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Compatibility of Acid Dyes on Nylon

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ABSTRACT

The selection of trichromatic acid dyes with good compatibility for nylon is more complicated than that for cationic-dye/acrylic-fiber dyeing because the dyeing-temperature range in nylon dyeing is much wider than that in acrylic-fiber dyeing.

Forty-six commercially available acid dyes have been divided into five groups according to their change in dyeing rate with dyeing temperature, i.e. activation energy. Discussion is made in terms of the molecular weight of the dye, the number of sulfonate groups in the dye, the change in saturation value with pH, and the change in the time of half-dyeing with dyeing temperature. Trichromatic combinations in each group are described.

1 INTRODUCTION

One of the most important factors required for good levelness in textile dyeing is the compatibility of dyes used in combination.

In cationic-dye/acrylic-fiber dyeing systems, a mixture parameter,[1] or *K* value,[2] is readily obtained as a compatibility parameter and it can be applied to the dyeing with high reliability for the following reasons:

- (i) the saturation value of acrylic fiber is stable at pH 4–6;
- (ii) the temperature range for the absorption of a cationic dye is very narrow (80–100°C), and the test for compatibility is carried out at around 95°C;
- (iii) most cationic dyes have only one quaternary ammonium group, i.e. one positive charge.

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On the other hand, in acid-dye/nylon dyeing systems, the behavior of the dye is more complicated because:

(i) saturation values vary widely with dyebath pH;
(ii) the temperature range for the absorption of acid dyes is very wide (40–100°C) and the compatibility of acid dyes may change within this temperature range;
(iii) each acid dye has a different number of sulfonate groups, i.e. one or two negative charges.

According to Atherton *et al.*[3] in the case of the dyeing of nylon with two acid dyes, the ratio of each dye on the fiber surface depends on its affinity to the fiber. Thus the ratio of two dyes absorbed is given by eqn (1):

$$\frac{dQ_1/dt}{dQ_2/dt} = \frac{D_1 Z_1 C_1}{D_2 Z_2 C_2} \exp\left\{\frac{-(\Delta\mu_1^0 - \Delta\mu_2^0)}{RT}\right\} \tag{1}$$

where Q, $\Delta\mu^0$, D, Z, and C represent the amount of dye absorbed, the affinity, the diffusion coefficient, the basicity, and the concentration of dye in the bath, respectively (suffixes 1 and 2 refer to the respective two dyes).

The compatibility K is given by eqn (2):

$$K = \frac{D_1 Z_1}{D_2 Z_2} \exp\left\{\frac{\Delta\mu_1^0 - \Delta\mu_2^0}{RT}\right\} \tag{2}$$

If $K = 1$, two dyes have good compatibility with each other and will give good levelness in combination dyeing.

Beckmann *et al.*[4] obtained K values for the cationic-dye/acrylic-fiber system at 100°C; in this case, the activation energy E does not change within the dyeing-temperature range. These K values cannot always be applied to practical dyeing, because of the complications of the acid dye/nylon system.

In this paper, 46 commercially available dyes have been divided into groups according to their change of dyeing rate by dyeing temperature, i.e. activation energy, and dye compatibility within these groups is discussed.

2 EXPERIMENTAL

2.1 Materials

Spun yarns of nylon 6 (Toray) were pretreated with hot water before dyeing commenced.

The following commercial acid dyes were used:

C.I. Acid Yellow 19, 25, 29, 49, 72, 78, 110, 219
C.I. Acid Orange 19, 43, 51, 67

C.I. Acid Red 32, 57, 111, 114, 131, 134, 138, 154, 249, 257, 266, 337
C.I. Acid Violet 43, 48
C.I. Acid Blue 40, 62, 78, 113, 117, 120, 126, 127:1, 129, 183
C.I. Acid Green 25, 27, 28
C.I. Acid Brown 2, 13, 301
C.I. Acid Black 21, 24, 26, 48

2.2 Measurements of saturation value

The saturation value of each dye was obtained under the following dyeing conditions:

dyeing depth: 0·5–1·0–2·0–to saturation value;
pH: $4 \pm 0{\cdot}2$ and $6 \pm 0{\cdot}3$ (controlled by acetic acid and sodium acetate);
dyeing temperature: 100°C;
liquor ratio: 1:50;
dyeing time: 90 min.

The absorbance of the residual dyebath was measured by using a Shimadzu spectrophotometer, with a 10-mm quartz cell at the appropriate absorbance maxima (Tables 1–5).

The dye uptake was plotted against the dyeing concentration in the dyebath, and the saturation value was then obtained from the turning point of the plot.

