Dyes and Pigments 21 (1993) 185–203

Dyeing in the Presence of Free Radical Initiators. Part 1—The Dyeing of Polyester Fabric with CI Disperse Yellow 54

S. M. Burkinshaw

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

&

Jiann Guang Lu

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

(Received 5 October 1992; accepted 2 November 1992)

ABSTRACT

The dyeing of polyester fabric with CI Disperse Yellow 54 has been carried out in the presence of ammonium persulphate. The oxidant markedly reduces the pH of the dyebath, necessitating the use of a buffer of strong buffer capacity. FTIR attenuated total reflectance (ATR) spectroscopy has been used to investigate the enhanced colour yield and improved fastness to DMF extraction imparted to the dyeings by the oxidant; no evidence was found to confirm covalent attachment of the dye to the substrate.

INTRODUCTION

Several authors[1–15] have studied the effects of oxidising and reducing agents on the dyeing behaviour of various dye classes on several types of fibres. Keralina *et al.*[1] observed that the wash fastness properties of several acid and basic dyes on wool were improved when the dyed samples were treated in a redox system comprising potassium persulphate and potassium pyrosulphate. In IR spectroscopic studies of the effects of hydrogen peroxide and potassium persulphate on dyeing with basic dyes,

Dyes and Pigments 0143-7208/93/$06.00

Ereshchenko *et al.*[2] proposed that the dyes were covalently bound to the N-vicinal methylene group of nylon and Bhattachary[3] concluded that the dyes were attached to the methylene group adjacent to the nitrile carbon atom in acrylic fibres. Shenai *et al.*,[4,5] in a study of the dyeing of wool, silk and nylon 6 with acid dyes and also the dyeing of cotton and viscose with direct dyes, suggested that redox systems could bring about covalent fixation of the dyes, induce grafting of certain monomers to the fibres[4,5] or protonate the amino groups of the protein fibre generating cationic sites for acid dyes.[6] Ibrahim *et al.*[7–13] proposed a free radical mechanism to account for the effects of redox systems in the dyeing of wool, nylon 6 and wool/acrylic blends with acid dyes, nylon 6 with disperse dyes and also cotton, viscose, wool and nylon 6 with direct dyes. Topiwala[14] observed that various oxidising and reducing agents improved both the wet fastness properties and colour yield of several disperse dyes on polyester and nylon 6·6 fibres. In a study of the low temperature dyeing of silk with acid dyes in the presence of hydrogen peroxide and glucose, Luo[15] also postulated that covalent attachment of the dye to the fibre occurred during dyeing.

However, such previous studies of the effects of radical initiator systems on the dyeing behaviour of various classes of dye on several types of fibres have clearly demonstrated that the precise mechanism of dyeing in the presence of free radical initiators is both complicated and unclear. The objectives of this work were to investigate the effects of radical initiators on the dyeing of several types of fibre (polyester, nylon and wool) with various chemical classes of disperse dye and to elucidate the mechanism of dyeing in the presence of free radical initiators. In this part of the work, the effects of ammonium persulphate on the dyeing of PET fabric with CI Disperse Yellow 54 were studied and an attempt made to find the mechanism.

EXPERIMENTAL

Materials

Fibres

Scoured, knitted (98 g m^{-2}) PET fabrics obtained from Whalleys were used.

Dyes and auxiliaries

A commercial sample of CI Disperse Yellow 54, kindly supplied by Yorkshire Chemicals Plc (YCL) was used. Commercial samples of Dyapol PT (YCL), which was employed as dispersing agent in dyeing and Sandozin

NIE (Sandoz) which was used in the reduction clearing of dyed PET, were supplied by the respective maker.

Chemicals

All chemicals used in this work were laboratory grade reagents obtained from either Aldrich of BDH; sodium acetate, acetic acid (99% w/w) and sulphuric acid (98% w/w) were used to control dyebath pH; sodium hydroxide and sodium dithionite were used for reduction clearing of dyed PET.

Procedures

Dyeing

Dyeing was carried out in sealed, stainless steel pots of 300 cm^3 capacity housed in a John Jeffries laboratory-scale dyeing machine. The dyebath was set with 2% o.w.f. CI Disperse Yellow 54 and 1 g $litre^{-1}$ Dyapol PT in either the presence or absence of ammonium persulphate using a liquor ratio of 30:1; the pH of the dyebath was adjusted to 5·5 using acetic acid or 0·02 M acetic acid/0·17 M sodium acetate buffer. Dyeing was commenced at 60°C, the temperature then raised to 130°C at a rate of 2°C/min and dyeing continued at 130°C for a further 60 min. At the end of dyeing the rinsed (cold tap water) dyed samples were treated for 30 min at 70°C in a stirred aqueous (distilled water) solution (30:1 liquor ratio) containing sodium dithionite (2 g $litre^{-1}$), sodium hydroxide (pellets) (2 g $litre^{-1}$), and Sandozin NIE (Sandoz) (1 g $litre^{-1}$). The reduction cleared samples were then rinsed thoroughly in cold tap water and allowed to dry in the open air.

DMF extraction

A sample (0·35 g) of the reduction cleared, dyed fabric was extracted in 40 cm^3 of DMF at 100°C for 30 min in a 100 cm^3 round-bottom flask equipped with condenser; at the end of extraction, the sample was rinsed thoroughly in cold tap water and allowed to dry in the open air.

Colour measurement

The reflectance values of the dry, reduction cleared, dyed samples and the DMF-extracted, dyed samples were measured using an ICS Micromatch 2000 colour measurement system under the following viewing conditions:

illuminant D_{65};
10° standard observer;
UV component included;
specular component excluded.

The CIELab coordinates and Kubelka-Munk (K/S) values (the latter at 440 nm) were calculated from the reflectance values. Each sample was folded twice to provide a total of four thicknesses of fabric; each sample was presented so that measurement was carried out on the same side of the fabric using identical orientation.

ATR analysis

IR analysis of PET fibres was carried out using a Perkin-Elmer 1740 Infrared Fourier Transform Spectrometer equipped with a vertical ATR attachment that comprised a thallium iodide (KRS5) crystal.

