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The degradation of dyed cotton fabrics by the sensitised production of singlet oxygen via an aqueous soluble phthalocyanine dye

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Abstract

The sensitised production of singlet oxygen is known to play an important role in polymer photo-oxidation reactions. Zinc phthalocyanine sulfonate (ZnPcS) is a known singlet oxygen sensitiser. However, the role of zinc phthalocyanine sulfonate as a sensitiser of singlet oxygen within a polymer matrix and its contribution to degradation is not well documented. In this investigation the photo-stability and photochemistry of dyed polymer fabrics, treated with ZnPcS, was undertaken to establish the nature of the mechanisms involved. The photo-stability of a range of dyes as well as the treated fabric has been investigated coupled with methods of stabilisation. ZnPcS was found to be detrimental to the photo-stability of dyed fabrics after a washing treatment. The sensitisation of singlet oxygen production in these fabrics and mechanisms of dye fading, were confirmed using various photochemical and analytical techniques. These included flash photolysis, which indicated that triplet energy transfer and intersystem crossing were major contributory factors in the sensitised production of singlet oxygen by ZnPcS. The degradation of dyed polymer fabrics treated with ZnPcS could be significantly reduced by the introduction of a safe trapping agent into the system. A peroxy radical scavenger decreased the concentration of hydroperoxide formed in treated fabrics that had been exposed to light and washed, while the addition of a radical trap after each wash was found to reduce photo-fading, i.e. improving the photo-stability. The mechanistic implications of these processes are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Singlet-oxygen; Photo-stability; Cotton; Dyes; Quenching; Degradation

1. Introduction

The degradation of dyed polymer textiles due to light exposure and washing is of great importance in terms of prolonging the lifetime of clothing. The number of wash cycles, combined with the amount of light exposure that textiles can endure is of particular interest to clothing and detergent manufacturers. The essential features of the polymer chain in cotton cellulose are: the main sequence of intermediate units, the non-reducing end groups and the glycosidic linkages as shown in Fig. 1.

All cotton fabrics used in this study had been mercerised and bleached. Mercerisation is a treatment using a strong caustic soda solution; without tension, strength and dye substantivity is improved, if tension is applied lustre is also improved. These

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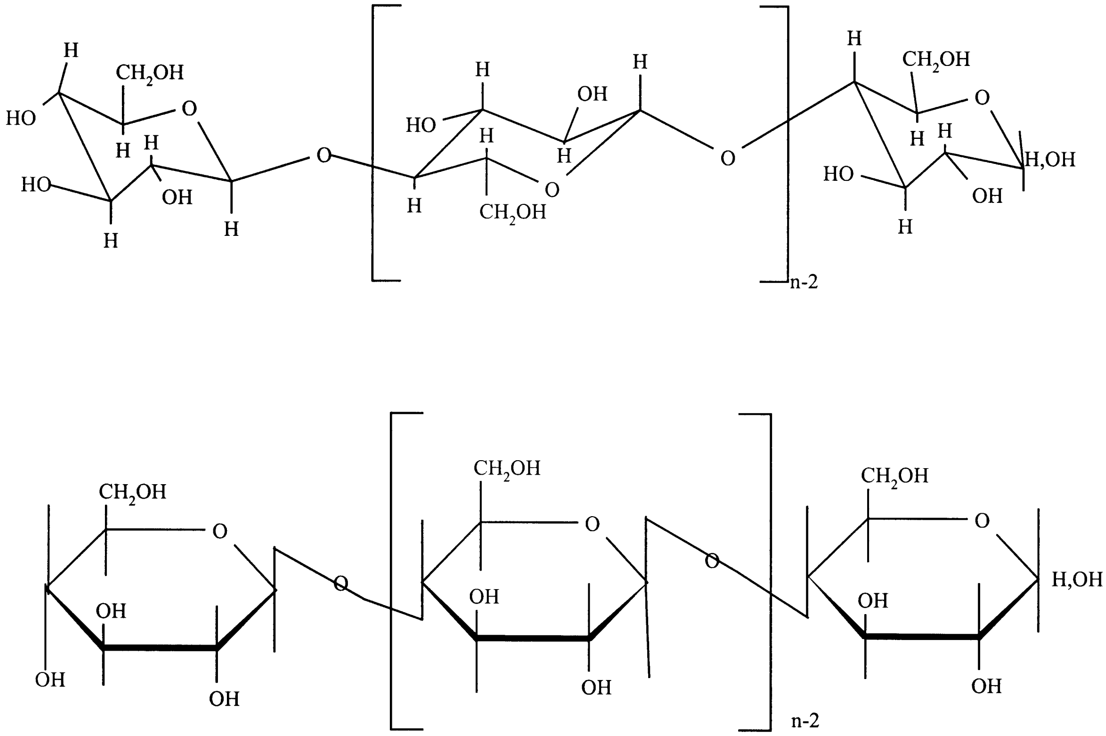


Fig. 1. Cellulose molecule.

effects tend to be confined to the surface of the fabric, as full penetration of concentrated caustic is not obtained at low temperature. Bleaching is carried out using hypochlorite, sodium chlorite or hydrogen peroxide. Mercerised cotton is more susceptible to dye uptake than the untreated fabric as a result of fibre expansion and internal re-orientation within the polymer during chemical treatment. This creates more sites for chemical and physical bonding of dye molecules to cotton fibres.

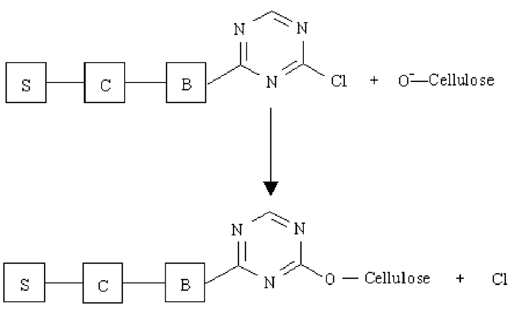
Three types of dyestuff are used on cotton; reactive, direct and vat dyes.

1. Reactive dyes are bonded to the cotton fabric by covalent bonds. Reactive dyes have four characteristic structural features in common.

where S = Solubilising group
C = Coloured molecule
B = Bridging group
X = Reactive group

The reactive dyes used here are monochlorotriazine dyes such as that shown in Fig. 2.

Monochlorotriazine dyes react by nucleophilic substitution with the monochlorotriazine bridging group as shown in Eq. (1).



(1)

Nucleophilic Substitution In Monochlorotriazine Dyes

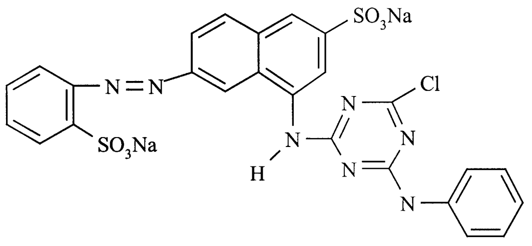
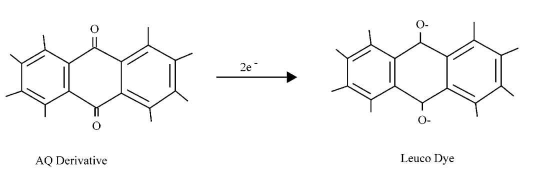


Fig. 2. Azo-bis-monochlorotriazine reactive dye.

Reactive dyes usually show excellent light and wash fastness, however, they are not usually fast to chlorine or other bleaches.

2. Direct dyes are bonded to cotton by absorption usually involving dipole interactions. It has been found that direct dyes are absorbed on specific sites in the polymer. In mercerised cotton dye uptake is good due to an open polymer structure. Direct dyes usually contain an azo chromophore with a triazine ring. These dyes tend to have good light-fastness properties but fairly poor wet-fastness, this was found in the photo-hydrolysis experiment discussed later.
3. Vat dyes work by reduction of a water insoluble dye into a water-soluble substantive compound called a leuco dye. This penetrates into the fibre and is reconverted via oxidation into the original insoluble form. Eq. (2) shows the conversion of an anthraquinone derivative in a vat dye into the leuco form of the dye [1].



(2)

Conversion of Anthraquinone into the Leuco Form

The chemical makeup of the dye influences the properties of its leuco form in the dyeing process, e.g. the rate of absorption, diffusion into the fibre, substantivity, thermal stability and levelling out properties. The green dye used here is an example of a dibenzanthrone (Fig. 3), which has very good light and wet-fastness properties.

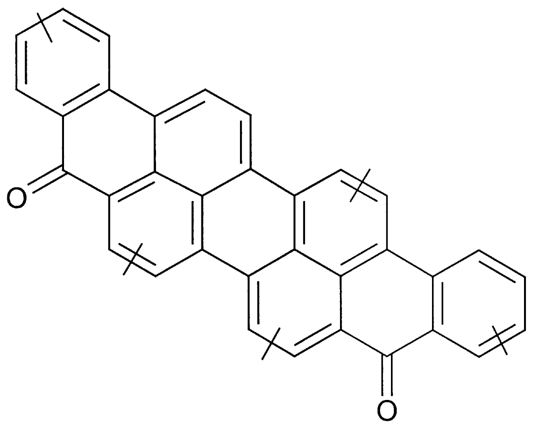


Fig. 3. Dibenzanthrone dye.

Photoluminescence of organic dyes in solution has shown that when illuminated, dyes absorb energy and are excited to higher energy states. Return to ground state can occur via fluorescence or phosphorescence. It has been shown that oxygen can quench the fluorescence of some irradiated dyes by an energy transfer process from the excited dye to oxygen, these energy transfer processes are shown in Eq. (3) [2], where D denotes a dye molecule.

$${}^3\mathrm{D} + {}^3\mathrm{O}_2 \xrightarrow{\text{isc}} {}^1\mathrm{D} + {}^1\mathrm{O}^*$$

Generation of ${}^1O_2$ *by triplet energy transfer.*

(3a)

$${}^1\mathrm{D}^* + {}^3\mathrm{O}_2 \xrightarrow{\text{isc}} {}^3\mathrm{D}^* + {}^1\mathrm{O}_2$$

Collisional energy transfer.

