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Silk and nylon or silk and polyester were successfully dyed in a common bath with disperse azo dyes Red 1, MHAB and Red 19, which are different in substituent amino groups. The adsorption isotherms of these dyes for silk and nylon were of the partition type. The uptake of these dyes was efficient in the order of nylon > silk > polyester. The adsorption isotherm of Orange 3 for silk and nylon was of the Freundlich type. The adsorption of this dye at the concentration of 2.0×10^{-5} M at pH 6 at 100℃ was almost equal between silk and polyester. The rate of dye uptake by silk and nylon was higher as the dye was lower in inorganicity/organicity-value, i.e. more hydrophobic.

Key words: simultaneous dyeing, silk/nylon, silk/polyester, disperse azo dyes, hydrophobicity

Recently consumption of silk is recovering owing to its excellent properties, which have been further improved by blending silk with natural and synthetic fibers. In this connection, it is necessary to develop techniques for dyeing constituent materials of blends simultaneously in the same bath. The authors have succeeded in dyeing silk together with nylon using disperse dyes having a malonic acid residue (DOHMYOU *et al.*, 1992) or reactive disperse dyes (DOHMYOU *et al.*, 1990). However, it was difficult to dye silk and polyester together in a common bath with the above dyes to the same extent. This may be due to the fact that polyester is more hydrophobic than silk. Recently we found the efficacy of hydrophobic dyes for dyeing silk and polyester at once. The present paper describes the dyeing of silk/nylon and silk/polyester with a series of disperse azo dyes.

Materials and Methods

Silk fabrics (14 *metsuke habutae*) were used

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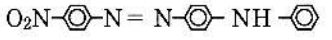
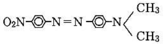
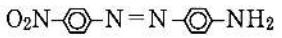
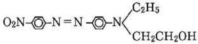
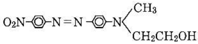
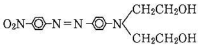
after scouring in 1.0 g/l solution of a nonionic surfactant Noygen HC (Daiichi Industrial Chemical Co. Ltd.) for 30 min at 80℃. The nylon 6 and polyester fabrics used were washed in water for 30 min at 80℃ and bone dried. C. I. Disperse Orange 1 and Orange 3 (Table 1) were purified by recrystallizing commercial products (Mitsui Toatsu Dye Co. Ltd.) from methanol solution. Other disperse dyes, DMAB, Red 1, MHAB and Red 19 (Table 1), were synthesized by coupling diazotized *p*-nitroaniline with *N*,*N*-disubstituted aniline. The characteristics including the structures of the dyes are shown in Table 1. The inorganicity / organicity-values (I / O-values) of Orange 1, Orange 3, DMAB, Red 1, MHAB and Red 19 were calculated to be 0.50, 0.57, 0.65, 0.77, 0.81 and 1.03, respectively, using previously reported formulas (KUROKI, 1974). The dyes were each solubilized at different concentrations in 2 ml ethanol and 200 ml 0.01 M acetate buffer, pH 6, and allowed to stand overnight at a constant temperature (70, 80 or 90℃). Silk (0.1 g) and nylon (0.1 g), or silk (0.1 g) and polyester (0.1 g), were immersed together in the dye solution until equilibrium was reached as far as possible. After dyeing, the fabrics were extracted with 50% dioxane solution. Each extract was diluted with 50% dioxane to a total volume of 100 ml. The dye concentration of the solution was determined by colorimetry by using U-1100 type Hitachi spectrophotometer and the amounts of absorbed dyes were calculated. To measure time course of dyeing, 25 ml of dye solution was pipetted into a measuring flask while the solution was hot and diluted with dioxane to a total volume of 50 ml and the concentration of residual dye was determined by colorimetry.

Results and Discussion

The adsorption rates of disperse azo dyes onto silk and nylon, or silk and polyester, immersed together in the same bath were measured at 70, 80 and 90℃. Fig. 1 shows

Table 1. Disperse azo dyes used.