RESULTS AND DISCUSSION

Effect of pH on dyeing

Since, of the various disperse dyes employed by Topiwala,[14] a hypsochromic shift in the λ_{max} of dyeings on polyester and nylon 6.6 was not observed for CI Disperse Yellow 54 in the presence of both oxidants and reductants, the initial part of the study involved this particular dye. A range of dyeings of polyester was carried out using CI Disperse Yellow 54 in the presence of various concentrations (1·25–250 mM) of ammonium persulphate (APS), the pH of each dyebath having been adjusted, prior to dyeing to 5·5 using acetic acid. It was found that the

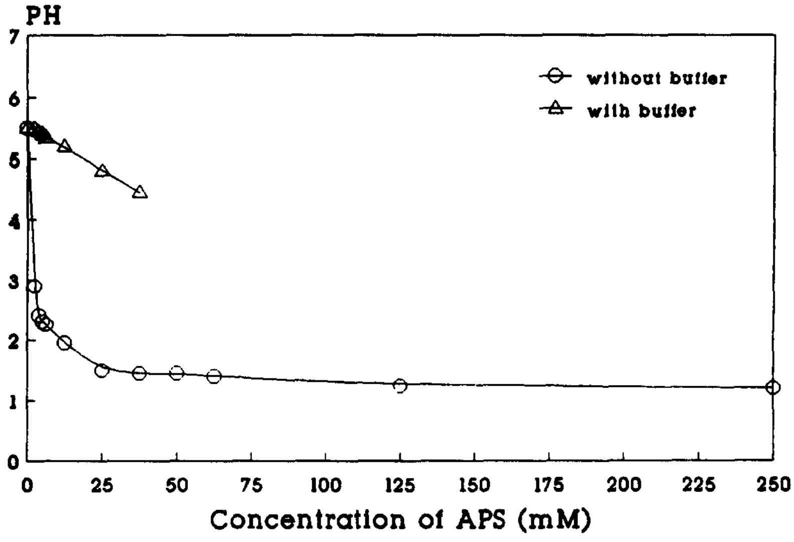


Fig. 1. pH of residual dyebaths.

pH of the residual dyebaths decreased with increasing concentration of APS used (Fig. 1) and that a marked change in shade of the dyeings had occurred. These results concur with those of Topiwala,[14] who found, during a study of the effects of various oxidising and reducing agents on the dyeing of nylon 6·6 and PET with disperse dyes using a 31·6 mM disodium hydrogen phosphate/9·2 mM citric acid buffer system, that when dyeing had been carried out in the presence of ammonium persulphate, the pH of the dyebath dropped from 6 to below 2 during dyeing and also that a marked shade change occurred for some of the dyes employed.

The observed reduction in dyebath pH was examined; the pH of several aqueous (distilled water) solutions ranging from 1·25 to 250 mM of APS at 20°C was measured (Fig. 2). Each solution was then rapidly heated to the boil and allowed to cool to 20°C and the pH of the cool, boiled solutions then measured (Fig. 2). It is evident (Fig. 2) that the pH of both the boiled and unboiled solutions decreased markedly with increasing concentration of APS up to about 50 mM after which the rate of decrease of pH was reduced; also, the pH of the boiled APS solutions was some two pH units lower than that of the unboiled solutions. Although studied by many authors[17–24] the precise mechanism of the thermal decomposition of persulphate ion remains unclear. Equations (1)–(3) are suggested to represent the stoichiometry of the decomposition of the persulphate ion under alkaline and neutral, weakly acidic and strongly acidic aqueous conditions respectively.[18]

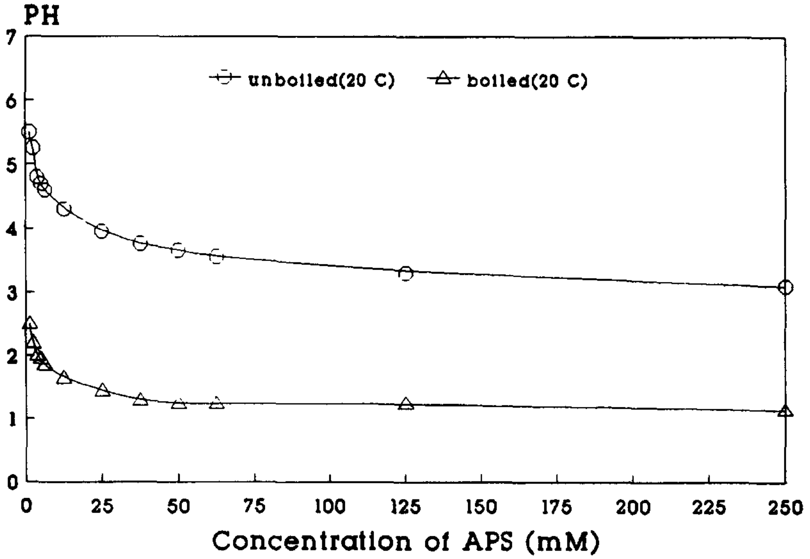


Fig. 2. pH of aqueous ammonium persulphate solutions.

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + 1/2O_2 \quad (1)$$
$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^- + H_2O_2 \quad (2)$$
$$S_2O_8^{2-} + H_2O \rightarrow H_2SO_5 + SO_4^{2-} \quad (3)$$

At pH values above 3, decomposition is initiated by unimolecular homolytic scission (eqn (4)), although a bimolecular mechanism (eqn (5)) has also been proposed.[17,19,20]

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\cdot} \quad (4)$$
$$S_2O_8^{2-} + H_2O \rightarrow SO_4^{-\cdot} + HO^{\cdot} + HSO_4^- \quad (5)$$

The sulphate radical anion ($SO_4^{-\cdot}$) then reacts with water yielding hydroxyl radicals (eqn (6)).

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^- + HO^{\cdot} \quad (6)$$

Further decomposition involves hydroxy radicals, oxygen being evolved possibly by decomposition of hydrogen peroxide produced by means of eqn (7);[20] the precise mechanism of the formation of oxygen remains unclear.[17,19,20]

$$2HO^{\cdot} \rightarrow H_2O_2 \quad (7)$$

Under strongly acidic conditions (below pH 3) acid catalysis of the persulphate ion contributes to decomposition (eqns (8) and (9)).

$$H^+ + S_2O_8^{2-} \rightarrow HS_2O_8^- \quad (8)$$
$$HS_2O_8^- + H_2O \rightarrow HSO_4^- + H^+ + HSO_5^- \quad (9)$$

Depending on pH, Caro's acid anion (HSO_5^-) may then react with $SO_4^{-\cdot}$ or $HO^{\cdot}$ radicals[20] yielding oxygen or, under acidic conditions, may hydrolyse producing sulphuric acid and hydrogen peroxide (eqn (10))[20] the latter generating oxygen (eqn (11)).

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \quad (10)$$
$$H_2O_2 \rightarrow H_2O + 1/2O_2 \quad (11)$$

Ozone may also be formed from the reaction between Caro's acid and hydrogen peroxide.[20]

The observed rapid decrease in pH of both the unboiled and boiled solutions of APS that accompanied an increase in concentration of the oxidant up to about 50 mM (Fig. 2), can, from the foregoing discussion of persulphate decomposition, be attributed to the rapid production of acidic components (e.g. HSO_4^-) during decomposition. The finding (Fig. 2) that the pH of boiled APS solutions were some 2 units lower than those of unboiled solutions may be due to the extent of decomposition of the oxidant having been increased by boiling. The reduction in the rate of pH decrease found for concentrations of APS in excess of about 50 mM (both boiled and unboiled solutions) may be attributable to a reduction in the rate of persulphate decomposition caused by the presence of such acidic products. The low pH generated by the thermal decomposition of APS (Fig. 2) coupled with the elevated dyeing temperature employed (130°C) could be expected to have a damaging effect on some dye chromophores and may thus explain the marked change in shade observed by Topiwala[14] and in the present work.

