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Dyeing in the Presence of Free Radical Initiators. Part 6: The Dyeing of Wool with Disperse Dyes

S. M. Burkinshaw

Department of Colour Chemistry and Dyeing, The University of Leeds,
Leeds, UK LS2 9JT

&

J. G. Lu

Department of Textile Engineering, Van Nung Institute of Technology,
Chung-Li, Taiwan

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ABSTRACT

The dyeing of wool fabrics with four nitrodiphenylamine, five azo, seven anthraquinone and two quinophthalone disperse dyes was carried out in the presence of ammonium persulphate or thiourea dioxide. The colour yield, shade change and wash and light fastness of the resultant dyeings are discussed in terms of the interactions occurring between the dye, substrate and radical initiators.

INTRODUCTION

Disperse dyes are not commercially used to dye wool since the hydrophobic, sparingly water-soluble dyes display low substantivity towards the substrate and yield pale dyeings of low wet fastness properties.[1–4] However, several workers have explored the possibility of modifying wool so as to increase its substantivity towards disperse dyes. Asquith *et al.*[2] showed that the substantivity of disperse dyes towards the fibre could be increased by increasing the hydrophobicity of the fibre by either chemically modifying or physically blocking the hydrophilic groups of the fibre. However, these workers[2] demonstrated that such treatments resulted in dyeings of low wet fastness, this being attributable to the facts that the compounds used to modify the fibre may be removed from wool in much the same way as acid dyes of low fastness are removed from the fibre and also that the washing process may result in destruction of the hydrophobic interaction operating between the modified wool and the disperse dye. In contrast to Asquith's work, Lewis and Pailthorp[5,6] showed that wool which had been chemically modified with various hydrophobic compounds possessed high substantivity towards disperse dyes and that such treatment improved both the wash fastness and light fastness of the dyes on the substrate.

The dyeing of wool (and also silk) with direct, basic and acid dyes in the presence of radical initiators has been studied[7–15] and previous parts of this paper[16–20] have discussed the effects of radical initiators on the dyeing of nylon and polyester fibres with various classes of disperse dye. This part of the paper describes the effects of two radical initiators on the dyeing of wool with four classes of disperse dye as well as the possible reactions occurring between the radical initiators and the substrate.

EXPERIMENTAL

Materials

Fibres, dyes and chemicals

Scoured and bleached woven wool fabric (236·6 g/m^2) obtained from the International Wool Secretariat was employed. A total of 18 commercial disperse dyes were used, namely four nitrodiphenylamine, five azo, seven anthraquinone and two quinophthalone dyes, each kindly supplied by the respective manufacturer shown in Table 1.

All chemicals used were laboratory grade reagents obtained from either Aldrich or BDH. Sodium acetate and acetic acid were used to control dyebath pH, and ammonium persulphate (APS) and thiourea dioxide (TDO) were used as radical initiators. Dyapol PT (YCL) was used as a dispersing agent and Sandozin NIE (S) as a wetting agent.

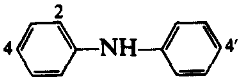
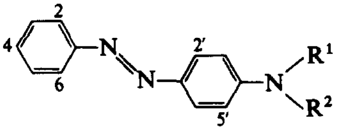
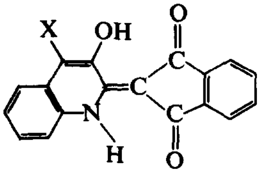
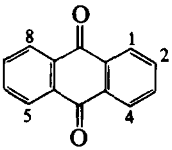
Procedures

All dyeings and treatments were carried out in sealed, stainless steel pots of 300 ml capacity housed in a John Jeffries laboratory-scale Rota Dyer.

Dyeing

The dyebath was set with 2% owf commercial disperse dye and 1 g/litre

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=C_2H_5, R^2=C_2H_4CN	Seriliene Orange 2RL	Orange 25	YCL
4-NO_2, R^1=C_2H_5, R^2=C_2H_4OH	Serisol Fast Scarlet BD	Red 1	YCL
2-CN, 4-NO_2, R^1=C_2H_2CN, R^2 = C_2H_5	Foron Rubine S-EGFL	Red 73	S
4-NO, 2'-Cl, R^1=R^2=C_2H_4OH	Celliton Scarlet R	Red 7	BASF
4-NO_2, 2'-CH_3, R^1=R^2=C_2H_4OH	Celliton Red GG	Red 17	BASF
Quinophthalone			
X=H	Seriliene 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-$NHCH_3$,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

Dyapol PT in either the absence or presence of various concentrations 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.[16] Dyeing was commenced at 40°C, and the temperature was raised to 98°C at a rate of 2°C/min and maintained at this temperature for 60 min. At the end of dyeing, the rinsed (cold tap water) dyed samples were scoured in a solution containing 2% owf Sandozin NIE at 98°C for 5 min, and the rinsed (cold tap water) dyed samples were then allowed to dry in the open air.

Treatment of wool with radical initiator for scanning electron microscopy (SEM) analysis

Treatment was carried out either in distilled water or in a dyebath containing 2% omf CI Disperse Violet 4 in both the absence and presence of various concentrations (10 M and 20 mM) of APS or TDO, the pH being adjusted to 5·5 using 0·02 M acetic acid/0·17 M sodium acetate buffer.[16] Treatment was commenced at 40°C, and the temperature was raised to 98°C at a rate of 2°C/min and maintained at this temperature for 60 min. For the treatment carried out in the absence of CI Disperse Violet 4, the treated samples were rinsed thoroughly in cold tap water and allowed to dry in the open air; in the case of the samples obtained using CI Disperse Violet 4, the composition of the dyebath and the scouring and drying procedures employed were identical to those described above.

Colour measurement

The CIELab coordinates and Kubelka–Munk (K/S) values were calculated from the reflectance values of dry, rinsed, dyed wool samples, which were measured using the instrument and procedure previously described.[16]

Wash and light fastness determination

The fastness of the dyed wool samples to washing (ISO CO2) and to light (ISO BO2) was determined according to the standard methods.[21]

SEM analysis

The fibre sample was mounted on a standard aluminium SEM stub and gold-coated using a Bio-Rad Diode Sputter coating unit (the thickness of the coating was *c.* 30 μm). The sample was magnified in the range of ×1200 to ×4000 and irradiated with a 6 to 15 kV electron beam using a Jeol JSM-820 scanning electron microscope. Electron micrographs were recorded using Ilford 120 FP4 35 mm roll film housed in a Mamiya medium format camera.

