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Dyeing in the Presence of Free Radical Initiators Part 4—The Effect of Radical Initiators on the Dyeing of Nylon 6.6 with Anthraquinone and Quinophthalone Disperse Dyes

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ABSTRACT

Nylon 6.6 was dyed with twelve anthraquinone and two quinophthalone disperse dyes in both the presence and absence of radical initiators. The colour yield, shade change, wash and light fastness of the dyeings imparted by the radical initiators are discussed in terms of the interactions occurring between the dye, fibre and radical initiators.

INTRODUCTION

Previous studies showed that the effect of radical initiators on the dyeing of polyester,[1] nylon 6[2] and nylon 6.6[3] with disperse dyes depends on the nature of both the dye and radical initiator. Certain nitrodiphenylamine and azo disperse dyes exhibited enhanced wash fastness on nylon 6.6 when dyeing had been carried out in the presence of radical initiators; the shade changes observed when dyeing had been carried out in the presence of both

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ammonium persulphate and thiourea dioxide were attributed to the presence of mixtures of oxidative or reductive products of the dyes, to dye polymerization or to covalent dye–fibre attachment.[3] This part of the paper extends this previous study[3] of the dyeing of nylon 6.6 and is concerned with the effects of radical initiators on the dyeing behaviour of twelve anthraquinone and two quinophthalone commercial disperse dyes.

EXPERIMENTAL

Materials

Fibre

Scoured, knitted nylon 6.6 fabric (78f20; 230·5 $g\,m^{-2}$) obtained from ICI Fibres was used.

Dyes and auxiliaries

A total of 14 commercial disperse dyes were used in the work, namely 12 anthraquinone and two quinophthalone 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; ammonium persulphate (APS), potassium periodate (KIO_4), glucose and thiourea dioxide (TDO) were used as radical initiators.

Procedures

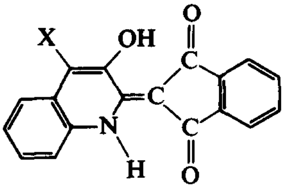
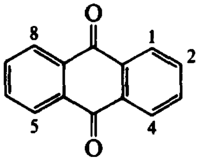
Dyeing

Dyeing was carried out using the equipment and procedures 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 dry, scoured, dyed nylon 6.6 samples which were measured using the instrument and procedure previously described.[2]

TABLE 1
Commercial Disperse Dyes Used

Structure	*Commercial name*	*CI Disperse*	*Supplier*
Quinophthalone			
X = H	Serilene Yellow 3GL	Yellow 54	YCL
X = Br	Palanil Yellow Violet 3G	Yellow 64	BASF
Anthraquinone			
1,4-di-NH_2	Serisol Brilliant Violet 2R	Violet 1	YCL
1-NH_2-4-$NHCH_3$	Celliton Violet 6B	Violet 4	BASF
1-NH_2-2-OCH_3-4-OH	Celliton Pink RF	Red 4	BASF
1,4-di-NH_2-2-OCH_3	Serisol Brilliant Red X3B	Red 11	YCL
1-NH_2-2-OC_6H_5-4-OH	Serilene Red 2BL	Red 60	YCL
1-OH-4-NHC_6H_5	Foron Violet E-BLN	Violet 27	Sandoz
1-$NHCH_3$-4-$NHC_2H_4OC_2H_4OH$	Serisol Brilliant Blue BGN	Blue 3	YCL
1,4-di-NH_2-5-NO_2	Palanil Violet 3B	Violet 8	BASF
1,4-di-NHC_2H_4OH-5,8-di-OH	Dispersol Blue 7G	Blue 7	ICI
1,5-di-$NHCH_3$-4,8-di-OH	Dispersol Blue B-G	Blue 26	ICI
1,5-di-NH_2-2-Cl-4,8-di-OH	Serilene Blue RL	Blue 56	YCL
1,5-di-NH_2-4,8-di-OH-6-$C_6H_5OCH_3$	Foron Blue SBGL	Blue 73	Sandoz

Wash fastness

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

Light fastness

The light fastness of the dry, scoured, dyed samples was determined according to the ISO BO2 method[4] using a Microscal fading lamp.

RESULTS AND DISCUSSION

Table 2 shows the results obtained for the dyeing of nylon 6.6 using CI Disperse Yellow 54 in the presence of various concentrations (between 0 and 30 mM) of four radical initiators. It is evident that, as found previously for the dyeing of PET with CI Disperse Yellow 54 in the presence of APS,[1] the colour yield (as given by the K/S values) of the dyeings obtained using this particular dye on nylon 6.6 in the presence of each of the four radical initiators is different from that of the control dyeing (i.e. that carried out in the absence of radical initiator). This difference in colour yield between the

TABLE 2

Colorimetric (λ_{max} = 440 nm) and Wash Fastness (ISO C06/C2) Data for Nylon 6.6 Dyed with CI Disperse Yellow 54 at 98°C, pH 5·5 for 1 h