Effects of ammonium persulphate on PET dyeing

A further range of dyeings of PET using CI Disperse Yellow 54 was carried out in the presence of various concentrations (0–37·5 mM) of APS. Each dyebath comprised 90 cm^3 of an aqueous acetic acid/sodium acetate buffer system; several such systems of differing buffer capacity were employed. It was found (Fig. 1) that a 0·02 M acetic acid/0·17 M sodium acetate system exerted adequate buffering action over the particular concentration range of oxidant used. Table 1 shows the meritorious effect of this particular buffer system on the colorimetric data obtained for the dyeing of PET with CI Disperse Yellow 54. Dyeings which had been carried out using APS in the unbuffered dyebath were considerably different in hue, chroma and lightness to the control dyeing (i.e. that carried out in the absence of oxidant); generally, the extent of this difference in colour increased with increasing concentration of oxidant used. Table 1

TABLE 1

Colorimetric Data for Polyester Dyed with CI Disperse Yellow 54 in both the Absence and Presence of 0·02 M Acetic Acid/0·17 M Sodium Acetate Buffer

APS (mM)	*L**		*a**		*b**		*c**		*h°*		*K/S*		*pH*	
	Pres	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*
0	73·9	—	14·5	—	85·0	—	86·3	—	80·3	—	19·2	—	5·5	5·5
2·5	72·0	70·8	15·0	11·9	83·1	80·4	84·4	81·3	79·8	81·6	20·2	19·8	5·5	2·9
3·75	72·0	68·5	14·2	13·6	82·7	77·0	84·0	78·1	80·2	80·0	19·6	19·7	5·5	2·4
5	72·9	68·0	14·4	12·9	83·8	76·1	84·9	77·2	80·3	80·3	19·5	19·6	5·4	2·3
6·25	72·5	67·8	14·7	13·1	83·9	76·2	85·2	77·4	80·1	80·2	20·1	20·4	5·4	2·3
12·5	75·1	66·4	12·9	12·1	85·8	73·2	86·8	74·2	81·4	80·6	19·7	19·7	5·2	2·0
25	73·7	63·9	9·9	5·9	79·4	53·3	80·1	53·7	82·9	83·7	17·5	10·7	4·8	1·5
37·5	75·9	66·3	4·9	3·6	71·3	41·7	71·5	41·9	86·0	85·1	10·6	4·9	4·5	1·5
0[a]	—	72·4	—	11·5	—	82·2	—	83·0	—	82·1	—	19·9	—	1·9
0[a]	—	67·1	—	9·4	—	74·3	—	74·9	—	82·8	—	20·8	—	1·5
0[a]	—	63·1	—	8·5	—	68·2	—	68·8	—	82·9	—	20·6	—	0·9

Abs: in absence of buffer.
Pres: in presence of buffer.
[a] pH of dyebath adjusted using sulphuric acid.

shows that although at concentrations of up to 6·25 mM oxidant, the values of the five colorimetric parameters obtained when dyeing had been caried out in buffered APS dyebaths, were, in general, lower than those of the control dyeing, the samples were of a similar colour to that of the dyeing carried out in the absence of oxidant. The colour of dyeings obtained using concentrations of APS in excess of 6·25 mM in both buffered and unbuffered dyebaths was less similar to that of the control, the extent of this dissimilarity increasing with increase in concentration of ammonium persulphate employed; the values of these colorimetric parameters at concentrations of 25 and 37·5 mM APS greatly differed from those of the control dyeing. The results shown in Table 1 clearly demonstrate that dyeings obtained using up to 6·25 mM APS in the buffered dyebath were slightly duller (as given by the lower c^* values) and bluer (as shown by the lower b^* values), but deeper in shade (as given by the lower L^* values and higher K/S values) than the dyeing produced in the absence of oxidant.

Table 1 also shows that the pH of the residual dyebaths obtained for dyeings carried out in the absence of buffer were highly acidic, especially at the higher concentrations of oxidant used. This implies that the marked shade difference between such dyeings and the control (Table 1) could, as suggested earlier, be due to the low pH generated during thermal decomposition of persulphate having damaged the dye chromophore at the elevated dyeing temperature (130°C) used. The effect of pH on dyeing was examined by applying CI Disperse Yellow 54 to PET at 130°C at pH values 1, 1·5 and 2, the dyebath pH having been adjusted using sulphuric acid. The colorimetric data obtained (Table 1) show that the colour of the three dyeings differed to that of the control dyeing; however, the colour of the dyeings obtained at pH 1–2 using sulphuric acid were considerably closer to that of the control than was the colour of the dyeings obtained at similar pH values using APS in the unbuffered dyebath. This suggests that low pH was not alone responsible for the marked shade change obtained when dyeing had been carried out in the presence of the oxidant and therefore implies that APS contributed greatly to this colour change.

Table 2 shows the colorimetric data for dyeings carried out using various concentrations of oxidant in both the absence an presence of acetate buffer, which had been extracted with DMF. A comparison of Table 1 and Table 2 reveals that, as expected, DMF extraction resulted in dye loss from all dyeings, as represented by the higher L^* and lower K/S values of the extracted samples. DMF extraction also reduced the a^*, b^* and c^* but increased the $h°$ values of dyeings carried out in both the absence and presence of buffer (Tables 1 and 2); this change in colour of the

TABLE 2

Colorimetric Data for Dyeing of PET with CI Disperse Yellow 54 in the Absence and Presence of 0·02 M Acetic Acid/0·17 M Sodium Acetate Buffer after Extraction with DMF

APS (*mM*)	*L**		*a**		*b**		*c**		*h°*		*K/S*	
	Pres	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*
0	75·8	—	−0·2	—	73·3	—	73·3	—	270·1	—	13·9	—
2·5	74·2	72·0	1·0	0·8	71·9	66·2	71·9	66·2	89·2	89·3	14·4	12·6
3·75	74·0	70·7	0·8	2·1	71·0	66·5	71·0	66·5	89·3	88·2	14·0	14·0
5	75·9	70·5	−0·5	1·5	72·2	65·2	72·2	65·2	270·4	88·7	13·2	13·5
6·25	74·8	69·5	0·5	2·3	72·3	65·3	72·5	65·3	89·6	88·0	14·2	14·1
12·5	76·6	68·2	−0·6	2·7	73·0	63·2	73·0	63·3	270·5	87·6	13·0	13·9
25	73·9	64·7	1·7	3·7	67·9	40·9	67·9	41·1	88·6	84·9	10·6	4·9
37·5	74·9	66·3	−0·1	3·0	60·7	31·1	60·7	31·3	270·1	84·5	6·4	2·7
0[a]	—	75·7	—	−2·6	—	68·7	—	68·8	—	272·2	—	11·4
0[a]	—	69·7	—	−0·2	—	62·4	—	62·4	—	270·2	—	12·4
0[a]	—	67·9	—	0·0	—	59·0	—	59·0	—	270·0	—	12·0

