Journal of the Korean Society of Dyers and Finishers
Vol. 19, No. 5, pp. 8~16(2007. 10)

〈Research Paper〉

Dye-resist Properties of Reactive Dye-resist Agents in Reactive Dyeing of Silk

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(Received: August 13, 2007/Revised: October 12, 2007/Accepted: October 19, 2007)

Abstract— The dye-resist effect of reactive dye-resist agents in reactive dyeing of silk was investigated. The dichlorotriazine-based dye-resists achieved a higher effectiveness than others since they make a charge barrier of diffusion in the silk fiber periphery due to high reactivity of dichlorotriazine group. Similarly, in the case of hetero-multifunctional dye-resist agent, the dye-resist agent containing both a dichlorotriazine and an α-bromoacrylamide reactive groups achieved better resist effectiveness than those containing both a monochlorotriazine and an α-bromoacrylamide groups. Also, their resist effectiveness was improved by increasing the number of sulfonate groups in the dye-resist agents and the number of reactive groups in the reactive dyes applied to them.

Keywords: *dye-resist, reactive dye, silk, dye-resist agent, α-bromoacrylamide*

1. Introduction

Tone-on-tore effects, white or colored patterns on contrasting ground shades in textile dyeing and printing, have become more popular as customers have come to regard these aesthetic aspects as highly valuable. These patterned effects produced can be achieved by either discharge or resist processes. In a discharge process, the fabric is dyed first and then the pattern is obtained by printing with a discharging agent that destroys the dye in the printed area. On the other hand, in resist printing the fabric is first printed with a resist agent and then dyed.

Conventionally, patterned effects have been mainly achieved by the discharge method. However, textile materials can be easily damaged during the treatment conditions of discharge methods because of the necessity to utilize strong oxidizing or reducing agents for braking down the chromophore of the ground dye.

This adversely affects physical properties of textile goods such as handle or tensile strength. However, the advantage of resist methods lies in the facile utilization of various dyestuffs. Even dyestuffs which are classified as not being dischargeable or having poor dischargeability can be applied in dye resist methods.

A dye resist process is one in which the dye uptake is slower or less than that on the untreated substrate[1)] and can be obtained by either physical methods or chemical modification of the substrate which is to be resist printed. This effect can only be achieved when the interaction between dye and fiber is effectively prevented. This may be achieved in three different ways : electrostatic repulsion between dye molecules and fiber, hindrance of dye diffusion into the fiber, and deactivation of dye binding sites[2)].

A variety of chemicals has been designed and studied for imparting dye-resist effects to wool[3-6)].

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Among them, reactive dye-resist agents are preferred as appropriate compounds for dye-resist of protein fibers with regard to handling and application of dye-resist agents[2]. However, the study on these reactive dye-resist agents has been limited only on the dichlorotriazine-based type ones even though various reactive systems can be applied for dye-resist agents for wool[2,3,7,8], Haarer et al. showed that dichlorotriazine-based reactive dye-resist agents, due to their very high reactivity and low migration ability, reacted only with nucleophilic groups to the fiber periphery leaving the interior untreated[7]. Thus, treatment with dichlorotriazine based dye-resist agents might impair levelness and reproducibility. Therefore, if reactive dye-resist agent with lower reactivity is used, levelness and reproducibility will be improved.

The α-bromoacrylamide reactive system, which is commercially know as Lanasol dyes, has been applied to reactive dyeing of silk. This reactive group has lower reactivity than dichlorotriazine type and reacts with nucleophilic groups in the silk fiber at about 70℃, and below the temperature they have all the dyeing properties of leveling-type acid dyes. Thus α-bromoacrylamide based dye-resist agents are expected to produce more uniform distribution than dichlorotriazine-based ones.

Various chemicals have been designed and applied for imparting dye-resist effect on cellulosic fibers and wool. However, in the case of silk fiber, little work has been done on the resist effectiveness of reactive dye-resist agents.