(3b)

$${}^3\mathrm{D}^* + {}^3\mathrm{O}_2 \rightarrow \underset{\substack{\text{triplet}\\ \text{exciplex}}}{{}^3(\mathrm{DO}_2)_n^*} \rightarrow \underset{\substack{\text{lowest}\\ \text{excited}\\ \text{singlet}\\ \text{exciplex}}}{{}^3(\mathrm{DO})_1^*} \xrightarrow{\substack{\text{spin}\\ \text{allowed}}} \underset{\substack{\text{ground}\\ \text{state}}}{{}^1\mathrm{D} + {}^3\mathrm{O}_2}$$

Intersystem crossing to the ground state

(3c)

Singlet oxygen can oxidise dyes, which do not react with ground state oxygen. In dyes containing an azo chromophore oxidation takes place via a concerted ‘ene’ reaction with the ketohydrazone form of the dye forming hydroperoxide [3]. Kuramoto and Kitao [4] reported that some anthraquinone dyes undergo photodecompostion via the production of singlet oxygen, generated by the dye itself or by a sensitiser. It would appear that singlet oxygen attaches to the dye itself. In fabrics, however, the process is more complex due to dye–substrate interactions [5,6]. Kuramoto and Kitao suggested that an efficient singlet oxygen quencher would improve photo-stability in dye substrate systems. Further investigations by the same authors [7] confirmed the involvement of singlet oxygen in the photo-oxidation of anthraquinone dyes. However, little evidence was found for a self-sensitised reaction, and the effect of a singlet oxygen quencher (DABCO) was confirmed. Egerton [8] proposed a mechanism in which the photo-active excited state of the dye (D), normally the triplet can be quenched by ground state molecular oxygen to produce active singlet oxygen. Excited state oxygen then reacts with the polymer (P) or water (under moist conditions) to form hydroperoxide radicals, which may then induce oxidative breakdown of the polymer as shown in Eq. (4).

$$\mathrm{D} \xrightarrow{\mathrm{hv}} {}^1\mathrm{D} \xrightarrow{\mathrm{isc}} {}^3\mathrm{D} \tag{4a}$$

$$ {}^3\mathrm{D}^* + {}^3\mathrm{O}_2 \rightarrow \mathrm{D} + {}^1\mathrm{O}_2 \tag{4b}$$

$$ {}^1\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{H}_2\mathrm{O}_2 \tag{4c}$$

Formation of hydrogen peroxide.

$$\mathrm{H}_2\mathrm{O}_2 + \mathrm{P{-}H} \rightarrow \text{Oxidation Products} \tag{4d}$$

Polymer breakdown.

Phthalocyanines are known to be effective photo-sensitisers. The photosensitising activity depends on the nature of the central metal atom and the substituents on the benzene rings. Photo-oxidation is initiated by an excited state, usually the triplet, of the sensitiser and is promoted by phthalocyanines as they have high triplet quantum yields and appropriate triplet lifetime. The central metal atom (see Fig. 4) promotes intersystem crossing, as Zn is diamagnetic, ZnPcS is an effective sensitiser, a paramagnetic central metal atom would shorten triplet lifetime and render the phthalocyanine inactive [9].

ZnPcS may form stacked aggregates, especially in aqueous solution, which could also lower photo-activity, as the major pathway for deactivation is through internal conversion to the ground state. Singlet oxygen production is sensitised by the transfer of excited state energy of the sensitiser to ground state oxygen, shown in Eq. (5).

$$\begin{tikzcd}
 & S_0 & S_0 + O_2 & \\
S_0 \arrow[r, "\text{hí}"] & S_1 \arrow[u, "K_f"] \arrow[d] \arrow[r, "K_{isc}"] & T_1 \arrow[u, "O_2", "K'_{et}"'] \arrow[d] \arrow[r, "{K_{et},O_2}"] & {}^1O_2 + S_0 \arrow[d] \\
 & S_0 & S_0 & O_2
\end{tikzcd}$$

5

Triplet-Singlet Energy Transfer

(5)

The interaction of the triplet excited state of the sensitiser with ground state oxygen proceeds by energy transfer leading to the formation of singlet oxygen and the sensitiser in the ground state.

Zinc phthalocyanine sulfonate (ZnPcS) is a known singlet oxygen sensitiser, which is used as an additive in washing powders to improve the appearance of white fabrics (produces the “blue haze”). However, it is not well documented whether ZnPcS could sensitise singlet oxygen within a dyed polymer matrix and therefore contribute to the subsequent degradation of the fabric. As dyed textiles can fade by a number of different photochemical mechanisms, one of which involves the sensitised production of singlet oxygen [1,2] a study of the degradation of dyed textiles, treated with ZnPcS, was undertaken, to establish whether

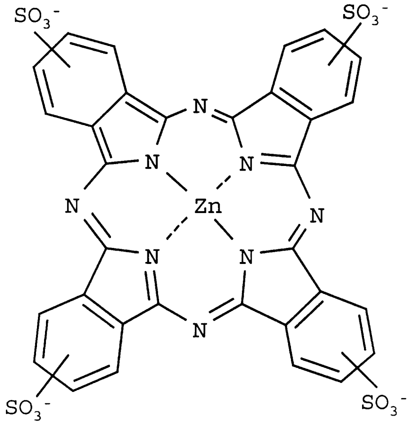


Fig. 4. Zinc phalocyanine sulfonate.

the singlet oxygen mechanism was significant. A high concentration of ZnPcS has been linked to stain removing properties when applied to white textiles, therefore, if ZnPcS was found to be insignificant in fading mechanisms its use as a stain remover could be further explored. Therefore, in most cases fabrics were saturated with ZnPcS before the appropriate analysis.

This study has two main themes. Firstly, the light-fastness properties of dyed polymer textiles treated with ZnPcS have been investigated, both before and after a number of simulated wash cycles (photo-hydrolysis). Photochemical analytical techniques including luminescence, flash photolysis and UV–Vis spectroscopy were used to establish the possible photo-degradation mechanisms occurring in these fabrics. Secondly, the sensitised production of singlet oxygen was found to be a very relevant mechanism in this system, therefore, singlet oxygen quenching studies were undertaken to establish whether a singlet oxygen quencher could significantly reduce photo-degradation and in turn prolong the life of dyed textiles.

2. Experimental

The following dyes, fabrics and trapping agents were used in the procedures described to establish dye/ZnPcS/fabric interactions. Reactive dyes were used to dye cotton in the laboratory, dyed fabrics provided were dyed with reactive, disperse, direct and vat dyes.

•Reactive dyes:	Procion Orange H –EXL, BASF Procion Crimson H-EXL, BASF	
•Fabrics:	Bleached cotton Dyed fabrics supplied by BASF	
•Treatment:	Zinc phthalocyanine sulfonate solution at varying concentrations, NaCl	
•Trapping agents:	Tetra-cyano-ethylene (TCE)	Electron trap
	Cadmium sulphate ($CdSO_4$)	Electron trap
	Potassium thiocyanate (KSCN)	Radical trap
	1,4-Diaza-bicyclo[2,2,2] octane (DABCO)	Singlet oxygen quencher
	Sodium benzene sulfonate (SbS)	Peroxy radical scavenger

2.1. Dyeing procedure

For Reactive dyes, the correct amount of dry dye powder, according to the percentage dyeing required was placed into a small beaker, a paste was formed using a little cold water. This was washed into a volumetric flask, using distilled water at 50 °C to produce a 250 cm^3 solution. The temperature of the dye solution was elevated to 100 °C and held at this temperature for 5 min then cooled.

Quantities of dyestuff required were calculated according to the equation:

$$\%\ \text{dyeing} = \big[(\text{vol. stock sol'n/weight of fabric}) \times (\text{mass of dye powder/total volume})\big] \times 100 \tag{6}$$

Reactive Procion dyes were used to carry out 0.2% dyeings on cotton.

The dry cloth (2.5 g) was rolled up and inserted into a sealable dyebath. The dye solution (20 cm^3) was added, and the dyebath was sealed. The dyebath was agitated for 5 min, after which salt (0.5 g) in water (2 cm^3) was added. After agitation for a further 20 min, the dyed material was withdrawn and soda ash (0.15g) ($NaCO_3$) was added, the fabric was then re-entered into the dyebath to continue agitation for a further 90 min.

This calculation of amount of dyestuff absorbed by the fabric was carried out using a solution depletion technique with UV/Vis absorbance spectroscopy.[1]

The dyed fabrics were treated with zinc phthalocyanine sulfonate (ZnPcS) of varying concentrations (10–500 ppm). ZnPcS was introduced into cotton fabric by soaking and agitation. Measuring the UV/Vis absorption of the solution at λ_{max} before and after treating the fabric monitored the amount of ZnPcS absorbed onto the fabric, the amount of ZnPcS absorbed was calculated in the same manner as for deposition of dyestuff.

After irradiation using a Sunchex Atlas Irradiation Unit, light-fastness monitoring on dyed fabrics was carried out using the procedure for light-fastness testing according Blue Wool (BS1006) and Grey Scale (BS1005) standards [10].

2.2. Singlet oxygen studies

Singlet oxygen detection methods were carried out, using a laser system with a germanium photodiode detector coupled to an oscilloscope. Bleached and unbleached cotton fabrics were treated with ZnPc. The fibre samples treated and untreated as well as a solution of ZnPc in D_2O were tested for singlet oxygen. The monochromator in the detection system was set at 1270 nm and using a germanium photodiode detector. Values of amplitude of trace (I_0) and rate constant (K) were calculated using a computer fitting program developed for this instrumentation. Specific lifetimes are given by $1/K$ and half-life values are given by $\ln 2/K$.

Quantum yields are calculated using perinaphthanone in acetonitrile as a standard. The quantum yield of this standard is 0.95, therefore quantum yields are given by:

$$I_{0\mu}(\text{standard})/I_{0\mu}(\text{sample}) \times 0.95 \tag{7}$$

2.3. Photo-hydrolysis

Samples were irradiated in sealed tubes, under humid conditions for up to 40 h using a Sunchex

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[1] Original absorbance at λ_{max} (before dyeing), $A_0 = 1.51$
Final absorbance at λ_{max} (after dyeing), $A_f = 0.021$

Beer Lambert Law: $A = \varepsilon c l$

A = Absorbance c = Concentration
l = Path length = 0.01 m ε = Extinction coefficient

Original stock dye solution: 0.5 g of dye powder in 250 cm^3 water ≡2 g/dm^3 ≡2000 g/m^3

Using the Beer Lambert Law:
$\varepsilon = 1.51/2000 \times 0.01 = 0.0755$

Using this value of ε to calculate the final concentration of dyestuff left in the dyebath after dyeing: $C_f = 0.021/0.0755 \times 0.01 = 27.81\ g/m^3$
$\equiv 27.81/1000 = 0.0278\ g/dm^3$

However in real terms, only 20 cm^3 of the dye solution was used, i.e. $2 \times 20/1000 = 0.04$ g of dyestuff actually used
This is equivalent to $g/dm^3/50$, therefore the amount of dyestuff left in the dyebath: $\equiv 0.0278/50 = 0.000556g$

So the amount of dyestuff actually taken up by the cotton fabric

As 4 g of cotton were dyed this equates to:
$0.394/4 = 0.0098$ g of dyestuff taken up by each gram of fabric.