Reagent	*Conc. (mM)*	*K/S*	*L**	*a**	*b**	*c**	*h°*	*E*	*N*	*C*
APS	0	15·0	81·0	2·8	80·0	80·1	88·0	3–4	1	2–3
	1	15·4	79·3	3·5	77·9	78·0	87·4	3–4	1	2–3
	3	15·8	77·9	3·9	76·4	76·5	87·1	3–4	1	2–3
	5	16·1	77·3	4·2	75·8	75·9	86·8	3–4	1	2–3
	6·25	16·3	77·5	4·1	76·0	76·1	86·9	3–4	1	2–3
	10	16·8	76·6	4·6	75·4	75·5	86·5	3–4	1	2–3
	20	19·4	76·9	5·7	78·5	78·7	85·8	3–4	1	3–3
	30	17·9	76·4	5·7	76·5	76·7	85·7	4–5	1	3
KIO_4	1	15·2	79·4	3·1	77·5	77·6	87·7	3–4	1	2–3
	3	15·7	78·4	3·4	76·6	76·7	87·5	3–4	1	2–3
	5	15·8	78·7	3·4	76·9	77·0	87·5	3–4	1	2–3
	6·25	15·9	79·1	3·4	77·5	77·6	87·5	3–4	1	2–3
	10	15·7	80·1	3·2	78·6	78·7	87·7	3–4	1	2–3
	20	15·3	81·3	2·7	79·7	79·8	88·1	3–4	1	2–3
	30	15·2	81·6	2·3	79·9	79·9	88·4	3–4	1	2–3
TDO	1	14·9	81·5	2·2	79·8	79·8	88·4	3–4	1	2–3
	3	15·1	81·5	2·4	80·2	80·2	88·3	3–4	1	2–3
	5	15·3	81·6	2·4	80·3	80·3	88·3	3–4	1	2–3
	6·25	15·2	81·8	2·2	80·6	80·6	88·4	3–4	1	2–3
	10	15·3	81·9	1·9	80·8	80·8	88·7	3–4	1	2–3
	20	15·4	81·9	1·7	80·9	80·9	88·8	3–4	1	2–3
	30	15·7	82·0	1·6	61·3	81·3	88·9	3–4	1	2–3
Glucose	1	15·1	81·1	2·4	79·6	79·6	88·3	3–4	1	2–3
	3	15·2	81·3	2·3	79·9	79·9	88·4	3–4	1	2–3
	5	15·1	81·2	2·4	79·7	79·7	88·3	3–4	1	2–3
	6	15·3	81·1	2·4	79·7	79·7	88·3	3–4	1	2–3
	10	15·1	81·2	2·4	79·8	79·8	88·3	3–4	1	2–3
	20	15·2	81·3	2·3	79·9	79·9	88·4	3–4	1	2–3
	30	15·2	81·4	2·3	80·0	80·0	88·4	3–4	1	2–3

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

control dyeing and dyeings carried out in the presence of radical initiator was least in the case of glucose. Figure 1 and Table 2 show that, generally, the K/S values of APS, KIO_4 and TDO dyeings increased with increasing concentration of these reagents used, although at concentrations greater than 20 mM APS and 6·25 mM KIO_4, this increase in colour yield decreased. Table 2 also shows that the dyeings obtained in the presence of APS differed in terms of hue, chroma and lightness from the control dyeing and that this difference increased with increasing concentrations of APS employed. The results (Table 2) clearly demonstrate that dyeings on nylon 6.6 secured using APS were deeper in shade (as given by the lower L^* values and higher K/S values) but slightly duller (as evidenced by the lower c^* values) and more orange (as shown by the higher a^* values and lower h° values) than the control dyeing. These results differ from those previously obtained for this particular dye on PET[1] in so far as dyeings on PET obtained in the presence of APS were greener than the control dyeing; this difference in shade change observed for the same dye on the two substrates implies that the dyeing properties of CI Disperse Yellow 54 in the presence of the oxidant depend on the nature of the fibre. It is known that the shade obtained for a given disperse dye on nylon differs slightly from that on PET;[5] the difference in shade has been attributed to a difference in the interactions occurring between the dye and the two substrates, it being considered that strong hydrogen-bonding occurs between disperse dyes and nylon, whereas this particular type of interaction is much weaker in the case of the disperse dye–

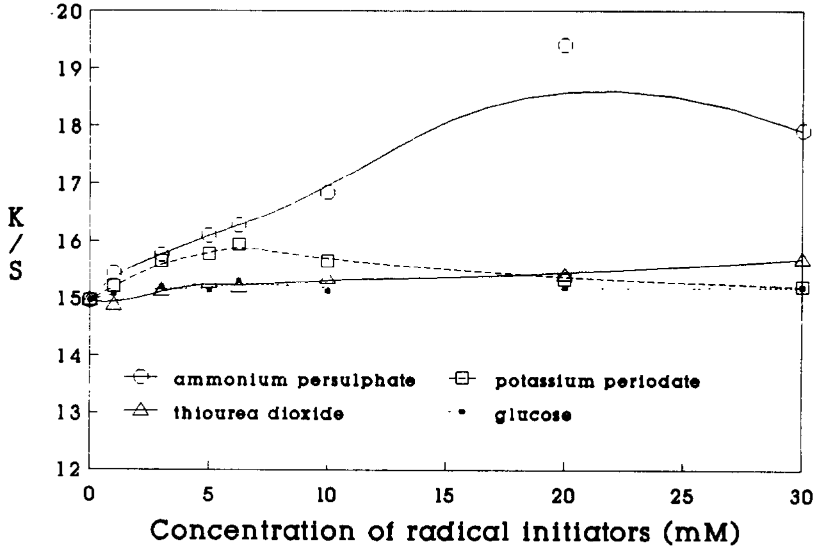


Fig. 1. Colour yield of nylon 6.6 dyed with CI Disperse Yellow 54 in the presence of various concentrations of radical initiator.

