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Dyeing in the Presence of Free Radical Initiators. 2. The Dyeing of Nylon 6 with Disperse Dyes

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ABSTRACT

The dyeing behaviour of four disperse dyes on Nylon 6 in both the absence and presence of ammonium persulphate and also thiourea dioxide has been studied. The radical initiators differed in the extent to which they altered the colour yield, shade and fastness to washing and DMF extraction of the dyes on the substrate; of the four dyes used, CI Disperse Yellow 54 was least effected by the radical initiators. Reflectance spectroscopy of the dyeings together with absorbance spectroscopy and TLC analysis of the dyebath residues indicated that the effects of the two radical initiators on the dyeings may be attributable to dye–fibre covalent reaction and/or dye polymerisation.

INTRODUCTION

In an investigation of the dyeing of Nylon 6.6 with several disperse dyes, Topiwala[1] found that both the brilliancy and colour yield of the dyeings were enhanced when dyeing had been carried out in the presence of various oxidants and/or reductants, including ammonium persulphate (APS) and thiourea dioxide (TDO); Ibrahim and Dawoud[2] proposed a free radical mechanism to account for the effects of redox systems on the dyeing of Nylon 6 with disperse dyes. In the previous part of this paper[3] that concerned the dyeing of polyester fabric with CI Disperse Yellow 54, enhanced colour yield and improved fastness to DMF extraction of the dyeings was achieved when dyeing had been carried out in the presence of APS; this part of the paper concerns the effects of APS and TDO on the dyeing of Nylon 6 with four commercial disperse dyes.

EXPERIMENTAL

Materials

Fibres
Scoured, woven Nylon 6 fabric (69·2 $\mathrm{g\,m^{-2}}$) obtained from Whalleys was used.

Dyes and auxiliaries
Four commercial disperse dyes, namely CI Disperse Yellow 1, CI Disperse Blue 3, CI Disperse Blue 56 and CI Disperse Yellow 54, each kindly supplied by Yorkshire Chemicals plc (YCL), were used. Commercial samples of Dyapol PT (YCL), which was used as dispersing agent in dyeing and Sandozin NIE (Sandoz), which was employed in the scouring of dyed Nylon 6, were supplied by the respective manufacturer.

Chemicals
All chemicals used in the work were laboratory grade reagents from either Aldrich or BDH.

Procedures

Dyeing
All dyeings were carried out in sealed, stainless steel pots of 300 $\mathrm{cm^3}$ capacity housed in a John Jeffries laboratory-scale rota dyer. The dyebath was set with 2% on weight of fibre commercial disperse dyes and 1 g $\mathrm{litre^{-1}}$ Dyapol PT in either the presence or absence of free radical initiator; a liquor ratio of 30:1 was employed, the pH being adjusted to 5·5 using 0·02 M acetic acid/ 0·17 M sodium acetate buffer.[3] Dyeing was commenced at 40°C, the temperature raised to 98°C at a rate of 2°C $\mathrm{min^{-1}}$ and maintained at this temperature for a further 60 min. At the end of dyeing the rinsed (cold tap water) dyed samples were scoured in a solution containing 2% on weight of fibre Sandozin NIE at 98°C for 5 min and the rinsed (cold tap water) dyed samples then allowed to dry in the open air.

Colour measurement

The CIELab coordinates and Kubelka-Munk (K/S) values were calculated from the reflectance values of the dry, scoured, dyed samples which were measured using the instrument and procedure previously described.[3]

Wash fastness

The fastness of the dry, scoured, dyed samples to the ISO CO6/C2 wash test was determined using the standard method.[4]

Ultraviolet/visible spectroscopy

UV/visible analysis of residual dyebaths were carried out using a Pye Unicam SP800A Ultraviolet Spectrophotometer (Philips, UK) using a 1 cm path length quartz cell and a slit width of 0·2 mm. A 1:1 acetone:distilled water mixture was used as solvent for the dyebath residue and as reference solvent.

