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Photofading of Vinylsulfonyl Reactive Dyes on Cellulose under Wet Conditions

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ABSTRACT

*The fading on cellulose of six vinylsulfonyl (VS) reactive dyes, an aminopyrazolinyl azo dye (**1**), C.I. Reactive Red 22 (**2**), a copper-complex azo dye (**3**), a copper phthalocyanine dye (**4**), C.I. Reactive Blue 19 (**5**) and Black 5 (**6**) was investigated under wet conditions. The rate of fading for VS dyes on cellulose, except for dye **2**, decreased with increase in the concentration; that for dye **2** increased. The rate of fading for the VS dyes examined was in the following order: **2** > **1** > **3** > **6** > **4** > **5**. This order was similar to that for the rate of fading for VS dyes on cellulose on which Rose Bengal was adsorbed, except for the reversal between dyes **1** and **2**. The photosensitivity of VS dyes was confirmed by exposing films dyed with a mixture of **1** with the other dyes and by shielding dye **1** by the use of a filter (> 510 nm). No fading of these dyes on cellulose in deaerated water occurs under a nitrogen atmosphere. These results suggest a singlet oxygen mechanism for the fading of VS dyes on cellulose under wet conditions. The rate of fading for a VS dye was dependent mainly on the ease with which it was oxidized and secondly on its efficiency and that of the partner dye to generate singlet oxygen.*

1 INTRODUCTION

Reactive dyes are now the largest dye-class for cellulose in Japan. Vinylsulfonyl (VS) dyes amount to about 60% of reactive dyes and C.I.

Reactive Black 5 especially is used in large quantities. In spite of the popularity of these dyes, there are some problems associated with them. The lightfastness of reactive dyes has been extensively studied,[1] but much remains to be elucidated, especially on the fastness under wet conditions. The mechanism of fading for monochlorotriazinyl reactive azo dyes under wet conditions has been studied by Datyner *et al.*,[2] who proposed some primary photochemical reactions in the fading of these dyes.

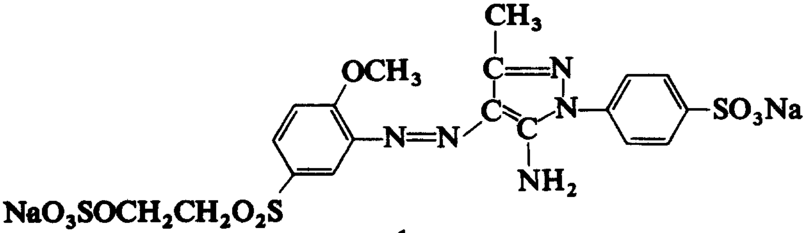
In a previous paper,[3] an anomalous fading was observed in VS dyeings using a mixture of a yellow azo dye and a blue phthalocyanine dye under wet conditions and this was shown to be due to the singlet oxygen mechanism.

In this present paper, the photosensitivity to generate singlet oxygen, the oxidizability and the concentration dependence of fading for six VS dyes are examined under dry and wet conditions. The photofading mechanism is also studied using the method previously described.[3]

2 EXPERIMENTAL

2.1 Dyes used

Six VS dyes, an aminopyrazolinyl azo dye **1**, C.I. Reactive Red 22 **2**, a copper-complex azo dye **3**, a copper phthalocyanine dye **4**, C.I. Reactive Blue 19 **5** and C.I. Reactive Black 5 **6**, were used. They have the structures shown.



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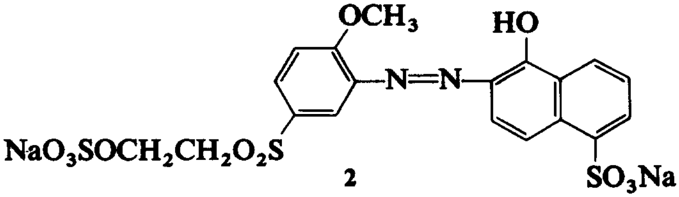

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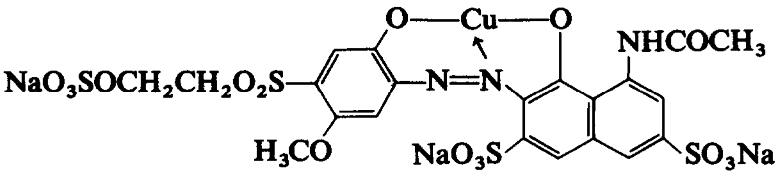