In this study, the dye-resist effectiveness of reactive dye-resist agents in reactive dyeing of silk was investigated. The effectiveness of dye-resist containing reactive groups of 2,4-dichloro-s-triazine, α-bromoacrylamide, and a 2,4-dichloro-s-triazine and an α-bromoacrylamide were compared.

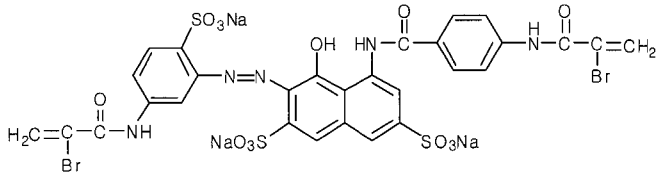
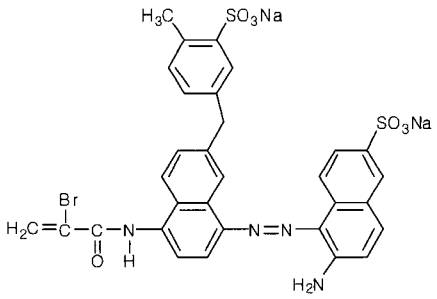
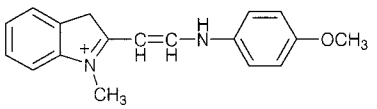
2. Experimental

2.1 Materials

The scoured silk fabrics (KS K 0905) were used for dyeing. The dyes used in this study were Lanasol Red G (**1**) (C.I. Reactive Red 83), Lanasol Red 6G (**2**) (C.I. Reactive Red 84) and Maxilon Yellow 5GL (C.I. Basic Yellow 13), which were supplied by Ciba Specialty Chemicals Korea (Table 1).

Albegal FFA was used as a wetting agent.

Table 1. Dyes used in this study

Classification	Dye No.	Chemical structures	Generic Name
Reactive dye	**1**		C.I. Reactive Red 83 (Lanasol Red G)
	2		C.I. Reactive Red 84 (Lanasol Red 6G)
Cationic dye	**3**		C.I. Basic Yellow 13 (Maxilon Yellow 5GL)

All the chemicals used in this study were of laboratory-reagent grade.

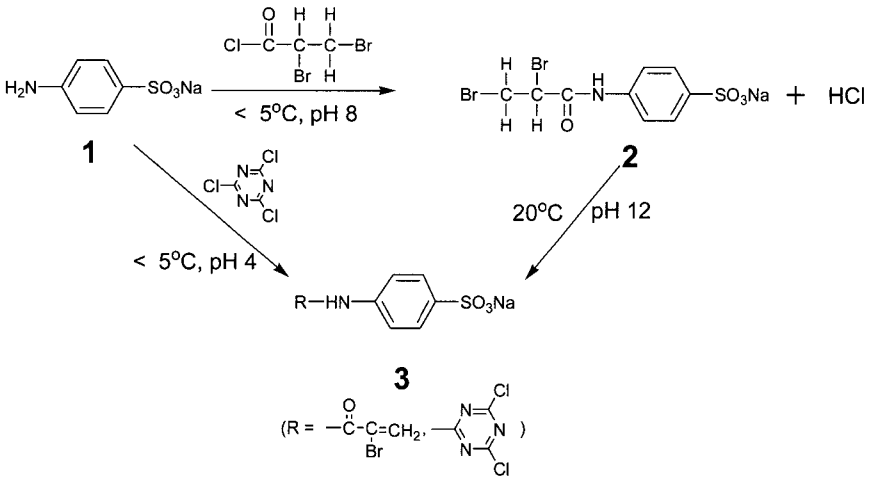
2.2 Synthesis of dye-resist agents

The synthesis of reactive dye-resist agents has been described in the previous work (Schemes 1 and 2)[9,10].