DMF extraction

This was carried out on scoured, dyed Nylon 6 samples using the procedure previously described.[3]

Thin layer chromatography TLC)

A small aliquot of residual dyebath was spotted on to TLC polyester sheets precoated with silica gel (mean pore diameter 60 Å, mean particle size 2–25 μm) obtained from Aldrich and eluted using an 8:2:1 toluene:ethyl acetate:acetic acid mixture. The sheets were removed after the solvent front had migrated about three-quarters of the length of the sheets, the solvent allowed to evaporate and the R_f value measured.

RESULTS AND DISCUSSION

In the previous study[3] of the dyeing of polyester fabric with CI Disperse Yellow 54 in the presence of APS, it was found that the use of a 0·02 M acetic acid/0·17 M sodium acetate buffer system was required in order to counteract the marked decrease in dyebath pH that resulted from the thermal decomposition of the oxidant. Consequently, an initial study was made of the suitability of this particular buffer system for the dyeing of Nylon 6 with CI Disperse Yellow 54 in the presence of various concentrations (between 0 and 30 mM) of TDO; it was found (Fig. 1) that the pH of the residual dyebaths decreased with increasing concentration of thiourea dioxide used.

Thiourea dioxide (formamidine sulphinic acid) is more stable than sodium dithionite under neutral and acidic aqueous conditions[5] owing to

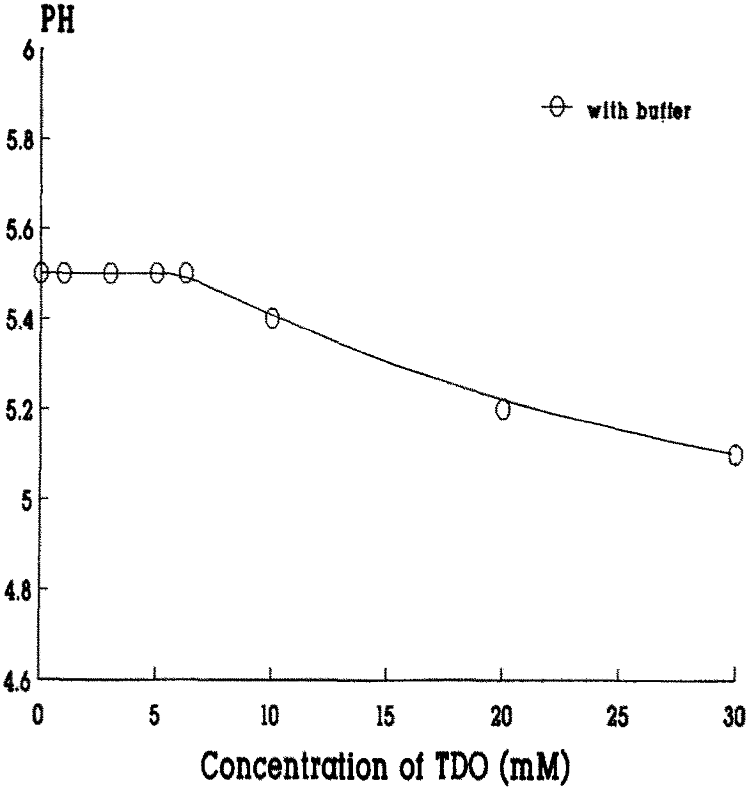
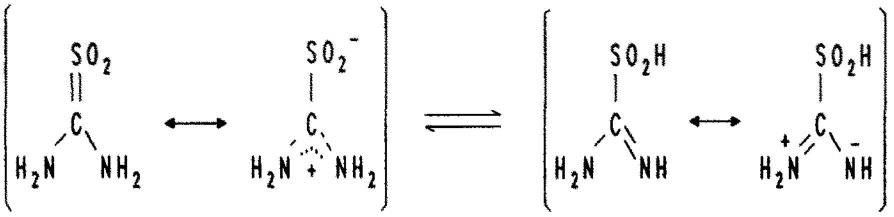


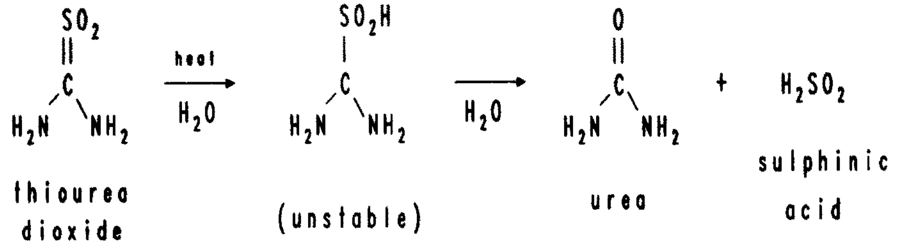
Fig. 1. pH of residual dyebaths.