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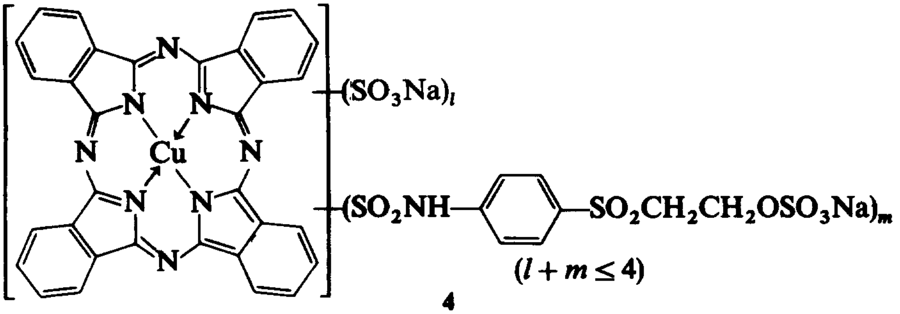

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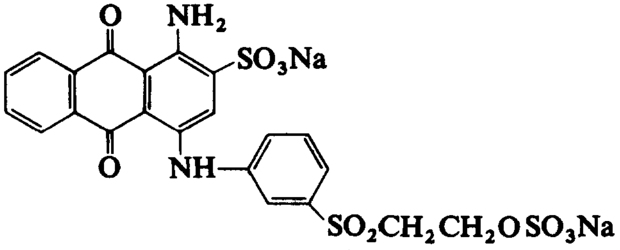

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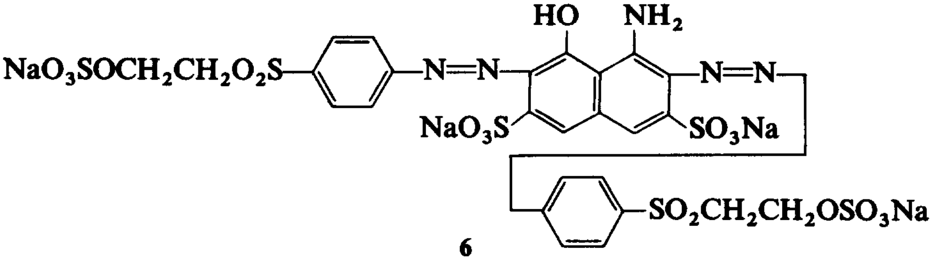

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Dye **3** was supplied by the Mitsubishi Kasei Corporation and the other dyes by Sumitomo Chemical Industries Ltd. They were used for dyeing without further purification.

The molar concentration was determined using films dyed with the purified hydrolyzed species of each dye. The sulfatoethylsulfonyl species was allowed to hydrolyze in 0·1M-NaOH at 80°C for 2 h. After neutralizing, the hydrolyzed species was salted out three times with potassium acetate and was then extracted with absolute alcohol. Dye **3** was purified with organic solvents according to Mehta *et al.*[4] For dye **6**, the hydrolyzed species was purified by column chromatography on alumina, the principal band being extracted with 15% aqueous pyridine and the product isolated using freeze-drying. Impurities such as the vinylsulfonyl and bis-aryl ethers in the purified sample were monitored by high-pressure liquid chromatography.[5]

2.2 Method of dyeing

The VS dyes, except for dye **1**, were applied by the one-bath method at 50°C from a dyebath containing sodium sulfate and borax as shown in Table 1.

TABLE 1
Dyeing Method for Cellophane Films

VS dye	*Concn of dye* ($g\ litre^{-1}$)	Na_2SO_4 ($g\ litre^{-1}$)	$Na_2B_4O_7 . 10H_2O$ ($g\ litre^{-1}$)
2	2·0	10	11·7
3	1·0	10	11·7
4	1·0	10	11·7
5	1·0	10	11·7
6	1·0	0	11·7

Dye **1** was dyed by the alkali-shock method at 50°C using a dyebath containing 1·0 g litre^{-1} dye and 20 g litre^{-1} Na_2SO_4 and an alkali bath containing 20 g litre^{-1} Na_2CO_3 and 50 g litre^{-1} Na_2SO_4. The dyed films were thoroughly scoured in boiling distilled water for at least 15 min until no coloration of the scouring solution was observed after renewing the scouring bath. The cellophane films, the apparatus and the method of exposure (>290 nm, in water at 50°C) were the same as those used in previous studies.[3] The relative fading (A/A_0, where A_0 and A are the optical densities before and after exposure, respectively) was estimated at the wavelength of the maximum absorption, except for dye **4**, which was estimated by a use of the isosbestic point.