PET system.[5] Griffiths[6] proposed that dye adsorption on to a fibre can be considered as a special case of solvent–solute interaction, as a consequence of which solvatochromism may occur when a given dye is applied to different substrates. Thus, it is also possible that such solvatochromism may account for the observed difference in shade obtained for the APS dyeings of CI Disperse Yellow 54 on nylon 6.6 and PET and, therefore, that the difference in the nature of the interactions occurring between CI Disperse Yellow 54 and PET and the dye and nylon 6.6 may result in the observed difference in shade observed for the dye on the two substrates.

Table 2 shows that the effects on dyeing imparted by KIO_4 were virtually identical to those obtained using APS, in that dyeings obtained using up to 10 mM KIO_4 were deeper in shade (as given by the higher K/S values and lower L^* values), more orange (as evidenced by the higher a^* values and lower h° values) and duller (as given by the lower c^* values) than the control dyeing. However, at concentrations above 10 mM, the effects of the two oxidants on dyeing differed; in the case of APS, the dyeings became a deeper orange colour, whilst the KIO_4 dyeings became paler and more yellow. For both oxidants, the colour of the dyeings obtained, using a concentration in excess of 10 mM, was considerably different from that obtained for oxidant concentrations of 10 mM and below.

In contrast to the results found for APS and KIO_4, those obtained using TDO revealed that with increasing concentration of reductant, the dyeings became gradually brighter (as given by the higher c^* values), deeper (as evidenced by the higher K/S values) and yellower (as shown by the higher b^* and h° values) than the control dyeing; furthermore, the difference in colour between the control dyeing and those carried out in the presence of TDO was considerably less than that obtained between the control dyeing and the dyeings obtained using APS and KIO_4. It was found (Table 2) that glucose imparted very little change in colour to the dyeings at each of the concentrations used and also that there was little difference between the shade obtained for the control dyeing and those carried out in the presence of glucose.

In a previous study,[1] it was concluded that in the presence of APS, CI Disperse Yellow 54 may become covalently attached to PET or may be present within the substrate in the form of a polymer. This conclusion was made as a result of the findings that APS brought about a marked change in the shade of the dyeings and that the APS dyeings exhibited higher resistance to extraction with DMF than the corresponding dyeing obtained in the absence of oxidant. Consequently, it can be suggested that if dye polymerization and/or covalent attachment of the dye to nylon 6.6 had occurred during dyeing in the presence of the four radical initiators used, the wash fastness of the dyeings should have been improved. However, Table 2 shows that the wash fastness of the dyeings (with the exception of that achieved using 30 mM APS) was not enhanced using each of the four radical initiators; consequently, although APS, KIO_4 and TDO each affected the dyeing of nylon 6.6 with CI Disperse Yellow 54, in so far as each reagent imparted a shade change, this effect clearly cannot be attributed to either dye polymerization and/or covalent attachment of the dye to the fibre having occurred. A possible explanation of the colour change and increased depth in shade (Table 2) obtained when CI Disperse Yellow 54 had been applied to nylon 6.6 in the presence of APS, KIO_4 and TDO, follows from the observation that the radical initiators damaged the fibre surface (this finding is to be discussed in the next part of this paper), such damage resulting in an increase in the rate of dye diffusion into the substrate and thus greater dye uptake.

The results shown in Table 2 clearly demonstrate that the effects imparted by APS and KIO_4 to CI Disperse Yellow 54 differed markedly from those imparted by TDO and glucose to the dye on nylon 6.6 with CI Disperse Yellow 54; also, whereas the two oxidants imparted virtually identical effects to the dye in terms of shade change and wash fastness, the two reductants differed in their effects on the dyes. These findings agree with those previously obtained for the effects imparted by APS, KIO_4, TDO and glucose to CI Disperse Yellow 1 on nylon 6.6.[3] The two oxidants (APS and KIO_4) are powerful oxidizing agents each having similar high positive potentials (persulphate 2·0 V;[7] $H_5IO_6 = 1{\cdot}7\,V$ where $IO_4^- + 2H_2O = H_4IO_6^-$)[7,8] whereas glucose is a weaker reducing agent (−0·41 V at 0·22 M in 1·0 aqueous KOH)[9] than TDO (−1·04 V at 5 g/litre in 15 g/litre aqueous NaOH).[10] Consequently, the similarity in the effects imparted by the two oxidants and the dissimilarity in the effects imparted by the reductants may be attributable to their respective redox potentials.