Abs: in absence of buffer.
Pres: in presence of buffer.
[a] pH of dyebath adjusted using sulphuric acid.

dyeings that occurred during DMF extraction was not caused by APS since it was observed for the control dyeing and also for the three dyeings obtained using sulphuric acid in the absence of oxidant. It was initially considered that the colour change which occurred upon DMF extraction could be due to solvatochromism caused by the presence of residual DMF within the dyed fibre. Consequently, each of the DMF extracted dyeings was boiled in distilled water for 30 min and allowed to dry in the open air in order to remove all residual DMF. However, this aqueous treatment had little effect on the colour of the dyeings (Table 3) and therefore demonstrated that solvatochromism was not responsible for the observed change in colour of the dyeings that had occurred upon DMF extraction. Since treatment of polyester with polar solvents is known to induce marked conformational changes in the physical structure of the substrate,[25–27] treatment with boiling DMF may have resulted in conformational changes not only of the fibre but also of the dye within the substrate; however, this aspect of the work requires further examination.

The results shown in Table 2 show identical trends to those of Table 1 in that dyeings which had been carried out using APS in the unbuffered dyebath were much different in colour to the control dyeing, while dyeings carried out in the presence of buffer were of a similar colour to the control. Table 2 also shows that, as previously observed (Table 1), the colour of dyeings obtained using concentrations of the oxidant in excess of 6·25 mM,

TABLE 3

Colorimetric Data for Dyeing of PET with CI Disperse Yellow 54 in the Absence and Presence of 0·02 M Acetic Acid/0·17 M Sodium Acetate Buffer after Extraction with DMF and Boiling in Distilled Water for 30 min

APS (mM)	*L**		*a**		*b**		*c**		*h°*		*K/S*	
	Pres	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*	*Pres*	*Abs*
0	75·7	—	−0·0	—	73·2	—	73·3	—	90·0	—	13·8	—
2·5	74·3	71·8	1·2	0·8	72·3	66·1	72·3	66·6	89·1	89·4	14·3	12·5
3·75	74·2	70·6	0·0	2·0	71·3	66·6	71·3	66·6	89·3	88·5	13·8	13·9
5	75·8	70·1	−0·2	1·7	72·8	65·2	72·8	65·2	270·1	88·5	13·4	13·6
6·25	75·1	69·3	0·3	2·6	72·8	65·7	72·8	65·8	89·8	87·8	14·0	14·5
12·5	76·7	68·2	−0·5	2·7	73·2	63·4	73·2	63·5	270·4	87·5	12·8	13·8
25	74·0	64·7	1·9	3·6	68·1	41·3	68·1	41·4	88·4	85·1	10·5	5·0
37·5	75·0	66·4	0·1	2·8	61·0	31·4	61·0	31·5	89·9	84·8	6·4	2·7
0[a]	—	75·6	—	−2·4	—	69·0	—	69·0	—	272·0	—	11·6
0[a]	—	69·7	—	0·0	—	62·6	—	62·6	—	270·0	—	12·4
0[a]	—	67·7	—	0·2	—	59·2	—	59·2	—	89·8	—	12·2

Abs: in absence of buffer.
Pres: in presence of buffer.
[a] pH of dyebath adjusted using sulphuric acid.

in both the absence and presence of buffer, was considerably different to that of the control dyeing. It was previously observed (Table 1) that the inclusion of APS in the buffered dyebath at concentrations of up to 6·25 mM resulted in an increase in depth of shade; Table 2 demonstrates that after DMF extraction, these particular samples remained generally deeper in shade than the control. This implies that not only has APS increased the depth of shade but also that the fastness of such dyeings to DMF extraction was comparable to that of the control dyeing. It was also previously observed (Table 2) that dyeing at low pH using sulphuric acid increased the depth of shade, although the colour of the dyeings obtained at pH 1 and 1·5 was considerably different to that of the control. Table 2 shows that the fastness to DMF extraction of the three dyeings produced using sulphuric acid was lower than that of dyeings obtained using APS (as given by the low *K/S* values of the DMF extracted samples) which suggests that low pH, in the absence of oxidant, yields dyeings of low fastness to DMF extraction.

Ibrahim & Haggag[10] proposed a free radical dyeing mechanism, based on the scheme originally suggested by Bartlett & Cotman,[17] to account for the improved depth of shade obtained when nylon 6 had been dyed with disperse dyes in the presence of redox systems based on ammonium persulphate as oxidant and potassium pyrosulphite, glucose or thiourea dioxide as reductant. This mechanism involved the formation of covalent bonds between the dye and fibre, as shown in Scheme 1 for the dyeing of nylon 6 with disperse dyes:

$$\begin{gathered}S_2O_8^{2-} \rightarrow 2SO_4^{-\cdot}\\ SO_4^{-\cdot} + H_2O \rightarrow HSO_4^- + HO^\cdot\\ SO_4^{-\cdot} + \text{Ny-H} \rightarrow \text{Ny}^\cdot + HSO_4^-\\ \text{D-XH} + SO_4^{-\cdot} \rightarrow \text{D-X}^\cdot + HSO_4^-\\ \text{Ny}^\cdot + \text{D-X}^\cdot \rightarrow \text{Ny-X-D}\end{gathered}$$

Scheme 1

where Ny-H and D-XH (XH = OH, NH_2, NHR, etc.) represent the nylon and dye, respectively.

Scheme 1 implies that sulphate radical anions are responsible for covalent attachment of the dye to the substrate. However, eqns (4)–(7) show that, under the pH conditions prevalent with the buffer system employed in this work (pH 5·5–4·5), at least three intermediates ($SO_4^{-\cdot}$, $HO^\cdot$ and H_2O_2) may be involved in the thermal decomposition of persulphate ion and thus in the free radical attack of both CI Disperse Yellow 54 and PET. The decomposition of hydrogen peroxide, especially when catalysts (e.g. $SO_4^{-\cdot}$ and $HO^\cdot$) are present, can be very rapid,[20] eqns (12)–(16) having been reported in this context.

$$HO^\cdot + H_2O_2 \rightarrow H_2O + HOO^\cdot \quad (12)$$

$$SO_4^{-\cdot} + H_2O_2 \rightarrow HSO_4^- + HO_2^\cdot \quad (13)$$

$$HO_2^\cdot \leftrightarrow O_2^{-\cdot} + H^+ \quad (14)$$

$$HO_2^{-\cdot} + S_2O_8^{2-} \rightarrow HSO_4^- + SO_4^{-\cdot} + O_2 \quad (15)$$

$$O_2^{-\cdot} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{-\cdot} + O_2 \quad (16)$$

It can therefore be suggested that owing to such rapid decomposition, H_2O_2 (and thus $HOO^\cdot$)may contribute less to free radical attack on both dye and fibre than the $SO_4^{-\cdot}$ and $HO^\cdot$ radicals. Norman *et al.*,[21] Gilbert *et al*,[22] and Chawla & Fessonden[23] found, using ESR, that the sulphate radical can generate radicals from a number of both inorganic and organic compounds in a manner similar to that displayed by the hydroxyl radical, but the former radical shows a greater tendency towards direct oxidation by one electron transfer. In general, the hydroxyl radical is more reactive than the sulphate radical and the sulphate radical is less reactive towards water than towards other substrates.[20,21,23,24] Thus eqns (17) and (18) could contribute to free radical attack on both dye and substrate and these two equations may therefore be inserted into Scheme 1.