3 RESULTS AND DISCUSSION

3.1 Rate of fading in aerated water

In a previous paper,[3] it was shown, under wet conditions, that dye **1** on cellulose showed a large initial rate of fading and a constant rate of subsequent fading and that when it was dyed on cellulose in admixture with dye **4**, it was anomalously faded by the photosensitization of dye **4**.

The concentration dependence of fading for the other four dyes was initially examined by exposing the dyed films in aerated water. As in the case of dye **1**,[3] the fading of four VS dyes was shown to occur at a similar rate at each wavelength in the visible region under the given conditions. The results are shown in Figs 1 and 2. The relative rate of fading for dyes **3**, **5** and **6** on cellulose decreased with increase in the concentration as in the case of dyes **1** and **4**,[3] whilst that for dye **2** increased, i.e. **2** showed a 'positive' concentration dependence on fading. Dye **2** had the largest rate of fading and dye **5** the smallest. When values of A/A_0 for an 8 h exposure were compared, the order of the rate of fading for the dyes was as follows:

$$\mathbf{2} > \mathbf{1} > \mathbf{3} > \mathbf{6} > \mathbf{4} > \mathbf{5} \qquad (1)$$

The reasons for this order of the fading are discussed below.

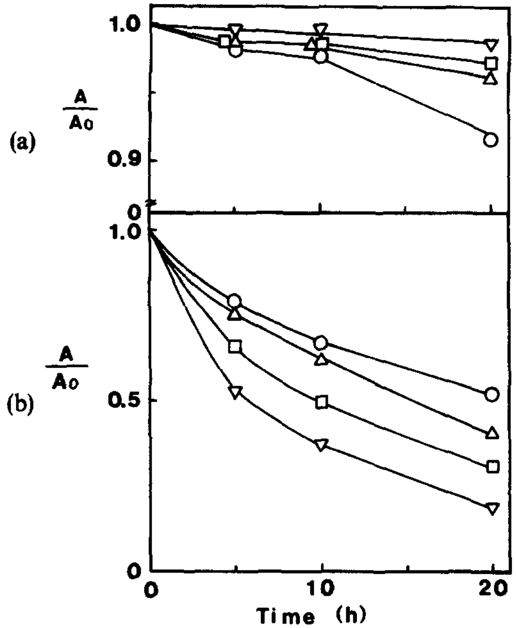

Fig. 1. (a) Relative rate of fading for dye 5 on cellophane (○, $2{\cdot}93 \times 10^{-3}$ mol kg^{-1}; △, $6{\cdot}55 \times 10^{-3}$ mol kg^{-1}; □, $1{\cdot}15 \times 10^{-2}$ mol kg^{-1}; ▽, $2{\cdot}25 \times 10^{-2}$ mol kg^{-1}), and (b) that for dye 2 on cellophane (○, $3{\cdot}39 \times 10^{-3}$ mol kg^{-1}; △, $8{\cdot}00 \times 10^{-3}$ mol kg^{-1}; □, $1{\cdot}77 \times 10^{-2}$ mol kg^{-1}; ▽, $3{\cdot}82 \times 10^{-2}$ mol kg^{-1}) in aerated water.

