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Dyeing in the Presence of Free Radical Initiators. Part 7: The Dyeing of Silk Fibres

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ABSTRACT

The dyeing of silk fabric, at various pH values, with two nonmetallised acid dyes and two disperse dyes was carried out in the absence and presence of various radical initiator systems, namely ammonium persulphate, potassium periodate, hydrogen peroxide, glucose, thiourea dioxide, thiourea and ferrous sulphate. The six radical initiators used, imparted similar changes to the shade, colour yield and wash fastness of all four dyes on silk; for each of the four dyes employed, ammonium persulphate and $FeSO_4/H_2O_2$ *yielded dyeings that were most different, in terms of shade, colour yield and enhanced wash fastness, to the respective control dyeings at each of the pH values used. The effects imparted by the radical initiators were found to be dependent on both the nature and concentration of the initiator used, but appeared to be independent of the chemical class of dye employed.*

INTRODUCTION

Previous studies by the authors have considered the effects of radical initiators on the dyeing of polyester,[1] nylon 6,[2] nylon 6.6[3–5] and wool[6] with disperse dyes; the dyeing of wool and also silk with direct, basic and acid dyes in the presence of radical initiators has been studied by various workers[7–15] and several radical initiator dyeing systems have been proposed for use on silk[11–15] by means of which enhanced colour yield and wash fastness are achievable. The present paper concerns the effects of several radical initiators on the colour yield, shade and wash fastness of nonmetallised acid dyes as well as disperse dyes on silk. Since hydrogen peroxide/thiourea,[11] potassium periodate/glucose[12–14] and hydrogen peroxide/glucose[15] radical initiator systems have previously been employed in silk dyeing, these systems were selected for use in this work; in addition, the traditional ferrous sulphate/hydrogen peroxide[16] redox initiator system was also used.

EXPERIMENTAL

Materials

Fibre

Scoured, woven silk fabric (48·6 g m^{-2}) obtained from Whalleys was used.

Dyes and auxiliaries

Two commercial nonmetallised acid dyes, namely Airedale Orange II (YCL) (CI Acid Orange 7) and Sandolan Red MF-2BL (Sandoz) (CI Acid Red 336), together with two commercial disperse dyes, namely Serisol Fast Yellow PL (YCL) (CI Disperse Yellow 9) and Serisol Brilliant Violet 2R (YCL) (CI Disperse Violet l), were used in the work, each kindly supplied by the respective manufacturer. Commercial samples of Dyapol PT (YCL), which was employed as dispersing agent in dyeing, and Sandozin NIE (S), which was used in the scouring of the dyed silk, were also supplied by the respective manufacturer.

Chemicals

All chemicals used in the work were laboratory grade reagents obtained from either Aldrich or BDH; ammonium persulphate (APS), potassium periodate (KIO_4), hydrogen peroxide (H_2O_2), glucose, thiourea dioxide (TDO), thiourea and ferrous sulphate ($FeSO_4$) were used as radical initiators.

Procedures

Dyeing

All dyeings were carried out in sealed, stainless steel dyepots of 300 cm^3 capacity housed in a John Jeffries laboratory-scale Rota Dyer. The dyebath comprised either 2% omf commercial disperse dye and 1 g/litre Dyapol PT or 2% omf commercial nonmetallised acid dye and the presence or absence of free radical initiator; a liquor ratio of 30:1 was employed. Dyeing was carried out at various pH values, the pH values being adjusted to 4 using either acetic acid or 0·014M acetic acid/0·04M sodium acetate buffer, and pH 5·5 using 0·2M acetic acid/0·17M sodium acetate buffer. Dyeing was commenced at 40°C, and the temperature was raised to 70°C at a rate of $2°\mathrm{C/min}^{-1}$ 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% omf 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.