The results obtained for the dyeing of nylon 6.6 with twelve commercial anthraquinone disperse dyes in both the absence and presence of 10 mM ammonium persulphate or 20 mM thiourea dioxide are shown in Table 3. A hypsochromic shift occurred in the λ_{max} of the APS dyeings using CI Disperse Violet 1, CI Disperse Violet 4, CI Disperse Red 4, CI Disperse Red 11, CI Disperse Blue 7 and CI Disperse Blue 26, as well as for the TDO dyeings obtained using CI Disperse Red 4 and CI Disperse Red 11; for each of the remaining dyes, no shift in λ_{max} was observed. For the red AQ disperse dyes used, dyeings carried out in the presence of APS were generally duller (as given by the lower c^* values) and more orange (as evidenced by the lower a^* values and the higher b^* and $h°$ values) than the control dyeings. In general, APS imparted a pale (as shown by the lower K/S values and higher L^* values), dull (as given by the lower c^* values) and greener hue (as evidenced by the lower a^* values, higher b^* values and lower $h°$ values) to the five blue dyes used and a dull (as given by the lower c^* values), bluer hue (as

TABLE 3
Colorimetric and Fastness Data (ISO CO6/C2 and BO2) for Nylon 6.6 Dyed with Anthraquinone Disperse Dyes at 98°C, pH 5·5 for 1 h

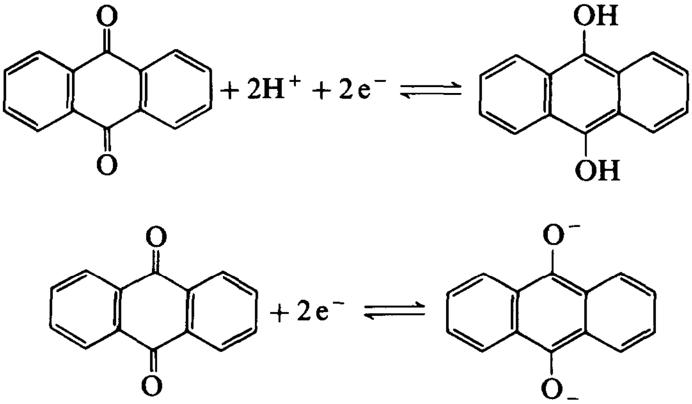
CI Disperse	*Reagent*	*K/S*	λ_{max} (*nm*)	*L**	*a**	*b**	*c**	*h°*	*E*	*N*	*C*	*LF*
Violet 1	NIL	19·4	600	28·0	33·3	−41·8	53·4	308·5	2	1	2	6
	APS	6·1	580	34·2	7·8	−7·3	10·7	316·9	4	2	4–5	5
	TDO	10·2	600	33·2	18·3	−24·0	30·2	307·3	2	1	3	4
Violet 4	NIL	15·7	600	29·1	19·7	−43·1	47·4	294·6	1–2	1	2–3	3
	APS	4·3	580	39·4	1·4	−6·1	6·3	282·9	4	2	4–5	3
	TDO	7·2	600	36·7	9·2	−24·1	25·8	290·9	2–3	1	3–4	3
Red 4	NIL	8·9	520	49·5	57·0	1·1	57·0	1·1	2	1	2	6
	APS	2·0	400	60·1	10·2	14·1	17·4	54·1	4–5	2–3	5	2
	TDO	3·7	420	70·7	13·2	35·3	37·7	69·5	2	1–2	4	4
Red 11	NIL	16·1	580	33·6	49·2	−29·3	57·3	329·2	2–3	1	2	6
	APS	4·1	540	41·0	12·4	−1·3	12·5	354·0	4–5	2	4–5	4
	TDO	14·8	540	34·4	46·9	−22·1	51·8	334·8	2–3	1	2	6
Red 60	NIL	6·2	520	49·4	53·1	−6·6	53·5	352·9	3	1	3	6
	APS	6·7	520	46·4	45·7	1·5	45·7	1·9	3	1	3	6
	TDO	6·8	520	46·5	46·0	4·8	46·3	5·9	2–3	1	3–4	5
Violet 27	NIL	4·9	580	42·6	10·8	−35·4	37·0	287·0	2–3	1	3–4	3
	APS	5·4	580	39·7	4·1	−21·3	21·7	280·9	2–3	1	3–4	3
	TDO	7·1	580	36·4	6·1	−25·3	26·0	283·6	3	1	3–4	4
Blue 3	NIL	14·4	600	36·8	1·0	−40·4	40·4	271·4	2–3	1	3	4
	APS	4·2	600	40·7	−1·3	−7·9	8·0	260·7	4	2	4–5	4
	TDO	6·1	600	36·8	1·4	−10·6	10·7	277·5	2	1	4	4
Violet 8	NIL	15·9	580	30·7	16·5	−42·9	46·0	291·0	2	1	3	3
	APS	4·8	580	39·3	−2·7	−9·2	9·6	253·6	4	2–3	5	3
	TDO	19·1	580	27·4	13·0	−35·5	37·8	290·1	2–3	1	2–3	5
Blue 7	NIL	22·6	680	38·7	−20·0	−23·9	31·2	230·1	3	1	3–4	3
	APS	3·0	620	48·7	−10·3	−5·5	11·7	208·1	4–5	2–3	4–5	3
	TDO	16·8	680	39·7	−16·3	−22·2	27·5	233·7	3–4	1–2	4	4
Blue 26	NIL	15·8	640	34·9	2·2	−40·5	40·6	273·1	2–3	1	3	4
	APS	3·8	620	44·7	−8·2	−9·2	12·3	228·3	4–5	2–3	4–5	3
	TDO	13·4	640	36·5	−1·4	−36·2	36·2	267·8	3	1	3–4	6
Blue 56	NIL	18·8	640	31·9	3·8	−39·7	39·9	275·5	3–4	1	3–4	4
	APS	11·9	640	35·5	−8·6	−24·3	25·8	250·5	4	1–2	4	4
	TDO	13·9	640	35·8	−2·0	−34·5	34·6	266·7	3–4	1	3	6
Blue 73	NIL	17·4	640	32·6	−2·1	−34·1	34·2	266·5	4	1	4	6
	APS	6·2	640	40·5	−10·7	−13·7	17·4	232·0	4–5	2	4–5	4
	TDO	16·3	640	33·3	−2·9	−32·9	33·0	265·0	4	1	4	6