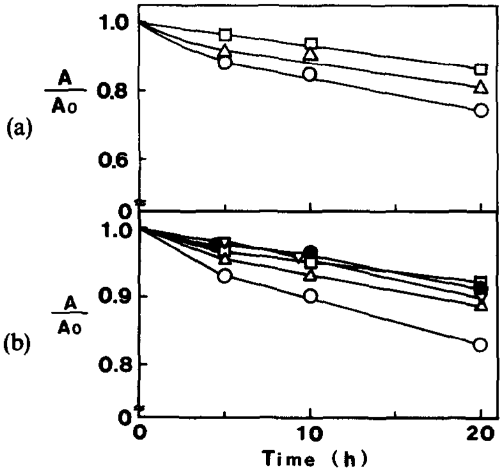

Fig. 2. (a) Relative rate of fading for dye 3 on cellophane (○, $5{\cdot}61 \times 10^{-3}$ mol kg^{-1}; △, $1{\cdot}04 \times 10^{-2}$ mol kg^{-1}; □, $1{\cdot}65 \times 10^{-2}$ mol kg^{-1}), and (b) that for dye 6 on cellophane (○, $9{\cdot}66 \times 10^{-4}$ mol kg^{-1}; △, $3{\cdot}64 \times 10^{-3}$ mol kg^{-1}; □, $6{\cdot}15 \times 10^{-3}$ mol kg^{-1}; ▽, $7{\cdot}79 \times 10^{-3}$ mol kg^{-1}; ●, $1{\cdot}16 \times 10^{-2}$ mol kg^{-1}) in aerated water.

3.2 Effect of Rose Bengal on the fading of VS dyes under wet conditions

In order to elucidate the mechanism relevant to the fading of these dyes, the effect of Rose Bengal (RB), a strong sensitizer in generating singlet oxygen,[6,7] on the fading of VS dyes on cellulose was examined under wet conditions. Sodium sulfate was also added, because a delayed fading was observed due to no adsorption of RB in the absence of the salt.[3] Cellophane films were dyed to obtain an optical density in the range 0·8–1·0 at the wavelength of the maximum absorption. The molar concentrations in the film, however, varied with the dyes, because of the difference in their molar extinction coefficient. RB was allowed to adsorb on the dyed film for 1 h at 50°C under the given condition prior to exposure. The results of the exposure are shown in Table 2. It was concluded that the superposition of the absorption spectra characteristics of the VS dyes onto that of RB and the different concentrations of RB on the film resulted in only a small effect on the rate of fading under the experimental conditions examined (Fig. 3).[8] The relative rate of fading for VS dyes sensitized by RB or the ease with which VS dyes are oxidized by singlet oxygen was in the following order:

$$\mathbf{1} \gg \mathbf{2} \gg \mathbf{3} > \mathbf{6} > \mathbf{4} > \mathbf{5} \qquad (2)$$

The order (2) is similar to the order (1) for the rate of fading obtained above, except for the reversal between dyes **1** and **2**. It may be concluded therefore that the rate of fading for VS dyes on cellulose in water is mainly dependent on the ease with which they are oxidized by singlet oxygen.

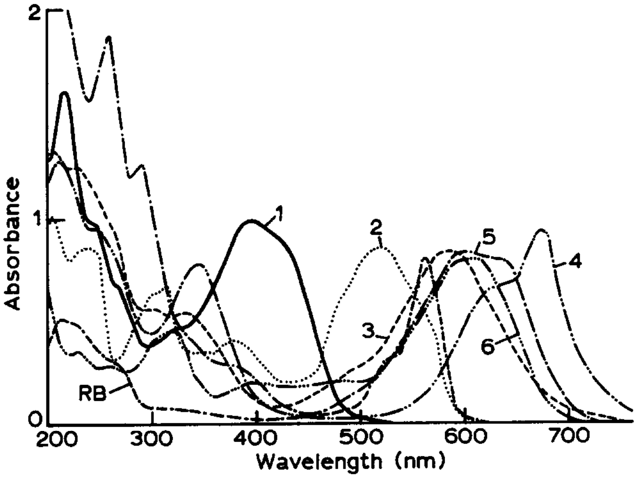

Fig. 3. Absorption spectra of VS dyes and of Rose Bengal on cellophane. Dye **1**, $1{\cdot}83 \times 10^{-2}$ mol kg^{-1} (——); **2**, $2{\cdot}28 \times 10^{-2}$ mol kg^{-1} (·····); **3**, $1{\cdot}29 \times 10^{-2}$ mol kg^{-1} (– – –); **5**, $1{\cdot}39 \times 10^{-2}$ mol kg^{-1} (–·–·–); **4**, $6{\cdot}80 \times 10^{-3}$ mol kg^{-1} (–··–··–); **6**, $5{\cdot}46 \times 10^{-3}$ mol kg^{-1} (–···–···–); and RB, $2{\cdot}30 \times 10^{-3}$ mol kg^{-1} (——·——·——).