RESULTS AND DISCUSSION

Effect of concentration of radical initiator in wool dyeing

An initial study, using an an anthraquinone (CI Disperse Violet 4) and an azo (CI Disperse Red 7) disperse dye, was made on the effect of concentration of reductant and oxidant on dyeing. The results obtained for the dyeing of wool with CI Disperse Violet 4 in both the absence and presence of various concentrations (between 0 and 30 mM) of ammonium persulphate or thiourea dioxide are shown in Table 2. The results clearly demonstrate that at each of the four concentrations of APS used the wash fastness of the dyeings was considerably higher than that of the control dyeing and, also, that the fastness to washing increased with increasing concentrations of APS employed; in contrast, only concentrations of 20 and 30 mM TDO resulted in enhanced wash fastness, this enhancement being only marginal. Table 2 also shows that both APS and TDO enhanced the light fastness of the dye on wool, this enhancement increasing with increase in concentration of the radical initiator employed. However, both APS and TDO reduced the colour yield of the dyeings (as shown by the lower K/S values) and, especially in the case of

TABLE 2

Colorimetric and Fastness Data (ISO CO2 and BO2) of Wool Dyed with CI Disperse Violet 4 in the Presence of Various Concentrations of Radical Initiator at 98°C for 60 min

Reagent	*(mM)*	*K/S*	λ_{max} *(nm)*	*L**	*a**	*b**	*c**	*h°*	*E*	*W*	*C*	*LF*
	0	7·3	580	37·2	9·3	−32·4	33·7	286·0	1	1–2	3	2
	6·25	5·3	580	37·1	−1·4	−7·9	8·0	260·0	3	4	4–5	3
APS	10	4·6	400	39·3	0·0	−2·8	2·8	270·0	3–4	4–5	4–5	4
	20	5·2	400	43·6	4·5	6·4	7·8	54·9	4	4–5	5	4
	30	4·7	400	49·0	7·6	12·2	14·4	58·1	4–5	5	5	4
	6·25	10·2	580	33·0	12·0	−34·0	36·1	289·4	1	1	2–3	2
TDO	10	10·0	580	33·3	12·0	−34·3	36·3	289·3	1	1	2–3	2
	20	3·4	560	43·0	7·7	−5·0	9·2	327·0	1	2–3	3–4	3
	30	3·1	480	47·1	12·4	6·1	13·8	26·2	1–2	3	4–5	3

E: effect on shade; W: staining of wool adjacent; C: staining of cotton adjacent; LF: light fastness.

TABLE 3
Colorimetric and Fastness Data (ISO CO2 and BO2) of Wool Dyed with CI Disperse Red 7 in the Presence of Various Concentrations of Radical Initiator at 98°C for 60 min

Reagent	*(mM)*	*K/S*	λ_{max} *(nm)*	L^*	a^*	b^*	c^*	h°	*E*	*W*	*C*	*LF*
APS	0	10·5	500	43·3	41·2	22·3	46·9	28·4	1	2	3	3
	6·25	8·3	480	46·3	38·2	27·3	47·0	35·6	1	3	4	4
	10	7·0	480	48·7	35·1	29·5	45·9	40·4	1	3	4	4
	20	5·8	440	54·5	29·3	36·3	46·7	51·1	1	4	4–5	4
	30	4·9	400	62·1	19·8	36·6	41·6	61·6	2	4–5	5	4
TDO	6·25	7·2	500	47·2	38·5	21·8	44·2	29·5	1	2–3	3–4	4
	10	3·5	480	54·3	30·1	19·2	35·7	32·5	1	3-4	4–5	4
	20	0·9	400	79·2	0·1	14·1	14·1	89·6	—[a]	—[a]	—[a]	—[a]
	30	0·7	400	85·2	−1·3	15·2	15·3	94·9	—[a]	—[a]	—[a]	—[a]

E: effect on shade; W: staining of wool adjacent; C: staining of cotton adjacent; LF: light fastness.

[a] No measurement made owing to low colour yield obtained.

APS, markedly altered both the chroma and chromaticeness of the dyeings, these effects being greatest for concentrations of 20 and 30 mM of each radical initiator. In the case of APS, the colour of the dyeings obtained using a concentration in excess of 6·25 mM was considerably different to that obtained using a concentration of 6·25 mM. The results (Table 2) show that, in general, the dyeings obtained using APS were paler (as shown by the lower K/S values and higher L^* values), duller (as shown by the lower c^* values) and of a much different hue (as evidenced by the lower a^* values and higher b^* values) than the control dyeing, the hue of the APS dyeings varying for the different concentrations of APS used. The dyeings secured using TDO were paler (as given by the higher L^* values) and redder (as evidenced by the similar a^* values, but higher b^* values and higher h° values) and, in the cases of 20 and 30 mM TDO much duller (as shown by the lower c^* values) than the control dyeing. Table 2 also shows that high concentrations of both APS and TDO imparted a hypsochromic shift to the dyeings.

Table 3 shows that, when wool was dyed using CI Disperse Red 7 in both the absence and presence of various concentrations (between 0 and 30 mM) of APS or TDO, a hypsochromic shift in λ_{max} of the dyeings was observed. The dyeings obtained using APS were paler (as given by the lower K/S values and higher L^* values), more orange (as evidenced by the lower a^* values, higher b^* values and higher h° values) and duller (as shown by the lower c^* values) than the control dyeing. In contrast to the results obtained for the APS dyeings, those obtained in the presence of TDO were paler (as given by the lower K/S values and higher L^* values), duller (as shown by the lower c^* values) and more yellow (as evidenced by the lower a^* values, lower b^* values and higher h° values) than the control dyeing. This observed difference in colour between the control dyeing and the dyeings carried out in the presence of APS and TDO increased with increasing concentrations of the radical initiators used; indeed, the TDO dyeings became virtually colourless when a concentration in excess of 10 mM was used. Both the APS and TDO dyeings exhibited slightly greater fastness to both washing and light than the control dyeing, the wash fastness of the APS dyeings increasing with increase in concentration of oxidant used.

As discussed in previous studies,[18,19] the light fastness of a dyeing is influenced by several factors; generally, the photodegradation of a dye occurs via oxidative decomposition on nonprotein fibres and via reductive degradation on protein fibres.[22–25] It has been proposed that the histidine and perhaps also the tryptophan residues in wool are responsible for the photoreduction of dyes on the substrate,[22–25] this suggestion gaining support from the observation that photoreduction occurred on nonprotein fibres into which histidine had been incorporated.[22] Additionally, the high light scattering properties of the scaler surface of wool may retard the fading of dyes owing to a reduction in the amount of light absorbed by the dye.[22] No attempt was made in this work to elucidate the cause of the observed increase in light fastness of the two dyes imparted by both the oxidant and the reductant (Tables 2 and 3), this being the subject of further investigations.

Despite the considerable shift in λ_{max} that occurred for the dyeing of wool with CI Disperse Violet 4 and CI Disperse Red 7 in the presence of both APS and TDO, Tables 2 and 3 clearly show that both radical initiators enhanced the wash fastness of the dyes; indeed, the fastness rating of CI Disperse Violet 4 to ISO CO2 on the substrate was increased from 1 to 4–5 using APS. Such a marked increase in fastness to washing cannot solely be attributed to the radical initiator having enhanced those forces of interactions (dispersion, dipole–dipole, hydrogen bonding, etc.) considered to operate between a disperse dye and the wool substrate. Thus, as discussed in previous studies of the dyeing of nylon and polyester with disperse dyes in the presence of radical initiators,[18,19] the observed enhancement of wash fastness (Tables 2 and 3) may be attributable to covalent attachment of the dye to the fibre and/or the formation of a dye polymer within the substrate. Since the results shown in Tables 2 and 3 reveal that, as found for both the dyeing of polyester[16] and nylon 6.6[18,19] with disperse dyes in the presence of radical initiators, the effects imparted by the oxidant and reductant were significantly influenced by both the nature and concentration of radical initiator used, subsequent work was carried out in order to examine the effects of dye structure on the dyeing of wool in the presence of radical initiators.

