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New Dyeing Method for wild Silk Yarns Using Reactive Dyes

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Abstract

We observed that during the dyeing process of wild silk yarns with a reactive dye, dye uptake could occur in an alcohol-water solvent mixture bath that did not contain any salt. The K/S value of the wild silk yarn dyed by this process which is related to the dye uptake, increased with the increase of the alcohol content in the dye bath. At the some time, the K/S value was affected also by the kind of alcohol used. The effect on the K/S value decreased in the order of butyl alcohol, isopropyl alcohol and ethyl alcohol. However, if the solubility in water and the boiling point are taken into account, isopropyl alcohol was most suitable when a single alcohol was used. Even an alcohol with a low solubility in water could be used in the dye bath by combining it appropriately with isopropyl alcohol, and the K/S value could be improved. Based on the effect of the dye concentration, it appeared that dyeing in an alcohol-water solvent mixture was not suitable in terms of the dye buildup characteristics.

Discipline: Sericulture/Agricultural environment
Additional key words: alcohol-water solvent mixture bath, color depth, isopropyl alcohol, solvent-assisted dyeing

Introduction

Wild silk yarns from Japanese tusser (from *Antheraea yamamai*), Chinese tusser (from *Antheraea pernyi*), Indian tusser (from *Antheraea mylitta*), Oak-tusser (from *Antheraea proylei*), Muga (from *Antheraea assamensis*), Eri (from *Philosomia cynthia ricin*), etc. have a unique gloss and a feel with a rather rustic appeal, and are important silk materials. They are, however, generally difficult to dye compared to silkworm (from *Bombyx mori*) silk yarn. The dye uptake is lower, the development and clearness of color are inferior, and binding of the dye molecules to the yarn is weak. The following factors could be responsible for the difficulty in dyeing these yarns. Silk is generally dyed either in a neutral bath, in which neutral salts like Glauber's salt, sodium chloride, etc. are the dyeing auxiliaries, or in a weakly acidic bath containing acetic acid. In such neutral to weakly acidic baths, the wild silk yarns have a greater amount of charge than *mori* silk yarn. As a result, the electrostatic repulsion between the yarn and the anionic dye molecules is greater, which interferes with the dye absorption, regardless of the measures taken. Furthermore, wild silk yarns have a fiber structure in which water molecules cannot easily penetrate into the micellar spaces (amorphous region). Therefore, they do not swell readily and the internal surface area of the micellar spaces, which are the effective dye absorption sites, is smaller than in *mori* silk yarn. As a result, the color does not develop well even in highly concentrated dye baths, the dye buildup remains poor, and the color can not achieve depth. Dyeing to dark colors like black, dark blue and brown is particularly difficult.

We examined the solvent-assisted dyeing method of wild silk yarns with reactive dyes as a possible dyeing method that could enable to overcome the problems of dyeing of such yarns. Reactive dyes are a relatively new class of dyes that has been

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developed for cellulose fibers. Their colors are very clear and pure and they have a superior wet color fastness. Solvent-assisted dyeing is a method by which a small amount of solvent that is partly soluble in water is added to the dye bath to enhance the rate of dyeing[4]. The dyeing is performed at a relatively low temperature and the dye is absorbed in a short time.

Materials and methods

1) Silk material

Chinese tusser, *Antheraea pernyi* yarn produced in China was used after degumming with an enzyme (Papain C-400, activity 650 u/g). The degumming loss was 11.8%.

2) Reactive dyes

Two types of reactive dyes[2] were used, i.e. Levafix E type with dichloro-quinoxaline as the reactive group and Verofix type with monochloro-difluoro-pyrimidine as the reactive group[2] (both manufactured by Bayer Co.). The names of the dyes have been abbreviated in this paper, Blue E-BRA (for Levafix Brilliant Blue E-BRA) for instance.