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

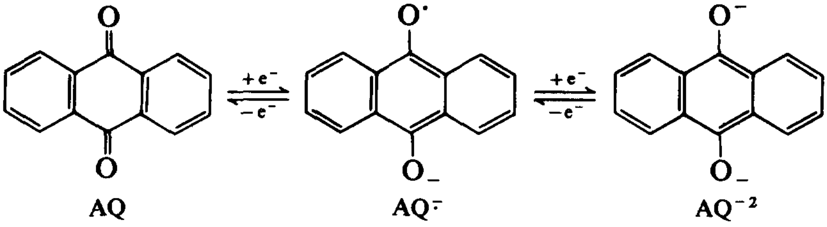
shown by the lower a^* values, higher b^* values and lower h° values) to the dyeings secured using the four violet dyes. In a manner similar to that observed using APS, TDO imparted a dull (as given by the lower c^* values) and more orange hue (as evidenced by the lower a^* values and the higher b^* and h° values) to the dyeings obtained using the three red dyes; for the five blue dyes used, the TDO dyeings were plaer (as shown by the lower K/S values and higher L^* values), duller (as given by the lower c^* values) and less blue (as evidenced by the higher b^* values) than the control dyeing, the hue of the dyeings varying between dyes, being either greener or redder than the control dyeing. The reductant imparted a duller (as evidenced by the lower c^* values) and more blue hue (as shown by the lower a^* values, higher b^* values and lower h° values) to the violet dyeings, the lightness of the TDO dyeings varying between dyes, being either deeper or paler than the control dyeing.

With the exception of CI Disperse Red 60, CI Disperse Violet 27 and CI Disperse Violet 8, it is clear that both APS and TDO reduced the colour yield of the dyeings and also that the APS dyeings were of lower colour yield than the TDO dyeings.

The reduction of AQ vat dyes may be represented as shown in Scheme 1;[11] under strongly acidic conditions the hydroquinone form of the dye is obtained, whilst under strongly alkaline conditions reduction produces the ionized quinonoid derivative. Hocking[9,12] studied the reduction of AQ with both glucose and sodium dithionite in aqueous alkaline solution by Electron Paramagnetic Resonance and obtained the anthrasemiquinone radical anion ($AQ^{-\cdot}$) produced via Scheme 2. Since, in this work, dyeing had been carried out under acidic conditions (pH 5·5) using a sodium acetate/acetic acid buffer system, it seems reasonable to propose that the AQ dyes were reduced to the hydroquinone form in the presence of TDO.