Effect of radical initiators on nitrodiphenylamine disperse dyes

The results obtained for the dyeing of wool with four commercial nitrodiphenylamine disperse dyes in both the absence and presence of 10 mM APS or 20 mM TDO are shown in Table 4. As observed for the dyeing of nylon 6.6 in the presence of the reductant,[18] Table 4 clearly shows that a bathochromic shift occurred in λ_{max} of the TDO dyeings using CI Disperse Yellow 1 and CI Disperse Yellow 9. The APS and TDO dyeings of CI Disperse Yellow I and CI Disperse Yellow 9 on wool were generally deeper (as given by the lower L^* values and higher K/S values) and redder (as evidenced by the higher a^* values and lower h° values) than the control dyeing. The dyeings obtained using CI Disperse Yellow 33 and CI Disperse Yellow 42 (2-nitrodiphenylamine) in the presence of APS were deeper (as shown by the higher K/S value and lower L^* value) and more orange (as given by the higher a^* value and lower h°

TABLE 4

Colorimetric and Fastness Data (ISO CO2 and BO2) of Wool Dyed with Nitrodiphenylamine Disperse Dyes at 98°C for 60 mins

CI Disperse	*Reagent*	*K/S*	λ_{max} *(nm)*	L^*	a^*	b^*	c^*	h°	*E*	*W*	*C*	*LF*
	NIL	8·5	400	69·0	10·7	49·1	50·3	77·7	1	3	4–5	3
Yellow 1	APS	19·8	400	55·2	17·2	49·5	52·4	70·8	1–2	4–5	5	4
	TDO	7·4	440	55·5	27·8	42·3	50·6	56·7	1–2	4–5	4–5	1
	NIL	6·3	400	66·2	15·0	45·2	47·6	71·6	1–2	3	4–5	4
Yellow 9	APS	16·0	400	54·3	16·1	43·6	46·5	69·7	3	4–5	4–5	5
	TDO	6·9	420	56·4	20·1	40·4	45·1	63·4	2	4	4–5	3
	NIL	2·4	420	78·5	2·3	46·0	46·1	87·1	1	4	5	6
Yellow 33	APS	5·2	420	68·1	11·1	48·3	49·6	77·1	2	4–5	5	6
	TDO	0·8	400	81·7	0·9	25·3	25·3	88·0	—[a]	—[a]	—[a]	—[a]
	NIL	3·1	420	77·5	2·0	49·1	49·1	87·7	1	4	5	4
Yellow 42	APS	4·1	400	72·1	6·1	46·2	46·6	82·5	1	4	5	6
	TDO	0·7	400	82·9	0·8	16·9	16·9	87·3	—[a]	—[a]	—[a]	—[a]

E: effect on shade; W: staining of wool adjacent; C: staining of cotton adjacent; LF: light fastness.

APS: 10 mM ammonium persulphate; TDO: 20 mM thiourea dioxide.

[a] No measurement made owing to low colour yield obtained.

value) than the control dyeing; in contrast, the dyeings obtained for the TDO dyeings of CI Disperse Yellow 33 and CI Disperse Yellow 42 were paler (as given by the lower K/S values and higher L^* values) and greener (as evidenced by the lower a^* values and lower b^* values) than the control dyeing. The shade changes observed for the dyeings carried out in the presence of the radical initiator may be attributed to the presence of degradative products of the dye, to dye polymer formation or to dye-fibre covalent attachment.

A hypsochromic shift in λ_{max} of the wool dyeings was found to have occurred for dyeings obtained using CI Disperse Yellow 42 in the presence of both APS and TDO as well as the TDO dyeings secured using CI Disperse Yellow 33; these effects were not observed for the corresponding nylon 6·6 dyeings.[18] Such a difference in shade change observed for the same dye on the two different substrates may be attributable to a difference in the interactions occurring between the dyes and the fibres;[26] a further possible cause of this difference in shade observed for the same dyes on nylon 6.6 and wool is that the radical initiators differed in their degradative effects on the two substrates.

For each of the four nitrodiphenylamine dyes, the dyeings obtained using APS exhibited higher colour yield than the respective control dyeings whilst the corresponding TDO dyeings (with the exception of CI Disperse Yellow 9), were of lower colour yield than the control dyeings. Indeed, the reductant imparted very low colour yield to CI Disperse Yellow 33 and CI Disperse Yellow 42, thus showing that these two 2-nitrodiphenylamine dyes were more susceptible to reduction by TDO than the two 2,4-dinitrodiphenylamine dyes (CI Disperse Yellow 1 and CI Disperse Yellow 9) on wool, as was previously observed for the dyeing of nylon 6.6 with the four dyes under consideration in the presence of APS and TDO.[18]

Table 4 clearly shows that CI Disperse Yellow 9 and CI Disperse Yellow I exhibited enhanced wash fastness on wool when dyeing had been carried out in the presence of each radical initiator; CI Disperse Yellow 33 displayed enhanced wash fastness when dyeing had been carried out in the presence of APS, whereas the wash fastness of CI Disperse Yellow 42 was little effected by both radical initiators. These findings are similar to those obtained when nylon 6.6 had been dyed using the four nitrodiphenylamine dyes in the presence of APS and TDO.[18] Table 4 also reveals that the light fastness of CI Disperse Yellow 1, CI Disperse Yellow 9 as well as CI Disperse Yellow 42 on wool was enhanced by APS and that the light fastness of the remaining dye was unaffected by the oxidant; these findings differ to those secured on nylon 6.6 where it was found that the light fastness of CI Disperse Yellow 1 and CI Disperse Yellow 9 was reduced and that of CI Disperse Yellow 33 and CI Disperse Yellow 42 was unchanged by the oxidant.[18] This result implies that the oxidized nitrodiphenylamine derivatives are more stable to photodegradation on wool than on nylon 6.6. In the case of TDO, no such direct comparison can be made between its effect on the light fastness of the four dyes on wool and on nylon 6.6, since, owing to the very low colour yield obtained for CI Disperse Yellow 33 and CI Disperse Yellow 42 on wool (Table 4), the light fastness of these two dyeings was not undertaken. However, since Table 4 clearly shows that TDO reduced the light fastness of CI Disperse Yellow 1 and CI Disperse Yellow 9 on wool and that the reductant lowered the light fastness of all four dyes on nylon 6.6,[18] it can be proffered that the reductant has a deleterious effect on the light fastness of nitrodiphenylamine dyes on both types of polyamide substrate.