Irradiation Unit. The samples were then washed in water at 50 °C, dried in the dark and re-irradiated under the same conditions. The absorbance of the solution after washing was monitored using a Perkin-Elmer Lambda 16 UV–vis Spectrophotometer and the fluorescence spectra of the fabrics were observed using a Perkin-Elmer LB 50 Spectrophotometer. The light-fastness at the end of the experiment was also observed and compared to the light-fastness observed after the same exposure time under dry conditions.

2.4. Nano-second laser flash photolysis

Nano-second laser flash photolysis experiments were carried out using a frequency tripled neodymium laser (J.K. Laser Ltd.) that delivered a 15 ns pulse at 355 nm irradiation having energy of <10 mJ. Transient absorption changes were measured by illuminating the quartz cell (path length 1 cm) with light from a pulsed xenon lamp. Wavelength selection was achieved with a diffraction grating high irradiance monochromator with a 10 nm bandwidth. Kinetic changes in the light signal at pre-selected wavelengths were detected and amplified using a Hamamatsu R1477 photo-multiplier, before collection by a Hewlett Packard 9000 series 3.0 computer. The time resolved spectra shown were obtained by repeating the procedure at successive wavelengths. The solutions used were degassed under white spot nitrogen (or oxygen for triplet state quenching studies) for 40 min before use.

2.5. Hydroperoxide analysis

Hydroperoxide analysis was carried out using a standard iodometric method [11].

Weighed amounts of the dyed fabrics (0.1 g) were cut into small pieces and placed into round bottomed flasks, with glacial acetic acid (0.5 cm^3), isopropanol (9.5 cm^3) and a small amount of sodium iodide.

These mixtures were refluxed for 30 min alongside a blank solution which was prepared in the absence of polymer. After the 30 min period had elapsed the solutions were quench cooled in a mixture of ice and water, then filtered through a fluted filter paper. During the reflux stage of the procedure, hydroperoxides in the polymer oxidise the iodide to iodine.

$$\mathrm{ROOH} + 2\mathrm{H}^+ + 2\mathrm{I}^- \rightarrow \mathrm{ROOH} + \mathrm{H_2O} + \mathrm{I_2} \quad (8)$$

Oxidation from iodide to iodine.

$$\mathrm{I_2} + \mathrm{I}^- \rightarrow \mathrm{I_3^-} \quad (9)$$

The iodine then complexes with the excess iodide producing a yellow colour.

The UV–vis absorbance of each solution was measured at 420 nm which corresponds to the shoulder of the peak produced by the I_3^- ion. This wavelength was chosen in order to minimise interference from any extractable products from the polymer.

The hydroperoxide concentrations were calculated using the equation of the calibration curve produced using cumene hydroperoxide as a standard.

$$\mathrm{Conc/g} = \left(\mathrm{A}/3 \times 10^{-3}\right) \times 10 \quad (10)$$

where: A = absorbance of filtered solution.

2.6. Microsecond flash photolysis

A 10^{-5} M solution of dyestuff or ZnPcS were made up in water, and anthraquinone was made up in iso-propanol. These solutions were saturated with nitrogen for measurement of triplet state interactions.

The transient absorption spectra for each solution was obtained using a FXP-1 Microsecond Kinetic Flash Unit, which uses two parallel 46 kV xenon filled lamps operating at 10 kV. A continuum interrogation beam is produced by a 150 W tungsten halogen light source. This passes through the sample and enters a Nortech MG10 grating monochromator, which determines the wavelength of the light analysed. The transient decay profile at the appropriate wavelength was recorded on a Gould 200 MHz digital storage oscilloscope type 1425.

The spectra were produced by plotting log $[I_o/(I_o-I_a)]$ versus wavelength. I_0 values were obtained using d.c. power and measuring the voltage at a series of wavelengths. I_a values were obtained using a.c. power and charging the capacitors to 10 kV, the flash is then fired in the shortest possible time. The maximum voltage of the transient produced is then recorded.

3. Results and discussion

3.1. Singlet oxygen detection

Preliminary studies of singlet oxygen detection in ZnPcS solutions and cotton fabrics treated with ZnPcS showed that singlet oxygen was detected in all samples also, the quantum yield was higher in ZnPcS solution in D_2O than in water. In cotton samples the highest quantum yield was found in bleached cotton fabric and the lowest was in dyed cotton fabric. The intense colour of the dyestuff here could have been absorbing laser light, thus masking some $^1O_2$ species. Singlet oxygen detection was then carried out on treated and untreated dyed cotton fabrics, provided by BASF. Although it was not possible to measure quantum yields, due to low ZnPcS concentrations and the effects of the dyestuff, singlet oxygen was detected for samples treated with ZnPcS and half-lives were measured. It was found that $^1O_2$ had a longer lifetime in treated samples than in untreated samples. This means that despite the very small quantum yield, singlet oxygen degradation mechanisms were indicated here. The small quantum yield could be attributed to a very short-lived species.

The results obtained from this analysis are summarised in Tables 1 and 2.

3.2. Light-fastness and photo-hydrolysis

Light-fastness measurements for both laboratory dyed and BASF supplied fabrics are shown in Table 3. It was found that in all cases, under dry conditions ZnPcS had no significant effect on the photo-stability of the fabrics. A light-fastness result of 6–8 is considered good, 4–5 is moderate and 3–1 is poor. All samples showed a good to moderate light-fastness under dry conditions, i.e. prior to the photo-hydrolysis experiment as shown in Table 3. The best photo-stability was found to occur for a vat dye on cotton and a disperse dye on polyester.

Photo-hydrolysis experiments on a selection of these samples, showed a significant decrease in the light-fastness of treated fabrics, dyed with direct or reactive dyes, after washing. Washing was found to have a significant effect on dyed cotton fabrics with the light-fastness being significantly reduced. Reactive and direct dyed fabrics treated with ZnPcS showed poor light-fastness after washing compared to moderate or good under dry conditions. The vat dye again was found to be the most photo-stable having moderate light-fastness after washing compared to good light-fastness under dry conditions. These results can be found

Table 1
Singlet oxygen detection

Sample	Specific lifetime 1/K/ms	Half-life $T_{1/2}$/ms	Quantum yield (perinaphthanone standard)
ZnPcS solution 7.04% light filter	43.1	29.9	0.354
ZnPcS in D_2O 7.04% light filter	64.6	44.8	0.524
ZnPcS on bleached cotton (dry)	308.0	214.0	0.127
ZnPcS on bleached cotton (wet with CCl_4)	250.0	174.0	0.125
ZnPcS on bleached cotton (high conc)	106.1	75.3	0.113
ZnPcS on unbleached cotton (dry)	134.9	93.5	0.084
ZnPcS on unbleached cotton (wet with CCl_4)	194.1	135.0	0.109
ZnPcS on bleached cotton dyed with procion orange	40.5	28.0	0.091

Table 2
Singlet oxygen results

Sample	Exposure time/h	Rate constant	Lifetime/μs (1/K)	$T_{1/2}$/μs (ln2/K)
Perinaphthanone in acetonitrile		1.39E4	74.79	50.98
Reactive Blue 171 untreated	0	6.82E4	14.66	10.16
Reactive Blue 171 untreated, washed only	0	No $^1O_2$ detected		
Reactive Blue 171 untreated	20	1.99E5	5.02	3.48
Reactive Blue 171 untreated	40	No $^1O_2$ detected		
Reactive Blue 171 36 ppm ZnPcS	0	6.81E4	14.67	10.17
Reactive Blue 171 36 ppm ZnPcS washed only	0	5.39E4	18.54	12.85
Reactive Blue 171 36 ppm ZnPcS	20	7.03E4	14.22	9.86
Reactive Blue 171 36 ppm ZnPcS	40	No $^1O_2$ detected		
Direct Blue 199 untreated	0	5.91E4	16.92	11.72
Direct Blue 199 untreated	182	6.78E4	14.75	10.22
Direct Blue 199 44 ppm ZnPcS	0	4.64E3	215.61	149.44
Direct Blue 199 44 ppm ZnPcS washed only	0	2.44E4	41.05	28.45
Direct Blue 199 44 ppm ZnPcS	182	3.31E4	30.18	20.92
Direct Blue 199 DABCO	0	4.25E4	23.51	16.30
Solanthrene Green untreated	0	4.76E4	21.01	14.57
Solanthrene Green untreated	80	7.29E5	1.37	0.950
Solanthrene Green 14.2 ppm ZnPcS	0	5.54E4	18.05	12.51
Solanthrene Green 14.2 ppm ZnPcS	80	8.38E4	11.92	8.26

Table 3
Light-fastness

Dye/fabric	Conc. ZnPcS Sol'n/ppm	Conc. ZnPcS Sol'n on fabric/ppm	Light-fastness
Direct Brown	0	0	5
116/Cotton	200	101.44	6
	100	23.04	6
	50	11.056	6
Direct Blue 199	0	0	6
Cotton	200	43.86	6
Direct Blue 71	0	0	6
Cotton	200	36.18	6
Reactive Blue 171	0	0	5
Cotton	200	36.05	6
Reactive Blue 160	0	0	5
Cotton	200	13.23	5
Reactive Red 141	0	0	5
Cotton	200	33.78	5
Reactive Yellow	0	0	5
84/cotton	200	22.43	5
Disperse Blue 369	0	0	5
Polyester	200	35.47	5
Disperse Red	0	0	6
167:1/polyester	200	5.69	6
	100	11.71	6
Disperse Yellow	0	0	8
218/polyester	200	15.90	8
	100	8.01	8
Solanthrene Green	0	0	8
(vat dye)/cotton	100	14.2	8

in Table 4, which shows light-fastness results for fabrics saturated with ZnPcS.

Light-fastness measurements and photo-hydrolysis experiments showed that ZnPcS could reduce the photo-stability of dyed fabrics significantly on washing. Fluorescence quenching investigations using a singlet oxygen quencher and nano-second laser flash photolysis were carried out in order to establish whether a singlet oxygen mechanism was taking place in order for this reduction in photo-stability to occur.

3.3. Fluorescence quenching

It was found that Stern Volmer Quenching takes places when a reactive dyestuff is added to ZnPcS solution. This suggested that the excited state of ZnPcS is quenched by the dyestuff by a mechanism such as intersystem crossing. A Stern Volmer quenching plot is shown in Fig. 5.

The quenching constant K_q is 0.1242 ± 7%. Here the Fluorescence intensity was steadily decreased as the concentration of the dyestuff was increased. The fluorescence spectra at the different concentrations are shown in Fig. 6. This illustrated that the dyestuff was acting as a fluorescence quencher for ZnPcS.