3) Dyeing

Fabric made of *A. pernyi* yarn was immersed for 30 min in a dye bath containing a suitable amount of alcohol to allow the fabric to take up the dye. Thereafter, sodium carbonate was added and the dyeing allowed to continue for another 60 min. The dyeing temperature remained constant at 40°C and the liquor ratio used was 1:30. The dyed fabric was washed first with water and then with warm water (57 ± 3°C), and air-dried.

4) Measurement of surface color depth (K/S value)

In this experiment, we did not determine the dye uptake because we considered that the characteristic smell of the alcohol present in the bath would complicate the work. We decided to evaluate the dyeing performance by determining the surface color depth, hereinafter referred to simply as the K/S value which stands for the surface depth of shade of silk yarns. The K/S values were calculated by determining the spectral reflectivity (R) at the peak absorption wavelength measured using a spectrophotometer (MPS-50L manufactured by Shimadzu Seisakusho) and the Kubelka-Munk function[3] as follows:

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

Results and discussion

1) Dyeing in alkaline baths

To evaluate the dyeing performance of the dichloro-quinoxaline type and monochloro-difluoro-pyrimidine type reactive dyes on *A. pernyi* fabric, ordinary alkali dyeing was performed at the dyeing temperature of 40°C and liquor ratio of 1:30, which were also used in the other dyeing trials. Fig. 1 shows the K/S values of the fabric dyed at different concentrations of anhydrous sodium sulfate in the bath. Blue E-BRA and Red BBL showed a similar trend, with a maximum K/S value at the sodium sulfate concentration of about 50 – 70 g/l. Although there was some uncertainty because the dye uptake was not directly measured, the results obtained here are slightly different from those obtained[1] with other reactive dyes like the sulfato-ethyl-sulfone type. The difference in the dyes used could perhaps be responsible for this discrepancy, but it appears that the difference in liquor ratio played a greater role. If we assume that the exhaustion percentage (percentage of the dye adsorbed in relation to the initial dye content of the bath) of a reactive dye by the *A. pernyi* fabric increases with the decrease in the liquor ratio, then by dyeing at a liquor ratio of 1:100, which was used with the sulfato-ethyl-sulfone type dye, the K/S value increased with the increase in the sodium sulfate concentration because the

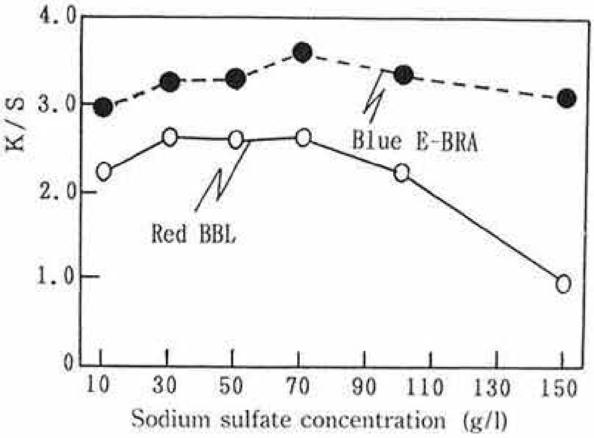

Fig. 1. Relationship between the K/S value and anhydrous sodium sulfate concentration in alkali dyeing

Dyeing conditions:

Dye concentration; 2% owf, Liquor ratio; 1:30, Temperature; 40°C, Duration; 30 min + 60 min after addition of alkali, Alkali; 2 g/l of sodium carbonate.

exhaustion percentage was lower compared to that in alkali dyeing as mentioned above at the liquor ratio of 1:30. At the low liquor ratio of 1:30, even when the content of the dye in relation to the fiber weight was the same, the dye concentration in the bath could increase and therefore the amount of dye uptake would be higher. Therefore, the extent of increase in dye uptake caused by the increase in the amount of sodium sulfate added decreased gradually as the dye adsorption sites on the fibers became saturated. When the salt concentration becomes very high, it competes with the dye and lowers the exhaustion percentage of the dye. What we have discussed here is only a hypothesis and the effect of the liquor ratio needs to be examined further in relation to the characteristics of the dyes.