2.3 Measurements of absorption isotherm

The absorption isotherm was measured under the following conditions:

dyeing depth: saturation value at pH 6;
auxiliary: ammonium sulfate 3% (o.w.f.);
dyeing temperature; 60°, 75°, and 90°C;
liquor ratio: 1:50;
dyeing time: 0–60 min.

3 RESULTS AND DISCUSSION

The most significant difference was found in the change in the time of half-dyeing, t_{50} (at 60°, 75°, and 90°C), and these dyes could be divided into five groups according to their change in t_{50}, namely:

Group I: $t_{50}(60°C)/t_{50}(90°C)$ 0–9·99

TABLE 1
Dyes of Group I

Dyes	MW	Number of sulfonate group	λ_{max} (nm)	Saturation value (% (o.w.f.))			Half-dyeing time (t_{50}) (min)			
				pH 6	pH 4	pH 4/pH 6	90°C	75°C	60°C	60°C/90°C
Acid Yellow 25	537	1	400	1·6	3·4	2·13	0·9	1·2	7·3	8·11
Yellow 49	448	1	420	2·4	3·6	1·50	0·8	1·7	6·6	8·25
Yellow 110	560	1	415	2·4	4·0	1·67	0·8	1·1	6·2	7·75
Yellow 219	448	1	410	2·5	4·0	1·60	0·8	1·5	4·3	5·38
Red 57	525	2	530	1·9	2·9	1·53	1·8	3·2	12·7	7·06
Red 257	521	1	530	2·7	3·6	1·33	1·6	2·2	10·1	6·31
Red 266	452	1	520	6·2	8·0	1·29	2·0	2·3	9·0	4·50
Red 337	417	1	520	3·0	5·0	1·67	0·9	1·8	3·5	3·89
Violet 43	383	1	580	1·6	2·8	1·75	1·2	2·2	6·0	5·00
Blue 40	449	1	620	3·0	3·9	1·30	1·8	2·2	9·0	5·00
Blue 62	422	1	645	2·9	3·5	1·21	2·1	2·5	7·6	3·62
Blue 78	500	1	640	3·0	4·0	1·33	1·9	2·3	9·5	5·00
Blue 129	458	1	620	3·0	3·6	1·20	1·7	2·3	8·7	5·12
Blue 183	484	1	635	8·0	10·4	1·30	2·3	3·0	7·0	3·04
Average	472	1·07				1·49				5·57

TABLE 2
Dyes of Group II

Dyes	*MW*	*Number of sulfonate group*	λ_{max} *(nm)*	*Saturation value (% (o.w.f.))*			*Half-dyeing time* (t_{50}) *(min)*			
				pH 6	*pH 4*	*pH 4/pH 6*	*90°C*	*75°C*	*60°C*	*60°C/90°C*
Acid Yellow 19	553	2	430	0·9	1·9	2·11	0·9	2·4	11·6	12·89
Yellow 29	554	1	400	1·7	4·0	2·35	1·0	2·4	12·5	12·50
Orange 19	505	1	490	2·8	4·0	1·43	1·1	2·0	11·6	10·54
Orange 43	605	1	480	1·4	2·2	1·57	1·9	4·2	19·5	10·26
Orange 51	604	1	470	3·6	6·4	1·78	1·1	4·5	31·4	18·47
Red 32	604	1	535	6·2	8·0	1·29	1·2	4·5	20·0	16·70
Green 25	622	2	645	1·2	2·1	1·75	2·4	6·7	43·5	18·12
Brown 2	516	1	560	3·8	4·5	1·18	2·0	4·5	25·7	12·85
Brown 13	732	2	425	2·9	3·2	1·10	1·7	5·0	33·0	19·41
Average	588	1·33				1·62				14·64

TABLE 3
Dyes of Group III

Dyes	*MW*	*Number of sulfonate group*	λ_{max} *(nm)*	*Saturation value (% (o.w.f.))*			*Half-dyeing time* (t_{50}) *(min)*			
				pH 6	*pH 4*	*pH 4/pH 6*	*90°C*	*75°C*	*60°C*	*60°C/90°C*
Acid Orange 67	590	1	440	4·0	5·1	1·28	0·9	4·0	19·5	21·67
Red 111	830	2	505	2·8	3·4	1·21	2·5	11·1	64·5	25·80
Red 131	677	2	530	1·7	2·4	1·41	1·9	6·2	48·3	25·42
Red 134	872	2	545	2·8	4·3	1·54	4·1	27·7	95·0	23·17
Red 138	653	2	550	2·5	3·7	1·48	0·8	3·9	23·8	29·75
Red 158	840	2	520	3·1	4·2	1·35	3·9	24·0	5·0	25·49
Red 249	748	2	525	2·3	3·3	1·43	1·9	7·5	46·0	24·21
Violet 48	764	2	600	2·5	3·3	1·32	3·1	16·0	87·0	28·06
Blue 117	537	1	580	2·7	4·4	1·63	1·0	5·5	28·8	28·80
Blue 126	566	1	625	4·2	5·2	1·24	1·0	3·6	27·3	27·30
Average	708	1·70				1·39				25·97

