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Improved Dyeing with Redox Systems: IV—Dyeing of Nylon-6 with Disperse Dyes

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SUMMARY

The dyeing of nylon-6 fabric with Terasil Red 2GL (CI Disperse Red 72), in the absence and presence of redox systems based on ammonium persulphate [$(NH_4)_2S_2O_8$] *as oxidant and potassium pyrosulphite* ($K_2S_2O_5$), *glucose* ($C_6H_{12}O_6$) *or thiourea* (CH_4N_2S) *as reductant, was studied. It was found that for a given set of dyeing conditions the colour strength, expressed as K/S, follows the order*

$$(NH_4)_2S_2O_8 > (NH_4)_2S_2O_8/C_6H_{12}O_6 > (NH_4)_2S_2O_8/K_2S_2O_5 > (NH_4)_2S_2O_8/CH_4N_2S > \textit{blank (without redox system)}$$

Increasing the $(NH_4)_2S_2O_8$ *concentration (0·00–0·03 M) as well as the duration (15–60 min) and temperature (65–95°C) of the dyeing process caused significant enhancement in the colour strength and dye fixation. It is postulated that the presence of* $(NH_4)_2S_2O_8$ *alters the mode of dye interaction. In the presence of the oxidant component, i.e.* $(NH_4)_2S_2O_8$, *attachment of the disperse dye to the nylon-6 substrate seems to involve covalent bonding in addition to the usual hydrogen bond. This is indicated by the significant colour strength remaining after DMF extraction for dyeings obtained using different disperse dyes and in the presence of* $(NH_4)_2S_2O_8$. *A free-radical mechanism for the covalent bond formation between nylon-6 and the disperse dyes is tentatively suggested.*

1 INTRODUCTION

In previous studies[1–3] we have shown that the colour strength and dye fixation are enhanced significantly during colorations in the presence of a

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redox system. The improvement in the dyeing properties of all the fibres studied, i.e. wool, wool/acrylic and nylon-6 with acid dyes, and cotton and viscose with direct dyes, suggests that in the presence of a redox system dyeing involves the formation of covalent bonds between substrate and dye via a free-radical mechanism in addition to the conventional interactions.[1–5] These results stimulated the present work, which aims to clarify the role of redox systems in the dyeing of nylon-6 with disperse dyes, and to improve the dyeing properties of disperse dyes on nylon-6.

2 EXPERIMENTAL

2.1 Materials

Substrate

Nylon-6 fabric (210 denier/35 filament) was scoured at 70°C for 1 h in a bath containing 5 g litre^{-1} Kieralon OL (BASF), thoroughly rinsed with water and air-dried.

Dyestuffs

Commercial disperse dyestuffs, namely Terasil Red 2GL (Ciba) (CI Disperse Red 72), Terasil Blue R (CI Disperse Blue 73), Terasil Brilliant Blue 2G (CI Disperse Blue 87), Samaron Red 2BSL (Hoechst) and Samaron Navy Blue GR, were used.

Chemicals

The oxidant used was ammonium persulphate $(NH_4)_2S_2O_8$; reductants included potassium pyrosulphite ($K_2S_2O_5$), glucose ($C_6H_{12}O_6$) and thiourea (CH_4N_2S). All were laboratory-grade chemicals. The non-ionic wetting agent (Invadine VBF) was kindly supplied by Ciba–Geigy. Kieralon OL (BASF) was used as a non-ionic/anionic surfactant, Laventin W (BASF) as a non-ionic wetting agent and the detergent, Avolan IS (Bayer), as a dispersing agent.

2.2 Dyeing procedure

Unless otherwise stated, the dyebaths were set with the requisite amount of dye (LR 1:30), dispersing agent (1 g litre^{-1}), non-ionic wetting agent (2 g litre^{-1}) and the reducing agent (0·x M). The fabrics were introduced, followed by the addition of the oxidizing agent (0·x M). Dyeing was carried out at 65–95°C for varying lengths of time (15–60 min) with continuous stirring. At the end of the dyeing, the dyed sample was rinsed with cold water, scoured at

65°C for 30 min in a solution containing 2 g litre^{-1} soda ash and 2 g litre^{-1} Laventin W, then rinsed and finally dried at ambient conditions. Dyed samples were extracted at the boil with DMF (50%).