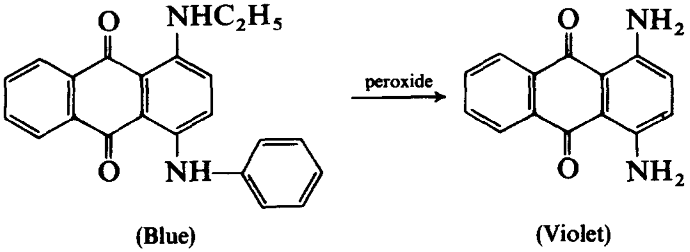
Scheme 1



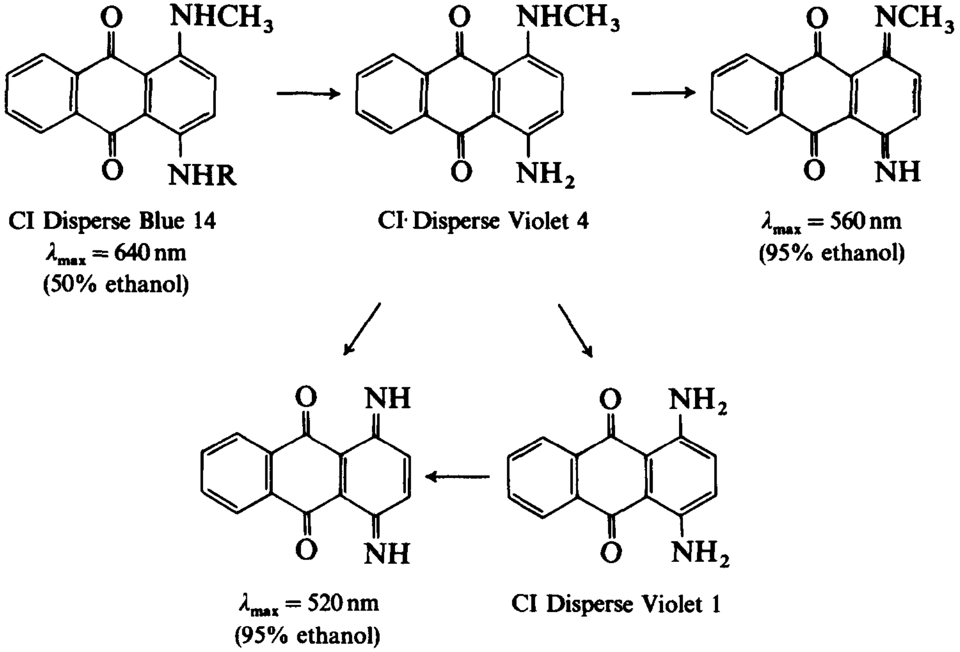
Scheme 2

Kail[13] assumed that there was some similarity between the degradative behaviour of AQ dyes when exposed to peroxide and their photofading behaviour; from TLC analysis, it was proposed that upon oxidation, 1-ethylamino-4-anilinoanthraquinone underwent *N*-dealkylation and *N*-dearylation to form 1,4-diaminoanthraquinone (Scheme 3). Giles and Sinclair[14] examined the photofading products of AQ dyes on PET and suggested that the following degradative mechanism (Scheme 4)[14,15] took place. In addition to the work of Giles and Sinclair,[14] the degradative products I[15] and II[16] have been proposed to be involved in the photofading reaction (see Structure 1). Consequently, from the foregoing, it seems reasonable to propose that as a result of treatment with APS or TDO, a variety of oxidation or reduction products, respectively, would be formed for each of the twelve AQ dyes studied and that such a mixture of degradation products could be responsible for the observed shade changes obtained when dyeing had been carried out in the presence of the two radical initiators (Table 3).

Table 3 shows that, generally, the wash fastness of the APS and TDO dyeings was higher than that of the respective control dyeing and also that the fastness to washing of the APS dyeings was generally higher than that of the TDO dyeings. It is noteworthy that of the twelve dyes studied, CI Disperse Red 60, CI Disperse Violet 27 and CI Disperse Blue 73, each of which contain a benzene substituent, together with CI Disperse Blue 56, which contains an electron withdrawing chlorine substituent, were little influenced by the two radical initiators. It has been suggested that the high



Scheme 3



CI Disperse Blue 14
$\lambda_{max} = 640$ nm
(50% ethanol)

CI Disperse Violet 4

$\lambda_{max} = 560$ nm
(95% ethanol)

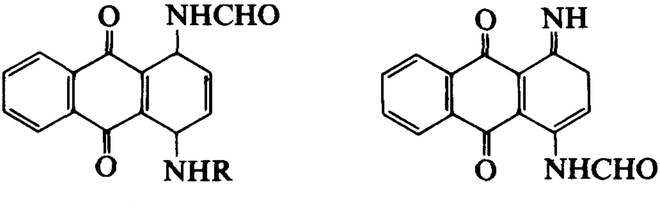
$\lambda_{max} = 520$ nm
(95% ethanol)

CI Disperse Violet 1

Scheme 4

light fastness of 1-arylamino substituted AQ dyes on both PET and nylon can be attributed to the benzene ring enhancing the rate of deactivation of the excited singlet state;[17,18] this may explain the finding that the three AQ dyes which contained a benzene substituent were little influenced by the two radical initiators. However, the observation that CI Disperse Blue 56, which contained a chloro group in the 2-position, was little affected by both TDO and APS, cannot be explained in view of the finding[18] that aminochloro AQ dyes exhibit low light fastness on nylon fibre.

Although the λ_{max} of the APS and TDO dyeings obtained using CI Disperse Blue 56 and CI Disperse Blue 73 was identical to that of the control



(I)
R = H
$\lambda_{max} = 524$ nm
(95% ethanol)

(II)

Structure 1

dyeing, the dyes most probably underwent degradation during dyeing in the presence of the two radical initiators, possibly via Schemes 1–4 discussed above, in so far as, for each of the two dyes, the oxidant and reductant each reduced the colour yields of the dyeings. In contrast to CI Disperse Blue 56 and CI Disperse Blue 73, the colour yield obtained for CI Disperse Red 60 and CI Disperse Violet 27 was enhanced by treatment with both APS and TDO; the λ_{max} of the dyeings was unaffected by both radical initiators. This latter finding implies that both CI Disperse Red 60 and CI Disperse Violet 27 were more resistant to degradation by the two radical initiators than were the other dyes used and, therefore, that the high colour yield obtained for CI Disperse Red 60 and CI Disperse Violet 27 may be due to the radical initiators having damaged the fibre surface, resulting in greater dye diffusion into the fibre and higher dye uptake.

It has been found[19–23] that treatment of *p*-phenylenediamine with oxidant resulted in the formation of *p*-benzoquinonediimine, which then coupled to the original dye forming a trimer. According to Scheme 4, the alkylamino anthraquinone derivative was dealkylated to 1,4-diimine-anthraquinone;[14] it is possible that this latter product could be covalently attached to the fibre. Furthermore, under acidic conditions, the alkylamino AQ derivative may be protonated and this protonated derivative may, in a manner similar to that of protonated *p*-benzoquinonediimine, undergo either dye polymerization or covalent attachment to the fibre. Consequently, it is proffered that the enhanced wash fastness obtained using APS (Table 3) may be attributable to the presence of either diimine or monoimine AQ derivatives which contain alkylamino groups that either couple to the original dye to form dimers, trimers or polymers or become covalently attached to the fibre. In the case of TDO, the observed enhanced fastness of the dyeings obtained in the case of alkylamino AQ dyes may be due to the generation of the corresponding anthrasemiquinone radical anion and its covalent attachment to a fibre radical; this particular mechanism will be given in detail in a later part of this paper.