the following resonance structures (Scheme 1); TDO can act as a reducing agent under various pH conditions.[6]

Although thiourea dioxide is stable in acidic solution,[5] its decomposition rate in aqueous solution increases with increasing pH above 5·5, with decreasing concentration of thiourea dioxide used and at temperatures over 50°C.[6] The decomposition mechanism of thiourea dioxide in aqueous medium is shown in Scheme 2; its degradation to sulphinic acid is considered responsible for its reducing action.[5,7,8] In a study of the use of thiourea



Scheme 1



Scheme 2

dioxide in the dyeing of cotton with vat dyes[7] as well as in wool bleaching,[6,8] it was found that sulphinic acid acted as a powerful reducing agent.

From the foregoing, the observed reduction in residual dyebath pH that accompanied an increase in concentration of TDO (Fig. 1) can be attributed to the generation of sulphinic acid during the decomposition of TDO.

In the previous study[3] of the dyeing of polyester with CI Disperse Yellow 54 in the presence of ammonium persulphate, optimum results, in terms of enhanced colour yield and fastness to DMF extraction of the dyeings, was obtained using a concentration of 6·25 mM of the oxidant; based on these findings, this particular concentration of TDO was selected for use in the present work. Figure 1 shows that at this concentration of the reductant (i.e. 6·25 mM), the buffer system used exhibited adequate buffer capacity; thus, as found previously for ammonium persulphate,[3] it is necessary to use a strong buffer-capacity system to minimise degradation of the disperse dye during dyeing in the presence of thiorea dioxide.

Each of the four dyes used in this work was applied to Nylon 6 in both the absence and presence of either 6·25 mM APS or TDO using the 0·02 M acetic acid/0·17 M sodium acetate buffer system described previously.[3] The colour yield of the scoured dyeings (as given by the K/S values) carried out using CI Disperse Yellow 1 and CI Disperse Yellow 54 increased in the presence of APS whereas the colour yield of dyeings obtained using CI Disperse Blue 3 and CI Disperse Blue 56 were reduced in the presence of the oxidant. Table 1 also shows that, with the exception of CI Disperse Yellow 54, dyeing in the presence of ammonium persulphate resulted in enhanced fastness of the dyeings to the ISO CO6/C2 wash test; furthermore, with the exception of CI Disperse Blue 56, dyeings carried out in the presence of the oxidant exhibited greater resistance to extraction with DMF. In contrast to the results secured using APS, those obtained using TDO (Table 1) revealed that for each of the four dyes used, the presence of the reductant reduced the colour yield of the dyeings. With the exception of CI Disperse Blue 56, the reductant slightly enhanced the wash fastness of the dyeings; TDO also slightly enhanced the resistance to DMF extraction of the dyeings obtained using CI Disperse Yellow 1 and CI Disperse Yellow 54.

TABLE 1
K/S Values and Wash Fastness Results Obtained for Dyeings Carried Out in Both the Absence and Presence of 6·25 mM of Radical Initiator

Dye	*Radical initiator*	*K/S*		*ISO CO6/C2*			*λ_{max} (nm)*
				E	*N*	*C*	
CI Disperse Yellow 1	Nil	4·0[a]	0·6[b]	2		5	400
	APS	5·0[a]	4·0[b]	4	5	5	400
	TDO	3·5[a]	0·8[b]	3	4–5	5	400
CI Disperse Blue 3	Nil	7·0[a]	1·4[b]	4	3	4	640
	APS	4·4[a]	2·7[b]	4–5	4	4–5	620
	TDO	6·7[a]	1·2[b]	4–5	3–4	4–5	640
CI Disperse Blue 56	Nil	8·2[a]	3·2[b]	4	4	4–5	640
	APS	5·8[a]	2·7[b]	4–5	4–5	4–5	640
	TDO	8·1[a]	3·0[b]	4	4	4–5	640
CI Disperse Yellow 54	Nil	7·7[a]	1·5[b]	4	2–3	3–4	440
	APS	7·9[a]	2·2[b]	4	2–3	3–4	440
	TDO	7·6[a]	1·7[b]	4	3	4	440

[a] Scoured dyeings.
[b] Dyeings extracted with DMF.
E, Effect on pattern; N, staining of Nylon 6 adjacent; C, staining of cotton adjacent.