2.3 Testing

Colour strength, expressed as K/S, was calculated from the reflectance values measured with a Hunter Reflectometer. The K/S values were calculated using the Kubelka–Munk equation:[6]

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

where R is the observed reflectance, K is the coefficient of reflectivity and S is the coefficient of light scattering.

Evaluation of washing and perspiration fastness properties were performed according to standard methods.[7]

3 RESULTS AND DISCUSSION

3.1 Redox components

Table 1 shows the effect of incorporation of $(NH_4)_2S_2O_8$ in the absence or presence of certain reductants, i.e. $K_2S_2O_5$, $C_6H_{12}O_6$ or CH_4N_2S, on the colour strength, expressed as K/S, of the dyed nylon samples with a disperse dye, namely Terasil Red 2GL. The data show that incorporation of $(NH_4)_2S_2O_8$, either alone or in the presence of the reductant, is accompanied by a significant enhancement in the K/S values. This is observed irrespective

TABLE 1

Effect of Nature of Reductant when Used with $(NH_4)_2S_2O_8$ on the Colour Strength (K/S) of Nylon-6 Fabric[a]

Reductant			
None	$K_2S_2O_5$	$C_6H_{12}O_6$	CH_4N_2S
1·40	1·18	1·30	1·12

[a] Redox components, 0·02 M each; Terasil Red 2GL, 2% based on weight of fabric (o.w.f.); Avolan IS, 1 g litre^{-1}; Invadine VBF, 2 g litre^{-1}; material-to-liquor ratio, 1:30; dyeing at 75°C for 45 min. K/S of blank (without redox components) = 1·03.

of the reductant used. Nevertheless, for a given set of dyeing conditions the colour strength of the dyed samples followed the order

$$(NH_4)_2S_2O_8 > (NH_4)_2S_2O_8/C_6H_{12}O_6 > (NH_4)_2S_2O_8/K_2S_2O_5 > (NH_4)_2S_2O_8/CH_4N_2S > \text{blank (without redox components)}$$

This order reflects the ability of $(NH_4)_2S_2O_8$ to form with the nylon and the dye an efficient redox system which contributes in creating reactive sites on the fibre and on the dye, and which are capable of combination additional to the conventional attachment via hydrogen bonding at the —HNCO— grouping of the nylon molecule.[8]

A further observation is that dyeing of nylon-6 in the presence of any of these reductants, together with $(NH_4)_2S_2O_8$, under the conditions used in this investigation appears to result in a loss of active sites, as evidenced by the substantial diminution in the colour strength of the dyed samples. On the other hand, differences in the colour strength values obtained using different reductants could be associated with differences between these reductants with respect to the nature and mode of interaction with other components of the dyeing formulation.

3.2 Concentration of $(NH_4)_2S_2O_8$

It is apparent from the above that $(NH_4)_2S_2O_8$ alone was the best component studied for the dyeing of nylon-6 with the disperse dye. It was,

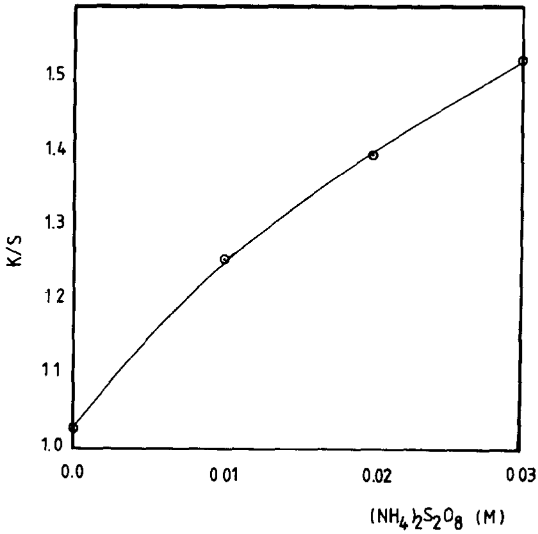

Fig. 1. Effect of concentrations of $(NH_4)_2S_2O_8$ on the colour strength (*K/S*) of nylon-6. Dyeing at 75°C for 45 min.

therefore, of interest to investigate the effect of the concentration of this oxidant on the colour strength of the dyed nylon-6 samples.