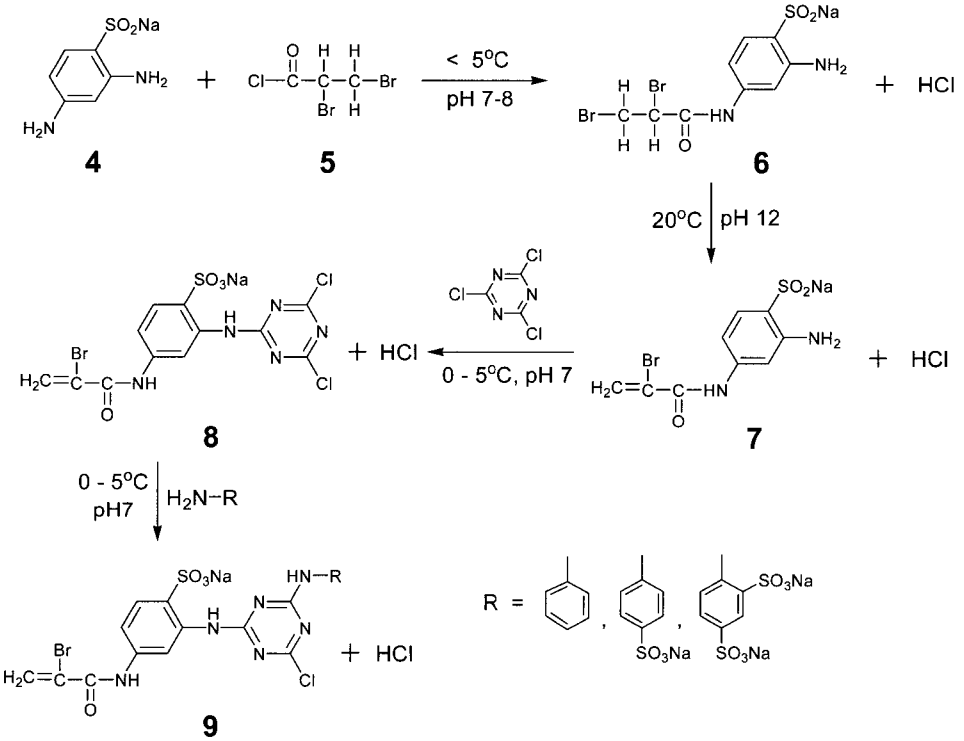
The synthesized dye-resist agents given in Table 2 were used throughout the study were given in Table 2.

2.3 Synthesis of reactive fluorescent brightening agents

In order to examine the leveling property of reactive dye-resist agents indirectly, the reactive fluorescent brightening agents with α-bromoacrylamide (FBA-1) and dichlorotriazine reactive group (FBA-2) as model compounds were prepared using a similar reaction process to the reactive dye-resist agents.

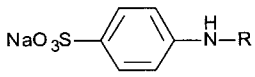
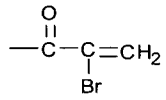
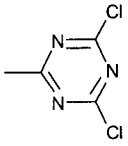
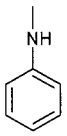
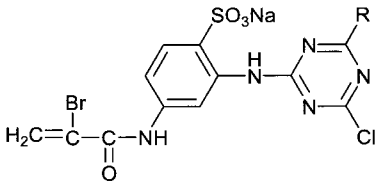
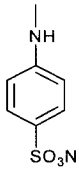
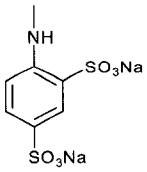


Scheme 1. Synthesis of mono-functional reactive dye-resist agents[9].



Scheme 2. Synthesis of hetero-multifunctional dye-resist agents[10].

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

Dye-resist	Structure	Reactive group	R
DR-1		α-Bromoacrylamide	
DR-2		Dichlorotriazine	
DR-3		α-Bromoacrylamide + Dichlorotriazine	-Cl
DR-4			
DR-5		α-Bromoacrylamide + Monochlorotriazine	
DR-6			

The chemical structures and ^{1}H-NMR spectral data are shown in Table 3.