The reflectance values of dyeings carried out using each of the four disperse dyes in both the absence and presence of APS and TDO are shown in Figs 2–5, from which it is evident that whilst the reflectance of CI Disperse Yellow 54 was unaffected by both reagents that of the other three dyes was altered by the oxidant. The change in the reflectance curves of CI Disperse Yellow 1, CI Disperse Blue 3 and CI Disperse 56 caused by APS (Figs 2, 3 and 5) were clearly apparent upon visual inspection of the dyed samples, the shade change observed in the case of CI Disperse Blue 56 being somewhat less marked than that for CI Disperse Yellow 1 and CI Disperse Blue 3. In contrast to the results obtained using APS, the reflectance curves of the TDO dyeings secured using each of the four dyes were similar to those of the control dyeing (Figs 2–5).

As previously discussed, several workers have suggested a free radical mechanism to explain the shade changes and enhanced fastness of dyeings obtained in the presence of radical initiators. Dye–fibre covalent reaction has been proposed to explain the shade changes observed for basic dyes on Nylon [9] and acrylic [10] when dyeing had been carried out in the presence of radical initiators. Consequently, it is possible that the shade change observed for the dyeings of CI Disperse Yellow 1, CI Disperse Blue 3 and CI

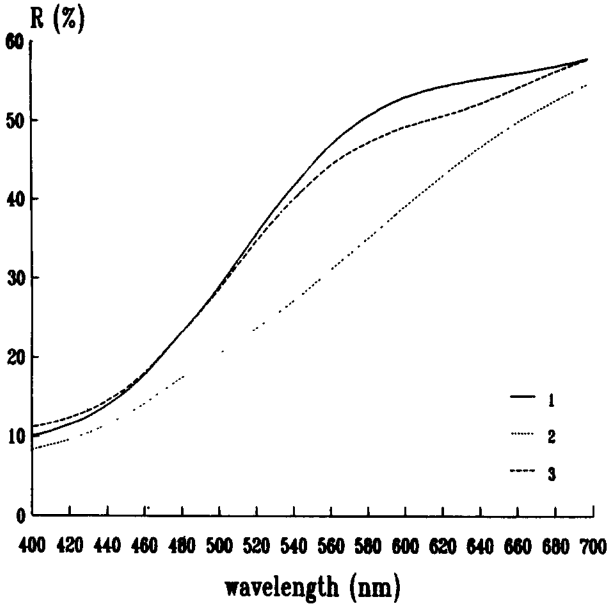


Fig. 2. Reflectance spectra of Nylon 6 dyed with CI Disperse Yellow 1 (1, dye alone; 2, dye + 6·25 mM APS; 3, dye + 6·25 mM TDO).