Colour measurement

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

Wash fastness

The fastness of the dry, scoured, dyed silk samples to the ISO CO2 wash test was determined using the standard method.[17]

RESULTS AND DISCUSSION

The dyeing of silk with nonmetallised acid dyes in the presence of radical initiators

As both CI Acid Red 336[15] and CI Acid Orange 7[11–13] have previously been employed in the dyeing of wool and silk in the presence of radical initiators, enhanced colour yield and wash fastness having been obtained, these two particular dyes were selected for use in the present work. In view of the results discussed earlier[1,2] concerning the effect of pH on dyeing with disperse dyes in the presence of radical initiators, a pH of 5·5, obtained using an acetic acid/sodium acetate buffer, was employed; since nonmetallised acid dyes are normally applied to silk under acidic (typically pH 3–5) conditions, a dyebath pH of 4 was also used, this being attained using acetic acid as well as an acetic acid/sodium acetate buffer system. As it was suggested[11–15] that free radical dyeing systems yielded

TABLE 1
Colorimetric and Fastness Data for Silk Dyed with CI Acid Red 336 at 70°C for 60 min

Radical initiator	*pH*	*K/S*	λ_{max} *(nm)*	L*	a*	b*	c*	h°	*ISO CO2*		
									E	*S*	*C*
Nil	4[a](5·5)	5·2	520	54·1	48·2	7·1	48·7	8·4	1	4–5	4–5
H_2O_2 (0·1M)/ glucose (0·1M)	4[a](5)	4·4	520	55·5	46·4	7·1	46·9	8·7	1–2	4–5	4–5
APS (10 mM)	4[a](3·3)	3·1	400	59·6	30·4	12·9	33·0	23·0	2	5	5
$FeSO_4$ (0·03M)/ H_2O_2 (0·03M)	4[a](3·2)	11·0	520	45·5	48·4	18·2	51·7	20·6	2	4	4–5
Nil	4(4·1)	7·1	520	51·2	50·5	9·2	51·3	10·3	1–2	4	4–5
H_2O_2 (0·03M)/ thiourea (0·05M)	4	7·8	520	50·6	51·5	10·2	52·5	11·2	1–2	4	4–5
H_2O_2 (0·1M)/ glucose (0·1M)	4(4)	7·1	520	51·1	49·9	9·6	50·8	10·9	1–2	4	4–5
KIO_4 (0·01M)/ glucose (1 g/litre)	4	7·1	520	51·1	50·0	9·3	50·9	10·5	1	4	4–5
APS (10 mM)	4(4)	2·7	400	57·3	32·2	11·9	34·3	20·3	2	4–5	5
$FeSO_4$ (0·03M)/ H_2O_2 (0·03M)	4(2·5)	7·4	400	47·0	36·8	22·6	43·2	31·5	2	4–5	4–5
$FeSO_4$ (0·01M)/ H_2O_2 (0·01M)	4	6·8	520	47·3	39·5	17·7	43·3	24·1	2	4–5	4–5
Nil	5·5(5·6)	6·6	520	51·8	49·8	8·6	50·5	9·8	1	4	4–5
H_2O_2 (0·03M)/ thiourea (0·05M)	5·5	6·7	520	51·8	49·7	8·5	50·4	9·7	1	4	4–5
H_2O_2 (0·1M)/ glucose (0·1M)	5·5(5·5)	5·8	520	52·9	48·6	7·9	49·2	9·3	1–2	4–5	4–5
KIO_4 (0·01M)/ glucose (1 g/litre)	5·5	5·8	520	53·1	48·7	7·5	49·3	8·8	1	4	4–5
TDO (20 mM)	5·5	6·4	520	52·4	50·0	7·9	50·6	9·0	1	4	4–5
APS (10 mM)	5·5(5·5)	4·2	520	54·0	41·0	9·2	42·0	12·6	1–2	4–5	4–5
$FeSO_4$ (0·03M)/ H_2O_2 (0·03M)	5·5(4·8)	5·2	400	54·6	30·8	20·8	37·2	34·0	1–2	4–5	5
$FeSO_4$ (0·01M)/ H_2O_2 (0·01M)	5·5	5·1	400	53·8	35·0	20·9	40·8	30·8	1–2	4–5	5