A concentration quenching effect was observed with ZnPcS, as an increase in concentration was accompanied by a decrease in fluorescence intensity. This was observed with increasing concentrations of ZnPcS and when increasing amounts on ZnPcS were added to a solution of a reactive dyestuff. The shoulder appearing at 750 nm in the spectra of ZnPcS which, increases with concentration and is accompanied by a decrease in fluorescence intensity, could be indicative of excimer formation and self-quenching. The spectra are shown in Fig. 7.

This self quenching effect was also observed in solutions of DABCO (singlet oxygen quencher) as can be seen from a plot of fluorescence intensity versus concentration as shown in Fig. 8. DABCO solutions show less evidence of excimer formation as no additional peaks were observed in the fluorescence spectra shown in Fig. 9. When DABCO is added to a solution of reactive dyestuff, ZnPcS or a mixture of both, the fluorescence intensity firstly increased then levels out. This suggests that the dyestuff and ZnPcS are not affected by the addition of DABCO and the self-quenching of DABCO takes place at higher concentrations.

3.4. Triplet state decay kinetics

In the decay kinetics of ZnPcS mixed with a reactive dyestuff (nano-second laser flash photolysis), it was found that the half-life of the triplet state decay of ZnPcS decreased with an increase in concentration of dyestuff as shown in Table 5, suggesting triplet energy transfer or intersystem crossing as shown in Eq. (5).

The triplet state decay was observed in nitrogen, air and oxygen saturated solutions, decay kinetics are shown in Table 6.

A mechanism in which triplet energy transfer takes place to produce singlet oxygen is suggested. In air and oxygen triplet energy transfer can take place as shown in Eq. (4) whereas in nitrogen, intersystem crossing to form a triplet ecxiplex is more likely. A mechanism involving singlet oxygen has already been suggested in solution quenching studies and ZnPcS was found to cause a significant decrease in photo stability of dyed

Table 4
Photo-hydrolysis

Sample	Light-fastness dry sample	Light-fastness of sample after washing
Direct Blue 199 untreated	6	5
Direct Blue 199 saturated with ZnPcS	6	<3
Reactive Blue 171 untreated	8	5
Reactive Blue 171 saturated with ZnPcS	8	<3
Solanthrene Green (vat dye) untreated	8	5
Solanthrene Green saturated with ZnPcS	8	5

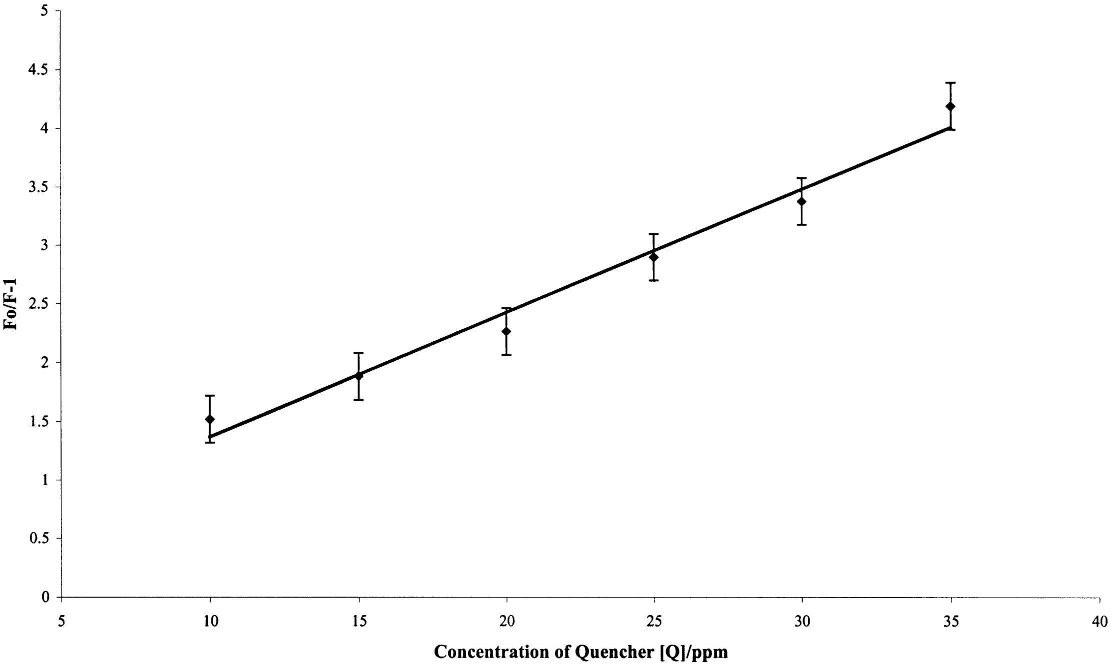

Fig. 5. Stern Volmer quenching plot for Procion Royal added to ZnPcS.

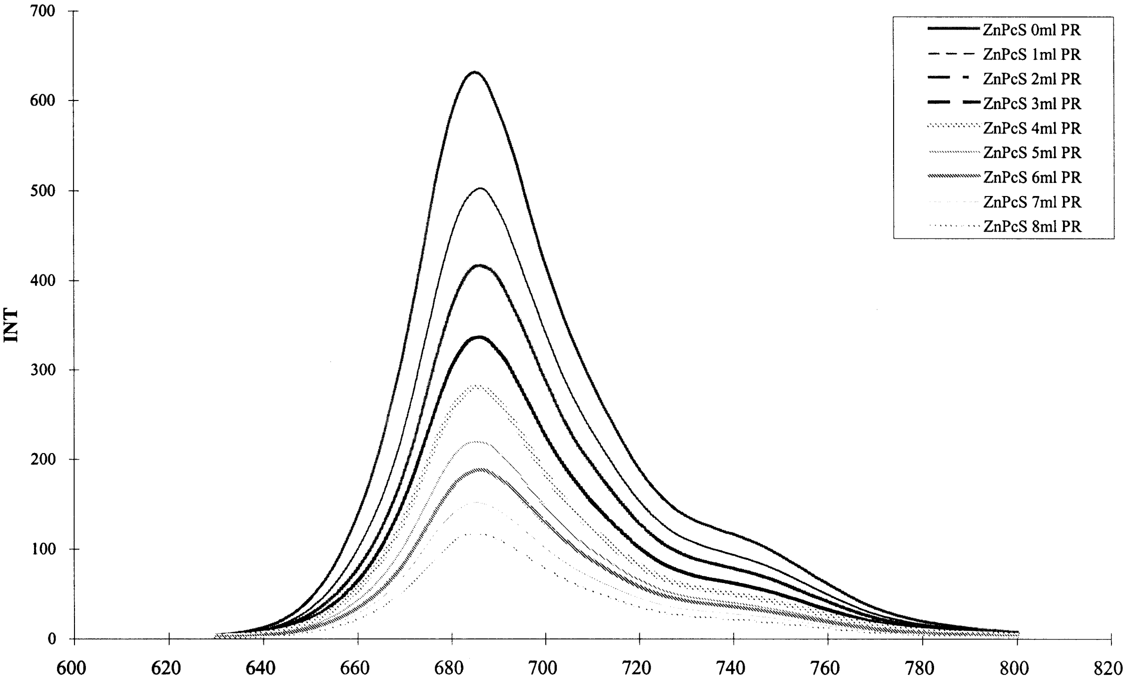

Fig. 6. Fluorescence spectra showing Stern Volmer quenching of ZnPcS using Procion Royal (reactive dye).

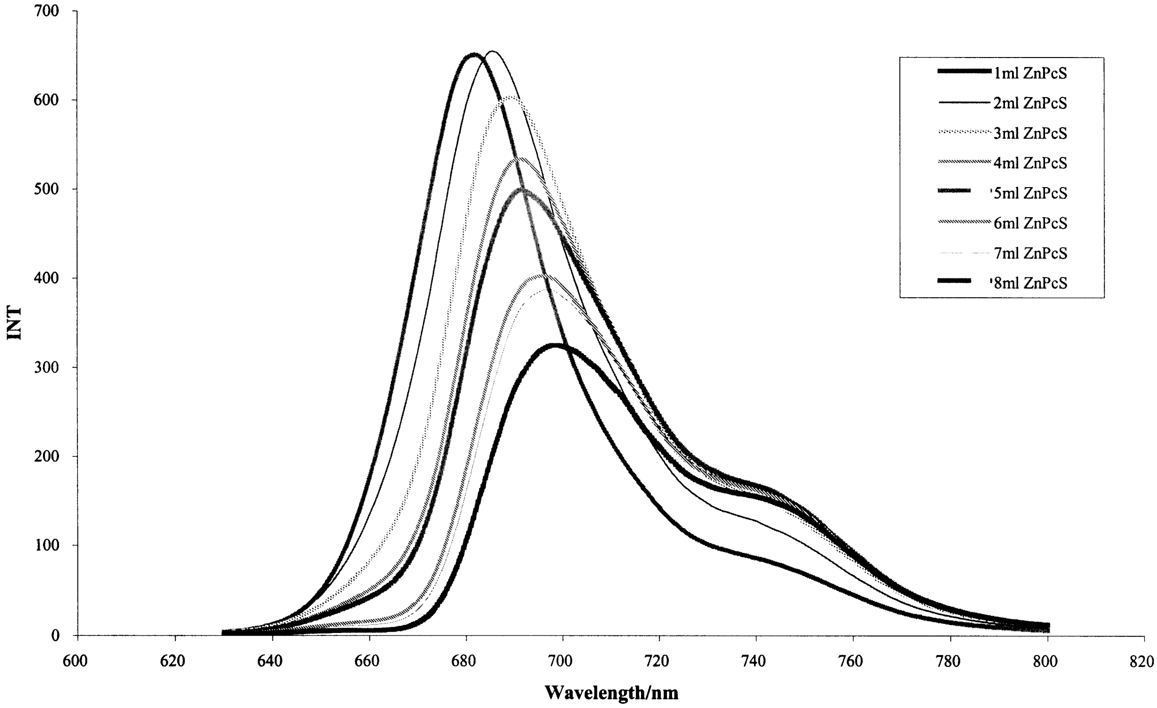

Fig. 7. Fluorescence spectra showing increasing concentrations of ZnPcS.

