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Dyeing in the Presence of Free Radical Initiators. Part 3: The Dyeing of Nylon 6.6 with Nitrodiphenylamine and Azo Disperse Dyes

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ABSTRACT

The effects imparted to the shade, colour yield and fastness to washing of CI Disperse Yellow 1 on nylon 6.6 by ammonium persulphate were found to be very similar to those secured using potassium periodate, but differed to the effects imparted by thiourea dioxide; glucose had little effect upon dyeing. Ammonium persulphate and thiourea dioxide differed in the extent to which they altered the colour yield, shade and fastness to washing and light of four nitrodiphenylamine and 12 azo disperse dyes on the substrate. The finding that the effects imparted by the two radical initiators to two 2,4-dinitrophenylamine dyes differed to those imparted to two 2-nitrodiphenylamine dyes are discussed in terms of the light stability of the two types of dye. The bathochromic or hypsochromic shifts imparted by the two radical initiators to some azo dyes and the very low colour yields obtained for dyeings carried out in the presence of TDO are discussed in terms of the reductive and oxidative degradation of the dyes. The effects of the radical initiators on dyeing are explained in terms of dye–fibre covalent reaction and/or dye polymerisation.

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INTRODUCTION

Previous studies demonstrated that the effects of ammonium persulphate (APS) on the dyeing of PET with disperse dyes[1] and of APS and thiourea dioxide (TDO) on the dyeing of nylon 6 with disperse dyes[2] depend on the nature of both the radical initiator and the dye. Potassium periodate (KIO_4)[3-5] and glucose[6,7] have been proposed to act as radical initiators and have also been employed in dyeing.[8-17] In this work, the dyeing of nylon 6.6 with four nitrodiphenylamine and 12 azo disperse dyes in the presence of ammonium persulphate, potassium periodate, thiourea dioxide and glucose was carried out in order to investigate the effects of these various radical initiators on dyeing.

EXPERIMENTAL

Materials

Fibres

Scoured, knitted nylon 6.6 fabric ($230{\cdot}5\,g\,m^{-2}$) obtained from ICI Fibres was used.

Dyes and auxiliaries

Sixteen commercial disperse dyes were used, namely four nitrodiphenylamine and 12 azo disperse dyes, each kindly supplied by the respective manufacturer shown in Table 1. Commercial samples of Dyapol PT (YCL), which was employed as dispersing agent in dyeing, and Sandozin NIE (Sandoz) which was used in the scouring of dyed nylon 6.6, were supplied by the respective manufacturer.

Chemicals

All chemicals used in this work were laboratory grade reagents obtained from either Aldrich or BDH.

Procedures

Dyeing

Dyeing was carried out using the equipment and procedure previously described.[2] The dyed samples were rinsed and scoured using the procedure described earlier[2] and 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.[2]

Wash fastness

The fastness of the dry, scoured, dyed samples to the ISO CO6/C2 wash test was determined using the standard method.[18]

Light fastness

The light fastness of the dry, scoured, dyed samples was determined according to ISO BO2[18] using a Microscal fading lamp.

RESULTS AND DISCUSSIONS

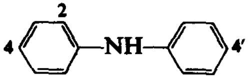
Previous work[2] demonstrated that the dyeing of CI Disperse Yellow 1 on nylon 6 obtained in the presence of APS exhibited higher wash fastness and colour yield than the comparative dyeing obtained in the absence of radical initiator. Further work was carried out to examine the effects of various concentrations (between 0 and 30 mM) of four radical initiators on the dyeing of nylon 6.6 with CI Disperse Yellow 1. Table 2 shows that at concentrations upto 10 mM both APS and KIO_4 yielded dyeings which were deeper (as shown by the higher K/S values and lower L^* values), more orange (as evidenced by the higher a^* values and lower b^* and h° values) and duller (as given by the lower c^* values) than the control dyeing (i.e. that carried out in the absence of radical initiator). The dyeings obtained using concentrations in excess of 10 mM APS and KIO_4 were markedly paler (as given by the lower K/S values) and more yellow (as shown by the lower a^* values) than the control dyeing; at concentrations in excess of 10 mM, the colour of the dyeings obtained using the two oxidants was considerable different to those obtained using oxidant concentrations of less than 10 mM.

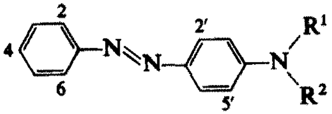
The dyeings obtained using CI Disperse Yellow 1 in the presence of TDO (Table 2) were identical to those obtained using APS and KIO_4, insofar as, at concentrations of the reductant of up to 10 mM, the dyeings were deeper in shade, more orange and duller than the control dyeing; the colour of the dyeings obtained using the two oxidants was considerably different to those obtained using oxidant concentrations of less than 10 mM.

A bathochromic shift was observed when a concentration of 20 mM TDO had been employed, the ensuing golden brown shade of this dyeing contrasting with the pale brown colour of the dyeings secured both in the absence of radical initiator and in the presence of concentrations of up to 10 mM of the reductant. Glucose imparted little change in colour to the dyeings obtained using CI Disperse Yellow 1 at each of the concentrations cmployed, in that there was little difference between the shade obtained for the control dyeing and those carried out in the presence of gluclose.

Figure 1 and Table 2 show that, generally, the colour yield (K/S) of the

TABLE 1
Commercial Disperse Dyes Used

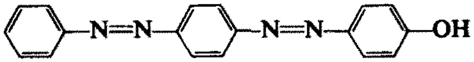
Structure		Commercial name	CI Disperse	Supplier
Nitrodiphenylamine				
2,4-di-NO_2, 4′-OH		Serisol Fast Yellow A	Yellow 1	YCL
2,4-di-NO_2, 4′-NH_2		Serisol Fast Yellow PL	Yellow 9	YCL
2-NO_2, 4-SO_2NH_2		Serisol Fast Yellow GGL	Yellow 33	YCL
2-NO_2, 4-$SO_2NHC_6H_5$		Palanil Yellow GE	Yellow 42	BASF