E: Effect on shade; S: staining of silk adjacent; C: staining of cotton adjacent.
pH 4: obtained using 0·14M acetic acid/0·04M sodium acetate buffer.
pH 5·5: obtained using 0·02M acetic acid/0·17M sodium acetate buffer.
[a] pH 4: adjusted by acetic acid.
( ): pH of the residual dyebath.

dyeings of similar colour yield, but higher wash fastness than those achieved using high temperature dyeing in the absence of radical initiator, a temperature of 70°C was employed in this work.

The results obtained for the dyeing of silk with CI Acid Red 336 at 70°C for 60 min in both the absence and presence of various radical initiators are shown in Table 1, from which it is evident that, when dyeing had been carried out in the absence of a free radical initiator, the colour yield of the dyeings increased in the order pH 4 (acetic acid) < pH 5·5 < pH 4 (buffer). Also, the chromaticeness of the dyeing obtained at pH 4 using acetic acid differed from that of the two dyeings obtained at pH 4 with buffer and at pH 5·5 with buffer, the chromaticeness of the two buffered dyeings being similar. These findings can be explained in terms of the pH values of the residual dyebaths (Table 1). In the case of the dyeing that had been carried out at pH 4 using acetic acid, the pH of the residual dyebath was 5·5, thus implying that, for part of the dyeing process, the pH of the dyebath was much higher than the initial value of 4; at the end of the dyeing carried out using pH 5.5 buffer, the dyebath had a pH of 5·6; each of these two residual dyebath pH values was much higher than the value of 4·1 recorded for the pH 4 (buffer) dyeing. Since, in general, nonmetallised acid dyes are applied to silk under acidic (pH 3–5) conditions, the observation that higher colour yield was obtained when dyeing had been carried out at pH 4 (buffer) than at pH 4 (acetic acid) and pH 5·5 (buffer) can be attributed to the higher substantivity of the nonmetallised acid dye at the lower pH value. Furthermore, although these findings therefore show that, in terms of colour yield, it is preferable to employ buffer for dyeing and that highest colour yield was secured at pH 4, Table 1 demonstrates that there was little difference in wash fastness of the three dyeings that had been carried out in the absence of radical initiator.

It is apparent (Table 1) that at a pH of 4 (adjusted using acetic acid) the dyeings of CI Acid Red 336 obtained using H_2O_2 (0·1M)/glucose (0.1M) and also APS were paler (as given by the lower K/S values and higher L^* values), duller (as shown by the lower c^* values) and more orange (as evidenced by the lower a^* values and higher $h°$ values) than the control dyeing; in contrast, the dyeing obtained using $FeSO_4$ (0·03M)/ H_2O_2 (0·03M) was deeper (as given by the higher K/S value and lower L^* value), cleaner (as shown by the higher c^* value) and more orange (as evidenced by the higher a^* value, higher b^* value and higher $h°$ value) than the control dyeing. For each of these three radical initiator systems, the dyeings obtained at pH 4 using acetic acid exhibited enhanced wash fastness (Table 1). A hypsochromic shift in λ_{max} occurred for the dyeing carried out in the presence of APS, in contrast to which, the dyeings obtained using $FeSO_4$ (0·03M)/H_2O_2 (0·03M) and H_2O_2 (0·1M)/glucose (0.1M) were of the same λ_{max} as the control dyeing.