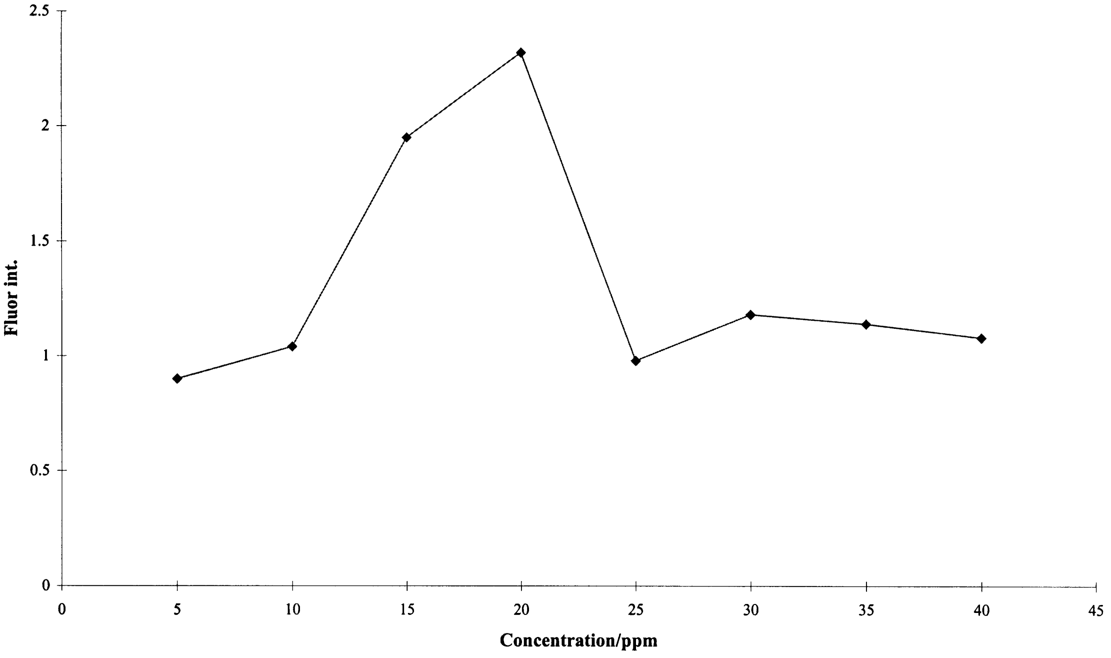

Fig. 8. Fluorescence intensity vs concentration for DABCO.

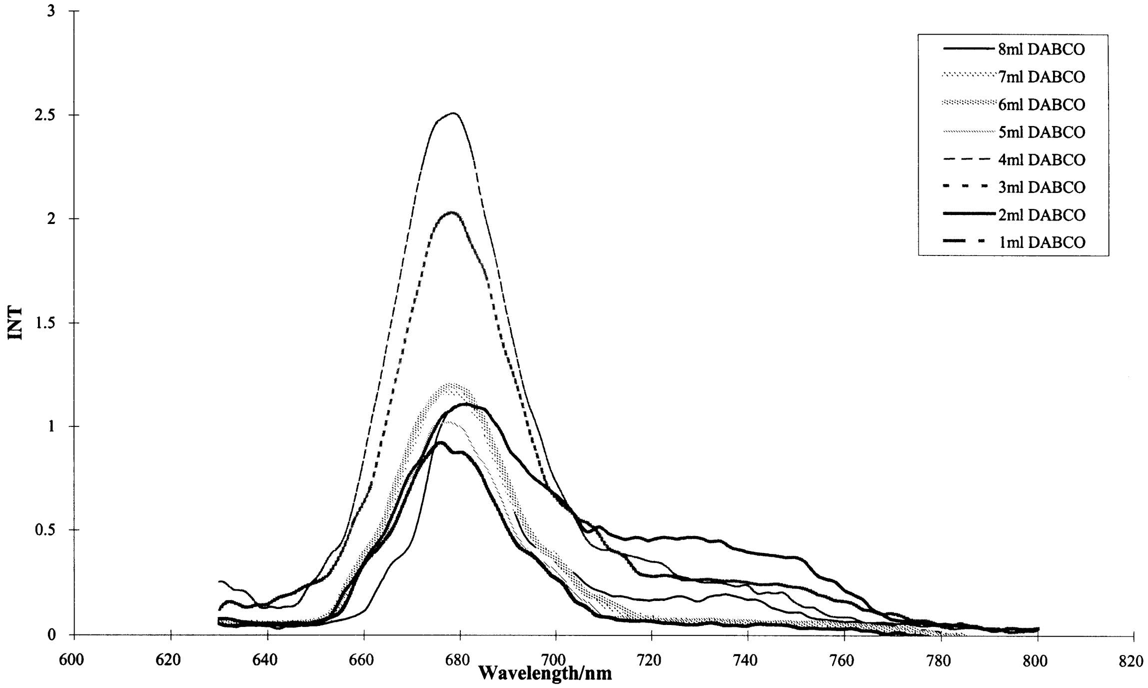

Fig. 9. Fluorescence spectra for increasing concentrations of DABCO.

Table 5
Decay kinetics in nitrogen saturated solutions

Solution N_2 saturated	Rate constant K	$t_{1/2}$ (ln2/K)/ms
ZnPcS only (10 ppm)	4.31E04	16.1
ZnPcS (10 ppm) with 0.25% Procion Orange H-EXL	4.90E04	14.1
ZnPcS (10 ppm) with 0.5% Procion Orange H-EXL	7.73E04	8.97

Table 6
Decay kinetics in nitrogen, air and oxygen saturated solutions

Solution	% Oxygen	Rate constant K	$t_{1/2}$ (ln2/K)/ms
ZnPcS 10 ppm	0	4.31E+04	1.61E-05
	20	5.26E+05	1.32E-06
	100	2.93E+06	2.37E-07

fabrics on washing; therefore it seemed that a singlet oxygen mechanism was causing this decrease in photo stability.

In order to investigate this further, solid-state fluorescence was carried out on dyed fabrics treated with ZnPcS, which suggested an increased diffusion of ZnPcS into the fabric on washing. This would enhance the photochemical activity of the ZnPcS due to disaggregation [12], therefore also enhancing the production of singlet oxygen, by increasing the probability of collisions, and subsequent degradation of both dye and polymer.

Therefore the effect of the build up and increased diffusion of ZnPcS into dyed fabrics was investigated using hydroperoxide analysis.

3.5. The effect of the build-up of ZnPcS on washed, irradiated fabrics

It was found that hydroperoxide radical concentrations were increased on light exposure and subsequent treatment with ZnPcS. This significant increase was followed by a rapid decrease, showing that the formation and subsequent photodecomposition of hydroperoxide radicals plays an important role in the degradation process of dyed fabrics. A similar trend was observed in untreated fabrics, which were washed with water only after each period of light exposure. The results obtained are shown in Table 7. This also indicates the sensitised production of singlet oxygen by ZnPcS, followed by degradation of the dye and polymer as shown in Eqs. (4) and (5).

The increase in hydroperoxide radical concentration was accompanied by a decrease in light-fastness for the samples treated with ZnPcS. This decrease in light-fastness was not observed with the control samples shown in Table 8. This again suggests dye and polymer degradation via the formation of peroxy radicals.

3.6. The effect of a peroxy radical scavenger

Having found that the formation of peroxy radicals was a probable cause of degradation, an investigation of the effect of a peroxy radical scavenger was undertaken in order to try to slow down the degradation process.

The peroxy radical scavenger appeared to eliminate any accelerated fade on washing the fabric samples. Table 9 shows that the peroxy radical scavenger inhibits the photo-fading process so that ZnPcS no longer had a detrimental effect on the photo-stability of the dyed fabric. The peroxy radical scavenger, sodium benzene sulfonate was

Table 7
Hydroperoxide results for dyed, treated fabrics

Fabric/dye	Exposure time/h	[ROOH]/g ZnPcS treated	[ROOH]/g washed only
Cotton	0	242.3	228.6
Solanthrene Violet	100	633.5	473.7
(vat dye)	153	5262.1	500.0
	253	379.6	290.9
Cotton	0	181.2	208.3
Procion Red 4%	100	398.7	551.9
(reactive dye)	153	1986.2	506.5
	253	341.3	331.5
Cotton	0	179.4	113.8
Diazol Red	100	311.1	412.7
(direct dye)	153	1992.7	373.3
	253	334.4	11.1
Polyester	0	210.8	152.3
Dispersol Red	100	281.9	542.0
(disperse dye)	153	1388.4	229.1
	253	375.5	2.0

Table 8
Light-fastness results for treated and washed fabrics

Fabric/dye	Light-fastness (control fabric)	Light-fastness (fabric treated with ZnPcS)	Light-fastness (washed fabric only)
Cotton/Solanthrene Violet	8	5	8
Cotton/Procion Red	5	4	5
Cotton/Diazol Red	5–6	4	5–6
Polyester/Dispersol Red	6	4	6

Table 9
Light-fastness results showing the effect of a peroxy radical scavenger

Fabric/dye	Exposure time/h	Light-fastness untreated		LF. treated with sodium benzene sulfonate		LF. treated with sodium benzene sulfonate and ZnPcS	
			Washed		Washed		Washed
Cotton	0	8	8	8	8	8	8
Solanthrene	100	8	8	8	8	8	8
Yellow	200	8	6	8	8	8	8
Vat dye	300	8	6	8	8	8	8
Cotton	0	8	8	8	8	8	8
Procion Red	100	5	5	5	5	5	5
Reactive	200	5–4	5–4	5–4	5–4	5–4	5–4
Dye	300	4	4	4	4	4	4
Cotton	0	8	8	8	8	8	8
Diazol Red	100	4	4	4	4	4	4
Direct Dye	200	3	3	3	3	3	3
	300	<3	<3	<3	<3	<3	<3
Polyester	0	8	8	8	8	8	8
Dispersol	100	8	8	8	8	8	8
Green	200	6	6	6	6	6	6
Disperse Dye	300	4	4	4	4	4	4

also found to cause a significant decrease in the concentration of hydroperoxide radicals produced in fabrics treated with ZnPcS, which is shown in Figs. 10–13. These two effects confirmed that the suggested degradation mechanism by the sensitised formation of singlet oxygen shown in Eq. (4) is probable.

3.7. *Other photo-chemical mechanisms*

To investigate the possibility of other photochemical mechanisms taking place, microsecond flash photolysis spectra were produced from solutions of dyestuffs, ZnPcS and a combination of these with electron trapping agents and singlet oxygen quenchers.

It was found that the electron trapping agent tetra-cyano-ethylene did not have a quenching effect on a mixture of anthraquinone and ZnPcS; however, the addition of cadmium sulphate to a mixture of a vat dye and ZnPcS did produce a slight quenching effect. This suggests that some electron transfer or complexation may be taking place between the two species. Given that the effect is so small electron trapping is unlikely to be the predominant mechanism taking place. Figs. 14 and 15 show the microsecond flash photolysis spectra for solutions containing electron-trapping agents.