Monoazo

4-NO$_2$, R^1 = H, R^2 = C$_6$H$_5$	Serilene Orange 5R	Orange 1	YCL
4-NO$_2$, R^1 = C$_2$H$_5$, R^2 = C$_2$H$_4$CN	Serilene Orange 2RL	Orange 25	YCL
4-NO$_2$, R^1 = C$_2$H$_5$, R^2 = C$_2$H$_4$OH	Serisol Fast Scarlet BD	Red 1	YCL
2-CN, 4-NO$_2$, R^1 = C$_2$H$_2$CN, R^2 = C$_2$H$_5$	Foron Rubine S-EGFL	Red 73	Sandoz
4-NO$_2$, 2′-Cl, R^1 = R^2 = C$_2$H$_4$OH	Celliton Scarlet R	Red 7	BASF
4-NO$_2$, 2′-CH$_3$, R^1 = R^2 = C$_2$H$_4$OH	Celliton Red GG	Red 17	BASF
2,6,2′-tri-Cl, 4-NO$_2$, R^1 = R^2 = C$_2$H$_4$OH	Serilene Red Brown R-FS	Brown 1	YCL
2,6-di-Cl, 4-NO$_2$, R^1 = C$_2$H$_4$CN, R^2 = C$_2$H$_4$OCOCH$_3$	Serilene Yellow Brown R-LS	Orange 30	YCL
2-CN, 4-NO$_2$, 2′-CH$_3$, R^1 = R^2 = C$_2$H$_4$OCOCH$_3$	Dispersol Rubine C-B	Violet 33	ICI
2,4-di-NO$_2$, 6-Br, 2′-NHCOCH$_3$, 5′-OC$_2$H$_5$ R^1 = R^2 = C$_2$H$_4$OCOCH$_3$	Serilene Navy Blue 2GN-LS	Blue 78	YCL
2-OH, 5-CH$_3$, R^1 = H, R^2 = COCH$_3$	Dispersol Yellow AG	Yellow 3	ICI

Disazo



	Foron Yellow E-RGFL	Yellow 23	Sandoz

TABLE 2
Colorimetric and Wash Fastness (ISO CO6/C2) Data for Nylon 6.6 Dyed with CI Disperse Yellow 1 at 98°C for 1 h

	Concention (mM)	*K/S*	λ_{max} *(nm)*	L^*	a^*	b^*	c^*	$h°$	*E*	*N*	*C*
APS	0	12·7	400	69·6	15·2	60·1	62·0	75·8	1	1	4–5
	1	13·3	400	67·8	15·1	57·9	59·8	75·4	1	1	4–5
	3	13·9	400	62·0	14·8	49·9	52·1	73·5	1–2	1	4–5
	5	14·3	400	55·8	15·5	42·1	44·9	69·8	2–3	1	4–5
	6·25	14·5	400	53·5	15·5	38·7	41·7	68·2	3	1–2	5
	10	12·9	400	52·6	15·4	35·4	38·6	66·5	4	2	5
	20	8·9	400	57·8	13·1	35·3	37·7	69·6	4	2–3	5
	30	5·9	400	64·0	10·8	35·3	36·9	73·0	4–5	3–4	5
KIO_4	1	13·6	400	65·5	15·4	54·7	56·8	74·3	1	1	4–5
	3	14·2	400	58·7	16·0	45·3	48·0	70·5	1–2	1	4–5
	5	14·7	400	54·5	16·4	39·5	42·8	67·5	2	1	4–5
	6·25	14·5	400	53·3	16·5	37·5	41·0	66·3	2–3	1	4–5
	10	12·2	400	53·0	15·9	33·1	36·7	64·3	3	1–2	5
	20	8·9	400	57·0	14·8	32·5	35·7	65·5	4	2	5
	30	7·4	400	60·0	13·6	32·7	35·4	67·4	4	2	5
	1	12·6	400	67·5	15·2	56·4	58·4	74·9	1	1	4–5
	3	12·4	400	67·8	15·8	57·2	59·3	74·6	1	1	4–5
	5	12·3	400	68·1	15·4	57·1	59·1	74·9	1	1	4–5
	6·25	12·7	400	68·1	15·5	57·5	59·6	74·9	1	1	4–5
	10	12·7	400	67·4	16·0	57·4	59·6	74·4	1	1	4–5
	20	8·4	420	62·0	21·0	53·4	57·4	68·5	1–2	1–2	5
	30	1·7	400	73·3	10·8	27·2	29·3	68·3	3	4	5
Glucose	1	13·2	400	69·4	15·2	59·4	61·3	75·6	1	1	4–5
	3	13·5	400	69·2	15·6	60·1	62·1	75·5	1	1	4–5
	5	13·5	400	69·2	15·4	59·7	61·7	75·5	1	1	4–5
	6·25	13·5	400	69·1	15·4	59·6	61·6	75·5	1	1	4
	10	13·5	400	69·3	15·4	59·9	61·8	75·6	1	1	4–5
	20	14·1	400	69·1	15·9	60·5	62·6	75·3	1	1	4–5
	30	13·8	400	69·1	15·5	60·0	62·0	75·5	1	1	4–5

E, Effect on shade; N, staining of nylon 6.6 adjacent; C, staining of cotton adjacent.

dyeings obtained using CI Disperse Yellow 1 increased with increasing concentration of the four radical initiators used up to a concentration of 6·25 mM of both APS and KIO_4 or 10 mM TDO, after which the colour yield of the dyeings markedly reduced. Table 2 also shows that both APS and KIO_4 increased the wash fastness of CI Disperse Yellow 1 on nylon 6.6, the extent of the improvement increasing gradually with increase in concentration of each oxidant used; it is also apparent that the extent by which a given concentration of each oxidant enhanced the wash fastness of the dye was of similar magnitude. In contrast, glucose did not increase the wash