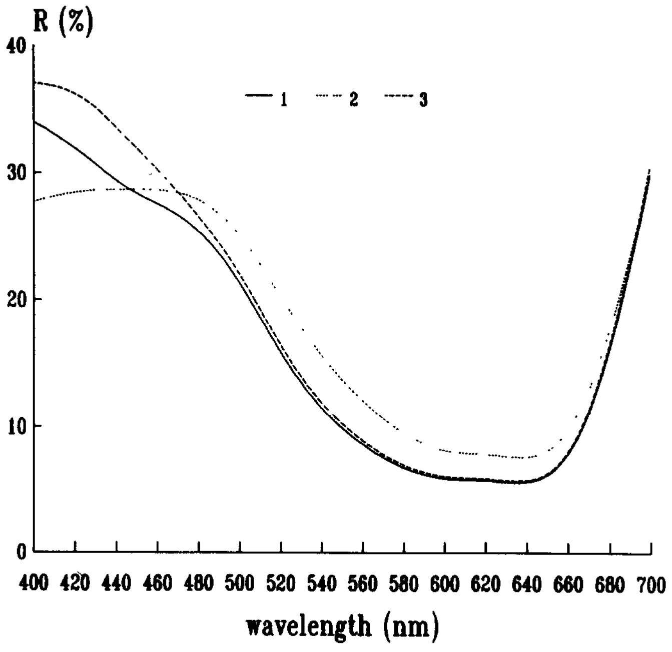


Fig. 3. Reflectance spectra of Nylon 6 dyed with CI Disperse Blue 3 (1, dye alone; 2, dye + 6·25 mM APS; 3, dye + 6·25 mM TDO).

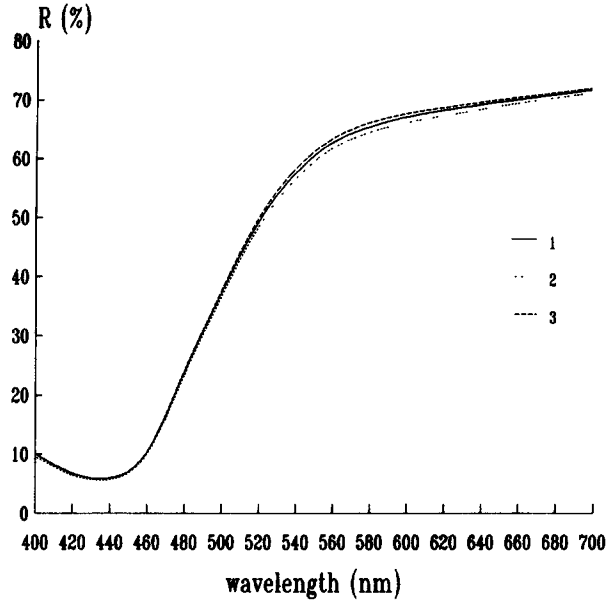


Fig. 4. Reflectance spectra of Nylon 6 dyed with CI Disperse Yellow 54 (1, dye alone; 2, dye + 6·25 mM APS; 3, dye + 6·25 mM TDO).

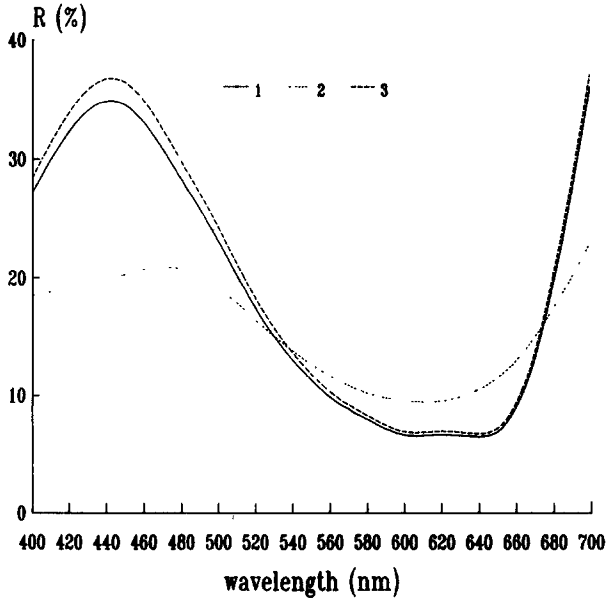


Fig. 5. Reflectance spectra of Nylon 6 dyed with CI Disperse Blue 56 (1, dye alone; 2, dye + 6·25 mM APS; 3, dye + 6.25 mM TDO).

Disperse Blue 56 obtained in the presence of APS (Figs 2, 3 and 5) may be attributable to covalent attachment of the dyes to Nylon 6; furthermore, such covalent dye–fibre attachment would also explain the enhanced wash fastness and resistance to DMF extraction of the dyeings (Table 1) obtained in the presence of APS. However, although covalent attachment of the dye to the fibre might explain the enhanced fastness of the disperse dyes on Nylon 6 imparted by APS and TDO (Table 1) and, as Ereshchenko *et al.*[9] and Bhattachary[10] proposed, may also explain the change in shade observed for dyeing with CI Disperse Yellow 1, CI Disperse Blue 3 and CI Disperse Blue 56 carried out using APS, the findings that no shade change (shift in λ_{max}) occurred in the case of dyeing with each of the four disperse dyes in the presence of TDO and also in the case of dyeing with CI Disperse Yellow 54 in the presence of APS, implies that such covalent dye–fibre interaction may not be the sole mechanism operating during dyeing in the presence of the two radical initiators.