The addition of a singlet oxygen quencher, DABCO, to a solution of ZnPcS produced a quenching effect both in nitrogen and oxygen saturated solutions is indicated in Fig. 16. The spectra indicate the same mechanism as previous results where ZnPcS produces singlet oxygen via intersystem crossing followed by triplet–triplet energy transfer, which would in turn sensitise the breakdown of the dyestuff via a concerted ‘‘ene’’ reaction [3]. Singlet oxygen can also attack the polymer, breaking it down by the formation of hydroperoxide radicals. Both these mechanisms, shown in Eq. (11) are reflected in the hydroperoxide analysis by the decrease in peroxide concentrations on the introduction of a peroxy radical scavenger, sodium benzene sulfonate onto the dyed treated fabric.

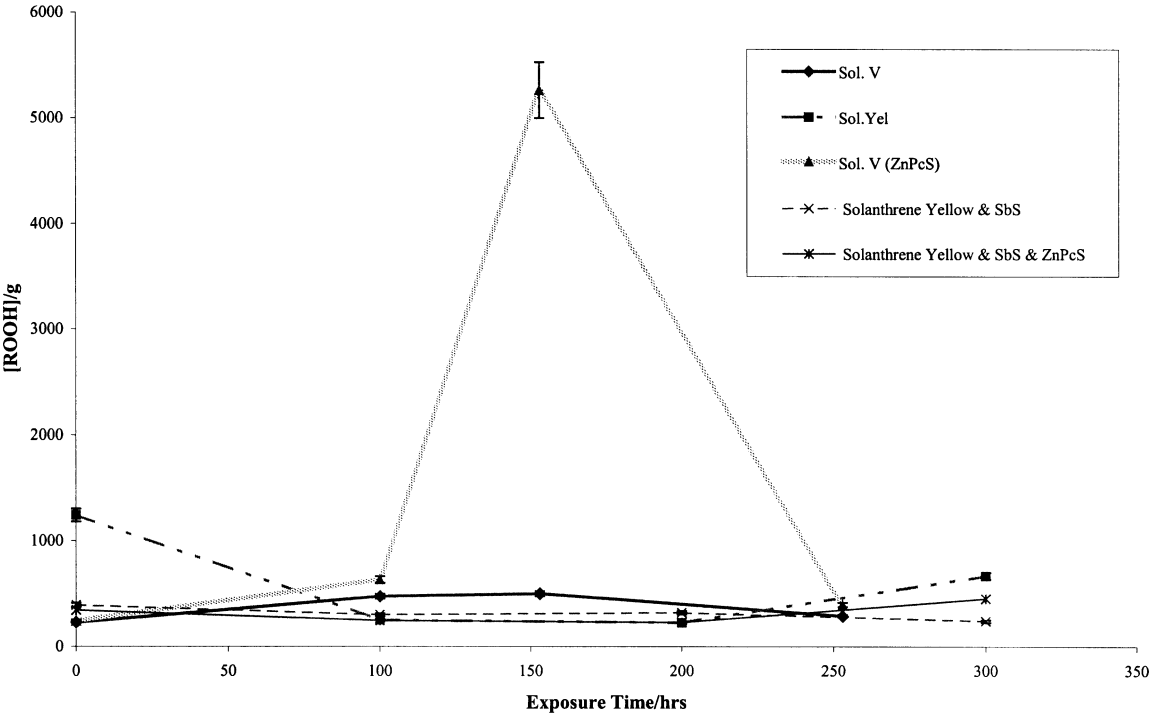

Fig. 10. Hydroperoxide analysis for cotton fabric dyed with vat dyes.

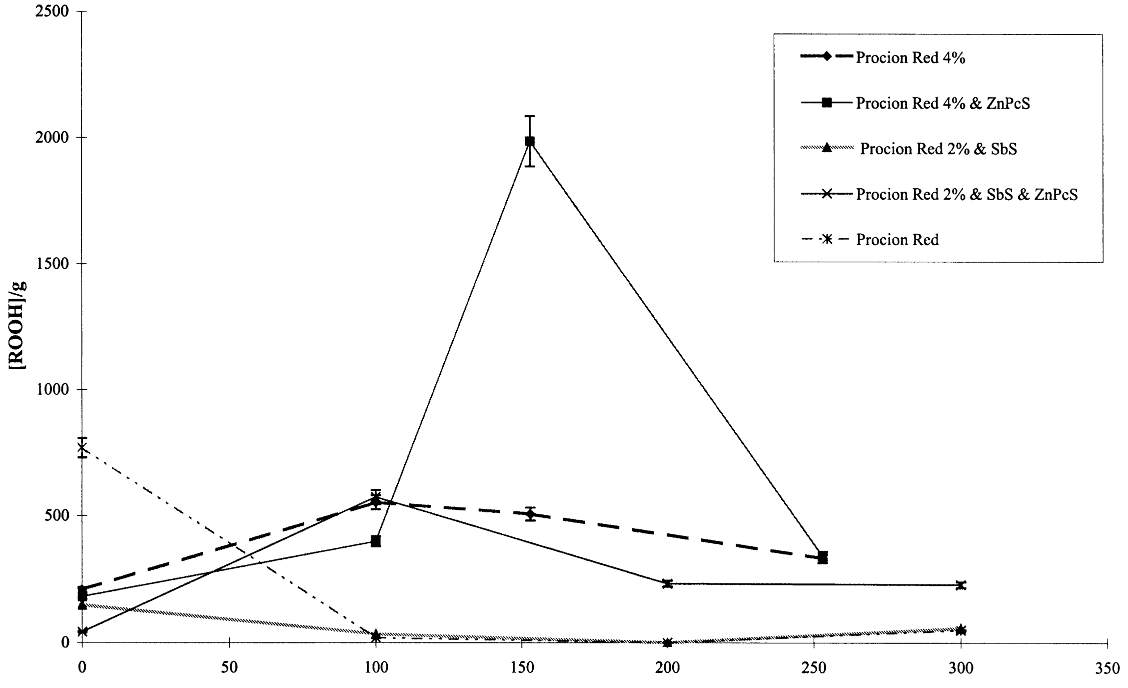

Fig. 11. Hydroperoxide analysis for cotton fabric dyed with a reactive dye.

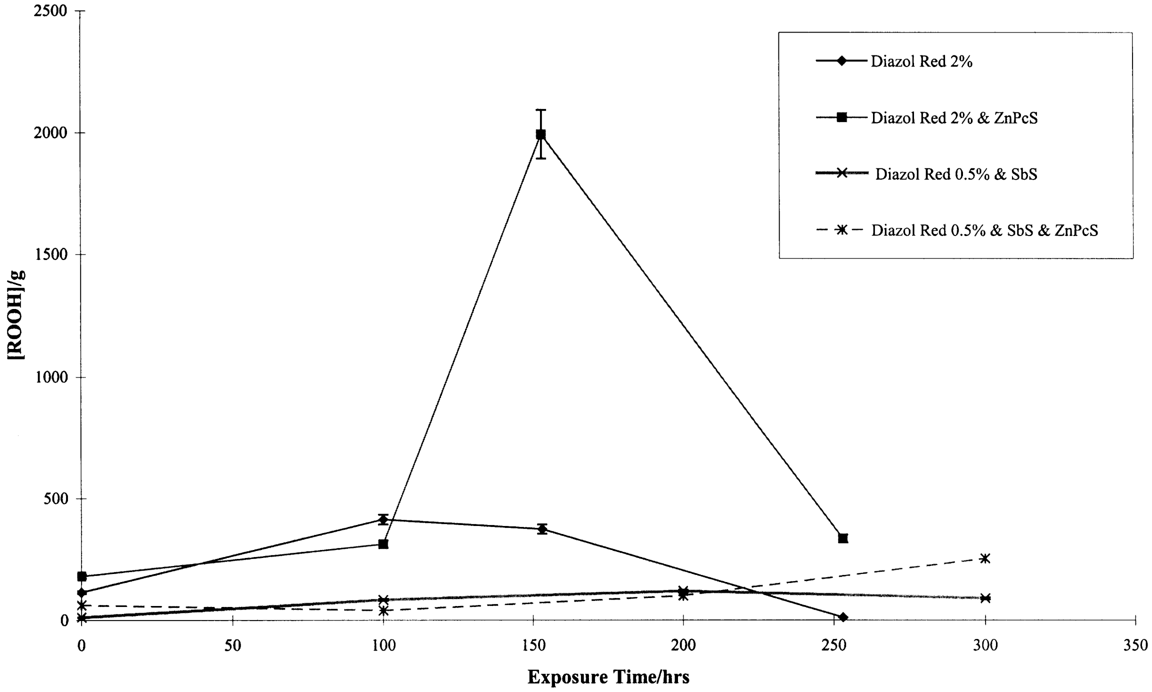

Fig. 12. Hydroperoxide analysis for cotton fabric dyed with a direct dye.

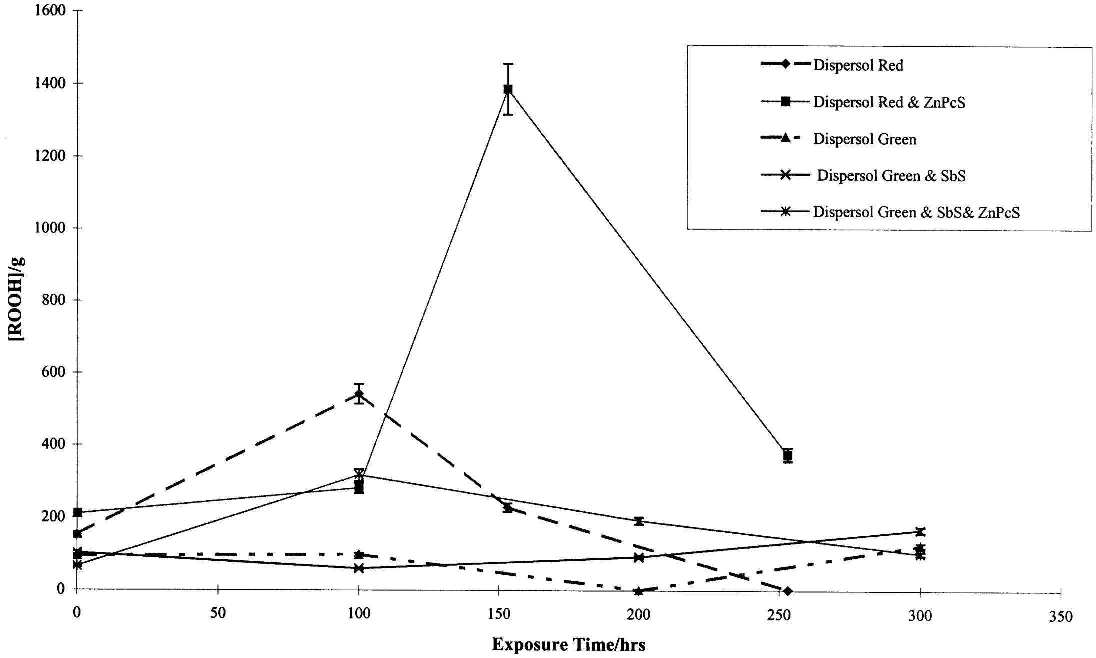

Fig. 13. Hydroperoxide analysis for polyester fabric dyed with a disperse dye.