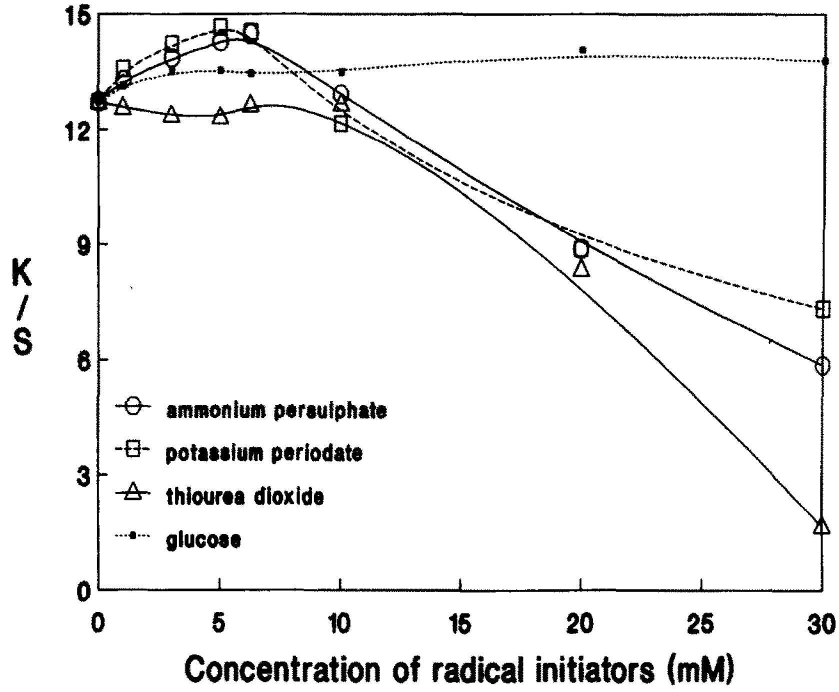


Fig. 1. Colour yield of nylon 6.6 dyed with CI Disperse Yellow 1 in the presence of radical initiators.

fastness of the dye on the substrate; in the case of TDO, enhanced fastness to washing was observed only for concentrations of 20 and 30 mM, such concentrations, as discussed above, being accompanied by a marked change in the shade of the dyeing.

Based on the above results, subsequent studies of the effects of radical initiators on nitrodiphenylamine and azo disperse dyes were confined to the use of APS at a concentration of 10 mM and TDO at a concentration of 20 mM.

The results obtained for the dyeing of nylon 6.6 with the four commercial nitrodiphenylamine disperse dyes under consideration in both the presence and absence of 10 mM APS and 20 mM TDO are shown in Table 3. For both CI Disperse Yellow 1 and CI Disperse Yellow 9, the dyeings secured in the absence of radical initiator were pale brown in colour and exhibited low wash fastness; in contrast, the APS dyeings of both dyes were dark brown in colour and of a deeper (as given by the higher K/S values and lower L^* values), duller (as shown by the lower c^* values) and more orange (as evidenced by the higher a^* values and the lower b^* and h° values) shade and possessed significantly higher wash fastness than the control dyeing. TDO imparted a bathochromic shift in λ_{max} of these two particular dyes on nylon

TABLE 3
Colorimetric and Fastness Data (ISO CO6/C2 and BO2) for Nylon 6.6 Dyed with Nitrodiphenylamine Disperse Dyes at 98°C for 1 h

CI Disperse	*Reagent*	*K/S*	λ_{max} *(nm)*	*L**	*a**	*b**	*c**	*h°*	*E*	*N*	*C*	*LF*
Yellow 1	NIL	12·7	400	69·6	15·2	60·1	62·0	75·8	1	1	4–5	3
	APS	12·9	400	52·6	15·4	35·4	38·6	66·5	4	2	5	2
	TDO	8·4	420	62·0	21·0	53·4	57·4	68·5	1–2	1–2	5	2
Yellow 9	NIL	6·2	400	64·8	15·0	42·0	44·6	70·3	1–2	1	4	4
	APS	11·9	400	52·2	17·4	34·3	38·5	63·1	4	2	5	2
	TDO	5·2	420	60·4	18·5	39·3	43·4	64·8	2	1–2	5	3
Yellow 33	NIL	3·2	420	77·5	6·0	49·3	49·7	83·1	1	1–2	5	3
	APS	5·6	420	67·5	13·1	48·8	50·5	75·0	3	2–3	5	3
	TDO	1·3	420	82·3	−1·5	36·1	36·1	92·4	1	2–3	5	1
Yellow 42	NIL	8·9	420	76·0	8·7	67·6	68·2	82·7	1	1	4	5
	APS	10·8	420	72·0	9·0	65·0	65·6	82·1	1	1–2	4–5	5
	TDO	6·4	420	79·2	2·9	65·4	65·5	87·5	1	1–2	4–5	1

E, Effect on shade; N, staining of nylon 6.6 adjacent; C, staining of cotton adjacent; LF, light fastness; APS, 10 mM ammonium persulphate; TDO, 20 mM thiourea dioxide.

6.6 (Table 2); the TDO dyeings were golden brown in colour, being slightly duller (as given by the lower *c** values) and more orange (as evidenced by the higher *a** values and lower *b** values) than the control dyeings. Although the TDO dyeings of CI Disperse Yellow 1 and CI Disperse Yellow 9 were of lower colour yield than the control dyeing, they exhibited slightly enhanced wash fastness.

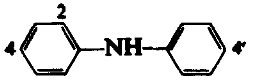
The colorimetric data for the APS dyeings obtained using CI Disperse Yellow 33 and CI Disperse Yellow 42 show that the dyeings were deeper (as given by the higher *K/S* values and lower *L** values) and more orange (as evidenced by the higher *a** values and the lower *b** and *h°* values) than the control dyeing; in contrast, the TDO dyeings of CI Disperse Yellow 33 and CI Disperse Yellow 42 were paler (as shown by the lower *K/S* values and higher *L** values) and more yellow (as evidenced by the lower *a** values and higher *h°* values) than the control dyeing. TDO imparted no change to the λ_{max} of these particular two dyes, this being in contrast to the effect of the reductant on both CI Disperse Yellow 1 and CI Disperse Yellow 9; APS imparted no change to the λ_{max} of the two dyes. Both the oxidant and the reductant enhanced the wash fastness of CI Disperse Yellow 33 and CI Disperse Yellow 42 on nylon 6.6 (Table 3), this effect being only slight in the case of the latter dye.