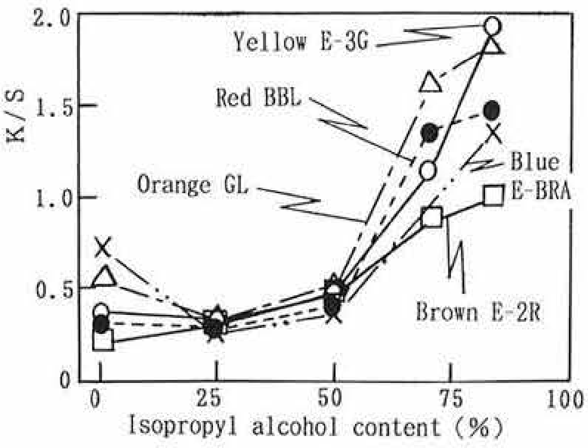

Fig. 2. Effect of isopropyl alcohol content on K/S values of *A. pernyi*
Dye concentration: 2% owf (4% owf for Brown E-2R).

2) *Alcohol content in the dye bath*

For dyeing in an alcohol-water solvent mixture, firstly a suitable mixing ratio of the alcohol and water must be determined. Therefore, we carried out dyeing trials at different ratios of isopropyl alcohol and water in the bath at a dye concentration of 2% owf (except for Brown E-2R in which case 4% owf was used) and a sodium carbonate concentration of 2 g/l, and observed the change in K/S value. With all the dyes, the K/S value increased with the increase in the alcohol content of the bath (Fig. 2). This result suggests that in the dyeing of *A. pernyi* fabric with reactive dyes, the uptake and fixation of the dye from an alcohol-water solvent mixture can occur even when there is no salt. It seems preferable that the alcohol content in the dye bath is high.

3) *Type of alcohol*

Reactive dyes are not readily soluble in alcohols. Therefore, the alcohol used in this method of dyeing must be a lower alcohol that is soluble in water. Although the dyeing temperature does not have a very strong effect on the dyeing performance of reactive dyes[1], the raising of the dyeing temperature to some extent would improve penetration and diffusion of the dye. The boiling point and the solubility in water of saturated monohydric alcohols are as

Table 1. Effect of the type of alcohol on K/S values of *A. pernyi*

Dye[a]	Alcohol	Alcohol content (%)	Spectral reflectivity at peak sorption wavelength (%)	K/S value
Scarlet E-2GA	Ethyl alcohol	60	16.4	2.13
		80	13.1	2.88
	Isopropyl alcohol	60	12.7	3.00
		80	8.8	4.73
	Butyl alcohol	60	9.5	4.31
		80	8.1	5.21
Yellow E-3G	Ethyl alcohol	60	35.0	0.61
		80	25.6	1.08
	Isopropyl alcohol	60	24.1	1.20
		80	13.5	2.77
	Butyl alcohol	60	25.6	1.08
		80	15.0	2.41

Dye concentration: 4% owf.
a): Dye with dichloro-quioxaline as the reactive group.

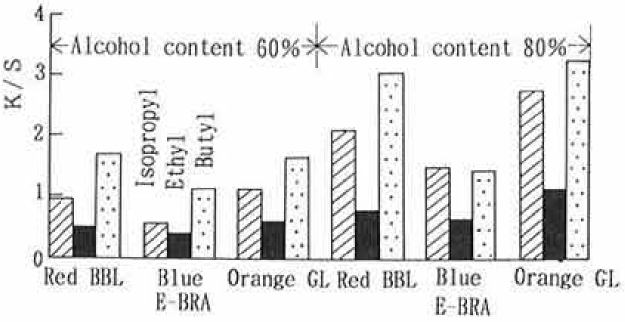

Fig. 3. Effect of the type of alcohol on K/S values of *A. pernyi*
Dye concentration: 2% owf.
Dye: Monochloro-difluoro-pyrimidine as the reactive group.