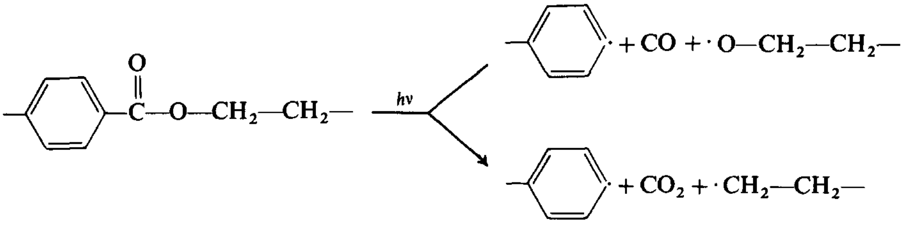
$$OH^\cdot + \text{Dye-XH} \rightarrow \text{Dye-X}^\cdot + H_2O \quad (17)$$

$$OH^\cdot + \text{Ny-H} \rightarrow \text{Ny}^\cdot + H_2O \quad (18)$$

From the foregoing, the observed increase in depth of shade secured by the inclusion of ammonium persulphate (at concentrations of up to 6·25 mM) in the buffered CI Disperse Yellow 54 dyebath may arise by virtue of the dye and fibre having reacted with both hydroxyl and sulphate radicals. The observed change in shade that occurred when dyeing had been carried out both in the absence of buffer and at concentrations in excess of 6·25 mM APS in the presence of buffer (Tables 1 and 2) may be attributed to destruction of the chromophore resulting from a combination of the low pH generated by thermal decomposition of the oxidant and the high dyeing temperature used as well as by oxidative decomposition.

ATR analysis of the polyester fibres

The photo-oxidative degradation of polyester has been studied by many authors.[28-32] Marcotte *et al.*[28] used ESR to study the photo-degradation of PET caused by exposure to light at 253·7 and 313 nm and proposed the mechanism shown in Scheme 2; crosslinking of the fibre was considered to occur by combination of the phenyl radicals in adjacent polymer chains.[28]

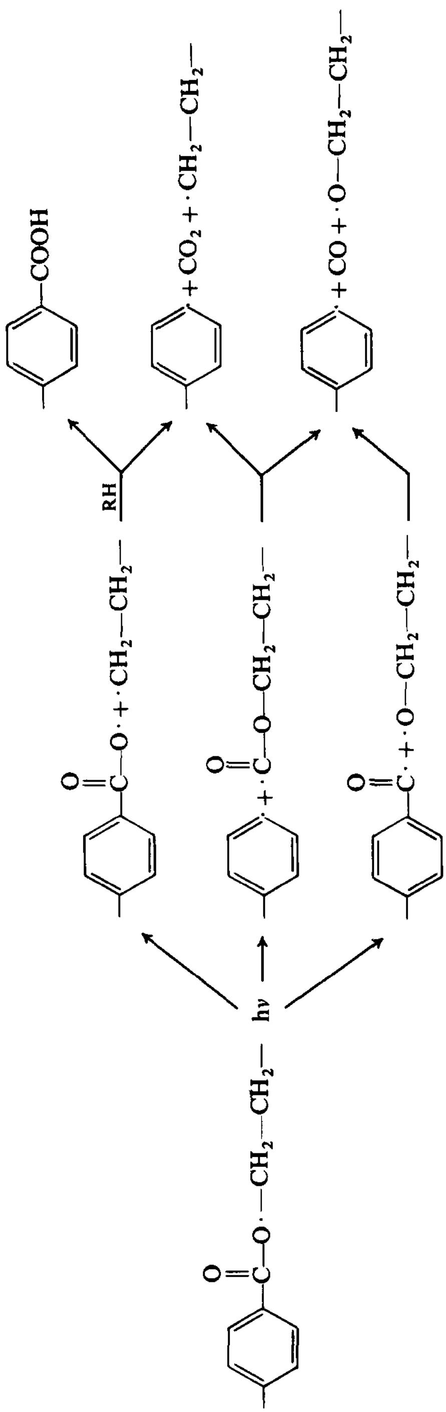


Scheme 2

Day & Wiles[29,30] observed that photo-degradation of PET involved the formation of carboxyl end groups (Scheme 3); over 90% of the volatile degradation products were found to be either carbon monoxide or carbon dioxide Hydroxylated polyesters were also detected when PET was exposed in air to ultraviolet irradiation.[31]

Other workers[30,32] have proposed that the photo-degradation of PET involves the formation of various species such as aromatic hydroxyl, aliphatic and aromatic aldehyde, aromatic carboxyl and aliphatic C=C bonds.

The ATR spectrum of PET which had been treated in sodium acetate/acetic acid buffer at pH 5·5 for 60 min at 130°C is shown in Fig. 3; Fig. 4 shows the corresponding spectrum of PET which had been treated with



Scheme 3

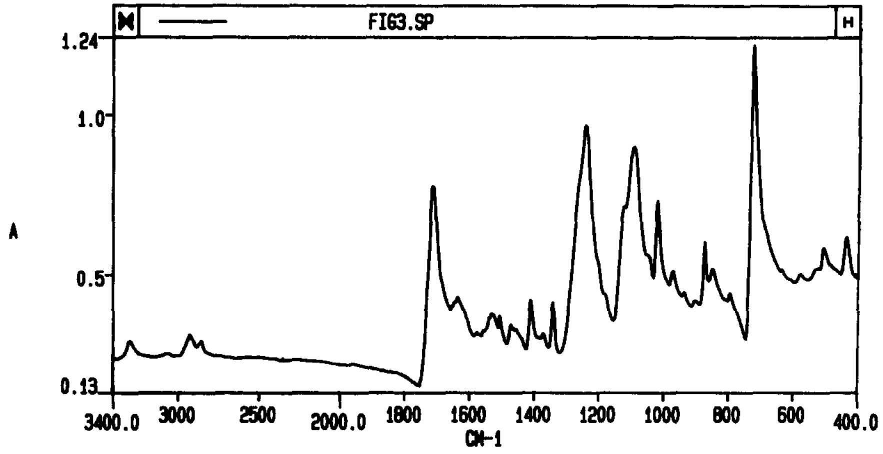


Fig. 3. ATR spectrum of PET treated in distilled water at 130°C for 60 min.