TABLE 2
Effect of Rose Bengal on the Fading of VS Dyes on Cellulose in Water Containing RB ($3{\cdot}3 \times 10^{-4}$ mol litre^{-1}) and Na_2SO_4 ($0{\cdot}05$ mol litre^{-1}) by Exposing for 4 h

VS dye	Concn of dye (mol kg^{-1})	Adsorption of RB (mol kg^{-1})	Relative rate of fading, A/A_0
1	$1{\cdot}46 \times 10^{-2}$	$2{\cdot}75 \times 10^{-3}$	0·851[a]
2	$2{\cdot}32 \times 10^{-2}$	$3{\cdot}48 \times 10^{-3}$	0·328
3	$2{\cdot}00 \times 10^{-2}$	$2{\cdot}82 \times 10^{-3}$	0·714
4	$7{\cdot}59 \times 10^{-3}$	$3{\cdot}86 \times 10^{-3}$	0·919
5	$1{\cdot}20 \times 10^{-2}$	$3{\cdot}40 \times 10^{-3}$	0·986
6	$5{\cdot}68 \times 10^{-3}$	$3{\cdot}45 \times 10^{-3}$	0·753

[a] The value for A/A_0 after 5 min exposure is shown; that for 10 min was 0·712.

3.3 Photosensitized fading of dye 1 by VS dyes

It has been reported that dye **4** sensitized the fading of dye **1** by generating singlet oxygen.[3] However, since dye **4** was present in cellulose in an aggregated state, the detailed mechanism of the photosensitization could not be investigated. The ability to oxidize the partner dyes on cellulose and to what degree VS dyes other than dye **1** sensitize the fading of dye **1** may be estimated by exposing the film dyed with a mixture of dye **1** and VS dyes. The films dyed in advance with the partner dye were dyed with dye **1** by the alkali-shock method so as to give the same concentration of dye **1** in all cases. The relative rate of fading dye **1** in the mixture dyeing, as well as that of the partner dye, are shown in Fig. 4. The rate of fading for dye **1** on cellulose increased in the mixture dyeings with dyes **2**, **3** and **6**, as in the case of **4**,[3] but was not changed in the mixture by dyeing with dye **3**, compared with the rate of fading for dye **1**, dyed singly at the same concentration. The efficiency of VS dyes to sensitize the fading of dye **1** was in the following order:

$$\mathrm{RB} > \mathbf{2} \sim \mathbf{4} \gg \mathbf{5} > \mathbf{6} > \mathbf{1} \sim \mathbf{3} \qquad (3)$$

This order (3) of the sensitivity varies widely with dyes and is considerably different from the order (1) for the apparent rate of fading. An anomalous fading of dye **1** is observed in a mixture of dyes **1** and **2** as in the case of dye **4**,[3] and a slight anomalous fading of dye **1** was also noticed in the mixture with dyes **5** or **6**.

In the mixture dyeings with dye **1**, the relative rate of fading for the partner dye was slightly accelerated in the case of dye **5** and dye **3**, and was suppressed in the case of dye **2** and dye **6**, when compared with that of the single dyeing at the same concentration.

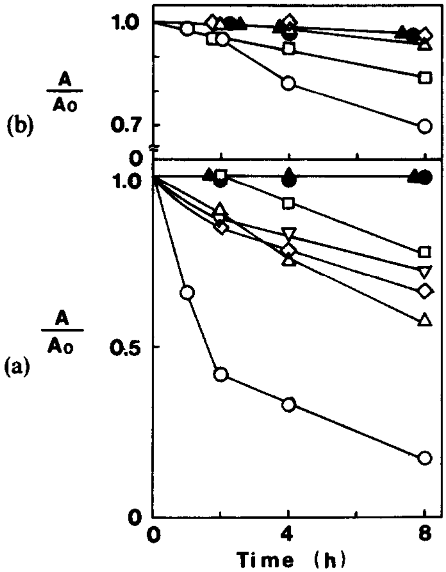

Fig. 4. (a) Relative rate of fading for dye 1 on water-swollen cellophane dyed singly and in admixture with other VS dyes, and (b) that for the partner dye on the same cellophane. No fading was observed in deaerated water under a nitrogen atmosphere, which is shown by the closed symbols.