TABLE 4
Dyes of Group IV

Dyes	*MW*	*Number of sulfonate group*	λ_{max} *(nm)*	*Saturation value (% (o.w.f.))*			*Half-dyeing time (t_{50}) (min)*			
				pH 6	*pH 4*	*pH 4/pH 6*	*90°C*	*75°C*	*60°C*	*60°C/90°C*
Acid Yellow 72	614	1	420	2·5	4·5	1·80	1·4	8·1	45·0	32·14
Red 114	814	2	515	4·2	4·8	1·14	2·6	15·0	80·0	30·77
Blue 113	649	2	590	3·8	4·4	1·16	1·1	7·1	43·5	39·55
Green 27	642	2	650	2·4	2·7	1·13	1·1	5·9	39·8	36·18
Green 28	738	2	640	3·4	3·8	1·12	1·5	7·8	55·0	36·67
Black 24	731	2	600	6·4	6·3	0·99	1·8	10·0	68·2	37·89
Black 26	697	2	590	3·7	4·1	1·11	2·3	15·0	72·5	31·52
Average	698	1·86				1·21				34·96

TABLE 5
Dyes of Group V

Dyes	*MW*	*Number of sulfonate group*	λ_{max} *(nm)*	*Saturation value (% (o.w.f.))*			*Half-dyeing time* (t_{50}) *(min)*			
				pH 6	*pH 4*	*pH 4/pH 6*	*90°C*	*75°C*	*60°C*	*60°C/90°C*
Acid Yellow 78	611	1	420	8·8	11·6	1·32	0·8	5·9	43·6	54·50
Blue 120	695	2	605	3·8	4·1	1·08	1·2	9·0	79·0	65·83
Blue 127:1	780	2	635	3·3	3·7	1·12	1·5	9·0	69·0	46·00
Brown 301	661	2	480	2·3	3·4	1·31	1·3	7·1	54·6	42·00
Black 21	745	2	620	5·2	5·2	1·00	1·8	13·0	80·0	44·44
Black 48	647	2	575	1·9	3·2	1·68	1·2	6·6	60·0	50·00
Average	690	1·83				1·25				50·46

Group II: $t_{50}(60°C)/t_{50}(90°C)$ 10·00–19·99
Group III: $t_{50}(60°C)/t_{50}(90°C)$ 20·00–29·99
Group IV: $t_{50}(60°C)/t_{50}(90°C)$ 30·00–39·99
Group V: $t_{50}(60°C)/t_{50}(90°C)$ 40·00–59·99

The molecular weight, number of sulfonate groups, saturation value at pH's 4 and 6, and t_{50} of each dye at 60°, 75°, and 90°C are summarized in Tables 1, 2, 3, 4, and 5, respectively.

The average molecular weight plotted against the average number of sulfonate groups, the average ratio of saturation values (pH 4/pH 6), and the average ratio of half-dyeing time (60°C/90°C) of each dye group are shown in Figs 1, 2, and 3, respectively.

With Groups I, II, and III, there are good correlations between the average molecular weight and the number of sulfonate groups and also between the average molecular weight and the average ratio of the time of half-dyeing (60°C/90°C). No good correlation was observed between the average molecular weight and the average ratio of the saturation value (pH 4/pH 6). Exceptions are found in the dyes of Groups IV and V because these dyes have a tendency to aggregation at lower temperature and require high energy for disaggregation to occur.

Dyes of different groups show different types of absorption behavior, i.e. different activation energy, in the dyeing-temperature range 60 –90 C. Thus the combination of the dyes of different groups gives a different absorption

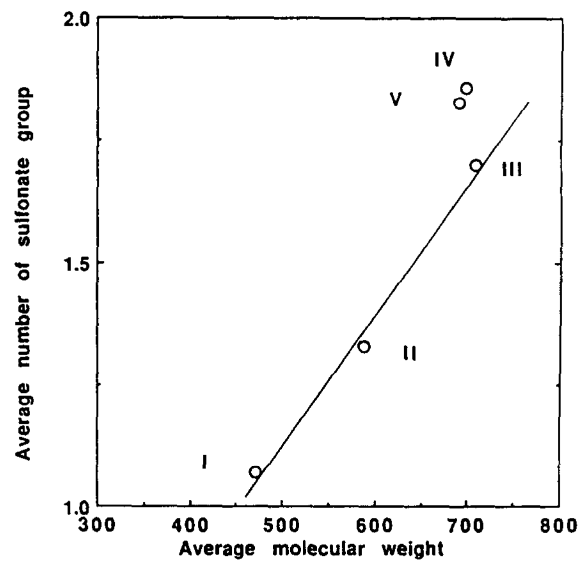

Fig. 1. Relationship between average molecular weight and average number of sulfonate group.