These results clearly demonstrate that ammonium persulphate and thiourea dioxide differ in their effects on the dyeing of Nylon 6 with disperse dyes and also that the effects of the two radical initiators depend on dye structure. Furthermore, since the precise mechanism involved in free radical assisted dyeing is unclear, further work was carried out to elucidate this mechanism.

UV/visible spectroscopic analysis of the residual dyebaths obtained from the dyeing of Nylon 6 with each of the four disperse dyes used in both the absence and presence of 6·25 mM APS or TDO (Figs 6–9) show that neither the oxidant nor the reductant altered the visible spectrum of CI Disperse Yellow 54 whereas APS changed the spectra of the three other dyes, this being evident as a hypsochromic shift in λ_{max} of the dyes, with the formation of single, broad peak in the case of CI Disperse Blue 3. If, as Ereshchenko *et al.*[9] and Bhattachary[10] proposed, the shade change of dyeings caused by both reagents was due to covalent attachment of the dye to the fibre, the visible spectrum of the dye in the residual dyebath, which obviously is not covalently attached to the fibre, should be different to the reflectance spectrum of the covalently attached dye on the fibre. However, it is evident that the changes in the visible spectra of the residual dyebaths for the three dyes (Figs 6, 7 and 9) caused by the presence of APS are identical to the changes obtained for the reflectance curves of the dyeings of the three dyes (Figs 2, 3 and 5). Consequently, covalent attachment of the dye to the fibre cannot be the sole cause of the shade change observed for CI Disperse Yellow 1, CI Disperse Blue 3 and CI Disperse Blue 56 and, therefore, some other mechanism must operate either in addition to or instead of covalent dye–fibre interaction.

Dye–fibre fixation, as proposed by various workers to explain the

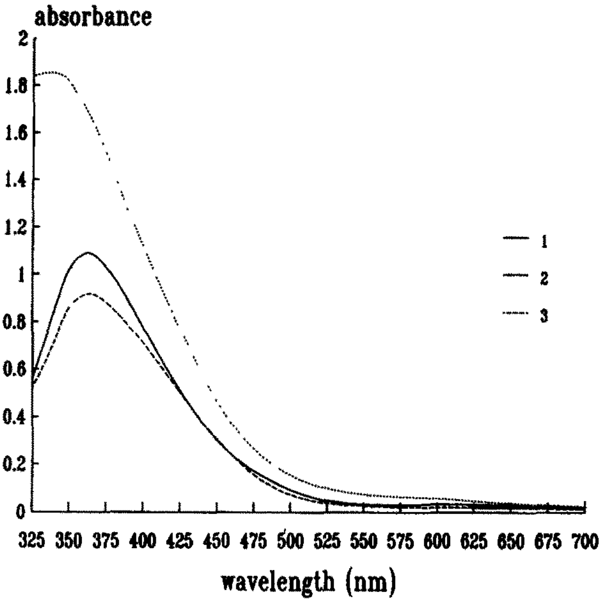


Fig. 6. UV/visible spectra of the residual dyebaths of CI Disperse Yellow 1 (1, dye alone; 2, dye + 6·25 mM APS; 3, dye + 6·25 mM TDO).