Dye (C. I. Disperse)	Chemical structure	Molecular weight	Inorganicity/ organicity	Abbreviation
Orange 1		318.33	0.50	Orange 1
		270.29	0.57	DMAB
Orange 3		242.24	0.65	Orange 3
Red 1		314.34	0.77	Red 1
		300.32	0.81	MHAB
Red 19		330.34	1.03	Red 19

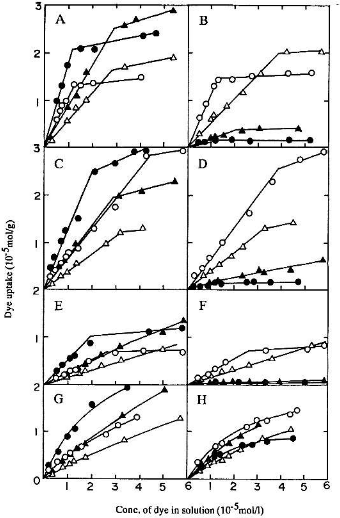


Fig. 1. Adsorption isotherms of Disperse azo dyes on silk and nylon or silk and polyester at pH 6. Open symbols for A to H indicate silk. Solid symbols for A, C, E and G show nylon and those for B, D, F and H show polyester. Circles, at 70℃; triangles, at 90℃. Plots at 80℃ were omitted. Dyes used were Red 1 (A,B), MHAB (C,D), Red 19 (E,F) and Orange 3 (G,H).

typical results. The adsorption isotherms of Red 1, MHAB and Red 19 on silk/nylon and silk/polyester were of the partition type (from A to F). The rates of uptake of these dyes by the fabrics were in the order, nylon > silk > polyester. Red 19 failed to be adsorbed onto the fabrics, in particular polyester, owing to the high hydrophilic character of the dye. On the other hand, the adsorption isotherms of Orange 3 on silk/nylon and silk/polyester were of the Freundlich type (G and H). This might be explained by the aggregation of the dye in the fibers. The uptake of Orange 3 by the fibers was efficient in the order of nylon >

Table 2. Thermodynamic parameters for adsorption of disperse azo dyes on silk, nylon and polyester at pH 6.

Dye	Fabrics	Temp. (℃)	K (l/g)	$-\Delta\mu^{\circ}$ (kcal/mol)	ΔH° (kcal/mol)	ΔS° (e.u.)
Red 1	Silk	70	1.16	5.68	−8.45	−8.19
		90	0.59	5.52		
	Nylon	70	1.91	6.58	−9.10	−7.40
		90	0.92	6.44		
	Silk	70	1.13	5.66	−9.09	−10.02
		90	0.54	5.46		
	Polyester	70				
		90				
MHAB	Silk	70	0.76	5.39	−7.03	−4.80
		90	0.43	5.30		
	Nylon	70	1.24	6.29	−7.16	−2.57
		90	0.69	6.24		
	Silk	70	0.66	5.29	−5.64	−0.99
		90	0.42	5.27		
	Polyester	70				
		90				
Red 19	Silk	70	0.28	4.70	−7.11	−7.07
		90	0.16	4.56		
	Nylon	70	0.48	5.65	−8.37	−8.00
		90	0.25	5.49		
	Silk	70	0.27	4.69	−7.09	−7.04
		90	0.15	4.55		
	Polyester	70				
		90				
Orange 3	Silk	70	0.53	5.14	−6.50	−3.82
		90	0.31	5.06		
	Nylon	70	0.86	6.04	−7.12	−3.18
		90	0.49	5.98		
	Silk	70	0.50	5.10	−7.52	−7.06
		90	0.27	4.96		
	Polyester	70				
		90				

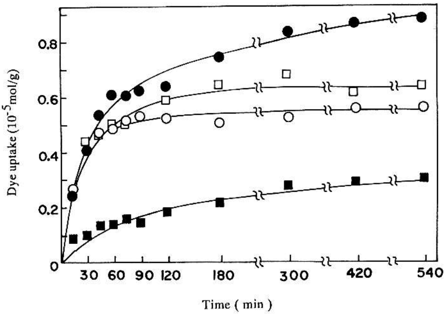


Fig. 2. Time course of dyeing with C. I. Disperse Orange 3 at a concentration of 2 × 10^{-5} M at pH 6 at 80℃. Silk and nylon (open circles and solid circles, respectively) or silk and polyester (open squares and solid squares, respectively) were treated simultaneously.