Symbol	*Concn of dye 1 (mol kg^{-1})*	*Partner dye*	*Concn (mol kg^{-1})*
▽	$1{\cdot}65 \times 10^{-2}$	None	—
○ (● under N_2)	$1{\cdot}99 \times 10^{-2}$	2	$1{\cdot}97 \times 10^{-2}$
□	$1{\cdot}49 \times 10^{-2}$	3	$1{\cdot}09 \times 10^{-2}$
△ (▲ under N_2)	$1{\cdot}88 \times 10^{-2}$	5	$1{\cdot}19 \times 10^{-2}$
◇	$1{\cdot}84 \times 10^{-2}$	6	$5{\cdot}62 \times 10^{-3}$

The rate of fading for VS dyes examined may be analyzed as follows. The rate of photosensitized fading of dye 1 by RB estimated in the previous paper[3] is larger than that by 2 in the present study. In the VS dyes examined, however, 2 has the highest efficiency in sensitizing the fading of the VS dye and a high oxidizability (next to dye 1). Dye 2, therefore, has the largest rate of fading as in the order (1).

In the VS dyes examined, the dye 1 is oxidized the most readily, as shown by the order (2). The rate of fading for the dye 1 on cellulose dyed in admixture with dye 3 was similar to that for dye 1 dyed alone. The photosensitivity of dye 3 was thus estimated to be small, but the results also show that dye 1 has the same efficiency in generating singlet oxygen as dye 3. As a result, the dye 1 has the second highest rate of fading of the VS dyes examined.

In spite of the high sensitivity of dyes **5** and **6**, the efficiency of which is the higher, **5** has the smallest rate of fading since it is oxidized the least readily (Table 2).

The sensitized fading of the dye **1** by VS dyes was also examined by exposing VS dyes on cellulose dyed in admixture with dye **1** and by shielding dye **1** with a Toshiba Y-50 filter (> 510 nm). The results (Fig. 5) show that dyes **2**, **3**, **5** and **6** sensitized the fading of **1** on cellulose in aerated water, as was found in the case of dye **4**.[3] The efficiency of sensitizing the fading of dye **1** on exposure with the filter was in the following order:

$$\mathbf{2} > \mathbf{4} > \mathbf{5} > \mathbf{6} \sim \mathbf{3} \qquad (4)$$

This order is similar to the order (3) and these results demonstrate the photosensitivity of VS dyes and the singlet oxygen mechanism in the fading of these dyes. The superposition of the absorption characteristics of dye **1** on

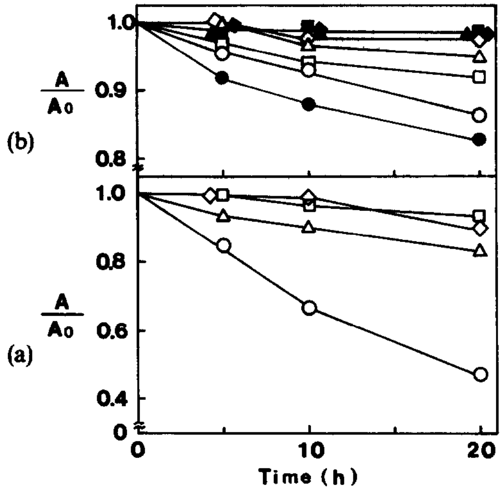

Fig. 5. (a) Apparent rate of fading for dye 1 on cellophane dyed in admixture with VS dyes on exposure through a Toshiba Y-50 filter (> 510 nm); (b) that of the VS dye on the same film dyed singly or in admixture with dye 1.

Symbol	*Concn of dye 1* (*mol kg*$^{-1}$)	*Partner dye*	*Concn* (*mol kg*$^{-1}$)
●	none	2	$2{\cdot}33 \times 10^{-2}$
○	$1{\cdot}73 \times 10^{-2}$	2	$2{\cdot}17 \times 10^{-2}$
■	none	3	$1{\cdot}32 \times 10^{-2}$
□	$1{\cdot}54 \times 10^{-2}$	3	$1{\cdot}13 \times 10^{-2}$
▲	none	5	$1{\cdot}24 \times 10^{-2}$
△	$1{\cdot}71 \times 10^{-2}$	5	$1{\cdot}19 \times 10^{-2}$
◆	none	6	$5{\cdot}89 \times 10^{-3}$
◇	$1{\cdot}74 \times 10^{-2}$	6	$5{\cdot}75 \times 10^{-3}$