For the four dyes examined, Table 3 shows that the enhancement of wash fastness imparted by APS to the dyeings was generally greater than that imparted by TDO; this finding supports those previously obtained in a study of the effects of APS and TDO on the dyeing of nylon 6 with disperse dyes.[2] The enhanced wash fastness obtained for the dyeings carried out in the presence of the two radical initiators may, as previously suggested,[2] be attributed to covalent attachment of the dyes to the fibre and/or the formation of a dye polymer within the fibre. In this context, an attempt was made to explain the finding (Table 3) that the wash fastness of CI Disperse Yellow 1 and CI Disperse Yellow 9 was enhanced to a greater extent than that of CI Disperse Yellow 33 and CI Disperse Yellow 42. It has been considered[19,20] that 2-nitrodiphenylamine dyes exhibit high light stability due to intramolecular hydrogen bonding and the formation of an additional *o*-quinonoid resonance structure, whereas 2,4-dinitrodiphenylamine dyes display lower light stability because of the presence of a tautomeric *p*-quinoid structure, which increases the tendency to photofading. The data presented in Table 4 clearly confirm this difference in light stability of the two types of dyes, inasmuch as the lightfastness of the two 2-nitrodiphenylamine dyes was higher on both PET and acetate fibres than the 2,4-dinitrodiphenylamine dyes.[21] Consequently, the observation that the extent of enhancement of wash fastness imparted by both APS and TDO was greater for the two 2,4-dinitrodiphenylamine dyes (CI Disperse Yellow 1 and CI Disperse Yellow 9) than the two 2-nitrodiphenylamine dyes (CI Disperse Yellow 33 and CI Disperse Yellow 42) (Table 3) may be due to the lower stability of the two 2,4-dinitrodiphenylamine dyes, as a result of which the latter type of dyes may be more susceptible to modification by the radical initiators and the consequent generation of dye radicals or quinone compounds which may form dye polymers or bind covalently to the fibre.

In the context of the above discussion concerning the difference in stability

TABLE 4

Light Fastness of Nitrodiphenylamine Disperse Dyes[21]

CI Disperse	*Structure*	*Light fastness (ISO BO2)*	
		Acetate	*PET*
			
Yellow 1	2,4-di-NO_2, 4'-OH	4–5	6
Yellow 9	2,4-di-NO_2, 4'-NH_2	5	5–6
Yellow 33	2-NO_2, 4-SO_2NH_2	6–7	7
Yellow 42	2-NO_2, 4-$SO_2NHC_6H_5$	6–7	6–7

to light of 2-nitrodiphenylamine and 2,4-dinitrophenylamine dyes, it follows that the light fastness of CI Disperse Yellow 1 and CI Disperse Yellow 9 should be lower than that of CI Disperse Yellow 33 and CI Disperse Yellow 42 on nylon 6.6 in the absence of radical initiator; the results shown in Table 3 do not entirely meet with this proposal. Table 3 shows that the light fastness of CI Disperse Yellow 1 and CI Disperse Yellow 9 on nylon 6.6 was reduced by both APS and TDO, whereas the light fastness of CI Disperse Yellow 33 and CI Disperse Yellow 42 was reduced only by TDO. Since it is well known that the fastness to light of a dyeing is determined by several factors, including the presence of 'impurities' such as oxidants and reductants,[22] the observed reduction in light fastness of the dyeings may have resulted from the presence of residual APS or TDO in the dyed samples. However, although no attempt was made to determine whether residual reductant or oxidant was present within the dyed samples, it seems reasonable to propose that the scouring treatments given to the dyed samples would have removed residual radical initiator from the dyeings, in which case, the deleterious effects of the two radical initiators on the light fastness of the dyes can be considered to have arisen during dyeing.

In this context, it is well known that many disperse dyes are degraded during dyeing and that such hydrolysis, oxidation or reduction of the dye results in shade change or loss of colour.[23–25] The reduced colour yields and marked alteration of shade obtained for each of the four dyes investigated when dyeing had been carried out in the presence of TDO (Table 3) implies that the dyes have undergone reductive degradation during dyeing; the finding that the reductant reduced the light fastness of the four dyes may be attributed to such modified dyes being more susceptible to photogradation than the original dyes. The observation that TDO had a far greater deleterious effect on the light fastness of the two 2-nitrodiphenylamine dyes (CI Disperse Yellow 33 and CI Disperse Yellow 42) than on the two 2,4-dinitrodiphenylamine dyes (CI Disperse Yellow 1 and CI Disperse Yellow 9) (Table 3) suggests that the TDO-modified forms of the former type of dye are more susceptible to photodegradation or, as the colorimetric data in Table 3 show, that the two 2-nitrodiphenylamine dyes are more susceptible to reductive degradation during dyeing in the presence of TDO. The observation that whilst APS enhanced the colour yield of each of the four dyes used the oxidant also imparted a shade change to the dyeings, implies that the dyes underwent modification during dyeing in the presence of the oxidant. However, the finding that APS reduced only the light fastness of CI Disperse Yellow 1 and CI Disperse Yellow 9 on nylon 6.6 implies that the APS-modified forms of these two 2,4-dinitrodiphenylamine dyes are more susceptible to photodegradation or, as discussed above the context of the enhanced wash fastness imparted by the radical initiators, that the two 2,4-

dinitrodiphenylamine dyes are more susceptible to modification during dyeing in the presence of APS. From the foregoing, it is apparent that the dyes vary with regards to the effect of the two radical initiators on their light fastness and also that the two radical initiators vary in their effect on the fastness to light of the four dyes on nylon 6.6.

The results obtained for the dyeing of nylon 6.6 with 12 commercial azo disperse dyes in both the absence and presence of either 10 mM ammonium persulphate or 20 mM thiourea dioxide are shown in Table 5. It is evident that a hypsochromic shift occurred in the λ_{max} of the APS dyeings furnished using CI Disperse Red 7, CI Disperse Red 17 and CI Disperse Yellow 3; for each of the remaining nine dyes, no shift in λ_{max} was obtained in the presence of the oxidant. Of the 12 azo dyes, the dyeings using the three orange, four red, one brown, and two yellow dyes in the presence of APS were generally yellower (as given by the lower a^* values and the higher b^* and h° values) and duller (as shown by the lower c^* values) than the control dyeings carried out in the absence of oxidant. APS imparted a dull (as evidenced by the lower c^* value), reddish hue (as given by the lower a^* value, higher b^* value and lower h° value) to the blue dye and a greener (as shown by the lower a^* value and the higher b^* and h° values) duller hue (as evidenced by the lower c^* value) to the violet dye. Enhanced colour yields were obtained when dyeing had been carried out in the presence of the oxidant in the cases of CI Disperse Orange 25, CI Disperse Red 73, CI Disperse Orange 30 and CI Disperse Violet 33, whilst reduced colour yield was secured for each of the remaining dyes used, with the exception of CI Disperse Yellow 23 for which no change in depth of shade was obtained. Although slightly enhanced wash fastness was imparted by the oxidant to CI Disperse Orange 25, CI Disperse Red 7, CI Disperse Red 17, CI Disperse Orange 30 and CI Disperse Yellow 3, APS had no effect on fastness to washing of the remaining seven dyes on nylon 6.6.