follows: methyl alcohol (64.7°C, ∞ g/100 g·H_2O), ethyl alcohol (78.3°C, ∞ g/100 g·H_2O), propyl alcohol (97.2°C, ∞ g/100 g·H_2O), butyl alcohol (117.5°C, 7.4 g/100 g·H_2O), and amyl alcohol (138°C, 2.5 g/100 g·H_2O). Based on the boiling point and solubility in water, ethyl alcohol and propyl alcohol and their isomers are the most suitable. It may be possible to use butyl alcohol although there are some problems with the solubility. On the basis of these considerations, we examined the suitability of ethyl alcohol, isopropyl alcohol and butyl alcohol. The enhancing effect on the K/S value decreased in the order of butyl alcohol, isopropyl alcohol and ethyl alcohol (Fig. 3, Table 1). Under the dyeing conditions in which the alcohol content is 60 and 80%, butyl alcohol was not completely dissolved and therefore the dye bath was not in a suitable condition. When only one type of alcohol is to be used, isopropyl alcohol appears to be most suitable.

4) Mixing ratio of isopropyl and butyl alcohols

The results given under 3) above suggest that butyl alcohol was more suitable than isopropyl alcohol for dyeing with dark colors. But since butyl alcohol is not very soluble in water, as mentioned earlier also, there is some limitation if it is to be used singly. To analyze this aspect, we investigated the effect of the combination of isopropyl and butyl alcohols on the K/S value, keeping the total alcohol content constant at 80%. Fig. 4 depicts the results obtained. Although only a few dyes were tested in this experiment, apparently the K/S value increased with increasing butyl alcohol content. The combined use of these two alcohols alleviated the problem of low solubility of butyl alcohol in water. For example, almost no undissolved alcohol fraction could be observed in a dye bath containing 70% butyl alcohol, 10% isopropyl alcohol and 20% water. This observation indicates that even with an alcohol with low solubility in water, the solubility in the dye solution could be improved by using it in combination with isopropyl alcohol in an appropriate ratio. Moreover, such combined use was more effective on the K/S value than when butyl alcohol was used alone. Also it may be possible to use a weaker alcohol for the dyeing.

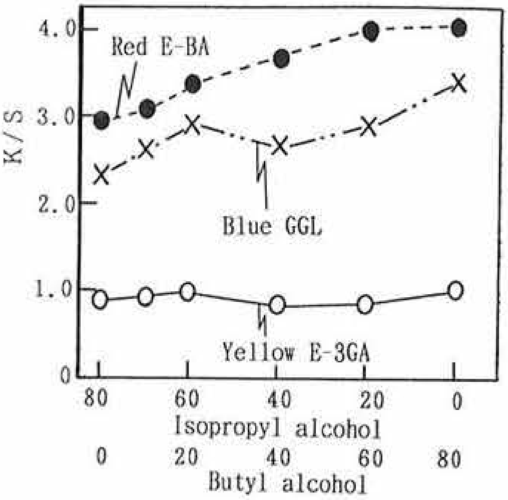

Fig. 4. Effect of the mixing ratio of isopropyl alcohol and butyl alcohol on K/S values of *A. pernyi*
Dye concentration: 2% owf.

5) Dye concentration

Fig. 5 shows the effect of the dye concentration on the K/S value when the fabric was dyed at an

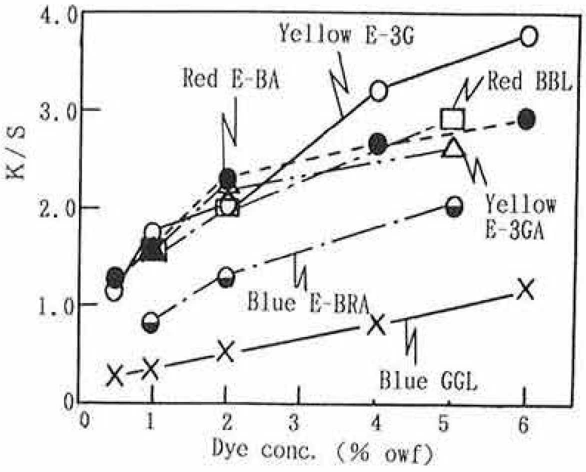

Fig. 5. Effect of dye concentration on K/S values of *A. pernyi*
Isopropyl alcohol content: 80%.