those of the other VS dyes seems to give only a small effect on the rate of fading. The order (3) for the sensitivity of these dyes did not change by filtering exposure to light of wavelength less than 500 nm, although the degree of shielding varied with the dyes. Moreover, although the light whose wavelength was less than 500 nm corresponded to half of the main absorption band (cf. Fig. 3), dye **2** caused a very large fading of dye **1** on cellulose under wet conditions. Dye **2** was thus shown to have a very high efficiency to generate singlet oxygen.

Dzhanashvili *et al.*[9] measured the quantum yield ϕ for the formation of singlet oxygen for some reactive dyes in an isopropanol/water (10:1) solution (0·5 for RB, $4{\cdot}8 \times 10^{-3}$ for **2** and $1{\cdot}7 \times 10^{-2}$ for **5**). The order of ϕ is different from the order (3) or (4) above. Griffiths has suggested that part of the low efficiency in the case of azo dyes may be self-reaction with singlet oxygen.[10] Further studies are required in respect of these differences.

3.4 Diagnostic test in the fading of VS dyes

Although the experiments above indicated a singlet oxygen mechanism in the fading of VS dyes under wet conditions, exposure under anaerobic conditions would yield a more positive confirmation for such a mechanism. The fading behavior examined in deaerated water under a nitrogen atmosphere is shown in Fig. 4, using as examples mixtures of dyes **1** and **2** and of dyes **1** and **5**. Since a trace of oxygen dissolved in the water could not be removed (this resulting in some fading), a glass plate was placed on the rear side of the dyed film to prevent penetration of oxygen from the external solution. No fading was observed for all the VS dyes thus examined in deaerated water under a nitrogen atmosphere.

From these results, it is concluded that all the VS dyes examined, including the dye **1**, generate singlet oxygen, which oxidizes not only the parent dye (self-sensitized fading) but also the partner dye, if dyed in admixture (photosensitized fading). The rate of fading for VS dyes, therefore, is related to their photosensitivity (the efficiency to generate singlet oxygen) and to that of the partner dye, and also to the ease with which VS dyes are oxidized. The latter property mainly determines the rate of fading under wet conditions.

3.5 Fading of VS dyes under dry conditions

The rate of fading for some VS dyes under dry conditions was also estimated by a prolonged exposure, using the same apparatus as above, but from which water was removed. In the bottom of the glass vessel, silica gel was added to maintain dry conditions. The rate of fading decreased considerably under dry conditions compared with that under wet conditions (Fig. 6). Moreover,

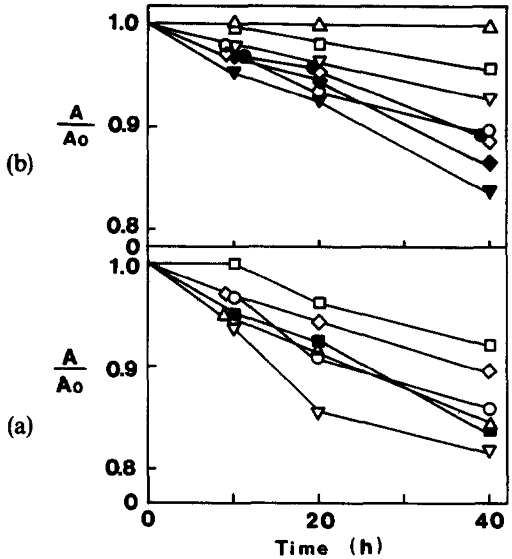

Fig. 6. (a) Relative rate of fading for dye 1 on cellulose dyed singly or in admixture with VS dyes under dry conditions; (b) that for VS dyes on the same film dyed singly or in admixture with dye 1.