Table 5 clearly shows that for each of the 12 dyes used, dyeing in the presence of TDO resulted in an often very marked reduction in colour yield (i.e. reduced K/S and higher L^* values of the TDO dyeings compared with the corresponding values for the control dyeing). In the case of CI Disperse Orange 25, CI Disperse Red 73, CI Disperse Red 7, CI Disperse Red 17, CI Disperse Brown 1, CI Disperse Orange 30, CI Disperse Violet 33, CI Disperse Blue 79 and CI Disperse Yellow 3, the chromaticeness of the TDO dyeings differed markedly to that of the respective control dyeing, the difference in the a^* and b^* values between the TDO dyeings and the control dyeing varying in either the positive or negative directions. Furthermore, the chroma of the TDO dyeings varied between dyes, being either higher or lower than the control dyeing, thereby yielding either cleaner or duller shades, respectively. With the exceptions of CI Disperse Red 1 and CI Disperse Red 17, the λ_{max} of the dyeings of the azo dyes underwent a

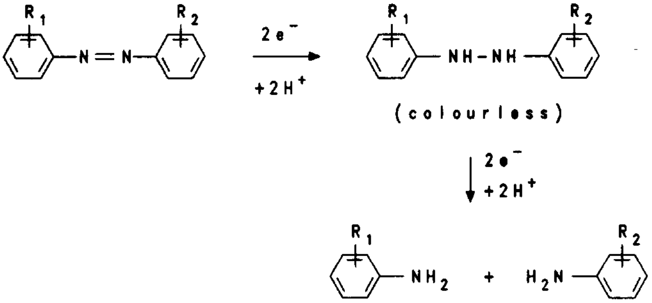
TABLE 5

Colorimetric and Fastness Data (ISO CO6/C2 and BO2) for Nylon 6.6 Dyed with Azo Disperse Dyes at 98°C for 1 h

CI Disperse	Reagent	K/S	λ_{max} (nm)	L*	a*	b*	c*	h°	E	N	C	LF
Orange 1	NIL	30·1	480	27·6	40·3	20·7	45·3	27·2	4	1	2	3
	APS	26·5	480	25·0	33·4	17·7	37·8	27·9	4	1	2	4
	TDO	11·5	500	41·7	41·9	23·8	48·2	29·6	3	1	3–4	3
Orange 25	NIL	11·0	480	51·9	46·7	40·9	62·1	41·2	2–3	1	3–4	6
	APS	14·2	480	48·7	45·7	43·2	62·9	43·4	3	1	3–4	6
	TDO	1·4	400	76·3	6·7	21·0	22·0	72·3	2–3	3	4–5	4
Red 1	NIL	29·5	500	28·5	41·7	21·0	46·7	26·8	3–4	1	1–2	3
	APS	25·3	500	32·7	42·2	26·5	49·8	32·1	3	1	2–3	3
	TDO	7·3	500	47·7	42·1	21·3	47·2	26·8	2–3	1	3–4	3
Red 73	NIL	24·8	520	25·2	38·4	−5·3	38·8	352·1	3–4	1	2–3	3
	APS	26·5	520	23·7	34·7	−0·3	34·7	359·5	3–4	1	2–3	4
	TDO	5·0	440	58·2	19·4	38·0	42·7	63·0	2–3	1	4–5	1
Red 7	NIL	20·9	500	40·9	48·6	31·5	57·9	32·9	2–3	1	2–3	4
	APS	16·4	480	42·9	45·1	33·1	55·9	36·3	3	1	3	3
	TDO	0·5	480	77·3	12·6	13·0	18·1	45·9	*	*	*	4
Red 17	NIL	29·9	520	27·0	41·6	12·9	43·6	17·2	3	1	1–2	5
	APS	17·0	500	36·7	41·6	24·4	48·2	30·4	3	1	3–4	4
	TDO	1·9	520	60·8	31·8	10·2	33·4	17·7	2–3	1–2	4–5	3
Brown 1	NIL	29·7	480	25·4	34·3	18·4	38·9	28·2	3–4	1	2	3
	APS	29·0	480	26·5	34·8	20·4	40·3	30·4	3	1	2	3
	TDO	3·3	400	56·0	22·8	20·5	30·7	42·0	3	2	4–5	3
Orange 30	NIL	9·4	440	53·5	36·0	45·4	57·9	51·6	2	1	3	3
	APS	12·1	440	51·6	35·8	47·1	59·2	52·8	2–3	1	3	3
	TDO	1·4	400	81·3	1·4	20·9	20·9	86·2	*	*	*	3
Violet 33	NIL	9·1	540	36·5	39·3	−15·5	42·2	338·5	4	1	4	3
	APS	9·8	540	34·9	34·7	−6·0	35·2	350·2	4	1	4	3
	TDO	0·6	400	77·7	7·1	17·9	19·3	68·4	*	*	*	3
Blue 79	NIL	11·9	620	35·4	−7·7	−24·4	26·5	253·1	4–5	2	4	1
	APS	11·5	620	34·0	−8·8	−19·8	21·7	246·0	4	2	4	1
	TDO	5·5	420	51·5	30·9	23·4	38·8	37·1	2–3	2	4–5	1
Yellow 3	NIL	23·9	420	73·4	13·6	86·0	87·1	81·0	2–3	1	2–3	6
	APS	21·5	400	66·6	13·6	72·7	74·0	79·4	3	1	3	3
	TDO	6·3	400	80·7	2·9	66·0	66·1	87·5	2	1	4–5	7
Yellow 23	NIL	27·1	420	60·8	32·8	71·4	78·6	65·3	2–3	1	2	6
	APS	27·1	420	61·0	31·2	71·4	77·9	66·4	2–3	1	2	6
	TDO	21·5	400	67·3	23·4	72·0	75·7	72·0	3	1	2–3	7