Figure 1 shows the variation of colour strength with the concentration of $(NH_4)_2S_2O_8$. It is apparent that, within the range examined, increasing the $(NH_4)_2S_2O_8$ concentration up to 0·03 M is accompanied by a significant enhancement in the colour strength of the dyed nylon-6 fabric. This improvement in colour strength resultant from the addition of $(NH_4)_2S_2O_8$ reflects the function of this component in

(a) enhancing the solubility of the disperse dye by moderating the pH of the dyebath to acidic and the favourable effect of this on diffusion, as well as improved exhaustion of the dye on to nylon-6;[8]
(b) causing gradual hydrolysis of the polymer with the production of new adsorption sites for the disperse dye, i.e. amine end groups;[9] and/or
(c) creating new active centres to yield nylon radicals as well as dye radicals.[2]

3.3 Rate of dyeing

Figure 2 shows the rates of dyeing of Terasil Red 2GL on nylon-6 in the absence and presence of $(NH_4)_2S_2O_8$. It is seen that the colour strength increases rapidly initially and then slows down. This was observed when the rates of dyeing were determined in both the absence and the presence of $(NH_4)_2S_2O_8$. Nevertheless, the rate of dyeing is greater in the presence of $(NH_4)_2S_2O_8$, reflecting the favourable effect of this compound on enhancing

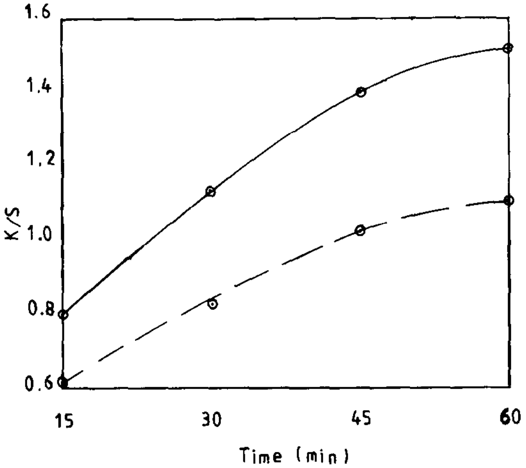

Fig. 2. Rate of dyeing of nylon-6 with Terasil Red 2GL in the absence and presence of $(NH_4)_2S_2O_8$: ——, with $(NH_4)_2S_2O_8$; ---, without $(NH_4)_2S_2O_8$. Concentration of $(NH_4)_2S_2O_8$, 0·02 M; dyeing at 75°C.

the *K/S* values. It is understandable that a proper duration is necessary for the convective transfer of dye from the bulk of the liquor to the fibre surface, adsorption, diffusion from the surface into the fibre itself and interaction of the dye with the fibre to occur.[10]

3.4 Temperature of dyeing

Figure 3 illustrates the effect of dyeing temperature on the colour strength of dyeings in the absence and the presence of $(NH_4)_2S_2O_8$. It is seen that, regardless of the presence or absence of $(NH_4)_2S_2O_8$, the colour strength increases significantly by raising the temperature from 65 to 95°C. Furthermore, the colour strength of the dyeings is improved by dyeing in the presence of $(NH_4)_2S_2O_8$.

Raising the dyeing temperature appears to result in

(a) opening of the nylon-6 structure;
(b) increase in its swellability;
(c) increasing the mobility of the macromolecular chains in the fibre as well as the solubility and mobility of the dye;
(d) accelerating the decomposition of the ammonium persulphate to generate free-radical species;
(e) creating new active centres on both the dye and the substrate; and
(f) enhancing the interaction of the dye with the substrate through the new active sites, i.e. free radicals, and/or via conventional hydrogen bonds.[2,11]

The net effect of all these factors leads to a higher colour strength with increase of temperature.