2.4 Application of reactive dye-resist agents on silk fabrics

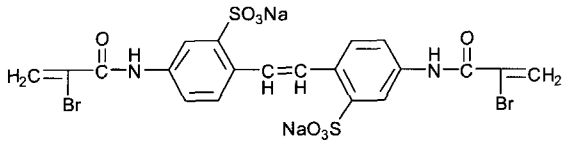
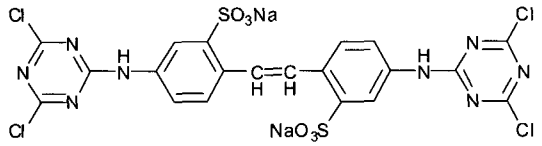
A 5.0 g silk sample was pre-treated with each reactive dye-resist agents at various concentrations (1, 2, 4, 8 and 16 %owf) by exhaustion process (liquor ratio = 20:1) using a laboratory IR dyeing machine (Ahiba Nuance, Datacolor, Switzerland). The pretreatment bath was composed of Albegal FFA(wetting agent, 0.25 g/l), dye-resist agents (x %owf) and buffer system (pH 4.5, acetic acid/ sodium acetate).

The process started at 40℃ and stayed for 10 minutes, and the dye-resist agents were added at pH 4.5. Then the dyebath was raised to the boil over 60 minutes (1℃/min) and maintained for 60 minutes at 100℃ and subsequently cooled down to 80℃ over 10 minutes. The samples were then rinsed and dried at room temperature.

2.5 Reactive dyeing of silk fabrics

The resist effectiveness of reactive dye-resist agents on silk was evaluated with reactive dyes (Table 1). The reactive dyes **1** and **2** has been chosen in order to investigate the effect of the number of reactive group and sulfonate group on the dye-resist effectivenss : dye **1** has two reactive groups and three sulfonate group and dye **2** has one reactive group and two sulfonate group. Also, dye **3** has been chosen in order to investigate the assist effect of dye-resist agents in cationic dyeing of silk.

Table 3. Chemical structures and 1H-NMR data of reactive fluorescent brightening agents synthesized in this study

FWA	Chemical structures	Yield (%)	Chemical shift (DMSO-d_6, δ)
FWA-1		67	6.3 (d,2H. CH_2= cis to -CBr-); 6.8 (d, 2H, CH_2= trans to -CBr-); 7.5-.8.1 (m, 6H, ArH); 10.3 (s, 2H, -NH-)
FWA-2		89	7.6-8.1 (m, 6H, ArH); 11.2 (s, 2H, -NH-)

The dyes were applied to silk treated with dye-resist agents at the same dye concentration (1.0 %owf) using a laboratory IR dyeing machine. In order to simulate commercial resist dyeing, competition dyeing method suggested by Bell et al.[3] was carried out with a 3:1 (w/w) ratio of untreated to treated silk at a liquor ratio of 40:1.

The reactive dyeing process of dye-resist treated-samples started at 50℃ and after 10 minutes duration at pH 4.5. The dye-bath was composed of Albegal FFA (0.25g/l), Albegal B (leveling agent, 1.0 %owf), reactive dye (1.0 %owf) and buffer system (pH 4.5, acetic acid/sodium acetate). The dyebath was then raised to the boil over 50 minutes (1℃/min), held for 60 minutes at 100℃ and cooled over 10 minutes to 80℃. The dyed samples were aftertreated with 3.0 %owf ammonia solution (28%) for 15 minutes at 85℃. The fabrics were washed and then dried at room temperature.

2.6 Cationic dyeing of silk fabrics

In order to confirm the number of sulfonate group effect on the dye-resist properties, the dye-assist effectiveness in cationic dyeing of dye-resist agent treated silk fabric was estimated. The cationic dyeing 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 consisted of Albegal FFA(0.25 g/l) and Glauber's salt (5 %owf) with different acid dye concentration (y %owf). Then the dyebath was raised to 100℃ over 30 min, held for 40 min and cooled over 10 min to 80 ℃. The samples were rinsed and dried at room temperature.