Table 1 also shows that at pH 4 (adjusted using buffer) the dyeings of CI Acid Red 336 obtained using the six radical initiator systems were generally duller (as given by the lower c^* values) and more orange (as evidenced by the lower a^* values, higher b^* values and higher $h°$ values) than the control dyeing. Of these radical initiator systems, APS, $FeSO_4$ (0·03M)/H_2O_2 (0·03M) and $FeSO_4$ (0·01M/H_2O_2 (0.01M) imparted slightly enhanced wash fastness to the dyeings; the other radical initiators had no effect upon wash fastness. A hypsochromic shift in the λ_{max} of the dyeings was observed in the cases of APS and $FeSO_4$ (0·03M)/H_2O_2 (0·03M). The colour yields of the dyeings obtained using H_2O_2/glucose and $FeSO_4$ (0·03M)/H_2O_2 (0·03M) were higher than that of the control dyeing; the other radical initiator systems, with the exception of APS which markedly reduced colour yield, exerted little influence on colour yield.

When applied at pH 5·5 with buffer, the dyeings obtained using APS, $FeSO_4$ (0·03M)/H_2O_2, (0·03M) and $FeSO_4$ (0·01M)/H_2O_2 (0·01M) were more orange (as evidenced by the higher b^* values and higher $h°$ values) than the control dyeing; each of the remaining radical initiator systems yielded dyeings that were redder (as given by the lower b^* values and lower $h°$ values) than the control dyeing (Table 1). It is also evident that, when applied at pH 5·5, increased colour yield was secured only for the H_2O_2/thiourea system and that each of the remaining six radical initiators reduced the colour yield of CI Acid Red 336. Four of the radical initiators, namely APS, H_2O_2/glucose and each of the $FeSO_4$/H_2O_2 systems used, imparted slightly enhanced wash fastness to the dyeings; the other three radical initiators had no effect on wash fastness. Furthermore, each of the $FeSO_4$/H_2O_2 systems imparted a hypsochromic shift to the λ_{max} of the dyeings.

Thus, although Table 1 clearly shows that both APS and $FeSO_4$/H_2O_2 enhanced the wash fastness of CI Acid Red 336 on silk when dyeing had been carried out at both pH 4 and 5·5, each of these radical initiator systems imparted a marked shade change to the dyeings, and APS resulted in a considerable reduction in colour yield.

Since, of the three pH systems employed, pH 4 (acetic acid) gave the lowest colour yield when dyeing had been carried out in the absence of radical initiator, in all further work on the dyeing of silk in the presence of radical initiators, pH values of 4 and 5·5 were used, the respective dyebath pH value being achieved using the appropriate buffer system.

Table 2 shows the colorimetric and fastness data obtained for CI Acid Orange 7, from which it is apparent that when dyeing had been carried out in the absence of radical initiator, the colour yield secured at pH 4

TABLE 2

Colorimetric and Fastness Data for Silk Dyed with CI Acid Orange 7 at 70°C for 60 min

Radical initiator	*pH*	*K/S*	λ_{max} *(nm)*	L*	a*	b*	c*	h°	*ISO CO2*		
									E	*S*	*C*
Nil	4	3·7	500	68·5	31·3	39·8	50·6	51·8	1	4	4–5
H_2O_2 (0·1M)/ glucose (0·1M)	4	3·2	500	68·7	30·3	36·8	47·7	50·5	1	4	4
H_2O_2 (0·03M)/ thiourea (0·05M)	4	3·4	500	68·8	31·1	38·0	49·1	50·7	1	4	4
KIO_4 (0·01M)/ glucose (1 g/litre)	4	4·1	500	67·5	32·2	41·2	52·3	52·0	1	4	4
APS (10 mM)	4	2·0	480	67·7	23·2	29·7	37·7	52·0	1	4–5	5
$FeSO_4$ (0·01M)/ H_2O_2 (0·01M)	4	5·5	400	49·2	20·7	24·7	32·2	50·0	1	4–5	5
Nil	5·5	1·4	500	73·6	21·7	24·7	32·9	48·7	1	4–5	4–5
H_2O_2 (0·1M)/ glucose (0·1M)	5·5	1·2	500	73·8	20·9	22·7	30·9	47·7	1	4–5	4–5
H_2O_2 (0·03M)/ thiourea (0·05M)	5·5	1·1	500	74·3	19·3	20·7	28·3	47·0	1	4–5	4–5
KIO_4 (0·01M)/ glucose (1 g/litre)	5·5	1·4	500	72·4	21·4	24·8	32·8	49·2	1	4–5	4–5
TDO (20 mM)	5·5	0·7	500	76·2	14·6	15·8	21·5	47·3	1	5	5
APS (10 mM)	5·5	1·5	480	70·3	18·0	27·5	32·9	56·8	1–2	5	4–5
$FeSO_4$ (0·03M)/ H_2O_2 (0·03M)	5·5	5·5	400	54·8	16·8	26·9	31·7	58·0	2–3	5	5
$FeSO_4$ (0·01M)/ H_2O_2 (0·01M)	5·5	4·0	400	58·3	20·8	28·5	35·3	53·9	1–2	4–5	4–5