Effect of radical initiators on azo disperse dyes

In view of the results shown in Table 3, namely that CI Disperse Red 7 on wool was readily degraded at concentrations of TDO in excess of 10 mM, the following work was carried out using a reductant concentration of 10 mM. Wool fibre was dyed using five commercial azo disperse dyes in both the absence and presence of 10 mM APS or 10 mM TDO at 98°C for 60 min.

Table 5 shows that, in general, the wash fastness of the five dyes on wool was slightly improved when dyeing had been carried out in the presence of each radical initiator and also that the shades of the resulting dyeings were significantly different to the respective control dyeing carried out in the absence of radical initiator. The dyeings obtained using APS were generally yellower (as evidenced by the higher b^* values and higher $h°$ values) and cleaner (as given by the higher c^* values) than the respective control dyeing; the TDO dyeings generally were also more yellow (as evidenced by the higher b^* values and higher $h°$ values) than the respective control dyeing. With the exception of the dyeings obtained using CI Disperse Orange 25 and CI Disperse Red 1 in the presence of TDO, both the reductant and the oxidant imparted a hypsochromic shift to the λ_{max} of the dyeings.

It has been found that the colour of the oxidative products obtained from an azo dye using oxidizing agents were similar to those of the photofading products of azo dyes.[22] As discussed in a previous study[18] of the dyeing of nylon with azo disperse dyes in the presence of radical initiators, since azo dyes can undergo both oxidative and reductive degradation, the shade changes observed for each of the five dyes on

TABLE 5
Colorimetric and Fastness Data (ISO CO2 and BO2) of Wool Dyed with Azo Disperse Dyes at 98°C for 60 mins

CI Disperse	*Reagent*	*K/S*	λ_{max} *(nm)*	*L**	*a**	*b**	*c**	*h°*	*E*	*W*	*C*	*LF*
	NIL	2·2	480	63·7	29·4	25·3	38·8	40·7	1	3	4	3
Orange 25	APS	3·6	460	58·6	29·1	32·2	43·4	47·9	1	3	4	3
	TDO	2·3	480	63·8	28·7	27·8	40·0	44·1	1	3–4	4	3
	NIL	7·2	500	44·7	35·8	20·3	41·2	29·6	1	2	2–3	4
Red 1	APS	11·9	480	40·2	34·6	27·3	44·1	38·3	1	3	4	4
	TDO	7·3	500	45·1	36·5	20·4	41·8	29·2	1	2	2–3	4
	NIL	4·4	540	43·2	24·7	−6·2	25·5	345·9	1	2	3	2
Red 73	APS	5·9	520	40·1	26·5	3·0	26·7	6·5	1	2	3–4	3
	TDO	6·1	500	41·3	29·5	12·5	32·0	23·0	1	2–3	4	3
	NIL	10·5	500	43·3	41·2	22·3	46·9	28·4	1	2	3	3
Red 7	APS	7·0	480	48·7	35·1	29·5	45·9	40·0	1	3	4	4
	TDO	3·5	480	54·3	30·1	19·2	35·7	32·5	1	3–4	4–5	4
	NIL	16·6	580	32·3	37·9	8·5	38·8	12·6	1	2	2–3	4
Red 17	APS	7·2	420	47·4	29·9	29·6	42·1	44·7	1–2	4–5	4–5	4
	TDO	3·1	500	52·5	30·0	12·1	32·3	22·0	1	4	4–5	4

E: effect on shade; W: staining of wool adjacent; C: staining of cotton adjacent; LF: light fastness.
APS: 10 mM ammonium persulphate; TDO: 10 mM thiourea dioxide.

wool (Table 5) may be due to the presence, within the fibre, of mixtures of degradative products imparted by the radical initiators.

It has been proposed that although electron withdrawing groups within the alkyl substituents in the electron donor ring increase the photostability of azo dyes on polyester, their presence decreases the stability of the dyes on nylon 6.6.[27,28] The results in Table 5 demonstrate that, on wool, the light fastness of CI Disperse Red 73, which contains a cyanoethyl group, and of CI Disperse Red 7, which contains a hydroxyethyl group, was slightly improved in the presence of both APS and TDO, and that the light fastness of CI Disperse Orange 25, which contains a cyanoethyl group, and also CI Disperse Red 1 and CI Disperse Red 17, both of which contain hydroxyethyl groups, was little affected by both APS and TDO. However, each of the five azo disperse dyes used exhibited slightly enhanced wash fastness when dyeing had been carried out in the presence of both radical initiators. These findings imply that no clear correlation exists between dye structure and the effects of both APS and TDO on the light fastness and enhanced wash fastness of azo disperse dyes on wool.

The shade and colour yield of the dyeings obtained on wool (Table 5) differed from those secured for the same five azo disperse dyes on nylon 6.6;[18] this may be attributed to the radical initiators differing in their effects on the two substrates as well as to differences in the interactions occurring between the modified substrates and the modified dye. It is, therefore, apparent that the effects imparted by the radical initiators vary for the two polyamide (wool and nylon) fibres and that further research is required to investigate this particular phenomenon.

Effect of radical initiators on anthraquinone disperse dyes

The results obtained for the dyeing of wool with seven commercial anthraquinone disperse dyes in both the absence and presence of 10 mM

TABLE 6

Colorimetric and Fastness Data (ISO C02 and BO2) of Wool Dyed with Anthraquinone Disperse Dyes

CI Disperse	*Reagent*	*K/S*	λ_{max} *(nm)*	*L**	*a**	*b**	*c**	*h°*	*E*	*W*	*C*	*LF*
Violet 1	NIL	6·9	560	38·6	20·6	−29·3	35·8	305·1	1	1–2	2–3	3
	APS	7·4	580	31·9	1·6	−6·1	6·3	284·7	3–4	3–4	4–5	4
	TDO	3·8	560	41·5	12·9	1·1	12·9	4·9	1	2	3–4	3
Violet 4	NIL	7·3	580	37·2	9·8	−32·4	33·9	286·8	1	1–2	3	2
	APS	4·6	400	39·3	0·0	−2·8	2·8	270·0	3–4	4–5	4–5	4
	TDO	3·4	560	43·0	7·7	−5·0	9·2	327·0	1	2–3	3–4	3
Red 4	NIL	1·7	520	62·2	33·0	1·7	33·0	2·9	1	2–3	3	4
	APS	3·6	400	54·1	9·8	15·1	18·0	57·0	3	4	4–5	4
	TDO	1·8	400	75·1	8·8	29·9	31·2	73·6	2	4–5	4–5	4
Red 11	NIL	4·4	540	47·5	35·4	−20·7	41·0	329·7	1	1–2	2	3
	APS	5·2	560	35·8	4·9	−0·5	4·9	354·2	4	4	4	4
	TDO	4·8	580	43·9	34·6	−10·8	36·3	342·7	1	1–2	2	4
Red 60	NIL	1·5	520	61·6	29·8	−0·3	29·8	359·4	1	3	4	3
	APS	2·4	400	57·4	23·1	11·3	25·7	26·1	1	3	4	4
	TDO	4·4	420	52·0	27·7	18·6	33·4	33·9	1	2–3	3–4	4
Blue 3	NIL	4·0	600	48·2	−6·6	−22·6	23·5	253·7	1	2–3	3–4	2
	APS	4·6	600	38·4	−2·0	−4·0	4·5	243·4	3–4	4	4–5	3
	TDO	3·2	600	43·1	3·9	−2·4	4·6	328·4	1	3	4–5	2
Violet 8	NIL	4·6	580	43·3	5·2	−27·5	28·0	280·7	1	1–2	3	5
	APS	6·1	600	36·8	−6·4	−6·7	9·3	226·3	3–4	4	4–5	5
	TDO	10·6	580	32·2	7·2	−26·2	27·2	285·4	1	1–2	2–3	5

E: effect on shade; W: staining of wool adjacent; C: staining of cotton adjacent; LF: light fastness.