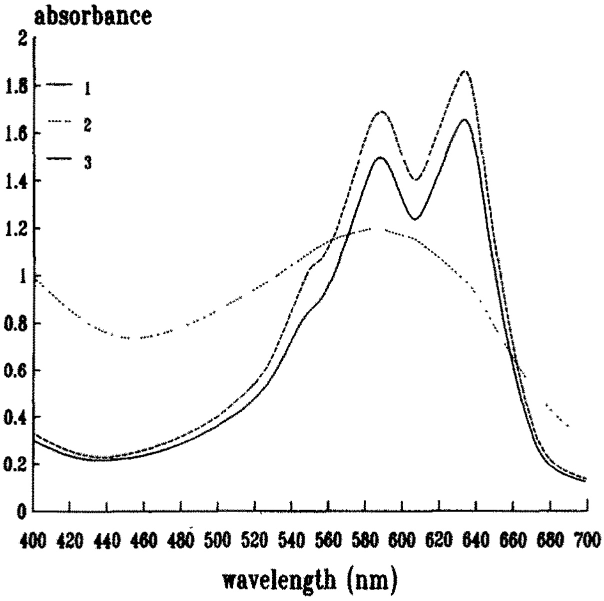


Fig. 7. Visible spectra of the residual dyebaths of CI Disperse Blue 3 (1, dye alone; 2, dye + 6·25 mM APS; 3, dye + 6·25 mM TDO).

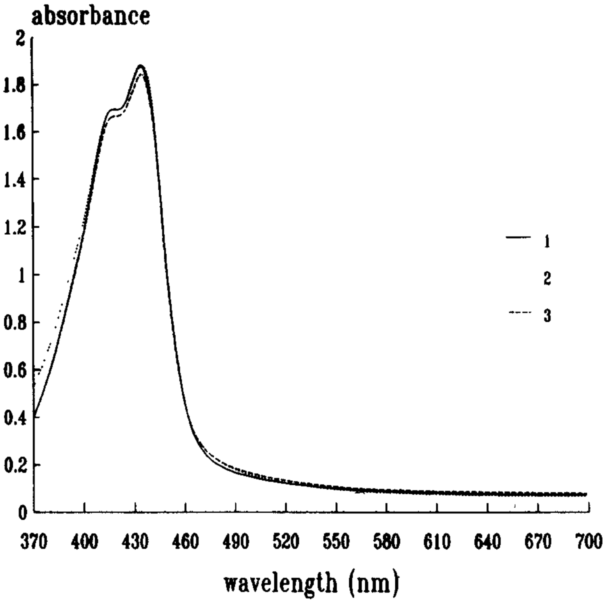


Fig. 8. UV/visible spectra of the residual dyebaths of CI Disperse Yellow 54 (1, dye alone; 2, dye + 6·25 mM APS; 3, dye + 6·25 mM TDO).

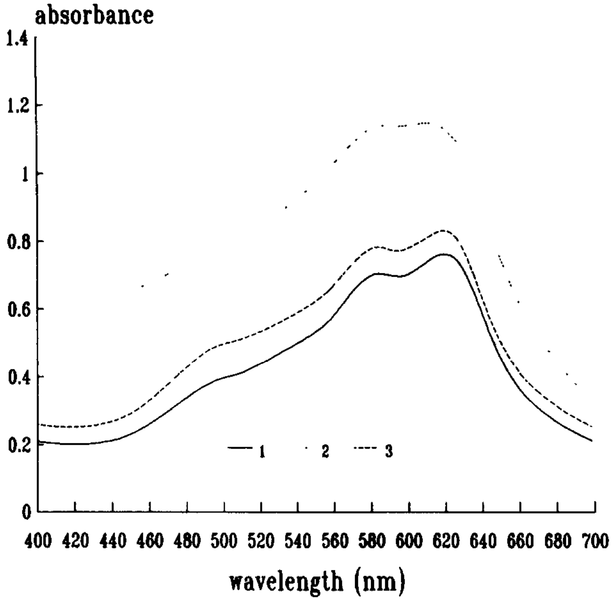


Fig. 9. Visible spectra of the residual dyebaths of CI Disperse Blue 56 (1, dye alone; 2, dye + 6·25 mM APS; 3, dye + 6·25 mM TDO).