2.7 Fluorescent dyeing and microscopy

The dyeing of silk with a reactive fluorescent compound (1% owf) was carried out using a similar dyeing procedure with that of reactive dye-resists on silk. The dyed silk samples were incorporated into an embedding-medium for frozen tissue specimens (Tissue-Tek O.C.T. compound) and frozen in a Leica CM 1900 chamber and cross-sections were prepared for each sample using a cryocutter. Cross-sections were observed by the Olympus BX50F4 incident light fluorescence microscope using a super high-pressure mercury lamp (Nikon H5-10101AF) as a fluorescence source.

The photo-micrographs were recorded using a Olympus PM-C35DX camera using a Kodak film.

2.8 Evaluation of dye-resist effect

The extent of resist effectiveness was quantified by using the following equation with K/S values of the dyed fabric on a spectrophotometer at the wavelength of maximum absorption (Color-Eye 3000, Macbeth, standard light D65, 10standard observer, specular component included). The percentage resist was then calculated by using equation 1[3]:

$$\%\text{Resist} = \frac{(K/S)_{untreated} - (K/S)_{treated}}{(K/S)_{untreated}} \times 100 \quad (1)$$

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

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

3. Results and Discussion

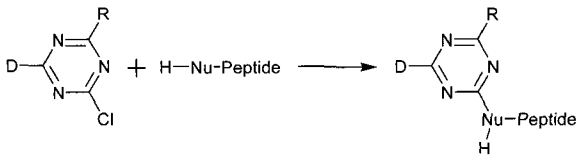
3.1 Dye-resist effect in reactive dyeing of silk

Reactive dye-resist effect can be achieved by two reaction mechanisms. Firstly, nucleophilic substitution reaction can be described in terms of the attraction of an electron-deficient carbon atom for the free lone pair of electrons on the nucleophiles (-SH, -NH_2 -OH) in protein fiber (Scheme 3). The reactive carbon atom is attached to a leaving group, usually halogen, sulfur or quaternary nitrogen. Reactive resist agent of chlorotriazine type can be explained in this mechanism. Secondly, the Michael addition reaction of dyes containing polarized, unsaturated carbon-carbon double bonds with nucleophiles can be considered to be a 1,2-trans-addition (Scheme 4).

The double bond is necessarily activated by the presence of an electron-withdrawing substituent such as a carbonyl or sulfonate group. Reactive resist agent of α-bromoacrylamide type can be explained in this mechanism.

It is known that, even though they do not make a great contribution to the bonding energy between dye and fiber, Coulombic forces have been shown to play an important role in the kinetics of dyeing.

Many of the earlier resist processes for protein fiber were primarily designed to disrupt the Coulombic forces of attraction between the positively charged ammonium groups in the fiber and the anionic dye molecules, e.g. acylation, sulfation with concentrated sulfuric acids, sulfation/sulfamation with sulfamic acid, application of formaldehyde-naphthosulfonic acid condensates and chlorination with alkaline hypochlorite.

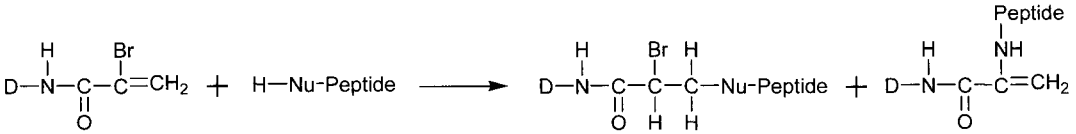


Scheme 3. Nucleophilic substitution reaction of dye-resist agent with silk fibers (D : dye-resist agent, Nu : nucleophiles).

Some of these chemical treatments would also disrupt the hydrophobic regions within the fiber, making the fiber more hydrophilic in character and thereby reducing the affinity of dyes for the fiber[3].