E: Effect on shade; S: staining of silk adjacent; C: staining of cotton adjacent.
pH 4: obtained using 0·14M acetic acid/0·04M sodium acetate buffer.
pH 5·5: obtained using 0·02M acetic acid/0·17M sodium acetate buffer.

was higher than that obtained at pH 5·5 and, also, that the wash fastness of the two dyeings was similar. These findings concur with those obtained for CI Acid Red 336 (Table 1); thus, as discussed for the results obtained for this latter dye, the observation that higher colour yield was obtained when CI Acid Orange 7 had been applied at pH 4 (buffer) than at pH 5·5 (buffer) can be attributed to the higher substantivity of the nonmetallised acid dye at the lower pH value.

Table 2 shows that, when dyeing had been carried out in the presence of various radical initiators, enhanced colour yield was secured in the cases of APS and each of the $FeSO_4/H_2O_2$ systems used at pH 5·5, as well as KIO_4/glucose and $FeSO_4$ (0·01M)/H_2O_2 (0·01M) at pH 4; all other radical initiator systems (with the exception of the dyeing secured using KIO_4/glucose at pH 5·5, which was of identical colour yield to the control dyeing) yielded dyeings that were of lower colour yield than the respective control dyeing at both pH values employed. Of the various free radical systems examined, APS and each of the $FeSO_4/H_2O_2$ systems imparted enhanced wash fastness to the dyeings at each pH value used and TDO resulted in slightly higher wash fastness at pH 5·5; all other radical initiators had little effect on fastness to washing.

Thus, although Table 2 shows that both APS and $FeSO_4/H_2O_2$ enhanced the wash fastness of CI Acid Orange 7 on silk when dyeing had been carried out at both pH 4 and 5·5, each of these radical initiator systems imparted a marked shade change and a hysochromic shift in the λ_{max} of the dyeings; also, APS resulted in a considerable reduction in colour yield of the dyeings. These findings concur with those obtained for CI Acid Red 336 (Table 1).

From the results shown in Tables 1 and 2, it is apparent that, for both CI Acid Red 336 and CI Acid Orange 7, dyeing at either pH 4 or 5·5, in the presence of both APS and $FeSO_4/H_2O_2$, imparted enhanced wash fastness. However, whilst $FeSO_4/H_2O_2$ resulted in higher colour yields, APS reduced the colour yield obtained using both nonmetallised acid dyes; furthermore, both APS and $FeSO_4/H_2O_2$ imparted marked shade changes to the dyeings. The findings displayed in Tables 1 and 2 also clearly show that the two nonmetallised acid dyes were very similar with regards the effects imparted to them by the various radical initiators.