enhanced fastness of dyeings achieved in the presence of radical initiators,[3] involves the generation of both dye and fibre radicals which then combine to yield a dye–fibre covalent bond. However, it is possible that in addition to this dye–fibre reaction, dye–dye reaction (eqns (1)–(3)) will also occur both within the fibre and the dyebath:

$$\mathrm{D.} + \mathrm{D} \rightarrow \mathrm{D{-}D} \tag{1}$$

$$\mathrm{D.} + \mathrm{D} \rightarrow \mathrm{D{-}D} \tag{2}$$

$$\mathrm{D.} + \mathrm{D{-}D} \rightarrow \mathrm{D{-}D{-}D} \tag{3}$$

Such a mechanism may yield dimers, trimers, etc., of dye and could perhaps result in dye polymerisation; such dimers, trimers, etc., of dye could, by virtue of their increased molecular size, consequent higher affinity for and lower diffusional power within the substrate, be anticipated to exhibit higher fastness to washing and DMF extraction than the dye monomer which, therefore, could account for the identical shade changes observed for both the dyeings and dyebath residues obtained for CI Disperse Yellow 1, CI Disperse Blue 3 and CI Disperse Blue 56.

Thin layer chromatographic studies carried out on the residual dyebaths (Table 2) show that for each of the four dyes used, the R_f values of the dyebath components obtained from TDO dyeings were identical to those for the components of the dyebaths obtained when dyeing had been carried out in the absence of radical initiator. However, in the case of CI Disperse Yellow 1 and CI Disperse Blue 3, the dyebath components obtained from

TABLE 2
TLC Analysis of Residual Dyebaths Obtained in Both the Absence and Presence of 6·25 mM of Radical Initiator

Dye	*Radical*	*R_f value*
CI Disperse Yellow 1	Nil	0·44
	APS	0·0
	TDO	0·44
CI Disperse Blue 3	Nil	0·41, 0·15
	APS	0·0
	TDO	0·41, 0·15
CI Disperse Blue 56	Nil	0·64, 0·44
	APS	0·64, 0·44
	TDP	0·64, 0·44
CI Disperse Yellow 54	Nil	0·67
	APS	0·67
	TDO	0·67

APS dyeing were unmoved, whereas the R_f values for the APS dyebath components of the other two dyes were identical to those of the dyebath components obtained when dyeing had been carried out in the absence of oxidant. As previously discussed, the dyeing of Nylon 6 with CI Disperse Blue 3 and CI Disperse Yellow 1 in the presence of APS resulted in a marked change of shade and hypsochromic shift in λ_{max} of the dyeings, this being attributable to covalent attachment of the dye to the fibre and/or dye polymerisation. Similarly, it is possible that the non-movement observed for the dyebath components of the APS dyeings of CI Disperse Blue 3 and CI Disperse Yellow 1 (Table 2) could be attributed to either the dyes being covalently bound to the silica gel or to the dyes having polymerised, the dye polymer being unmoved by the particular eluent system employed.

CONCLUSIONS

APS and TDO differ in the extent to which they alter the colour yield, shade and fastness to washing and DMF extraction of the four disperse dyes on Nylon 6; of the four dyes used, CI Disperse Yellow 54 was least effected by both radical initiators. The effects imparted by TDO and APS to the dyeings may be attributable to dye polymerisation and/or covalent attachment of the dye to the substrate.

REFERENCES

1. Topiwala, K., *The Effect of Reducing and/or Oxidising Agents on the Dyeing of Polyamide and Polyester Fabrics with Disperse Dyes.* MSc thesis, University of Leeds, UK, 1988.
2. Ibrahim, N. A. & Dawoud, M. A., *Amer. Dyest. Rep.*, **77** (1988) 35.
3. Burkinshaw, S. M. & Lu, J. G., *Dyes and Pigments* (in press).
4. *Methods of Test for Colour Fastness of Textiles and Leather* (4th edn). The Society of Dyers and Colorists, Bradford, UK, 1978.
5. Dsa, T. K., *Colourage*, **31**(26) (1984) 15.
6. Cegarra, J., Gacen, J., Caro, M. & Pepio, M., *JSDC.*, **104** (1988) 273.
7. He, Q., *Fangzhi Xuebao*, **4** (1983) 271; *Chemical Abstracts*, **100** (1975), 53013w.
8. Davidson, R. S., Ismail, G. M. & Lewis, D. M., *J.S.D.C.*, **103** (1987) 308.
9. Ereshchenko, A. G., Sepantsova, N. P. & Geller, B. E., *Tech. of Textile Industry USSR*, **4** (1971) 103.
10. Bhattachary, S. D., *Colourage*, **36**(8) (1989) 19.