It has been suggested that the 1-hydroxy-substituted AQ derivatives exhibit high light fastness on polyester due to the photoexcited dye being rapidly deactivated by a process involving reversible proton exchange across the strong intramolecular hydrogen bond; the low light fastness of such dyes on nylon fibres was attributed to the highly polar nature of the substrate which reduced such intramolecular hydrogen bonding.[16,18] Generally, AQ dyes such as 2-amino or 1-hydroxy derivatives, which can abstract an electron from an environment to form an excited AQ radical anion, usually possess low light fastness on hydrophobic fibres, whilst dyes such as 1-amino AQ and derivatives, which can abstract a hydrogen atom to form a semiquinone radical, display high light fastness on such substrates.[16,18] It is

TABLE 4

Colorimetric and Fastness Data (ISO CO6/C2 and BO2) for Nylon 6.6 Dyed with Quinophthalone Disperse Dyes at 98°C, pH 5·5 for 1 h

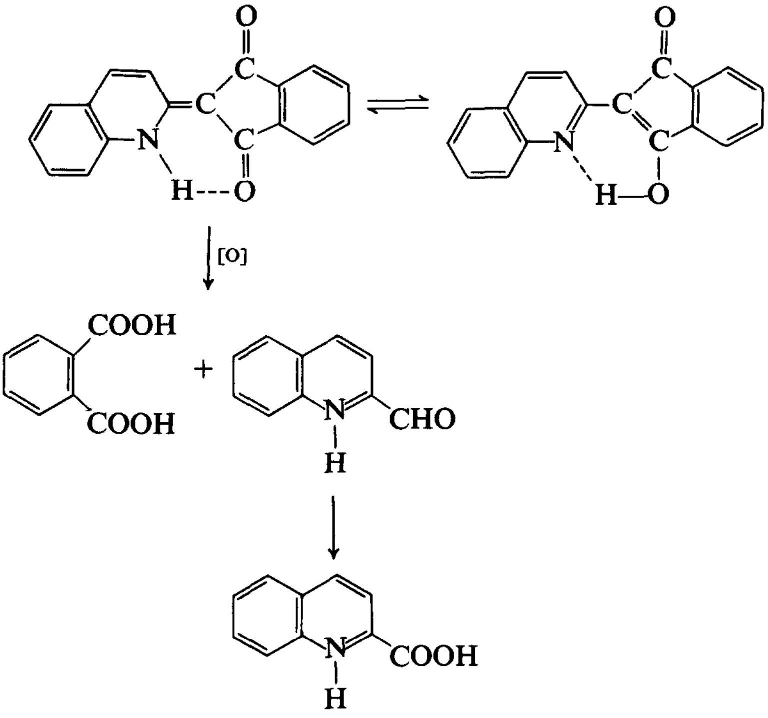
CI Disperse	*Reagent*	*K/S*	λ_{max} *(nm)*	L^*	a^*	b^*	c^*	h°	*E*	*N*	*C*	*LF*
Yellow 54	NIL	15·0	440	81·0	2·8	80·0	80·1	88·0	3–4	1	2–3	7
	APS	16·8	440	76·6	4·6	75·4	75·5	86·5	3–4	1	2–3	4
	TDO	15·4	440	81·9	1·7	80·9	80·9	88·8	3–4	1	2–3	7
Yellow 64	NIL	18·9	440	76·4	6·5	80·8	81·1	85·4	3–4	1	2–3	4
	APS	19·9	440	74·6	6·2	79·1	79·3	85·5	3–4	1	3	4
	TDO	19·3	440	76·1	2·8	80·5	80·5	88·0	3–4	1	3	6

E, Effect of 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.

considered that since nylon acts as an electron donor, the light fastness of AQ disperse dyes on nylon 6.6 is less predictable than that on PET.[16,18]

The results obtained for the dyeing of nylon 6.6 with two commercial quinophthalone disperse dyes in both the absence and presence of 10 mM ammonium persulphate or 20 mM thiourea dioxide are shown in Table 4. It is clear that the APS dyeings of these two dyes were deeper in shade (as given by the higher K/S values and lower L^* values), less yellow (as evidenced by the lower b^* values) and duller (as shown by the lower c^* values) than the control dyeing; the APS dyeings of CI Disperse Yellow 54 were more orange (as given by the higher a^* values and lower h° values) than the control dyeing whilst the corresponding CI Disperse Yellow 64 dyeings were more yellow than the control dyeing. The TDO dyeings of these two dyes were of higher colour yield (K/S) and more yellow (as evidenced by the lower a^* values and higher h° values) than the control dyeing. The TDO dyeing of CI Disperse Yellow 54 was cleaner (as evidenced by the higher c^* value) whereas the TDO dyeing of CI Disperse Yellow 64 was duller (as shown by the lower c^* value) than the respective control dyeing. The wash fastness of the dyeings was little effected by the two radical initiators.