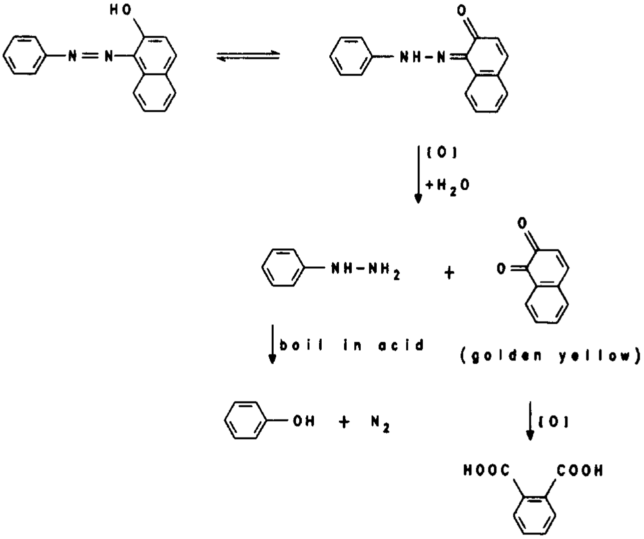
E, Effect on shade; N, staining of nylon 6.6 adjacent; C, staining of cotton adjacent; LF, light fastness; APS, 10 mM ammonium persulphate; TDO, 20 mM thiourea dioxide; *, fastness test not carried out owing to low colour yield obtained.

hypsocromic shift in the presence of TDO and the dyeing obtained using CI Disperse Orange 1 in the presence of the reduction exhibited a bathochromic shift. With the exception of CI Disperse Yellow 23 and CI Disperse Orange 25, for which was obtained slightly enhanced wash fastness in the presence of TDO, dyeing in the presence of the reductant reduced the wash fastness of the azo disperse dyes on the substrate.



Scheme 1

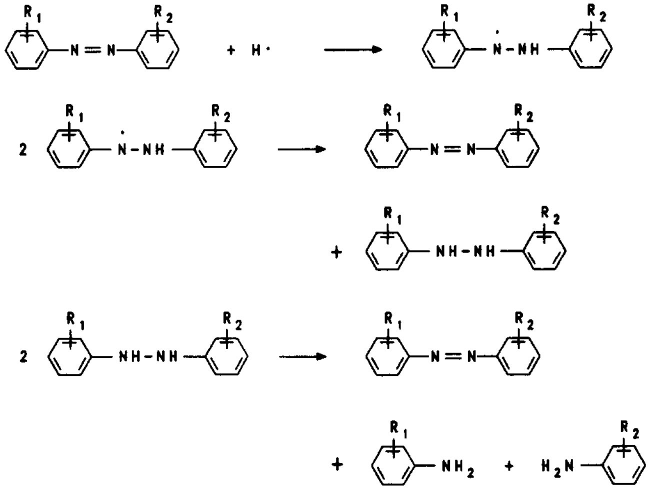
As previously mentioned, many disperse dyes are degraded during dyeing and it is considered that such hydrolysis, oxidation or reduction of the dye results in shade change or loss of colour.[23-25] The reduction of azo dyes was found to produce both hydrazo and amine compounds (Scheme 1)[25] whereas oxidation of the dye was considered to involve hydrolysis of the hydrazone form of the dye (scheme 2).[26]



Scheme 2

It has been reported[24] that the oxidative products of azo disperse dyes obtained using oxidising agents are of a similar colour to the products obtained by exposure of the dyes to light; consequently, an attempt was made to explain the colorimetric results displayed in Table 5 in terms of the photodegradation of azo dyes.

The photodegradative mechanism of azo dyes is complicated and both photooxidative and photoreductive reactions have been proposed, depending on the nature of the fibre and the environment.[27,28] Van Beek *et al.*[29,30] found that under anaerobic conditions, hydrazyl radicals and hydroazo compounds were formed during exposure to ultraviolet radiation, the radicals acting as powerful reducing agents; similar radicals, which also can act as reducing agents, were obtained using glucose. The hydroazo compounds are unstable and can decompose to form amines or regenerate the original dye (Scheme 3).[29,30]

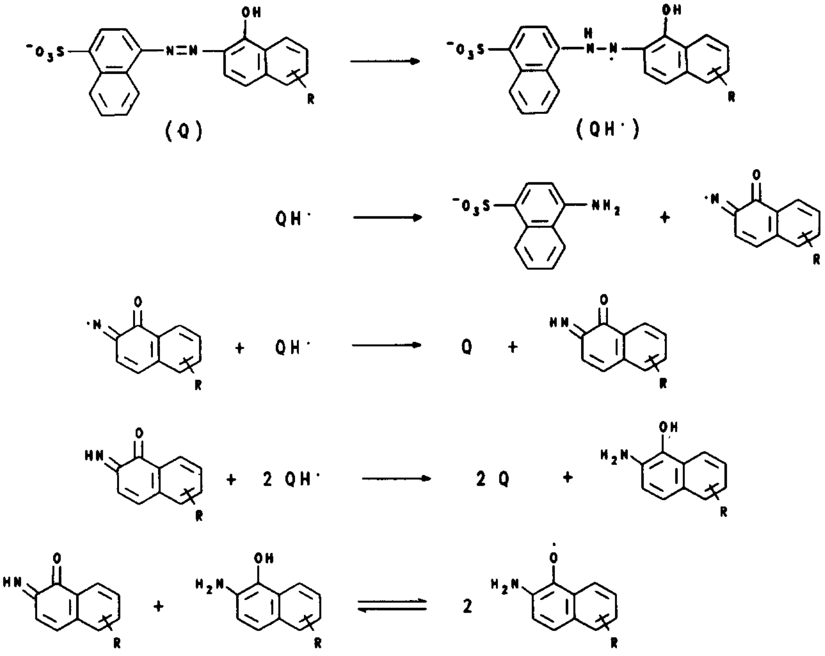


Scheme 3

Heijkoop and van Beek[31] used ESR to investigate the radical intermediates formed during the photoreduction of azo dyes; both hydrazyl and aminonaphthoxy radicals were identified and these authors proposed the following mode of decomposition of the hydrazyl radical (Scheme 4).[31]

Although the photoreductive degradation of azo dyes has been proposed by many authors, photooxidation has also been suggested to occur at the tertiary amino group generating dealkylation products (Scheme 5),[32] and at the azo linkage of the hydrazone tautomeric form of the dye (Scheme 6).[33]