It should be far more straightforward, in theory, to treat protein fiber in such a way that the protein fiber will resist reactive dyes. Providing the nucleophilic groups with the accessible regions of the protein fiber can be blocked, then there will be no sites for reaction available to fix the reactive dye to the protein fiber. By choosing reactive dyes of high reactivity but relatively low affinity it should be possible to achieve a very high level of resist. The principal nucleophilic groups available in protein fiber for reaction with reactive dyes are primary amino, secondary imino and free thiol groups. Reactive compounds that behave like colorless reactive dyes should achieve this objective.

A series of reactive dyes for silk were selected. Both the dyes are α-bromoacrylamide dyes, but Lanasol Red G has two reactive groups and three sulfonate groups, while Lanasol Red 6G have one reactive group and two sulfonate groups. With the aid of dyes **1** and **2**, the influence of the number of reactive groups and sulfonate groups of the reactive dyes for silk on the dye resist effect of reactive dye-resist agents can be indirectly estimated. All six reactive dye-resist agents can react with the nucleophilic sites normally available for reaction with reactive dye, and thereby decrease the extent of fixation possible between the reactive dye and the silk fiber. The resist effectiveness of dye-resists to the reactive dyes (**1** and **2**) examined in this work is given in Fig. 1.



Scheme 4. Michael addition reaction of dye-resist agent with silk fibers.

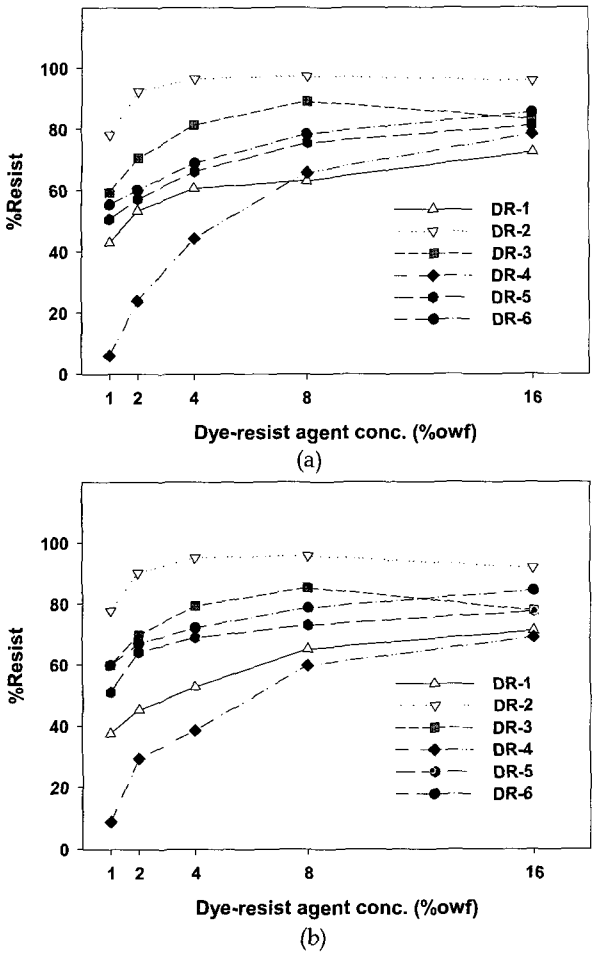


Fig. 1. Resist efficiency against dyes 1 and 2 on silk treated with various reactive dye-resist agents. (a) dye 1 (C.I. Reactive Red 83) (b) dye 2 (C.I. Reactive Red 84).

Although more dye-resist effectiveness was expected to dye **1** with the more sulfonated group (trisulfonated) than dye **2** (disulfonated), both the dyes **1** and **2** achieved similar dye-resist effectiveness. For reactive dyes, the more is the number of reactive groups in the dye molecule, the higher may be the possibility of reaction with the nucleophilic group in silk fiber. Therefore, it is thought that, although dye **1** has the more sulfonated groups, similar dye-resist effectiveness with dye **2** (one α-bromoacrylamide reactive group) is resulted due to two α-bromoacrylamide reactive groups.