6·25 mM of APS under identical conditions. Subtraction of Fig. 3 from Fig. 4 yields the difference spectrum (Fig. 5), from which it is clear that the oxidant has had a considerable effect on PET.

The strong absorption at 1703 cm^{-1} (Fig. 5) indicates stretching of the C=O groups[33–35] which may be due to the formation of aldehyde and/or carboxyl groups. Spectral changes occur for the bands at 1239 cm^{-1} which represent the modes associated with stretching of the C—O bonds[33–35] that may result from the formation of hydroxyl and or carboxyl groups; the bands appearing at 1089 cm^{-1} may be attributed to the formation of C=C double bonds and/or aldehyde groups.[33] The negative absorption

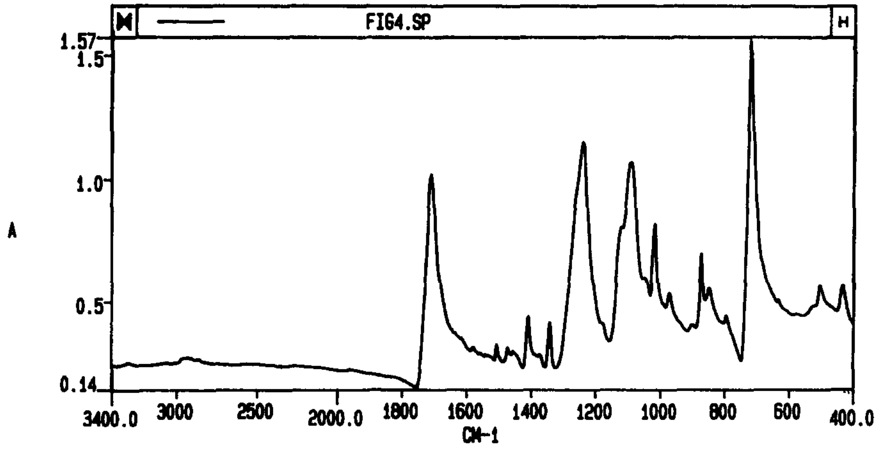


Fig. 4. ATR spectrum of PET treated in distilled water with 6·25 mM APS at 130°C for 60 min.

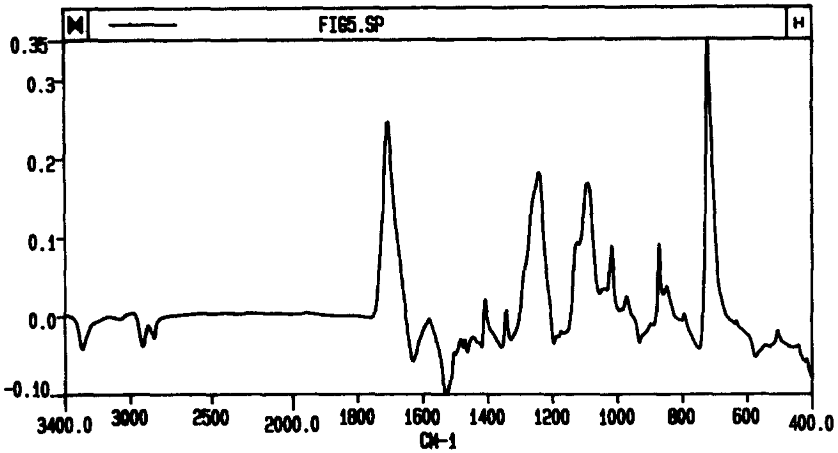


Fig. 5. Difference spectrum (Fig. 3 subtracted from Fig. 4).

appearing at 2929 cm^{-1} (Refs 36–38) and 2856 cm^{-1} (Ref. 39) reflect the loss of the stretching of aliphatic C—H bonds and the negative absorption in the region of 1475 cm^{-1} (Refs 36, 40, 41) and 1463 cm^{-1} (Refs 36, 37, 39–41) suggests loss of the bending of aliphatic C—H bonds; the spectral change in the band at 933 cm^{-1} also indicates the loss of bending of C—H bonds.[39] The disappearance of absorption at 3296 cm^{-1} implies the loss of hydroxyl end groups[33–35] due to the possible formation of aldehyde groups. The foregoing reveals that the mechanism of the oxidative degradation of PET is very complicated and the results shown in Fig. 5 agree with those obtained for the photo-degradation of PET, namely, that aromatic hydroxyl, aliphatic aldehyde, carboxyl and

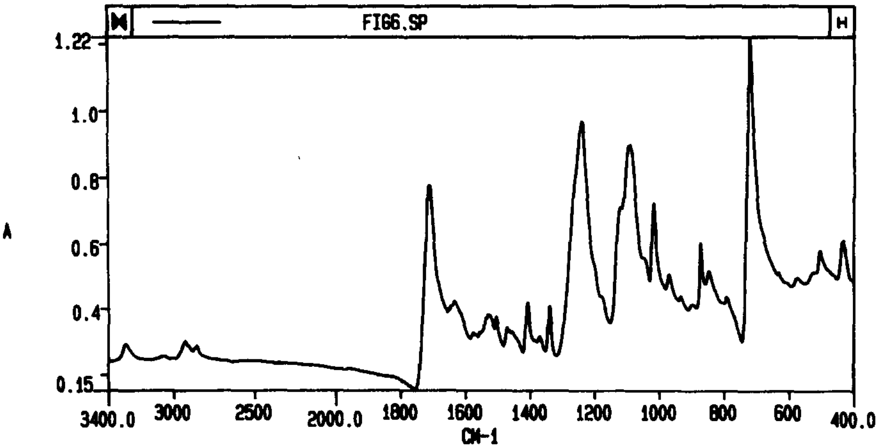


Fig. 6. ATR spectrum of PET dyed with CI Disperse Yellow 54 at 130°C for 60 min.