polyester ≧ silk. The amounts of all dyes adsorbed to silk and nylon were high at low temperature. This was in contrast to the results of polyester in which the uptake rates were high at high temperature. Namely, dyeing equilibrium was attained in the case of silk/nylon but not in the case of silk/polyester under the present experimental conditions. Probably this is ascribed to the compact structure of polyester. The profiles for the adsorption isothermsof Orange 1 and DMAB on silk/polyester were omitted since these dyes were undissolved. The uptake of these dyes did not increase even when large amounts of the dyes were used. The thermodynamic parameters for adsorption of the disperse azo dyes on silk and nylon were determined using the data shown in Fig. 1. The partition coefficient K, estimated from the slope at the lower dye concentration ranges in Fig. 1, is equal to $[D]_f/[D]_s V$, where $[D]_f$ means the dye uptake, $[D]_s$ indicates the concentration of free dye and V is the internal volume of a fiber. The values of V are 0.281 l/kg for silk (KANAMARU, 1959) and 0.122 l/kg for nylon (OKABE and IWATARE, 1988). Although the adsorption isotherms of Orange 3 was of the Freundlich type, the apparent values of K for this dye were also determined for comparison. The affinities of adsorption ($-\Delta\mu°$) were determined by substituting K in the equation $-\Delta\mu° = RT\ln K$, where R is the gas constant and T is a temperature. Standard adsorption heat ($\Delta H°$) and standard entropy change ($\Delta S°$) were calculated by the following equations: $\Delta\mu°/T = \Delta H°/T + C$ (C stands for the integral constant) and $\Delta\mu° = \Delta H° - T\Delta S°$. The results are listed in Table 2. The values for

K and $-\Delta\mu^\circ$ increase as the temperature decreases. Thus, the adsorption of these disperse azo dyes on silk and nylon were clearly of an exothermic reaction. The heat of dyeing ranges from −5.64 to −9.10 kcal/mol, and the entropy decreases. Table 2 indicates that the affinities of the dyes for silk and nylon are in the order, Red 1 > MHAB > Red 19. These dyes are common in fundamental structure but different in amino group substitution. The I/O-values of these three dyes increase in the above order (Table 1). The I/O-values of silk, nylon and polyester are 4.1 [calculated on the basis of the content of amino acids in silk (SHIMIZU, 1972)], 1.7 and 0.7 (KUROKI, 1974), respectively. It is likely that the affinity of dye for silk and nylon increases as the I/O-value reduces, i.e. the hydrophobicity of the dye increases. The affinities of the dyes for nylon, which is more hydrophobic than silk, are larger than those for silk. Red 1 and MHAB with one alkyl group and one hydroxyethyl group show high affinities for silk and nylon. This may be due to the hydrophobic property of alkyl group and the hydrophilic property of hydroxyethyl group. Red 19, which possesses two hydroxyethyl groups, shows a low affinity for all the fabrics because of its relatively high hydrophilicity.

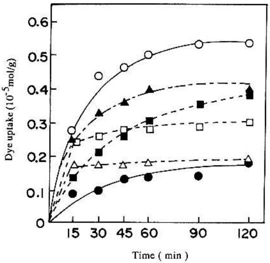


Fig. 3. Time course of dyeing with C. I. Disperse Orange 3 at a concentration of 2×10^{-5} M at pH 6 at various temperatures. Silk and polyester were dyed simultaneously at 80℃ (circles), 100℃ (squares) or 120℃ (triangles). Open symbols, silk; solid symbols, polyester.

The time course of dyeing of silk and nylon, or silk and polyester, with Orange 3 in the same bath was also determined (Fig. 2). An equilibrium state of silk dyeing was attained for about 120 min at 80℃. Beyond this time the dye uptake by nylon and polyester increases further. The curves for dyeing time course of silk and polyester simultaneously with Orange 3 at 80, 100 and 120℃ are shown in Fig. 3. The extent of dye uptake by silk and that by polyester are almost equal to each other at 100℃. These results suggest that silk and polyester can be dyed by the common bath method using Orange 3 at pH 6 at 100℃.

In conclusion, the present study shows the possibility that silk and nylon or silk and polyester can be dyed simultaneously at a constant temperature using the disperse azo dyes Red 1, MHAB, Red 19 and Orange 3, which resemble each other in the fundamental structure but differ in the substituent amino groups.

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道明美保子・清水慶昭・木村光雄・高岸 徹: 分散アゾ染料による絹/ナイロン, 絹/ポリエステルの一浴染色

分散アゾ染料を用いて, 絹/ナイロン, 絹/ポリエステルを一浴で一定温度で平衡染色した。これらの染料は基本構造は同じであるがアミノ基についている置換基が異なっている。Red1, MHAB, Red19 の絹とナイロンに対する吸着等温線は分配型を示した。これらの染料の染着量の順序はナイロン>絹>ポリエステルであった。一方, Orange 3 の絹とナイロンに対する吸着等温線はフロインドリッヒ型と推定された。Orange 3 の絹/ナイロン, 絹/ポリエステルに対する染色速度を測定した結果, 絹とポリエステルを pH 6, 100℃で一浴で染色することにより絹とポリエステルはほぼ同じ染着量が得られることが明らかとなった。絹とナイロンの染着量は染料の無機性/有機性-値が小さい (すなわち, より疎水性である) ほど増加した。