APS: 10 mM ammonium persulphate; TDO: 20 mM thiourea dioxide.

APS or 20 mM TDO are shown in Table 6. For the three red dyes used, the dyeings carried out in the presence of APS were generally 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 lower a^* values, higher b^* values and higher $h°$ values) than that carried out in the absence of oxidant. APS imparted a deeper (as shown by the higher K/S value and lower L^* value), duller (as evidenced by the lower c^* value) and more orange hue (as given by the higher a^* value, higher b^* values and lower $h°$ values) to the blue dye employed, whilst the APS dyeings obtained for the three violet dyes were duller (as evidenced by the lower c^* values) and greener (as given by the lower a^* values, higher b^* values and lower $h°$ values) than the control dyeing. The lightness (as given by the L^* values) of the APS dyeings varied between dyes, being either higher or lower than the control dyeings and therefore, either paler or deeper shades, respectively, were produced using the oxidant. In a manner similar to APS, TDO imparted a more orange hue (as evidenced by the lower a^* values, higher b^* values and higher $h°$ values) to the three red dyes; the lightness (L^*) and chroma (c^*) of the TDO dyeings obtained using the three red dyes varied. For the blue dye used, the dyeing carried out in the presence of TDO was duller (as shown by the lower c^* value) and more purple (as evidenced by the higher a^* value, higher b^* value and higher $h°$ value) than the control dyeing; the reductant imparted a duller (as given by the lower c^* values) and reddish hue (as shown by the higher b^* values and higher $h°$ values) to the three violet dyes, the lightness of these three latter dyeings varying between dyes.

The shade changes that were imparted to the dyeings by the radical initiators may be attributed to the presence of degradative products of the dye,[19] to dye polymer formation or to dye–fibre covalent attachment. The shade of the dyeings obtained on wool (Table 6) differed from those secured for the same anthraquinone disperse dyes on nylon 6.6;[19] this may be attributed to the different effects on the dye and the substrates imparted by the radical initiators and also to differences in the interactions between the modified substrates and the modified dyes.

The light fastness of several of the five dyes on wool was slightly improved when dyeing had been carried out in the presence of both APS and TDO; this may be due to the derivatives of the dyes produced by oxidation and reduction being more stable than the parent dyes to photofading on the substrate. The APS dyeings exhibited significantly improved wash fastness, whereas the dyeings obtained in the presence of TDO were either unaffected or showed only a slight increase in wash fastness. Table 6 also shows that the wash fastness of those dyes which contained amino, methylamino or hydroxyethylamino substituents were improved to a greater extent than that of CI Disperse Red 60 which contained a phenyl substituent, when dyeing had been carried in the presence of radical initiator. The finding[29,30] that 1-arylamino substituted anthraquinone disperse dyes exhibit high light fastness on both polyester and nylon, this being attributed to the benzene ring enhancing the rate of deactivation of the excited singlet state, may explain the finding that the light fastness of CI Disperse Red 60, which contained a phenyl substituent, was little influenced by the two radical initiators.

As proposed in a previous study of the dyeing of nylon 6.6 with anthraquinone disperse dyes in the presence of radical initiators,[19] the enhanced wash fastness of alkylamino anthraquinone dyes imparted by the radical initiators may be attributed to the presence of either diimine or monoimine anthraquinone derivatives which could either react with 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 anthraquinone dyes may be due to the generation of the corresponding anthrasemiquinone radical anion and its covalent attachment to a fibre radical or to the alkylamino group of the dye reacting with an amino end group of the substrate.

Effect of radical initiators on quinophthalone disperse dyes

The results obtained for the dyeing of wool with two commercial quinophthalone disperse dyes in both the absence and presence of 10 mM APS or 20 mM TDO are shown in Table 7. It is evident that the TDO

TABLE 7
Colorimetric and Fastness Data (ISO CO2 and BO2) of Wool Dyed with Quinophthalone Disperse Dyes

CI Disperse	*Reagent*	*K/S*	λ_{max} *(nm)*	L^*	a^*	b^*	c^*	h°	*E*	*W*	*C*	*LF*
Yellow 54	NIL	2·1	440	79·7	−1·6	42·6	42·6	92·2	1	3–4	3	6
	APS	3·3	400	73·2	4·2	43·1	43·3	84·4	1–2	3	2–3	5
	TDO	2·3	440	81·9	−2·2	47·7	47·8	92·6	1	3	2–3	3
Yellow 64	NIL	4·5	440	74·4	5·0	54·8	55·0	84·8	1	4	3–4	6
	APS	4·6	440	72·5	3·3	50·4	50·5	86·3	1	3–4	3	4
	TDO	5·3	440	78·7	1·9	64·0	64·0	88·3	1	4	3	3

E: effect on shade; W: staining of wool adjacent; C: staining of cotton adjacent; LF: light fastness.
APS: 10 mM ammonium persulphate; TDO: 20 mM thiourea dioxide.

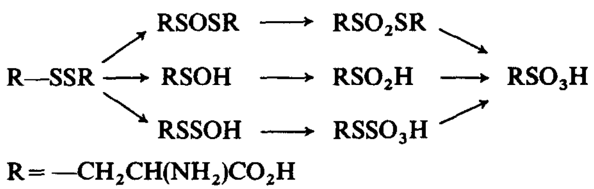
dyeings of these two dyes were brighter (as showed by the higher *c** values) and more yellow (as evidenced by the lower *a** values, higher *b** values and higher *h*° values) than the control dyeing. Although the APS dyeings of the two dyes were deeper (as shown by the lower *L** values and higher K/S values) than the control dyeings, the APS dyeing of CI Disperse Yellow 54 was brighter (as given by the higher *c** value) and more orange (as evidenced by the higher *a** value, higher *b** value and lower *h*° value) than the control dyeing, whilst the APS dyeing of CI Disperse Yellow 64 was duller (as shown by the lower *c** value) and more yellow (as given by the lower *a** value, lower *b** value and higher *h*° value) than the respective control dyeing. A hypsochromic shift occurred when wool had been dyed with CI Disperse Yellow 54 in the presence of APS, this being attributable to the degradation of quinophthalone.[31] The shade changes observed for the dyeings on wool obtained using the two quinophthalone disperse dyes in the presence of the radical initiators can, as discussed in the previous study of the application of the two dyes to nylon 6.6 in the presence of the radical initiators,[19] be attributed to the presence of mixtures of degradation products of the dyes within the substrate. The light fastness of the dyeings obtained using each of the two quinophthalone disperse dyes was reduced by both the oxidant and the reductant (Table 7); this may be due to the modified derivatives of the dyes being more susceptible to photodegradation on the substrate.