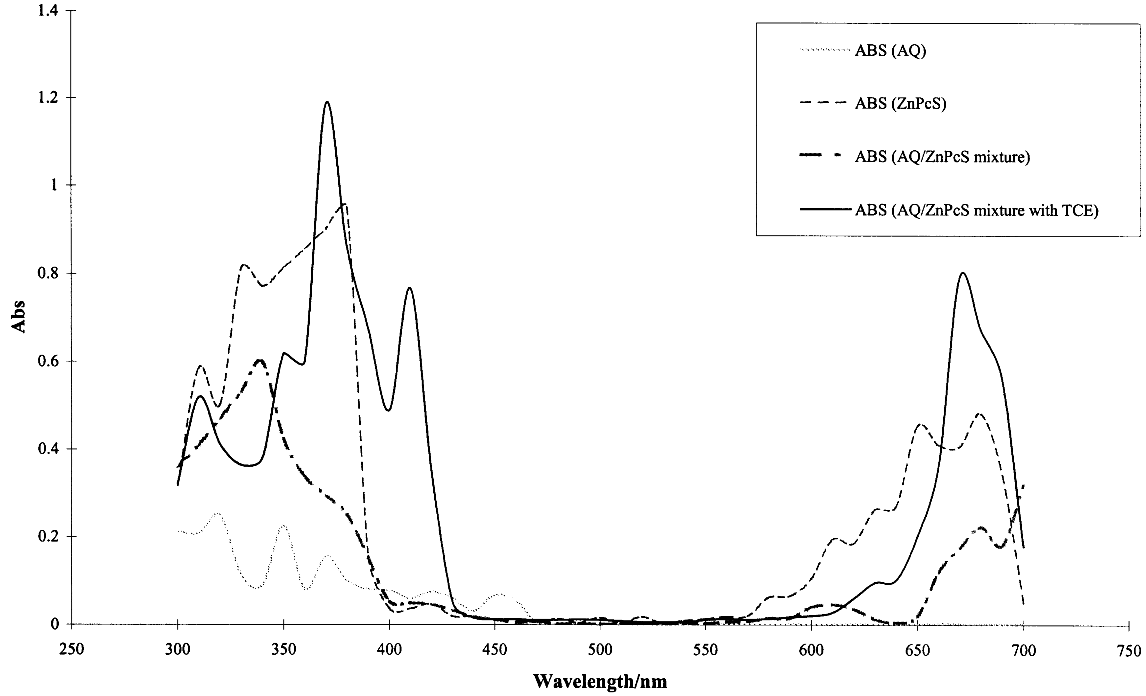

Fig. 14. Microsecond flash photolysis spectra of AQ/ZnPcS with tetra-cyano-ethylene.

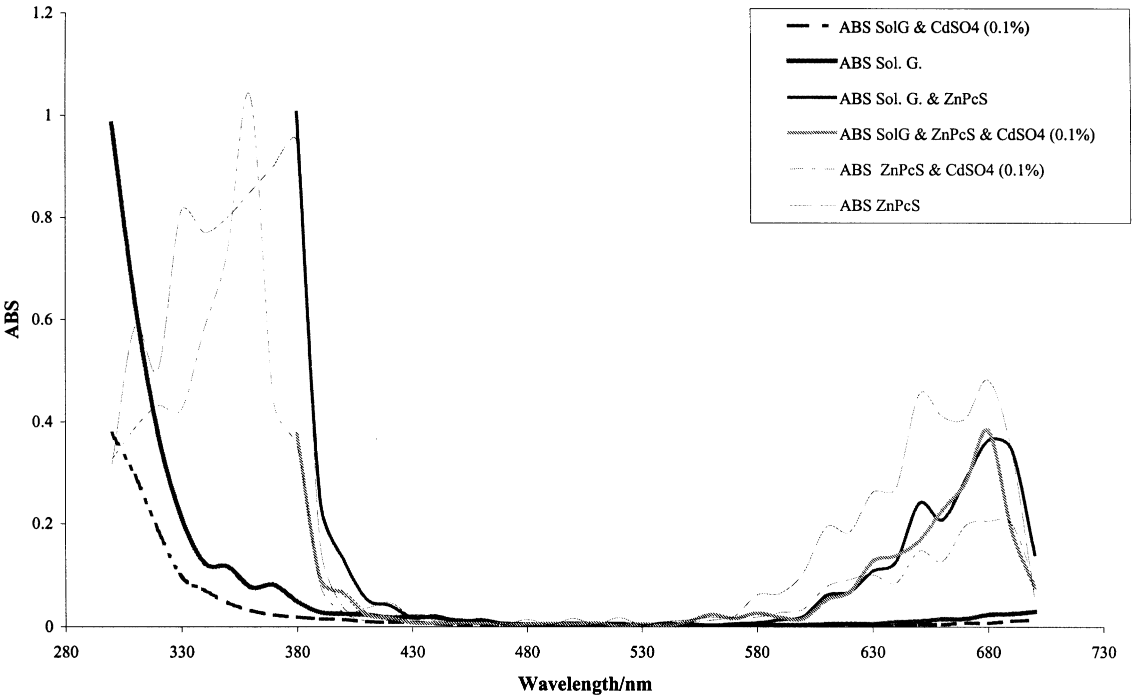

Fig. 15. Microsecond flash photolysis spectra for a Solanthrene Green/ZnPcS with $CdSO_4$..

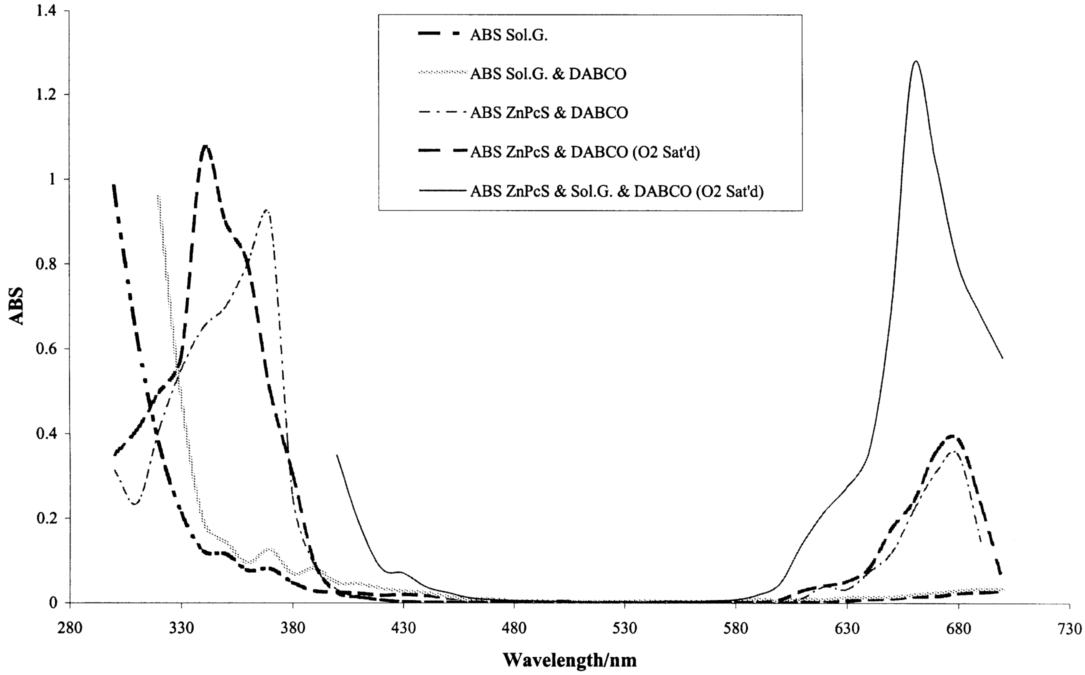

Fig. 16. Microsecond flash photolysis spectra for Solanthrene Green/ZnPcS with DABCO.

$$\mathrm{ZnPcS} \overset{h\nu}{\rightarrow} {}^1\mathrm{ZnPcS} \overset{isc}{\rightarrow} {}^3\mathrm{ZnPcS} \qquad (11a)$$

$$^3\mathrm{ZnPcS}^* + {}^3\mathrm{O}_2 \rightarrow \mathrm{ZnPcS} + {}^1\mathrm{O}_2 \qquad (11b)$$

$$^1\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{H}_2\mathrm{O}_2 \qquad (11c)$$

$$\mathrm{H}_2\mathrm{O}_2 + \mathrm{P} - \mathrm{H} \rightarrow \text{Oxidation Products} \qquad (11d)$$

Oxidative polymer breakdown induced by ZnPcS.

The enhanced absorbance observed in the peak produced by an oxygen saturated solution of the dyestuff, ZnPcS and DABCO, could be a result of the disaggregation of ZnPcS as this form is known to be more photosensitive when the molecules are aggregated [9]. This causes more photochemical breakdown, due to increased collisions with oxygen giving a higher absorbance. Complexation between ZnPcS and oxygen is also a possibility.

3.8. The effect of trapping agents in solutions and fabrics

The effect of trapping agents on solutions and fabrics was investigated in order to establish whether these trapping agents would slow down the dye fading mechanisms with or without ZnPcS. Also whether the accelerated fade found in dyes fabric samples treated with ZnPcS, discussed previously could be eliminated.