isopropyl alcohol content of 80% and sodium carbonate content of 2 g/l. If the K/S value could increase sharply with an increase of the dye concentration, the system would be superior in dye buildup characteristics and suitable for achieving a dark color. If we take the K/S value at a dye concentration of 0.5% owf as 100, the K/S value at 6.0% owf was 229 for Yellow E-3GA, 397 for Blue GGL, and 317 for Yellow E-3GA. Although comparable values can not be obtained for the buildup performance, it is likely that the relative increases are not appreciably large. However, as shown in Fig. 5, dyeing in a solvent mixture of isopropyl alcohol and water is appropriate.

6) *Effect of sodium carbonate*

To determine whether an alkali agent is necessary for dyeing in an alcohol-water solvent mixture, as in the case of alkali dyeing, the K/S value, the amount of dye that becomes desorbed by hot water treatment, etc. was examined by keeping the dye concentration in the bath at 2% owf and the isopropyl alcohol content of the bath at 80%, and changing the amount of sodium carbonate added, in the range of 0–5 g/l. With all the dyes used in this experiment, the K/S value was higher when dyeing was performed in the presence of sodium carbonate (Table 2).

The amount of dye removed by the hot water treatment (70°C, 20 min) was very large in the absence of sodium carbonate. With the addition of sodium carbonate to the dye bath, this amount decreased considerably. Thus, sodium carbonate had a distinct effect, suggesting that an alkali agent like sodium carbonate is essential for fixing the dye. In the case of sodium carbonate, about 2 g/l is the suitable amount, considering the amount of dye desorbed and the change in pH of the residual bath.

Next, the K/S value of an *A. pernyi* fabric dyed by standard alkali dyeing (control) was determined and compared with the results obtained in the dyeing in alcohol–water solvent mixtures. The dyeing conditions were the same as those adopted with the solvent mixture dyeing except that 100 g/l of sodium sulfate was used along with 2 g/l of sodium carbonate. The K/S values obtained for Red E-BA at 2% owf dye concentration were 2.72 for dyeing in 80% isopropyl alcohol and 20% water mixture and 2.57 in the alkali dyeing. The values were 3.37 and 2.94 with Blue E-4RA, 2.43 and 2.37 with Yellow E-3G, and 2.11 and 2.24 with Red BBL. Thus, the K/S values were almost the same in the two methods of dyeing.

Table 2. Relationship among sodium carbonate concentration in the dye bath, surface color depth of the dyed fabric and running of color in hot water

Dye	Sodium carbonate in dye bath (g/l)	K/S value	Removal of dye in hot water[a] ($\times 10^{-5}$ g·dye/g·fiber)	K/S value after the hot water treatment[a]	pH of residual bath
Red E-BA	0	1.75	78.5	1.24	5.95
	1	2.85	24.0	2.62	10.52
	2	2.72	20.5	2.50	10.69
	5	3.00	18.0	3.06	10.95
Blue E-4RA	0	1.50	56.0	1.43	6.02
	1	3.44	22.5	3.19	10.59
	2	3.37	20.0	3.48	10.71
	5	3.23	15.0	2.97	10.99
Yellow E-3G	0	0.77	44.5	0.67	–
	1	2.67	7.0	2.32	–
	2	2.43	6.5	2.51	–
	5	2.52	7.0	2.41	–
Brown E-2R	0	1.52	142.5	1.15	–
	1	1.80	4.5	1.75	–
	2	1.87	4.0	1.53	–
	5	1.84	3.0	1.65	–

Dye concentration: 2% owf.
Isopropyl alcohol content of bath: 80%.
a): Conditions of hot water treatment; Liquor ratio 1:50, Temperature 70 ± 2°C, Duration 20 min.

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