Previous workers observed that, after extraction with pyridine[7] or 50% aqueous, dimethylformamide,[15] a high proportion of acid dye remained on silk which had been dyed in the presence of radical initiators; the extent of this dye retention was found to depend on the pH of the dye-bath, with maximum retention being achieved at a pH value of 2·5.[7] It was postulated[7,15] that, in the case of dyeing silk with acid dyes in the presence of radical initiators, the dye was covalently attached to the substrate. The results shown in Tables 1 and 2 support the finding[7] that the effect of radical initiators on the dyeing of silk is pH dependent and, in addition, that the effects imparted depend on both the nature and concentration of the radical initiator used. The findings (Tables 1 and 2) that several radical initiator systems enhanced the wash fastness of the two nonmetallised acid dyes used can be considered to support the postulate[7,15] that, in the dyeing of silk with acid dyes in the presence of radical initiators, the dye is covalently attached to the substrate. However, although the enhanced fastness to washing imparted by the radical initiators indicates that a free radical reaction is probably involved, it is possible, as previously suggested by the present authors,[1–6] that the observed enhancement of wash fastness may also be attributable to dye polymerisation; clearly, further work is required to determine the precise nature of this free radical mechanism. It is of interest to note that previous workers[7,15] did not report that any shade change occurred during the dyeing of silk with acid dyes in the presence of radical initiators; the findings in Tables 1 and 2, however, clearly reveal that each of the six radical initiators used resulted in shade change, this being especially marked for some of the radical initiator systems employed.

The dyeing of silk with disperse dyes in the presence of radical initiators

In previous studies, the authors demonstrated that enhanced wash fastness was achieved using CI Disperse Yellow 9 and CI Disperse Violet 1 on both nylon 6.6[3,4] and wool[6] when dyeing had been carried out in the presence of radical initiators; consequently, these two dyes were selected for use in the present work. The results obtained for the dyeing of silk with CI Disperse Yellow 9 and CI Disperse Violet 1 at 70°C for 60 min, in both the absence and presence of various radical initiators, are shown in Tables 3 and 4, respectively, the pH of the dyebaths having been achieved using the appropriate buffer system.

Tables 3 and 4 show that, for each disperse dye, when dyeing had been carried out in the absence of radical initiator, the colour yield, shade and wash fastness of the dyeings were virtually identical for each of the two dyebath pH values employed. This result, was expected, as the adsorption of the nonionic disperse dyes on to silk should be pH independent.

Table 3 shows that, in the case of CI Disperse Yellow 9, the dyeings obtained at pH 4 and pH 5·5 using various radical initiator systems were generally deeper (as shown by the higher K/S values and lower L^* values), cleaner (as given by the higher c^* values) and more orange (as evidenced by the higher a^* values and lower $h°$ values) than the two respective control dyeings; it is also evident that each of the radical initiators increased the colour yield of the dyeings at both pH values employed. Inspection of the results in Table 3 clearly shows that enhanced wash fastness was achieved using H_2O_2/glucose and KIO_4/glucose at both pH 4 and 5·5 as well as using APS and each of the two $FeSO_4/H_2O_2$ systems at pH 5·5; furthermore, the difference in colour between the respective control dyeing and those carried out using each of these particular radical initiator systems was considerably greater than that obtained between the control dyeings and those dyeings obtained in the presence of the other radical initiator systems used. None of the radical initiators imparted a shift in the λ_{max} of the dyeings. Of the six radical initiator systems employed, APS and each of the $FeSO_4/H_2O_2$ systems

TABLE 3
Colorimetric and Fastness Data for Silk Dyed with CI Disperse Yellow 9 at 70°C for 60 min