Although photo-oxidation of quinophthalone dyes has been proposed[24] (Scheme 5), the photoreductive, oxidative and reductive degradation of the dye class have not been studied. The results shown in Table 4 demonstrate that the APS and TDO dyeings exhibited higher colour yield than the corresponding control dyeing (without radical initiators added); shade changes were found to have occurred for both APS and TDO dyeings even though the λ_{max} of the dyeings carried out in the presence of radical initiator were identical to those of the respective control dyeings. According to Scheme 5 it is possible that the observed shade change in the dyeings caused by APS may be attributed to the formation of the carboxylic acid and



Scheme 5

quinoline derivatives of each dye used. However, since no change in λ_{max} was observed for each dye when dyeing had been carried out in the presence of the oxidant, it can be proposed that only a low proportion of such degradative products was produced during treatment with APS. The enhanced colour yield of the APS dyeings therefore may not be due to the presence of such carboxylic acid and quinoline degradative products but may be attributed to an increase in the rate of diffusion of dye within the fibre that ensues from damage to the fibre surface caused by the oxidant.

As previously mentioned, although the reductive degradation of quinophthalone dyes has not been studied, it is possible that the observed shade change of the TDO dyeings (Table 4) may be attributed to the formation of reductive products; since no change in λ_{max} was observed for each dye when dyeing had been carried out in the presence of the reductant, then, as suggested above for the effects of APS on the dyes, only a low proportion of such degradative products may have been produced during dyeing in the presence of TDO. The enhanced colour yield of the TDO dyeings can also be attributed to damage of the fibre surface imparted by TDO and the corresponding increase in rate of dye diffusion within the fibre.

The light fastness of the APS dyeing obtained for CI Disperse Yellow 54 was lower whilst the light fastness of the TDO dyeing of CI Disperse Yellow 64 was higher than the respective control dyeings; this finding therefore implies that different degradative mechanisms apply in the cases of APS and TDO.

CONCLUSIONS

Selected anthraquinone 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 to either the formation of dye polymers or to dye–fibre covalent bonding. The shade changes observed for dyeings obtained 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 or to covalent dye–fibre attachment. In contrast, the wash fastness of quinophthalone disperse dyes on nylon 6.6 was unaffected by radical initiators; the alteration of shade observed for the dyeings carried out in the presence of the two radical initiators may be attributable to the presence of mixtures of the oxidative or reductive products of the dyes.

REFERENCES

1. Burkinshaw, S. M. & Lu, J. G., Part I. *Dyes and Pigments* (in press).
2. Burkinshaw, S. M. & Lu, J. G., Part II. *Dyes and Pigments* (in press).
3. Burkinshaw, S. M. & Lu, J. G., Part III. *Dyes and Pigments* (in press).
4. *Methods of Test for Colour Fastness of Textiles and Leather*, 4th edn. Society of Dyers and Colourists, Bradford, 1978.
5. Sinclair, R. S. & McAlpine, E., *J. Soc. Dyers Colour.*, **91** (1975) 399.
6. Griffiths, J., *Colour and Constitution of Organic Molecules.* Academic Press, London, 1976, p. 77.
7. Hunsberger, J. F., In *CRC Handbook of Chemistry and Physics*, 58th edn., ed. R. C. Weast. CRC Press, Boca Raton, FL, 1978, p. D141.
8. Downs, A. J. & Adams, C. J., In *Comprehensive Inorganic Chemistry, Vol. 12*, ed. J. C. Bailar. Pergamon Press, Oxford, 1973, Chap. 26.
9. Hocking, M. B. & Matter, S. M., *J. Magn. Reson.*, **47** (1982) 187.
10. Weiss, M., *Am. Dyest. Rep.*, **67**(8) (1978) 35.
11. Vickerstaff, T., *The Physical Chemistry of Dyeing.* Oliver & Boyd, London, 1954, Chap. 9.
12. Hocking, M. B., *Can. J. Chem.*, **58** (1980) 1983.
13. Kail, J. R., Final Year research project. The University of Leeds, 1985.
14. Giles, C. H. & Sinclair, R. S., *J. Soc. Dyers Colour.*, **88** (1972) 109.
15. Wegerle, D., *J. Soc. Dyers Colour.*, **89** (1973) 54.
16. Allen, N. S., *Rev. Prog. Col.*, **17** (1987) 61.
17. Griffiths, J., In *Developments in the Chemistry and Technology of Organic Dyes*, ed. J. Griffiths. Blackwell, Oxford, 1984, Chap. 1.

18. Allen, N. S. & McKellar, J. F., In *Developments in Polymer Photochemistry-1*, ed. N. S. Allen. Applied Science, London, 1980, Chap. 7.
19. Evans, N. A. & Stepleton, I. W., In *The Chemistry of Synthetic Dyes, Vol. V*, ed. K. Venkataraman. Academic Press, New York, 1978, Chap. 7.
20. Corbett, J. F., *J. Soc. Cosmet. Chem.*, **24** (1973) 103.
21. Brown, K. C. & Corbett, J. F., *J. Soc. Cosmet. Chem.*, **30** (1979) 191.
22. Brown, K. C., *J. Soc. Cosmet. Chem.*, **33** (1982) 375.
23. Pohl, S., *Cosmet. Toiletr.*, **103** (1988) 57.
24. Kuramoto, N., *J. Chem. Soc. Chem. Comm.* (1979) 379.