Although the colour yield of each of the dyes on wool was enhanced using each radical initiator, the dyeings exhibited little improvement in wash fastness and no change in λ_{max} occurred. Consequently, the enhanced colour yield imparted by both APS and TDO may be due to the radical initiator having damaged the wool epicuticle, resulting in an increase in both the rate and extent of penetration of the dye into the fibre.

The results obtained using the two quinophthalone disperse dyes on wool and also on nylon 6.6[19] therefore indicate that both dyes are little influenced by APS and TDO and that enhanced wash fastness cannot be achieved using this particular dyeing system.

Theoretical considerations regarding wool

A free radical dyeing mechanism has been proposed to explain the results obtained for the dyeing of wool with direct, basic and acid dyes in the presence of redox systems.[7–15] The oxidative and reductive bleaching of wool fibres has been widely studied[32] and the following comprises a brief account of this large area.



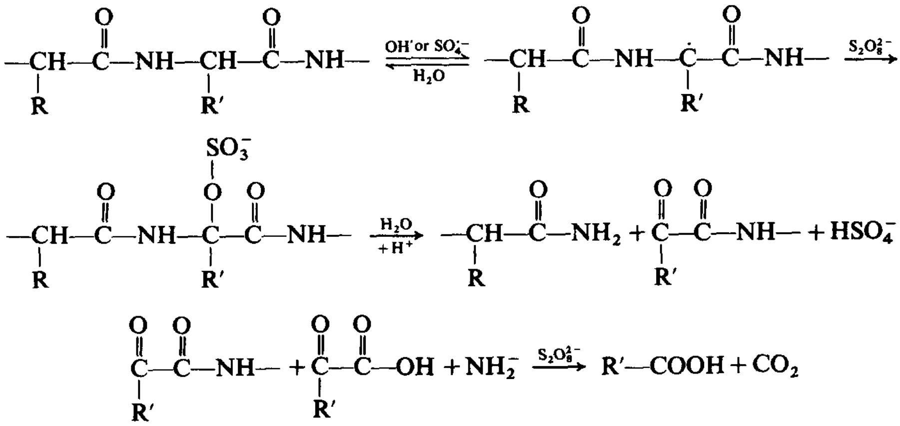
Scheme 1

The disulphide groups of many of the cystine residues in wool cross-link adjacent protein chains, thereby restraining the latter's conformational rearrangement which considerably influences many fibre properties. It has been proposed that oxidants react predominantly with cystine residues in wool, yielding cysteic acid residues (Scheme 1),[32] which can result in the enhanced uptake of basic dyes.

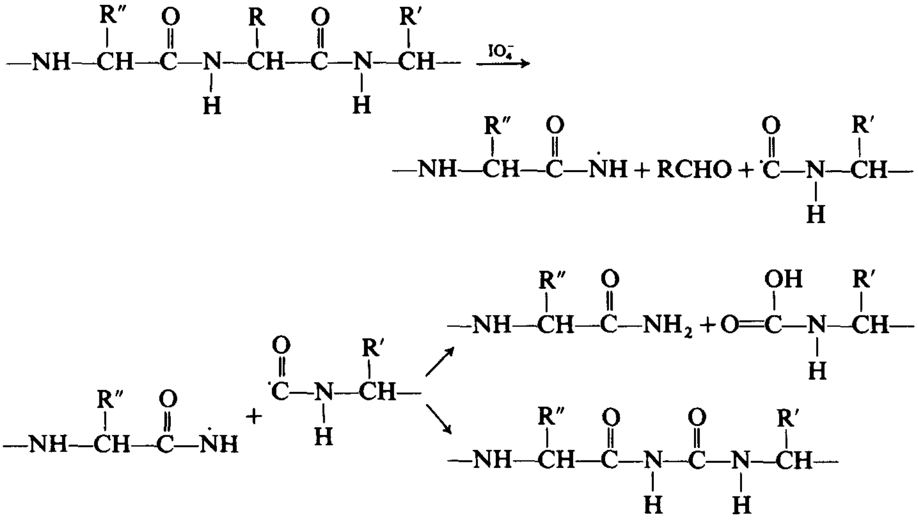
Needles[33] studied the degradation of wool with persulphate and concluded that cleavage of the protein chain was caused primarily by both sulphate and hydroxyl radicals (Scheme 2).

Kantouch and Bendak[34] proposed a different mechanism (Scheme 3) to describe the oxidation of wool with periodate.

Oxidative bleaching under alkaline conditions gives superior whiteness, but imparts slightly more damage to wool than does bleaching under acidic conditions; since oxidative bleaching also increases the sensitivity of wool to damage by acids, careful control of the pH of the dyebath is necessary so as to minimize fibre damage during the dyeing of wool which has been bleached with oxidants.[32] Lewis[35] proposed that wool fibres undergo hydrolysis during dyeing (Scheme 4) and concluded that



Scheme 2



Scheme 3

whilst damage that occurs within the pH range 1·8–3 is mainly due to amide bond splitting, that which occurs above pH 3 is increasingly associated with disulphide bond hydrolysis; under alkaline conditions, fibre damage involves both disulphide and amide bond cleavage.

Treatment of wool with reductants was found to convert disulfide groups into thiol groups, each cystine residue generating two cysteine residues (Scheme 5).[36]

Thiourea dioxide is an effective bleaching agent for wool and has less effect on the physical properties of the fibre than have other reducing bleaching agents.[37] Davidson[38] proposed that TDO can reduce the photo yellowing of wool and promote photobleaching of the fibre; the bleaching effect of TDO is considered to be due to the presence of sulphinic acid.[37–39] Oxidation–reduction bleaching has also been employed, which involves bleaching with hydrogen peroxide and subsequent treatment with a reducing agent.[39]