Radical initiator	*pH*	*K/S*	λ_{max} *(nm)*	L*	a*	b*	c*	h°	*ISO CO2*		
									E	*S*	*C*
Nil	4	1·7	400	76·7	3·3	30·6	30·8	83·8	1	3	5
H_2O_2 (0·1M)/ glucose (0·1M)	4	2·5	400	73·0	4·9	32·1	32·5	81·3	2	3	5
H_2O_2 (0·03M)/ thiourea (0·05M)	4	2·0	400	75·8	3·7	32·4	32·6	83·5	1	3	5
KIO_4 (0·01M)/ glucose (1 g/litre)	4	3·6	400	67·9	7·2	32·5	33·3	77·5	2–3	3	5
Nil	5·5	1·7	400	76·5	3·3	30·0	30·2	83·7	1	3	5
H_2O_2 (0·1M)/ glucose (0·1M)	5·5	1·9	400	75·3	4·0	30·6	30·9	82·6	1–2	3	5
H_2O_2 (0·03M)/ thiourea (0·05M)	5·5	1·8	400	76·2	3·6	31·3	31·5	83·4	1	3	4–5
KIO_4 (0·01M)/ glucose (1 g/litre)	5·5	2·6	400	71·9	5·4	31·6	32·1	80·3	2	3	5
TDO (20 mM)	5·5	1·8	400	76·4	3·3	30·9	31·1	83·9	1	3	5
APS (10 mM)	5·5	4·9	400	67·3	8·6	36·5	37·5	76·7	3	4	5
$FeSO_4$ (0·03M)/ H_2O_2 (0·03M)	5·5	6·9	400	63·8	12·0	39·1	40·9	72·9	3	3	5
$FeSO_4$ (0·01M)/ H_2O_2 (0·01M)	5·5	6·8	400	62·4	12·9	37·8	39·9	71·2	3–4	3–4	5

E: Effect on shade; S: staining of silk adjacent; C: staining of cotton adjacent.
pH 4: obtained using 0·14M acetic acid/0·04M sodium acetate buffer.
pH 5·5: obtained using 0·02M acetic acid/0·17M sodium acetate buffer.

employed imparted the most significant improvement to both the colour yield and wash fastness of CI Disperse Yellow 9 on silk.

Table 4 shows that enhanced colour yield was secured for the dyeings of CI Disperse Violet 1 in the presence of KIO_4/glucose and H_2O_2 at pH 4 and in the presence of APS and both $FeSO_4/H_2O_2$ systems at pH 5·5; all of the remaining radical initiators slightly reduced the colour yield of the dyeings. Although the largest increase in colour yield was obtained using APS and both $FeSO_4/H_2O_2$ systems at pH 5·5, these systems resulted in a marked alteration of the shade of the dyeings as evidenced by the shift in λ_{max} of these particular dyeings (Table 4). Indeed, the dyeings obtained in the presence of APS, $FeSO_4$ (0·03M)/H_2O_2 (0·03M) and $FeSO_4$ (0·01M)/H_2O_2 (0·01M) were duller (as shown by the lower c^* values) than the two respective control dyeings, the hue of the dyeings varying for the

TABLE 4
Colorimetric and Fastness Data for Silk Dyed with CI Disperse Violet 1 at 70°C for 60 min

Radical initiator	*pH*	*K/S*	λ_{max} *(nm)*	L*	a*	b*	c*	h°	*ISO CO2*		
									E	*S*	*C*
Nil	4	1·8	560	57·0	13·9	−26·5	29·9	297·7	1	2	4
H_2O_2 (0·1M)/ glucose (0·1M)	4	1·6	560	57·5	11·8	−20·8	23·9	299·6	1	2–3	4
H_2O_2 (0·03M)/ thiourea (0·05M)	4	2·1	560	55·2	15·5	−28·0	32·2	299·0	1	2	3–4
KIO_4 (0·01M)/ glucose (1 g/litre)	4	2·0	560	54·1	10·1	−17·4	20·1	300·1	1	2–3	4
Nil	5·5	2·2	560	54·5	16·2	−29·1	33·3	299·1	1	2	3–4
H_2O_2 (0·1M)/ glucose (0·1M)	5·5	2·1	560	55·2	15·6	−27·7	31·8	299·4	1	2	3–4
H_2O_2 (0·03M)/ thiourea (0·05M)	5·5	2·1	560	55·1	16·4	−29·2	33·5	299·3	1	2	3–4
KIO_4 (0·01M)/ glucose (1 g/litre)	5·5	2·1	560	54·4	13·3	−24·7	28·1	298·3	1	2	3–4
TDO (20 mM)	5·5	2·1	560	55·1	15·7	−28·3	32·4	299·0	1	2	3–4
APS (10 mM)	5·5	2·6	580	47·4	3·8	−9·5	10·2	291·8	4	4–5	5
$FeSO_4$ (0·03M)/ H_2O_2 (0·03M)	5·5	3·8	400	53·7	6·8	10·8	12·8	57·8	2–3	4	5
$FeSO_4$ (0·01M)/ H_2O_2 (0·01M)	5·5	2·4	560	48·6	6·7	3·6	7·6	28·2	1–2	2–3	4