The dichlorotriazine based dye-resist agents achieved a better resist effectiveness to the dyes than α-brormoacrylamide based one. There are two possible explanations that can account for this reason. Firstly, while the α-bromoacrylamide dye has the bifunctional group in itself, there is no direct evidence for 1:2 reaction (α-bromoacrylamide group:amino acid) but only for 1:1 reaction. Thus, it can be concluded that α-bromoacrylamide group reacts with one amino acid side chain of silk. Therefore, it is expected that the more leveling property could be obtained with α-bromoacrylamide based resists than the dichlorotriazine derivatives because of the lower reactivity.

Although α-bromoacrylamide-based resists produced more uniform distribution than those based on dichlorotriazine, they showed lower resist effectiveness than the dichlorotriazine based dye-resist probably due to their relatively lower reactivity.

Secondly, Haarer et. al. reported that, on their study of dichlorotriazine-based dye resist agents, they have low migration property due to high reactivity and the interior remains untreated[7].

Also, Evans reported that Lanasol dyes which has an α-brormoacrylamide system behave as reactive dyes at above 70℃, and below the temperature, they show the dyeing properties of leveling type acid dyes. Therefore, the silk treated with DR-1 (α-bromoacrylamide type) produces a uniform distribution while the silk treated with DR-2 (dichlorotriazine type) makes a barrier of dye diffusion in fiber interior due to non-uniform distribution.

Fig. 2 shows the photomicrographs for the silk dyed with reactive fluorescent compounds, FBA-1 with α-bromoacrylamide and FBA-2 with dichlorotriazine. Both compounds showed ring dyeing. However, the extent of ring dyeing differs from each other. Lewis et al. reported that FBA-2 penetrated the fiber markedly less than FBA-1 and produced ring dyeing most extreme ("peripherally ring dyeing")[3].

Fig. 2. Photomicrographs of silk dyed with reactive fluorescence whitening agents.

As expected, FBA-1 with α-bromoacrylamide group was localized in silk fiber less than FBA-2 with dichlorotriazine group. Therefore, it is presumed that the peripherally ring dyeing of dichlorotriazine based dye-resist agents could enhance their dye-resist effectiveness.

Of the multifunctional reactive dye-resist agent, triazine-based dye-resist agent (DR-3) has better resist effectiveness than the other dye-resist agents although it has low molecular weight and number of ionic charge compared with the hetero-multifunctional dye-resist agent (DR-4~DR-6) containing a monochlorotriazine and an α-bromoacrylamide. This result can be also explained by the aforementioned periphery dyeing of silk fiber due to the very high reactivity of triazinyl group; the more reactive dichlorotriazine group is able to react with nucleophilic group in the fiber periphery[2], which can make a barrier of dye diffusion and increase the local concentration of sulfonate group and accordingly increases the electrostatic repulsion with acid dyes.

According to the study reported by Haarer[7], DR-6 is expected to show maximum resist effectiveness since it has large molecular size for steric hindrance, reactive group for deactivating the dye-binding site, and uniform distribution of ionic charges over molecules for electrostatic repulsion. However, according to the experimental results, the maximum resist effectiveness was achieved with DR-2, irrespective of the dye type applied. This result could be ascribed to the dye diffusion barrier formation by more reactive dichlorotriazine group compared with the hetero-multifunctional dye-resist agents.

At 16% treatment of DR-2 and DR-3, the resist effectiveness is reduced a little more than that at 8%. A possible explanation is that the strong electrostatic repulsion developed by sulfonic acid groups restrains not only the dye molecules effectively, but the dye-resist agents themselves as well (a self-resist effect). This result could be confirmed by mass gain of reactive dye-resist agent on silk fiber in previous study (Fig. 3)[11].