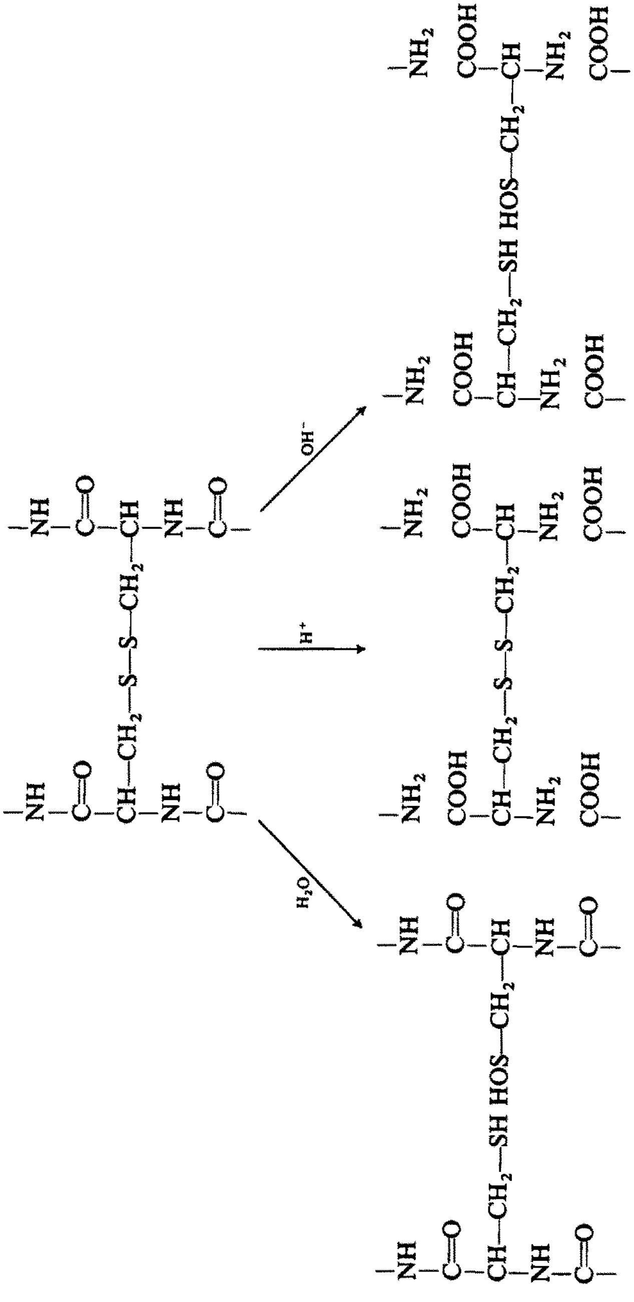
Electron spin resonance (ESR)[40,41] analysis of wool which had been irradiated with ionizing radiation revealed the following radicals:

(1) $>CH_2{-}S^{\cdot}$

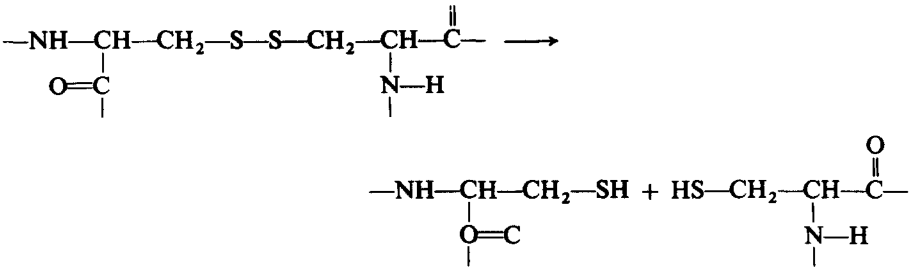
(2) $>C^{\cdot}{-}CH_3$

(3) $>C^{\cdot}{-}CH_2{-}R$

(4) $>C^{\cdot}H$



Scheme 4



Scheme 5

However, Barkakaty and Keighley[40,41] proposed a different mechanism to account for their ESR findings based on τ-irradiated wool, which included the production of the following radical species:

(1) $>CO^{\cdot}$ (doublet)

(2) $R-CH_2-CH_2-C^{\cdot}H-CH_2-R$ (quartet)

(3) the cystine type resonance (triplet).

From the above discussion, it can, therefore, be proposed that, during the dyeing of wool with disperse dyes in the presence of APS or TDO, various radical derivatives of the protein substrate are generated. Such fibre radicals can be considered to be capable of forming covalent linkages with dye radicals, which would account for the enhanced wash fastness observed for the dyeings carried out in the presence of both the oxidant and reductant. Furthermore, such fibre radical–dye radical interactions may also contribute to the shade changes and modified light fastness obtained for the APS and TDO dyeings.

SEM analysis of wool fibre

The results of an SEM investigation of the surface of wool fibre that had been treated with two concentrations (10 and 20 mM) of APS and TDO in the absence or presence of 2% owf CI Disperse Violet 4 at pH 5·5 for 60 min at 98°C are shown in Figs 1 and 2. Figure 1 clearly shows that treatment with both 10 and 20 mM of APS or TDO caused severe damage to the epicuticle of the fibre whilst Fig. 2 clearly demonstrates that, in the presence of CI Disperse Violet 4, the extent of damage to the epicuticle imparted by APS and TDO was lower than that imparted by the reagents in the absence of dye. These results imply that, in the presence of the disperse dye, both the oxidant and reductant attacked CI Disperse Violet 4 in preference to the substrate, as a consequence of which, less damage occurred at the wool surface. In a manner analogous to that