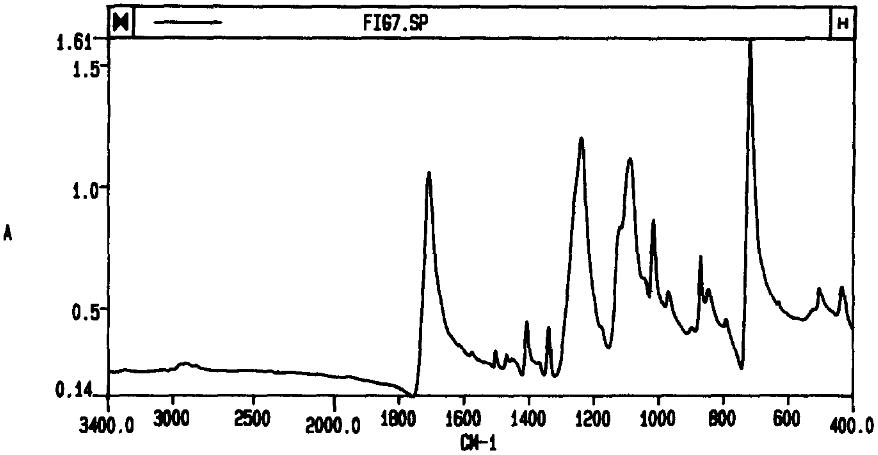


Fig. 7. ATR spectrum of PET dyed with CI Disperse Yellow 54 in the presence of 6·25 mM at 130°C for 60 min.

aliphatic C=C double bonds were formed by treatment of PET with ammonium persulphate.

The ATR spectrum of PET which had been dyed for 60 min at 130°C in sodium acetate/acetic acid buffer at pH 5·5 is shown in Fig. 6; Fig. 7 shows the corresponding spectrum of PET which had been dyed in the presence of 6·25 mM APS under identical conditions. Subtraction of Fig. 6 from Fig. 7 yields the difference spectrum (Fig. 8) which shows the effect of APS on PET dyeing. Figure 9 (Fig. 5 overlaid with Fig. 8) indicates that Fig. 8 displays similar results to Fig. 5. In order to obtain better resolution spectra the second order derivative spectra[42,43] of Fig. 9

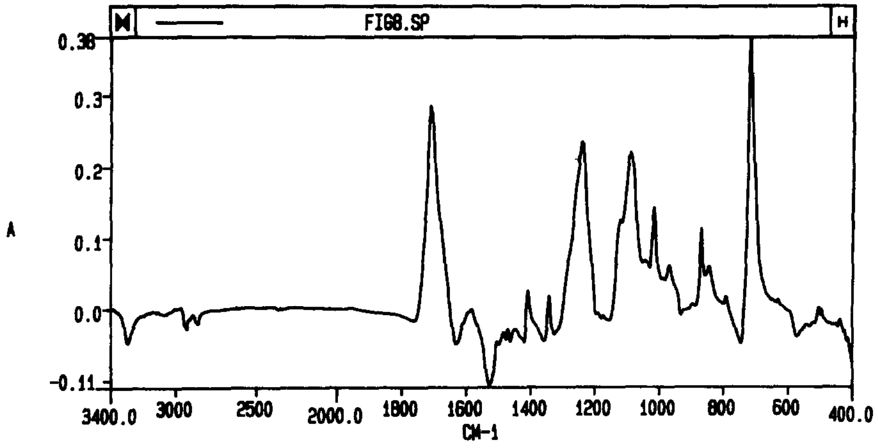


Fig. 8. Difference spectrum (Fig. 6 subtracted from Fig. 7).

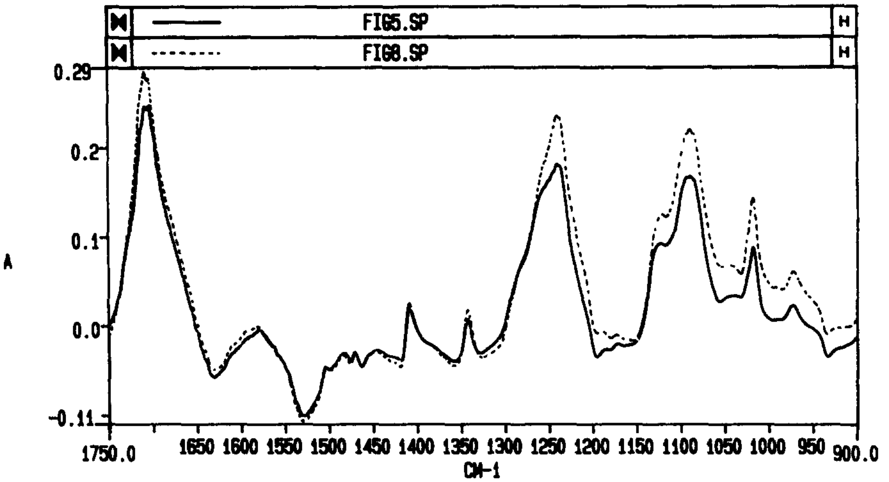
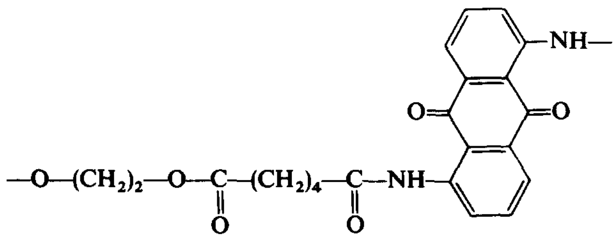


Fig. 9. The overlaid spectra of Figs 5 and 8.

are shown in Fig. 10. The bands appearing at 1022 cm^{-1} (Fig. 10) may be attributed to the loss of the bending of aromatic C—H bonds[36–39,41] as well as the stretching of C—H bonds[41] or of aromatic C—C bonds[38] the spectral change in the band at 1099 cm^{-1} (derivatised spectrum of Fig. 5) indicates the possible formation of an aliphatic aldehyde group,[33,34] C=C double bonds[33] and/or hydroxyl groups.[33–35]



Scheme 4

Although IR spectroscopy has been used to confirm the chemical binding of 1,5-diamino anthraquinone to an aliphatic polyester (Scheme 4)[44] during polymerisation of adipic acid, diethylene glycol, dimethylolpropane and 1,5-diamino anthraquinone in the presence of iron, ammonium molybdate and (MeO)$_4$Ti, according to Figs 9 and 10 no clear evidence was found in this work to confirm the covalent binding of CI Disperse Yellow 54 to the substrate; it appears that the primary effect of ammonium persulphate on PET dyeing is predominantly oxidative degradation.

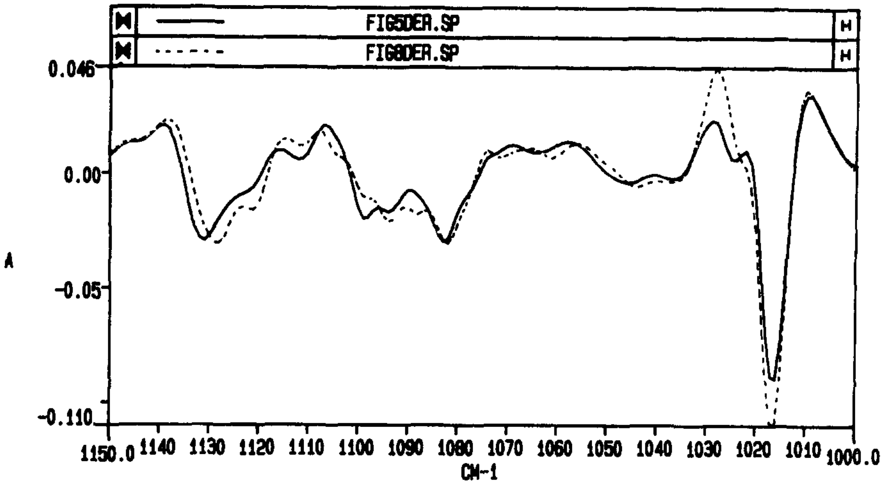


Fig. 10. Second order derivative spectra from Fig. 9.