Electron trapping agents ($CdSO_4$ and tetracyano-ethylene), a radical trapping agent (KSCN) and a singlet oxygen-trapping agent (DABCO) were added to anthraquinone and ZnPcS solutions. Second derivative UV spectroscopy was carried out the solutions after a series of light pulses from the flash photolysis unit. It was found that DABCO and KSCN significantly reduced the fading rate in both anthraquinone and ZnPcS (measured by the% decrease in intensity after irradiation). Both electron-trapping agents slightly reduced the fade in anthraquinone but had no effect on ZnPcS. Although this could at first indi-

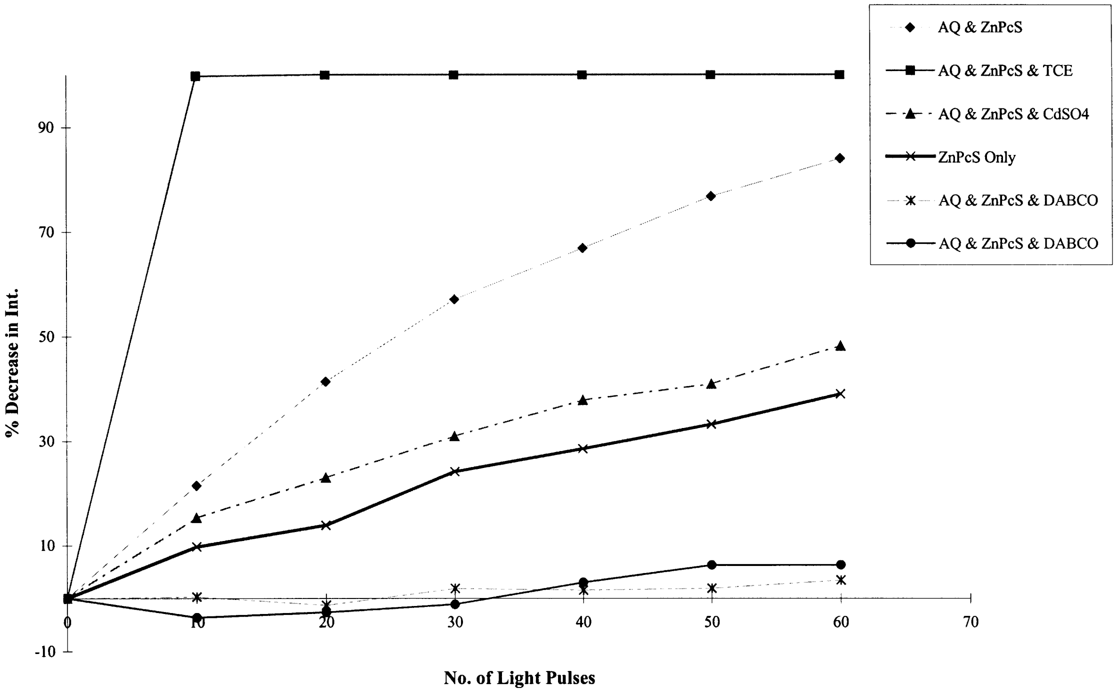

Fig. 17. Percentage decrease in UV intensity for solutions of ZnPcS.

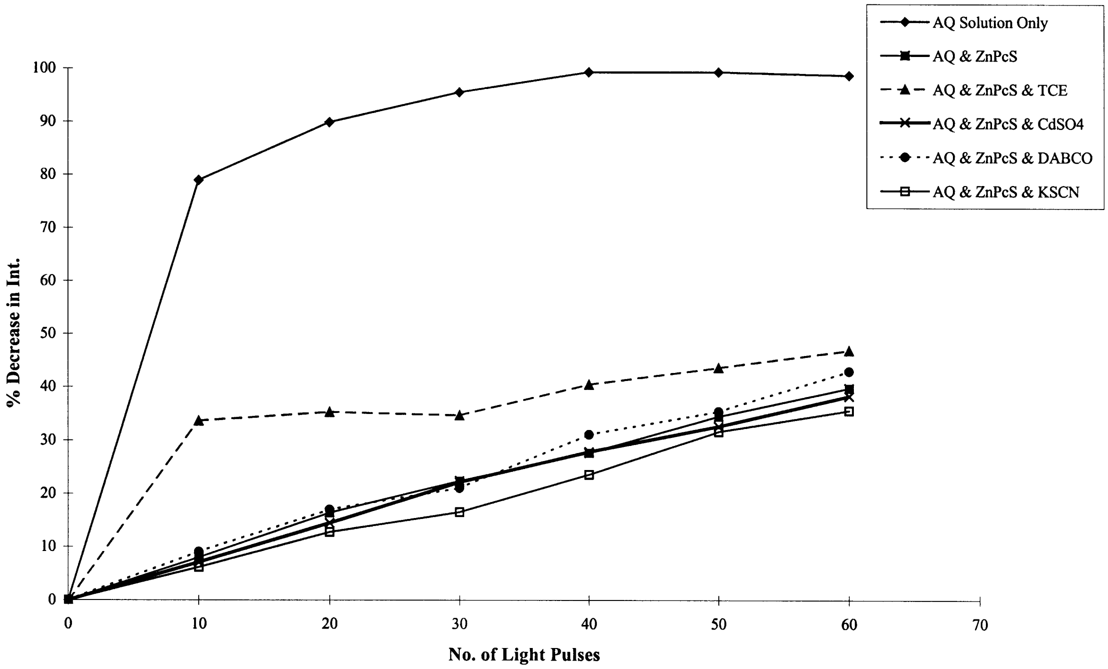

Fig. 18. Percentage decrease in 2D UV intensity for solutions of anthraquinone.

cate some electron transfer mechanism may be involved in the fading of anthraquinone and related dyestuffs, it is well documented that these dyestuffs breakdown via electron abstraction or hydrogen atom abstraction under anaerobic conditions and by photo-reduction producing a semiquinone intermediate or by reaction with singlet oxygen under aerobic conditions. A singlet oxygen mechanism postulated in Eq. (10) is therefore more likely to take place.

Graphs of % decrease in absorbance intensity for the solutions discussed here are shown in Figs. 17 and 18.

Cotton samples dyed with direct and reactive dyes were treated with $CdSO_4$ (electron trap), KSCN (hydroxyl radical trap) and DABCO (singlet oxygen trap). Light-fastness monitoring was carried out as the samples were subjected to various washing cycles. The samples were further treated with either KSCN or ZnPcS after each wash. This was done in order to establish whether repeated treatment with an electron-trapping agent would slow down dye fading.

Table 10 shows the results obtained. It was found that, in the case of the dyed only fabrics, the electron-trapping agent had no effect on the photo-stability of the fabric over a 300hr exposure period. In dyed fabrics treated with ZnPcS, the radical-trapping agent was found to have a stabilising effect on the light-fastness of the fabric. The accelerated fade previously observed in ZnPcS was found to be significantly reduced when KSCN was introduced into the system. This effect was especially noticeable in the samples dyed with a reactive dyestuff.

It was also significant that the radical trapping agent needed to be applied after each wash in order to increase photo-stability in the presence of ZnPcS, since pre-treatment with trapping agents and quenchers did not produce the same stabilising effect.

Table 10
Light-fastness results for fabrics treated with KSCN and ZnPcS

Dye/trapping agent	Exposure time/h	LF untreated		LF treated with KSCN only		LF treated with ZnPcS only		LF treated with ZnPcS and KSCN	
			Washed		Washed		Washed		Washed
Diazol	0	8	8	8	8	8	8	8	8
Black	50	3	3	3–4	3–4	3	3	4	4
Direct	100	4	3	4	4	4	3	4	4
Dye	200	<3	<3	<3	<3	<3	<3	<3	<3
DABCO	300	<3	<3	<3	<3	<3	<3	<3	<3
Procion	0	8	8	8	8	8	8	8	8
Red	50	8	8	8	8	4	4	8	8
Reactive	100	8	8	8	8	8	4	8	8
Dye	200	8	8	8	8	8	4	6	6
DABCO	300	8	8	8	8	4	4	6	5
Diazol	0	8	8	8	8	8	8	8	8
Yellow	50	8	8	8	8	4	4	4	4
Direct	100	8	8	8	8	6	4	4	4
Dye	200	8	8	8	8	6	4	4	4
$CdSO_4$	300	6	6	6	6	6	4	4	4
Procion	0	8	8	8	8	8	8	8	8
Navy	50	4	4	4	4	4	4	5	5
Reactive	100	8	4	8	4	8	4	8	5
Dye	200	6	4	6	5	8	<3	6	5
KSCN	300	5	4	6	4	6	<3	6	5

4. Conclusion

The theory that dyed cotton fabrics treated with ZnPcS degraded via the sensitised production of singlet oxygen was first indicated when singlet oxygen was detected on cotton treated with ZnPcS. The lifetimes of the singlet oxygen species in the dyed fabric was very short so further investigations were undertaken.

An extensive light-fastness screening program showed that under dry conditions ZnPcS did not adversely affect the photo-stability of dyed fabrics. However, a detrimental effect was observed in fabrics, which had been repeatedly washed and exposed to light, shown by photo-hydrolysis. Vat dyes on cotton were found to be the most photostable under dry and wet conditions.

Solution fluorescence quenching experiments showed that a Stern Volmer relationship exists between a reactive dyestuff and ZnPcS, where the dyestuff acts as a fluorescence quencher. ZnPcS and DABCO (singlet oxygen quencher) were found to self quench, therefore DABCO could not act as a fluorescence quencher for ZnPcS if either solution was at a high enough concentration for self quenching to occur.

Decay kinetics produced by nano-second laser flash photolysis suggested the significance of triplet state energy transfer and intersystem crossing in the sensitised formation of singlet oxygen by ZnPcS. Disaggregation and therefore increased diffusion of ZnPcS into the polymer on washing was indicated in the findings from solid-state fluorescence, this disaggregation effect could enhance the production of singlet oxygen by increasing the probability of collisions with excited state oxygen.

The significant increase in hydroperoxide concentrations in dyed fabrics treated with ZnPcS also indicated the production of singlet oxygen, which reacts with moisture forming hydrogen peroxide which in turn attacks the polymer causing degradation. This was further indicated by the introduction of a peroxy radical scavenger into the system, which significantly reduced the hydroperoxide concentration in the fabrics treated with ZnPcS. The accelerated decrease in the light-fastness of these fabrics was also eliminated by the addition of a hydroxyl radical scavenger.

Microsecond flash photolysis studies showed that some electron transfer between ZnPcS and a reactive dyestuff could also take place, but is unlikely to be the predominant mechanism. The introduction of the singlet oxygen quencher DABCO into solutions of ZnPcS mixed with dyestuff produced a quenching effecting, in this case, in both nitrogen and oxygen saturated environments. This suggests singlet oxygen production *via* intersystem crossing and triplet- triplet energy transfer from exited state ZnPcS to ground state oxygen. This sensitises the degradation of the dyestuff via a concerted ‘ene’ reaction.

The introduction of trapping agents into solutions of dyestuff and ZnPcS and into dyed fabrics during washing produced a very significant effect. Second derivative UV/Vis spectra of irradiated solutions of ZnPcS and dyestuff or anthraquinone with various trapping agents showed that DABCO eliminated fade in a solution of ZnPcS mixed with anthraquinone and the hydroxyl radical trapping agent KSCN had a significant quenching effect. The electron trapping agent however, had no effect on ZnPcS indicating that electron transfer was not the main pathway for degradation. On application of KSCN to dyed fabrics after each wash, the photo-stability of fabrics treated with ZnPcS was found to be significantly increased compared with previous results. This confirmed the finding that the mechanism by which the degradation of dyed polymer fabrics occurs is by the reaction with peroxy radicals produced by the sensitisation of singlet oxygen by zinc phthalocyanine sulfonate.

It is important to note that the concentrations of phthalocyanine used here are significantly greater than those used commercially in washing powders such that the effects of enhanced fade are minimised.

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