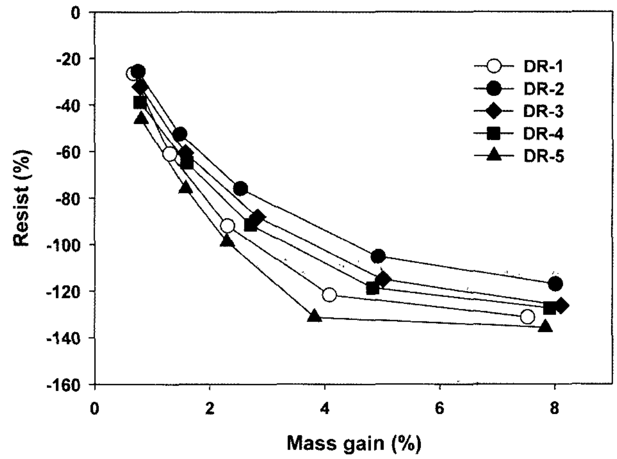


Figure 5. Dye assist effect of hetero-multifunctional reactive dye-resist agents in cationic dyeing of wool (dye 6, C.I. Basic Yellow 13).

Dye-assist Effect

A cationic dye, dye 6 (C.I. Basic Yellow 13) was applied to wool fiber in order to investigate the dye-assist effect (negative dye-resist effect) of hetero-multifunctional dye-resist agent in wool dyeing.

Figure 5 shows the dye-assist effect of hetero-multifunctional reactive dye-resist agents in wool dyeing with a cationic dye (dye 6, C.I. Basic Yellow 13). The dye-assist effect increased with increasing mass gain of dye-resist agents. The resist agents with more sulfonate groups showed better dye-assist effectivness, attributable to the increased electrostatic attraction between dye-resist agents and the cationic dye 6 (DR-2 < DR-3 < DR-4 < DR-5). This result demonstrates that the dye-resist agents reacted with wool fiber function as dye binding sites in cationic dyeing of wool.

Leveling Properties

The results of leveling test of reactive dye-resist agents for dye 3 are shown in Figure 6. Resist agents exhibiting smaller difference in %resist between the sample treated from 40 °C and that from 70 °C have higher leveling property. Dye-resist agent DR-1 having dichlorotriazine group showed poor leveling property compared with dye-resists agents DR-2~DR-5 having monochlorotriazine. This result indicates that reactive dye-resist agents having dichlorotriazine, due to their very high reactivity and low migration ability, reacted only with nucleophilic groups in the fiber periphery leaving the interior untreated, as was reported by Haarer and Höcker [6]. They have also suggested that to achieve better levelness

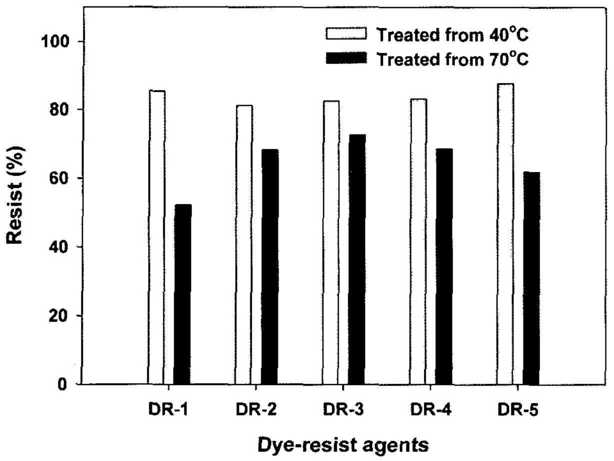


Figure 6. Leveling properties of hetero-multifunctional dye-resist agents for dye 3 at the mass gain for 80 % dye-resist (%).

and reproducibility, the reactive dichlorotriazine group could be substituted by less reactive groups such as the α-bromoacrylamide group or monochlorotriazine group. Therefore, it can be seen from Figure 6, dye-resist agents DR-2~DR-5 having less reactive groups, monochlorotriazine instead of dichlorotriazine, achieved better levelness. Also, the leveling properties of resist agents decreased as the number of sulfonate group increased (DR-3 > DR-4 > DR-5). It is presumed that the interaction of sulfonate group with wool fiber lowers the migration ability of dye-resist agents in wool fiber.

Conclusions

The dye-resist agent with the dichlorotriazinyl group achieved better resist effectiveness than the dye-resist agent with the monochlorotriazinyl group since more reactive dichlorotriazinyl group can deactivate the more dyeing sites compared with monochlorotriazinyl group. Also, when compare the resist effectiveness of dye-resists having same reactive groups, the resist agents with more sulfonate groups showed better resist effectivness due to the increased repulsion between dye-resist agents and dyes.

The resist effectiveness of the five reactive dye-resist agents varies greatly with the types of acid dyes used. An increase in the number of ionic groups in acid dyes leads to better electrostatic repulsion of reactive resist-treated wool and thus improves the resist effectiveness.

The dye-assist effect increased with increasing mass gain of dye-resist agents in basic dyeing of wool. The resist agents with more sulfonate groups showed better dye-assist effectivness, attributable to the increased electrostatic attraction between dye-resist agents and the cationic dye. This result demonstrates that the dye-resist agents reacted with wool fiber function as dye binding sites in basic dyeing of wool.

Dye-resist agents having dichlorotriazine group, due to their very; high reactivity and low migration ability, showed poor leveling property compared with dye-resist agents having monochlorotriazine. Also, the leveling properties of resist agents decreased with increasing the number of sulfonate group.

References

1. "Textile Terms and Definitions", 8th ed., Textile Institute, Manchester, 1986.
2. R. L. Elliot, R. Asquith, and M. A. Hobson. *J.S.D.C.*, **79**, 188 (1963).
3. J. Haarer and H. Höcker. *Text. Res. J.*, **64**, 480 (1994).
4. J. Frauenknecht and D. Schwer, *Can. Text. J.*, **10**, 75 (1971).
5. V. A. Bell, D. M. Lewis, and M. T. Pailthorpe, *J.S.D.C.*, **100**, 223 (1984).
6. J. Haarer and H. Höcker. *Text. Res J.*, **64**, 578 (1994).
7. B. D. Jeon, M. T. Pailthorpe, and S. K. David, *Dyes Pigm.*, **20**, 109 (1992).
8. J. Koh, I. S. Kim, S. S. Kim, W. S. Shim, and J. P. Kim, *Fibers and Polymers*, **5**, 44 (2004).
9. J. Koh, S. H. Park, G. H. Shim, D. H. Cho, and J. P. Kim, *Fibers and Polymers*, **5**, 110 (2004).
10. J. Koh and D. H. Cho, *Fibers and Polymers,* **5**, 134 (2004).
11. I. S. Kim, J. Koh, N. K. Han, and J. P. Kim, *Fibers and Polymers*, **5**, 219 (2004).
12. Y. J. Kwon, J. Koh, M. J. Oh, and S. D. Kim, *Fibers and Polymers*, **7**, 20 (2006).
13. M. J. Oh and J. P. Kim, *Dyes Pigm.*, **70**, 220 (2006).
14. M. J. Oh, J. P. Kim, and J. Koh, *Color. Technol.*, in press.
15. M. J. Oh, Ph.D Thesis, Seoul National University, 2002.
16. H. Zollinger, *Proc. 4th Internat. Wool Textile Res. Conf., Aachen*, **1**, 167 (1976).