3.2 Dye-assist effect in cationic dyeing of silk

A cationic dye, dye 3 (C.I. Basic Yellow 13) was applied to silk fiber in order to investigate the dye-assist effect (negative dye-resist effect) of reactive dye-resist agents in silk dyeing. Fig. 4 shows the dye-assist effect of reactive dye-resist agents in cationic dyeing of silk. The dye-assist effect increased with increasing mass gain of dye-resist agents. The resist agents with more sulfonate groups showed better dye-assist effectiveness, which is attributed to the increased electrostatic attraction between dye-resist agents and the cationic dye (DR-2 < DR-3 < DR-4 < DR-5 < DR-6). This result demonstrates that the dye-resist agents reacted with silk fiber function as dye

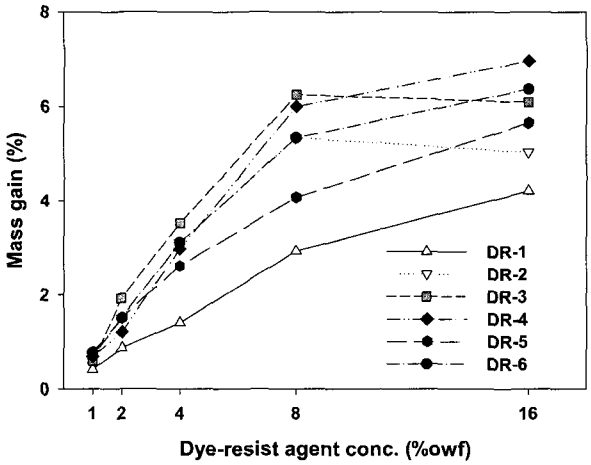


Fig. 3. Mass gain of reactive dye-resist agents at various treatment concentrations[13].

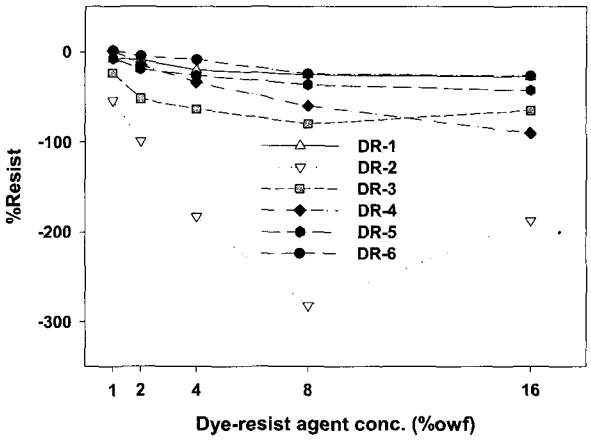


Fig. 4. Resist efficiency against cationic dye (3, C.I. Basic Yellow 13) on silk treated with reactive dye-resist agents.

binding sites in cationic dyeing of silk and the anionic property of sulfonate group plays an important role in ionic interactions.

4. Conclusions

The resist properties of monofunctional dye resist agents and multifunctional dye resist agents were compared in the reactive dyeing of silk.

The highest dye-resist effectiveness was achieved with dichlorotriazine-based dye-resist agent, irrespective of the dye type applied. This result could be ascribed to the diffusion barrier formation by more reactive dichlorotriazine group compared with the hetero-multifunctional dye-resist agents. Similarly, in the case of hetero-mulftifunctional dye-resist, the dye-resist agent containing a dichlorotriazine and α-bromoacrylamide achieved better resist effectiveness than those containing both monochlorotriazine and α-bromoacrylamide groups, probably because the more reactive dichlorotriazinyl group deactivates more dyeing sites. Also, when compare the resist effectiveness of dye-resists having same reactive groups, the resist agents with more sulfonate groups showed better resist effectiveness due to the increased repulsion between dye-resist agents and dyes.

In order to confirm the number of sulfonate group effect on the dye-resist properties, the dye-assist effectiveness in cationic dyeing of dye-resisted silk fabric was estimated. The resist agents with more sulfonate groups showed better dye-assist effectiveness, attributable to the increased electrostatic attraction between dye-resist agents and the cationic dye. This result demonstrates that the dye-resist agents reacted with silk fiber function as dye binding sites in cationic dyeing of silk and the anionic property of sulfonate group plays an important role in ionic interactions.

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