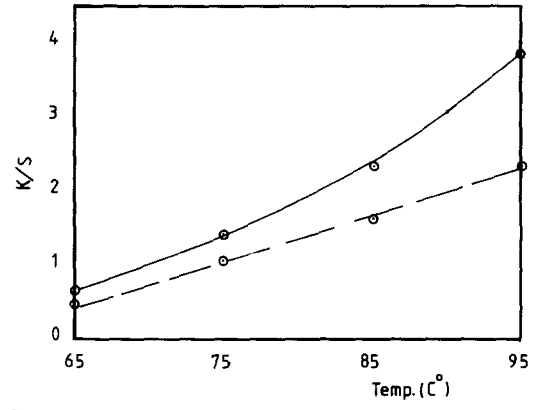

Fig. 3. Variation of the colour strength (*K/S*) by changing the temperature of dyeing: ——, with $(NH_4)_2S_2O_8$; - - -, without $(NH_4)_2S_2O_8$. Concentration of $(NH_4)_2S_2O_8$, 0·02 M; dyeing for 45 min.

TABLE 2

Effect of Nature of Dye on Colour Strength (K/S), Washing Fastness (WF) and Perspiration Fastness (PF) Properties of Nylon-6[a]

Disperse dye	*K/S*[b]		*WF at 60°C*[e]		*PF*[e]			
	Scoured[c]	*DMF*[d]	*St.*	*Alt.*	*Acidic*		*Alkaline*	
					St.	*Alt.*	*St.*	*Alt.*
Terasil Blue R	3·37 (2·80)	1·34 (0·98)	3–4	3–4	4	4	4	4
Terasil Brilliant Blue 2G	0·82 (0·56)	0·25 (0·10)	3–4	3–4	4	4	4	4
Terasil Red 2GL	1·40 (1·03)	0·39 (0·14)	4	3–4	3–4	4	3–4	4
Samaron Red 2BSL	0·97 (0·7)	0·33 (0·21)	4	3–4	4	3–4	4	3–4
Samaron Navy Blue GR	0·97 (0·59)	0·12 (0·05)	4	3	4	4	4	4

[a] $(NH_4)_2S_2O_8$, 0·02 M; dye, 2% (o.w.f.); Avolan IS, 1 g litre^{-1}; Invadine VBF, 2 g litre^{-1}; material-to-liquor ratio, 1:30; dyeing at 75°C for 45 min.

[b] The K/S values in parentheses are of dyeings in the absence of ammonium persulphate.

[c] The dyed samples were scoured with a solution containing 2 g litre^{-1} soda ash and 2 g litre^{-1} Laventin W (BASF) at 65°C for 30 min.

[d] The dyed samples were extracted with DMF (50%) for 30 min at the boil.

[e] St., staining of white wool; Alt., change of colour.

3.5 Nature of dye and mode of interaction

From the data above it may be concluded that the dyeing of nylon-6 in the presence of $(NH_4)_2S_2O_8$ gives rise to an improved colour strength, expressed as K/S, over the corresponding samples dyed in the absence of the oxidant, i.e. $(NH_4)_2S_2O_8$, irrespective of the dyeing conditions. It was thus of interest to study the effect on other disperse dyes, and evaluations were made using Terasil Blue R, Terasil Brilliant Blue 2G, Samaron Red 2BSL and Samaron Navy Blue GR.

The results (Table 2) indicate that for a given set of dyeing conditions with these dyes the magnitude of colour strength before and after dimethylformamide (DMF) extraction, and also the fastness properties of the dyeings, is determined by the nature of the dye, i.e. size, shape, configuration, number of dye sites, and the fibre dye capacity, as well as by the mode of interaction. In addition, Table 2 indicates that with all dyes examined colour retention was observed after DMF extraction. This suggests that, in addition to interaction of the disperse dye with nylon-6 by hydrogen bonds, the free-radical mechanism additionally involved[2,12] may be:

$$S_2O_8^{2-} \rightarrow 2\,SO_4^{-\cdot} \qquad (1)$$

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^- + HO^\cdot \qquad (2)$$

$$SO_4^{-\cdot} + \text{Ny—H} \rightarrow \text{Ny}^\cdot + HSO_4^- \qquad (3)$$

$$\text{D—XH} + SO_4^{-\cdot} \rightarrow \text{D—X}^\cdot + HSO_4^- \qquad (4)$$

$$\text{Ny}^\cdot + \text{D—X}^\cdot \rightarrow \text{Ny—X—D} \qquad (5)$$

where Ny—H and D—XH (—XH = OH, NH or NH_2) represent the nylon-6 and the dye respectively.

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