CONCLUSIONS

In the presence of ammonium persulphate, it is necessary to use a strong buffer to avoid damage to the dye during dyeing. The dyeing of PET with CI Disperse Yellow 54 in the presence of ammonium persulphate results in enhanced colour yield and improved fastness of the dyeings to extraction with DMF. No evidence has been found, using ATR IR analysis, to confirm that covalent bonding occurs between the disperse dye and the fibre.

ACKNOWLEDGEMENTS

The authors wish to thank the Committee of Vice-Chancellors and Principals of the Universities of the United Kingdom and the University of Leeds for the provision of a scholarship to Mr Lu

REFERENCES

1. Karelina, S. L., Sepantsova, N. P., Geller, B. E. & Ivanova, E. P., *Technol. Text. Ind. USSR*, **5** (1971) 75.
2. Ereshchenko, A. G., Sepantsova, N. P. & Geller, B. E., *Technol. Text. Ind. USSR*, **4** (1971) 103.
3. Bhattachary, S. D., *Colourage*, **36**(8) 19 (1989) 19.
4. Shenai, V. A. & Saraf, N. F., *Int. Dyer Text. Printer*, **163** (1980) 269.
5. Shenai, V. A. & Shah, H. C., *Colourage*, **28**(17) (1981) 7.
6. Shenai, V. A. & Chavada, B. P., *Text. Dyer & Printer*, **23**(20) (1990) 31.

7. Ibrahim, N. A., Haggag, K. & Hebeish, A., *Angew. Makromol. Chem.*, **131** (1985) 15.
8. Ibrahim, N. A., Haggag, K. & Hebeish, A., *Angew. Makromol. Chem.*, **132** (1985) 53.
9. Ibrahim, N. A., Aggour, Sh. Sh. & Hebeish, A., *Am. Dyest. Rep.*, **75**(4) (1986) 13.
10. Ibrahim, N. A. & Haggag, K., *Dyes and Pigments*, **8** (1987) 327.
11. Ibrahim, N. A. & Dawoud, M. A., *Am. Dyest. Rep.*, **77**(3) (1988) 35.
12. Ibrahim, N. A. & Dawoud, M. A., *Am. Dyest. Rep.*, **77**(6) (1988) 35.
13. Ibrahim, N. A. & Dawoud, M. A., *Am. Dyest. Rep.*, **77**(8) (1988) 56.
14. Topiwala, K., MSc thesis, University of Leeds, 1988.
15. Luo, J., *J. Soc. Dyers Col.*, **107** (1991) 117.
16. Kolthoff, I. M. & Miller, I. M., *J. Am. Chem. Soc.*, **73** (1951) 3055.
17. Bartlett, P. D. & Cotman, J. D., *J. Am. Chem. Soc.*, **71** (1949) 1419.
18. Kolthoff, I. M. & Miller, I. M., *J. Am. Chem. Soc.*, **73** (1951) 3055.
19. Fronaeus, S. & Ostman, A. C. O., *Acta Chem. Scand.*, **9** (1955) 902.
20. Behrman, E. J., *Rev. Inorg. Chem.*, **2** (1980) 179.
21. Norman, R. O. C., Stovey, P. M. & West, P. R., *J. Chem. Soc. (B)*, (1970) 1087.
22. Gilbert, B. C., Larkin, J. P. & Norman, R. O. C., *J. Chem. Soc. Perkin Trans. II*, (1972) 1272.
23. Chawla, O. P. & Fessonden, R. W., *J. Phys. Chem.*, **79** (1975) 2693.
24. Linck, R. G., In *Transition Metals in Homogeneous Catalysis*, ed. G, N, Schrauzer, Chapter 7. Marcel Dekker, New York, 1971.
25. Weigmann, H.-D., Scott, M. G., Ribnick, A. S. & Rebenfeld, L., *Text. Res. J.*, **46** (1976) 574.
26. Weigmann, H.-D., Scott, M. G., Ribnick, A. S. & Matkowsky, R. D., *Text. Res. J.*, **47** (1977) 745.
27. Weigmann, H.-D., Scott, M. G. & Ribnick, A. S., *Text. Res. J.*, **48** (1978) 4.
28. Marcotte, F. B., Campbell, D., Cleaveland, J. A. & Turner, D. T., *J. Polym. Sci. A-1*, **5** (1967) 481.
29. Day, M. & Wiles, D. M., *J. Appl. Sci.*, **16** (1972) 191.
30. Day, M. & Wiles, D. M., *J. Appl. Sci.*, **16** (1972) 203.
31. Bentley, P. *et al.*, *Rev. Prog. Coloration*, **5** (1974) 33.
32. Ranby, B. & Rabek, J. B., *Photodegradation, Photo-oxidation, Photo-stabilization of Polymers*, Chapter 4. John Wiley, London, 1975.
33. Dyer, J. R., *Application of Absorption Spectroscopy of Organic Compounds.* Prentice-Hall, Englewood Cliffs, NJ.
34. Pouchert, C. J., *The Aldrich Library of Infrared Spectra*, 3rd edn. Aldrich Chemical Company Inc., Milwaukee, USA, 1981.
35. Scheinmann, F., *An Introduction to Spectroscopic Methods for the Identification of Organic Compounds, Vol. 1.* Pergamon Press, Oxford, 1970, pp. 166–91.
36. Daniels, W. W. & Kitson, R. E., *J. Polym. Sci.*, **33** (1958) 161.
37. Gary, V., *Man-made Textiles in India* (1979) 491.
38. Bahl, S. K., PhD thesis, University of Cincinnati, 1974.
39. Manley, T. R. & Williams, D. A., *Polymer*, **10** (1969) 339.
40. Grime, D. & Ward, I. M., *Trans. Faraday Soc.*, **54** (1958) 959.
41. Sikka, S. S. & Kausch, H. H., *Coll. Polym. Sci.*, **257** (1979) 1060.
42. Bridge, T. P., Fell, A. F. & Wardman, R. F., *J. Soc. Dyers Col.*, **103** (1987) 17.
43. Joy, M. & Lewis, D. M., *Int. J. Cosmet. Sci.*, **13** (1991) 249.
44. Litvinenko, L. M., *Ukr. Khim. Zh.*, **46**(11) (1980) 1176 (CA 94(12) : 84914c).