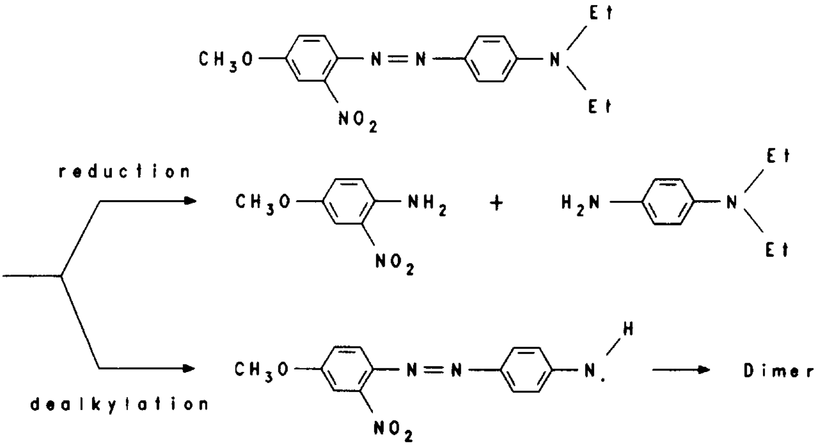
According to the above discussion, azo dyes can be reduced to colourless products (e.g. hydrazo and amine compounds) and oxidized to pale-



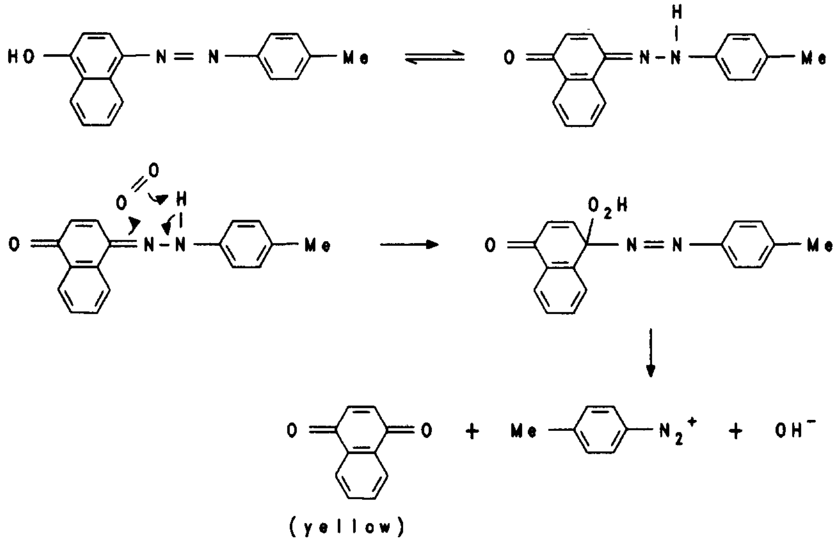
Scheme 4

coloured products (e.g. 1,2-naphthoquinone (golden yellow[34]) and 1,4-naphthoquinone (yellow)[34]).

The finding (Table 5) that TDO imparted a far greater reduction of colour yield and alteration of shade to the dyes than APS implies that the azo dyes are more susceptible to reductive, rather than oxidative, degradation during dyeing. Such reductive degradation may also explain the observation that



Scheme 5



Scheme 6

TDO caused a reduction in wash fastness of 10 of the 12 dyes used and imparted only slightly enhanced wash fastness to the two remaining dyes. Support for the above proposal that the azo dyes used were more susceptible to reductive rather than oxidative degradation accrues from the finding that slightly enhanced wash fastness was imparted to five of the 12 azo dyes by APS, the oxidant having no effect on the wash fastness of the remaining seven dyes. As previously proposed,[2] the enhanced wash fastness imparted by the two radical initiators may be attributed to the formation of a dye polymer and/or covalent attachment of the dye to the substrate.

The results shown in Table 5 clearly demonstrate that, in general, the colour yield and shade of dyeings obtained using azo disperse dyes in the presence of either APS or TDO differ markedly to those secured when dyeing had been carried out in the absence of oxidant or reductant. From the foregoing discussion of the reductive and oxidative degradation of such dyes, the bathochromic or hypsochromic shifts observed for the dyeings carried out in the presence of APS or TDO, together with the often marked shade change and low colour yields of the dyeings imparted by the two radical initiators (Table 5), can be attributed to such oxidative or reductive degradation, respectively, of the dyes and the presence of such oxidized or reduced products on the fibre. It is apparent that the degradation of azo disperse dyes on nylon 6.6 occurs primarily by means of a reductive mechanism and it seems reasonable to suggest that the degradation of azo dyes by TDO is worse than that caused by APS.

In the context of the light fastness results displayed in Table 5, a correlation has been obtained[35] between the light fastness of azo disperse dyes and the electronegativity of the substituents in the para position of the acceptor ring, with the *p*-nitro substituent yielding highest light fastness on PET; the introduction of a second subsequent into the *ortho* position of the acceptor ring was found to improve significantly the light fastness of such dyes on PET.[35] However, the results displayed in Table 5 clearly show that such substituents effects do not apply to dyeings on nylon 6.6, insofar, as, in the absence of radical initiator, the lightfastness of those dyes which contained only a nitro group in the *para* position of the acceptor ring (namely CI Disperse Red 1, CI Disperse Orange 25 and CI Disperse Orange 1) was similar to that of dyes that contaminated a second substituent in the *ortho* position of the acceptor ring (namely CI Disperse Red 73, CI Disperse Red 17, CI Disperse Violet 33 and CI Disperse Orange 30). Azo disperse dyes which contained nitro groups were found to exhibit low light fastness on nylon, this having been attributed to reduction of the nitro groups by the fibre.[36] The finding (Table 5) that both CI Disperse Yellow 3 and CI Disperse Yellow 23 displayed high light fastness on nylon 6.6 when dyeing had been carried out in the absence of radical initiator may be due to the absence of nitro groups within their structures which therefore supports this proposal. However, the high light fastness obtained for CI Disperse Orange 25 and CI Disperse Red 17 on nylon 6.6 in the absence of radical initiator (Table 5) contradicts this proposal; no explanation for this latter finding can be proffered, except that it appears to concur with the view[36] that generally the light fastness of disperse dyes on nylon fibre is less predictable than that on PET fibre.