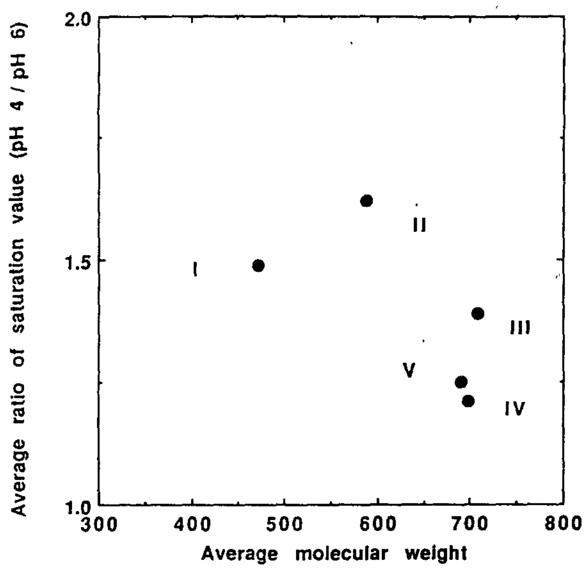

Fig. 2. Relationship between average molecular weight and average ratio of saturation value (pH 4/pH 6).

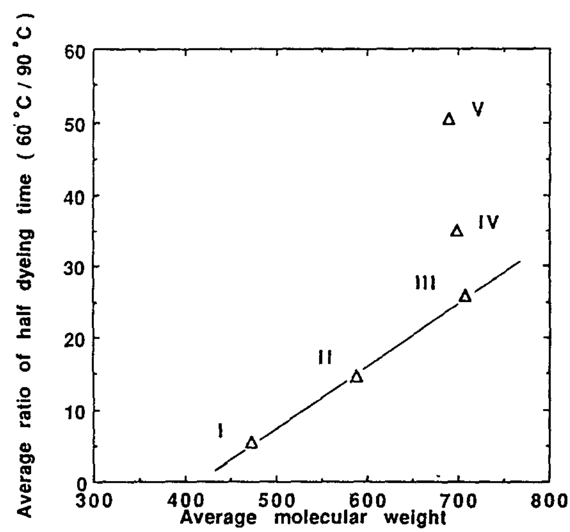

Fig. 3. Relationship between average molecular weight and average ratio of half-dyeing time (60°C/90°C).

rate in the practical dyeing process, when the dyeing is started at temperatures below 40°C and completed at around 100°C.

We examined whether there were fundamental dyes in each group, with the following conclusions:

Group I: four Yellows, four Reds, and five Blues;
Group II: two Yellows, one Red, and no Blue;
Group III: no Yellows, six Reds, and two Blues;
Group IV: one Yellow, one Red, and one Blue (navy blue);
Group V: one Yellow, no Red, and two Blues.

Thus only Group I dye can be selected providing a trichromatic dye combination. The SDC combination test[2] or another test[4] can be applied to determine which dye combination is better in Group I. It is likely that C.I. Acid Yellow 110, 219, Red 257, 266, 337, and Blue 40, 62, 129 are combinable in the dyeing of nylon 6, from our combination-test results.

The dyes used were all of commercial origin. Each dye contains a different diluent content. For example, C.I. Acid 266 contains much more diluent than C.I. Acid Blue 40. Thus the apparent saturation value of the former dye is higher than that of the latter. In this work, the saturation value at pH 4/pH 6 is more important. Although the saturation values of the two dyes differ significantly, the compatibility of C.I. Acid Red 266 and C.I. Acid Blue 40 is always good in any combination ratio in this dyeing system.

The best trichromatic combination should be selected from the aforementioned eight dyes for a given fiber and dyeing condition.

4 CONCLUSION

A range of commercially available acid dyes has been divided into five groups according to their change in t_{50} at 60°C/90°C, in other words, their activation energy of diffusion. Only in Group I, with the lowest activation energy, were there four or five fundamental dyes in each color (yellow, red, and blue) with good compatibility. The best combination for practical dyeing processes should be determined for individual coloration requirements.

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