E: Effect on shade; S: staining of silk adjacent; C: staining of cotton adjacent.
pH 4: obtained using 0·14M acetic acid/0·04M sodium acetate buffer.
pH 5·5: obtained using 0·02M acetic acid/0·17M sodium acetate buffer.

three radical initiator systems, with the APS dyeing being bluer (as given by the lower *h*° value) and the $FeSO_4/H_2O_2$ dyeings more orange (as shown by the higher *h*° values) than the respective control dyeings. Furthermore, as was previously found for CI Disperse Yellow 9 (Table 3), Table 4 clearly shows that the difference in colour obtained between the two control dyeings and those carried out using APS, $FeSO_4$ (0·03M)/ H_2O_2 (0·03M) and $FeSO_4$ (0·01M)/H_2O_2 (0·01M) was considerably greater than that obtained between the control dyeings and those dyeings obtained in the presence of other radical initiator systems.

The results presented in Tables 3 and 4 show that, of the six radical initiator systems employed, APS and $FeSO_4/H_2O_2$ imparted the most significant improvement to both the colour yield and wash fastness of both CI Disperse Violet 1 and CI Disperse Yellow 9; however, both APS and $FeSO_4/H_2O_2$ imparted marked shade changes to the dyeings. The findings displayed in Tables 3 and 4 also clearly show that the nitrodiphenylamine dye (CI Disperse Yellow 9) and the anthraquinone dye (CI Disperse Violet 1) were virtually identical with regards the effects imparted to them by the various radical initiators.

The different shades imparted by the various radical initiators to the dyeings of the two disperse dyes on silk can, as proposed for the dyeing of other fibres with anthraquinone and nitrodiphenylamine disperse dyes in the presence of free radical initiators,[2,3,5,6] be attributed to differences in the nature of the reduced and oxidised derivatives of the dye, to the formation of dye polymers, to dye–fibre covalent attachment or to a difference in the interactions occurring between the modified substrate and the modified dyes. The enhanced fastness of the two disperse dyes on silk imparted by the radical initiators can be attributed to dye polymerisation and/or dye–fibre covalent attachment.

CONCLUSIONS

A comparison of the results obtained for the two nonmetallised acid dyes and the two disperse dyes reveals that the six radical initiators used imparted similar changes to the shade, colour yield and wash fastness of all four dyes on silk, insofar as the extent of these changes increased in the order H_2O_2/thiourea ≈ TDO < H_2O_2/glucose < KIO_4/glucose < APS ≈ $FeSO_4/H_2O_2$; for each of the four dyes, APS and $FeSO_4/H_2O_2$ yielded dyeings that were most different, in terms of shade, colour yield and enhanced wash fastness, to the respective control dyeings at each of the pH values employed. This implies that, although the effects imparted by the radical initiators are dependent on both the nature and concentration of the initiators used, the effects appear to be independent of the chemical class of dye employed, as azo, nitrodiphenylamine and anthraquinone classes of dye were used in this study. The enhanced wash fastness of each of the four dyes on silk secured by the use of the radical initiators can be attributed to covalent attachment of the dye to the fibre or to dye polymer formation within the fibre; however, the enhancement of wash fastness is accompanied by a marked change in shade of the dyeing.

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