It has been assumed[37] that in general, the fading to light of azo dyes is accelerated by a decrease in the electron density at the azo linkage. Whereas electron withdrawing substituents in the alkyl groups of the electron donor ring can increase the photostability of azo dyes on PET, they can decrease the photostability on nylon, such alkyl-substituted dyes degrading by an oxidative process on PET and a reductive process on nylon.[27] However, the results shown in Table 5 do not entirely support this proposal, in that CI Disperse Orange 25, which contains a cyanoethyl group in the electron donor ring, exhibited high lightfastness on nylon 6.6 in the absence of radical initiator.

It has been reported that the light fastness of disperse dyes on hydrophobic fibres is influenced by the presence of various compounds, such as antioxidant,[24] oxidant or reductant[22] within the fibre; however, no explanation has been offered as to the mechanism by which an oxidant or reductant reduces the light fastness of disperse dyes. Thus, it seems reasonable to propose that the various reduction and oxidation products which, from the previous discussion, could be generated by the action of

TDO and APS on azo disperse dyes, may be responsible for the observed light fastness results.

CONCLUSIONS

The results obtained suggest that selected nitrodiphenylamine and disperse dyes exhibit enhanced wash fastness on nylon 6.6 when dyeing is carried out in the presence of radical initiators; this effect may be due either to the formation of dye polymers or to dye–fibre covalent bonding. The alteration of shade and colour yield observed for the dyeings carried out in the presence of both APS and TDO may be due to the presence of mixtures of the oxidative or reductive products of the dyes, to dye polymerization and/or to covalent dye–fibre attachment.

REFERENCES

1. Burkinshaw, S. M. & Lu, J. G., Part 1, *Dyes and Pigments*, **21** (1993) 185.
2. Burkinshaw, S. M. & Lu, J. G., Part 2, *Dyes and Pigments*, **22** (1993) 69.
3. Sklarz, B., *Quarterly Reviews*, **21** (1967) 3.
4. Kantouch, A., Hebeish, A. & Bendak, A., *Text. Research J.*, **42** (1972) 7.
5. Kantouch, A. & Bendak, A., *Text. Research J.*, **39** (1969) 858.
6. Wilson, R., *Electron Spin Resonance Studies of Free-Radicals in Solution*, PhD thesis, The University of Leeds, 1962.
7. Hocking, M. B. & Mattar, S. M., *J. Magnetic Resonance*, **47** (1982) 187.
8. Shenai, V. A. & Saraf, N. M., *International Dyer and Textile Printer*, **169** (1980) 269.
9. Shenai, V. A. & Shah, H. C., *Colourage*, **28**(17) (1981) 7.
10. Bendak, A. & Ali, J. H., *Annali di Chimica*, **75** (1985) 523.
11. Ibrahim, N. A., Haggag, K. & Hebeish, A., *Angew. Makromol. Chem.*, **131** (1985) 15.
12. Ibrahim, N. A., Aggour, Sh. Sh. & Hebeish, A., *Amer. Dyestuff Rep.*, **75**(4) (1986) 13.
13. Ibrahim, N. A. & Dawoud, M. A., *Amer. Dyestuff Rep.*, **77**(3) (1988) 35.
14. Ibrahim, N. A. & Dawoud, M. A., *Amer. Dyestuff Rep.*, **77**(6) (1988) 35.
15. Ibrahim, N. A. & Dawoud, M. A., *Amer. Dyestuff Rep.*, **77**(8) (1988) 56.
16. Topiwala, K., *The Effects of Reducing and/or Oxidising Agents on the Dyeing of Polyamide and Polyester Fibres with Disperse Dyes*, MSc thesis, The University of Leeds, 1988.
17. Luo, J., *J.S.D.C.*, **107** (1991) 117.
18. *Methods of Test for Colour Fastness of Textiles and Leather* (4th edn). Society of Dyers and Colourists, Bradford, 1978.
19. Asquith, R. S., Bridgeman, I. & Peters, A. T., *J.S.D.C.*, **81** (1965) 439.
20. Asquith, R. S. & Campbell, B., *J. S. D. C.*, **79** (1963) 678.
21. *Colour Index*. Society of Dyers and Colourists, Bradford, 1975.

22. Meier, H., In *The Chemistry of Synthetic Dyes, Vol. 4*, ed. K. Venkataraman. Academic Press, London, 1971, chap. 7.
23. Schnider, E. F., *Amer. Dyestuff Rep.*, **52** (1963) 370.
24. Giles, C. H. & McKay, R. B., *Text. Research J.*, **33** (1963) 527.
25. Dilling, P., AATCC International Conf., Quebec, Canada, 1985, AATCC, North Carolina, USA, pp. 253–7.
26. Desai, N. F. & Giles, C. H., *J.S.D.C.*, **65** (1949) 358.
27. Allen, N. S., *Rev. Prog. Coloration*, **17** (1987) 61.
28. Bentley, P., McKellar, J. F. & Phillips, G. O., *Rev. Prog. Coloration*, **5** (1974) 33.
29. Van Beek, H. C. A., Heertjes, P. M., Houtepen, C. & Retzloff, D., *J.S.D.C.*, **87** (1971) 87.
30. Van Beek, H. C. A., Heertjes, P. M. & Schaafsma, K., *J.S.D.C.*, **87** (1971) 342.
31. Heijkoop, G. & van Beek, H. C. A., *Recueil Trav. Chim.*, **96** (1977) 83.
32. Arcoria, A., Longo, M. L. & Parisi, G., *Dyes and Pigments*, **7** (1986) 299.
33. Griffiths, J. & Hawkins, C., *J. C. S. Perkin Trans.*, **2** (1977) 747.
34. Windholz, M., *The Merck Index* (9th edn), Merck & Co., Rahway, NJ, 1976, p. 831.
35. Abbott, C. A., *Structure-Property Relations in Azo Disperse Dyes*, PhD thesis, The University of Leeds, 1989.
36. Gordon, P. F. & Gregory, P., *Organic Chemistry in Colour*. Springer-Verlag, Berlin, 1983, chap. 6.
37. Seu, G., *Amer. Dyestuff Rep.*, **74**(3) (1985) 29.