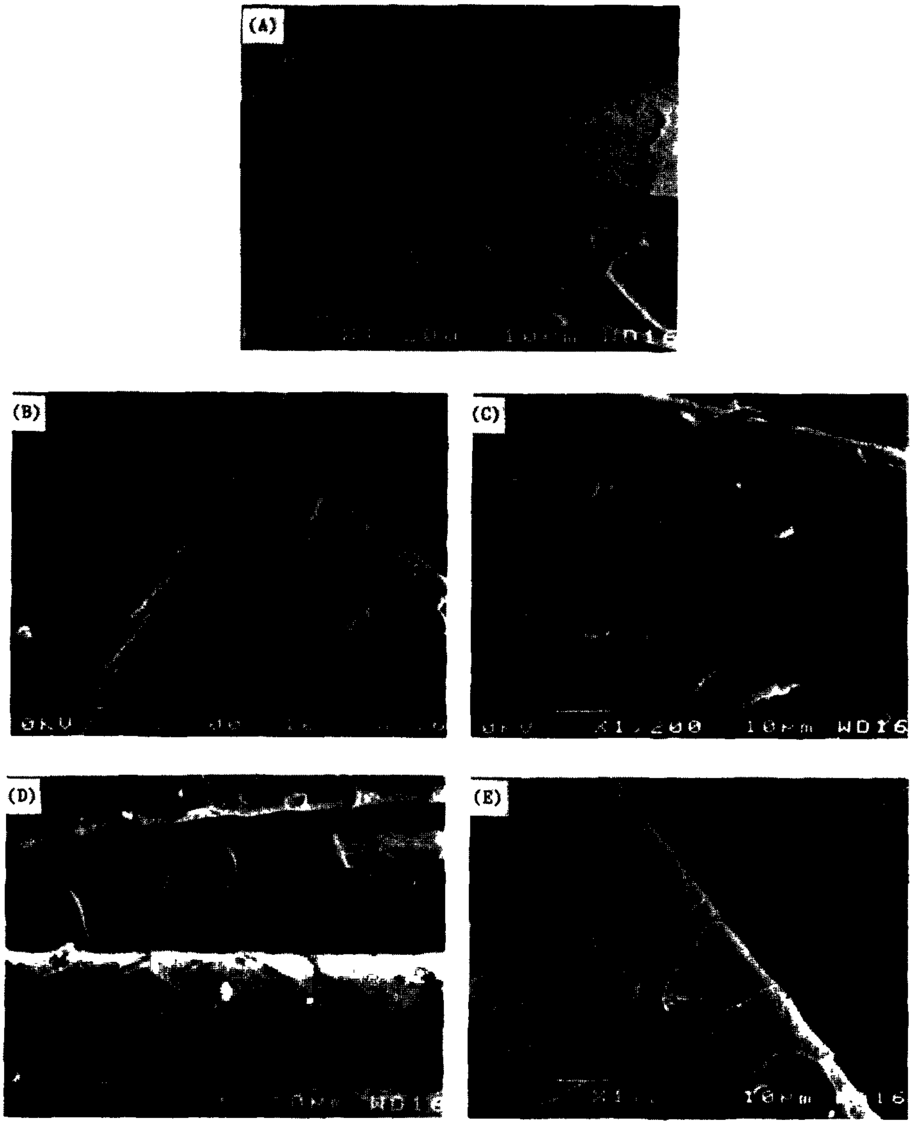


Fig. 1. SEM photomicrographs of wool treated with (a) distilled water alone; (b) 10 mM APS; (c) 20 mM APS; (d) 10 mM TDO; (e) 20 mM TDO.

discussed in a previous study[20] on the effects of radical initiators on nylon 6.6, the extent of damage caused to the wool by the radical initiators may have been reduced as a result of the radical initiator having interacted with the dye in the dyebath, or as a consequence of a reduction in the extent of the radical initiator–fibre reaction that accrued from the presence of adsorbed dye on the fibre.

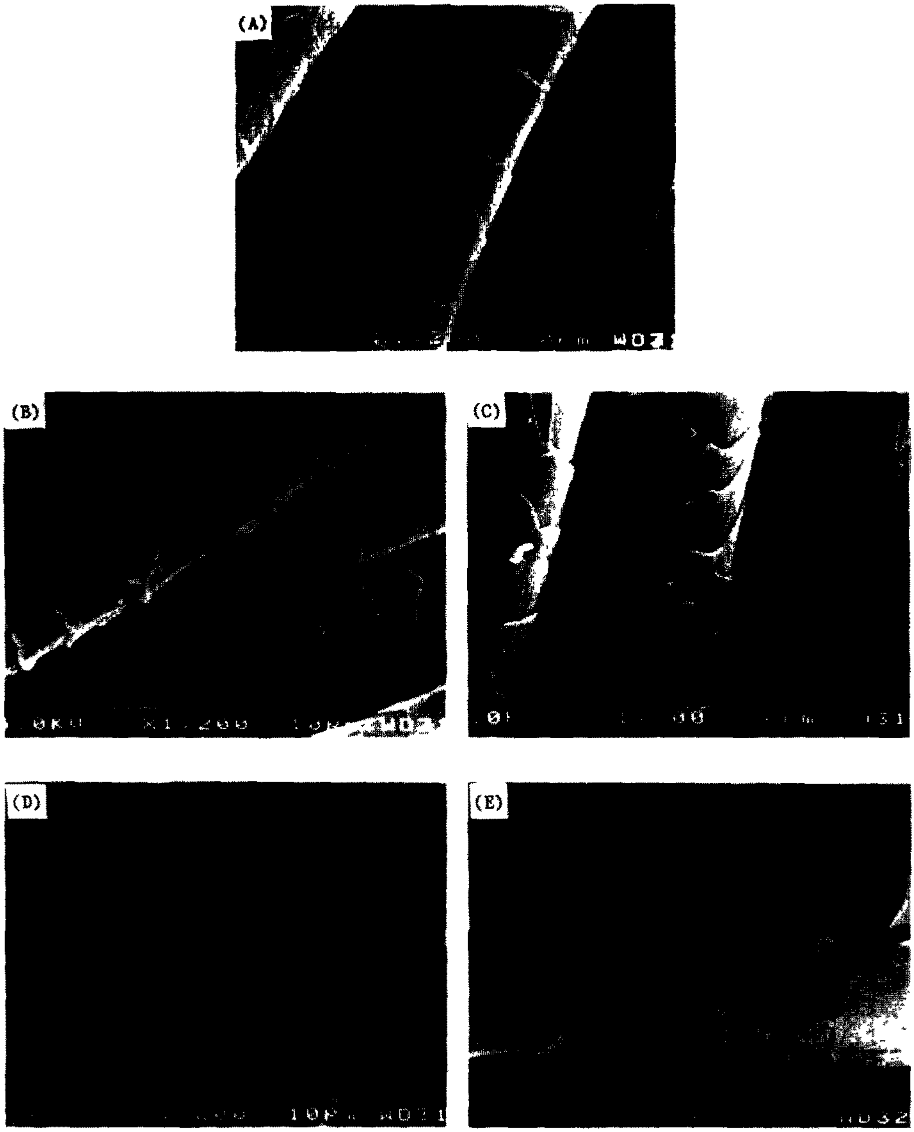


Fig. 2. SEM photomicrographs of wool dyed with CI Disperse Violet 4 in the presence of (a) dye alone; (b) 10 mM APS; (c) 20 mM APS; (d) 10 mM TDO; (e) 20 mM TDO.

CONCLUSIONS

Selected nitrodiphenylamine and anthraquinone disperse dyes display enhanced wash fastness when applied to wool in the presence of radical initiators. Such enhanced fastness to washing may be attributable to covalent dye–fibre attachment or dye polymerization within the fibre. If a covalent dye–fibre reaction occurs, then the wash fastness of the resultant dyeings should be comparable to that achieved using reactive dyes on wool, which, typically is rated at 4–5 to 5 to ISO CO6/B2.[42] However, the findings that dyeings on wool obtained using disperse dyes in the presence of a radical initiator achieved only a rating of 4–5 to ISO CO2 implies that covalent dye attachment to the fibre is not solely responsible for the observed enhanced wash fastness achieved using the radical initiator dyeing system and, therefore, that the mechanism involved is complicated. It can be proposed, however, that, as observed for reactive dyes on wool, a proportion of the adsorbed disperse dye is not covalently fixed to the fibre. In this context, it is postulated that, in contrast to reactive dyes, which typically enjoy high fixation efficiency (> 85%)[43] on wool, disperse dyes, when applied to the substrate in the presence of radical initiators, possess low fixation efficiency and, thus, the resultant dyeings exhibit lower wash fastness than that typically obtained using reactive dyes. Alternatively, it is possible that, in addition to dye–fibre covalent attachment, a proportion of the dye forms a dye polymer within the substrate. Furthermore, such dye–fibre covalent attachment and/or dye polymer formation may also contribute to the shade changes and modified light fastness observed for the APS and TDO dyeings.

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