Symbol	*Concn of dye 1 (mol kg^{-1})*	*Dye 2 or partner dyes*	*Concn (mol kg^{-1})*
■	$1{\cdot}60 \times 10^{-2}$	None	
▼	None	**2**	$7{\cdot}89 \times 10^{-3}$
◆	None	**2**	$2{\cdot}17 \times 10^{-2}$
●	None	**2**	$3{\cdot}64 \times 10^{-2}$
▽	$1{\cdot}57 \times 10^{-2}$	**2**	$2{\cdot}02 \times 10^{-2}$
□	$1{\cdot}38 \times 10^{-2}$	**3**	$1{\cdot}04 \times 10^{-2}$
○	$2{\cdot}70 \times 10^{-2}$	**4**	$7{\cdot}74 \times 10^{-3}$
△	$1{\cdot}71 \times 10^{-2}$	**5**	$1{\cdot}17 \times 10^{-2}$
◇	$1{\cdot}62 \times 10^{-2}$	**6**	$5{\cdot}61 \times 10^{-3}$

the rate of fading for dye **2** decreased with an increase in the concentration, as in the case of the dyes **1** and **4**.[3] Only under wet conditions does **2** show 'positive' concentration dependence on the rate of fading.

3.5.1 Fading of dyes 1 and 2

The *cis–trans* isomerism and/or azo–hydrazone tautomerism in dye **1** and in dye **2** may be restrained under dry conditions, as shown in Fig. 7. After exposure for 30 min, the absorption maximum of both dyes was shifted to shorter wavelength, by 7 nm for dye **1** and by 4 nm for dye **2**. If the film was stored in the dark under the dry conditions with silica gel, the absorption spectrum of dye **1** on the exposed film remained constant for several days,

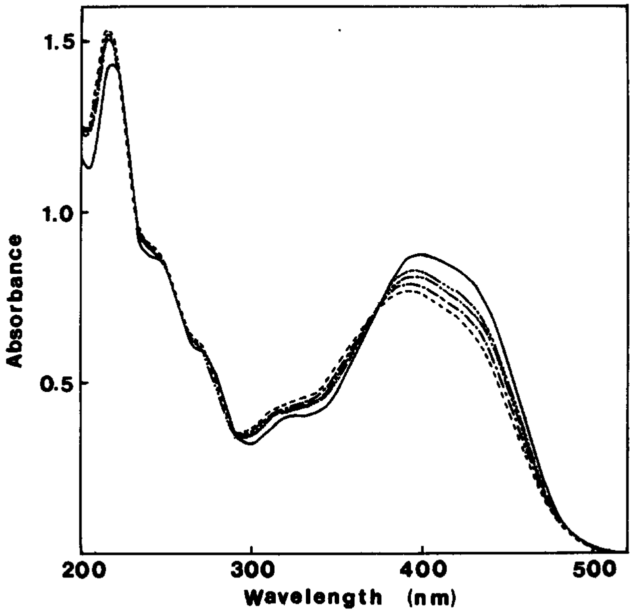

Fig. 7. Absorption spectra for dye 1 on cellophane ($1{\cdot}61 \times 10^{-2}$ mol kg^{-1}) after exposure for 30 min and variation in the ambient atmosphere (24·5°C and 75% RH) for 0·5 min (– – –), 5 min (–·–·–), 15 min (–· ·–· ·–) and 30 min (–· · ·–· · ·–), and that of no exposure (——) (cf. Fig. 8).

whilst that of dye **2** almost fully reverted in 2 days. When the absorption spectra of the exposed film were being measured in a laboratory, the absorption maximum was shifted to longer wavelength to give the final or stable spectra, the rate of shift depending on the relative humidity (Fig. 8). The humidity absorbed from the atmosphere appeared to remove the restraint of reversion. This was also inferred from the fact that swelling by water restored the final spectra instantly.

This behavior may be explained in terms of *cis–trans* isomerism and azo–hydrazone tautomerism.[11–13] The distinct features observed in the absorption spectra after exposure are (1) a hypso- and hypo-chromic effect of the A (main) band, (2) a small hyperchromic effect of the B band in the region around 300–350 nm and (3) a hyperchromic effect of the C band. The effect of (1) may be a typical feature of the *cis*-isomer,[14–17] though there remain some unresolved problems for (2) and (3).[16,17]

On the other hand, Fischer *et al.*[18–20] showed, using low-temperature techniques, that the *cis*-isomer of phenylazonaphthols was converted into the *trans*-isomer via the phenylhydrazone, and such a route was more energetically favorable than the direct *cis* → *trans* isomerization route. The time constant of the *cis–trans* isomerization for 1-phenylazo-2-naphthol is a

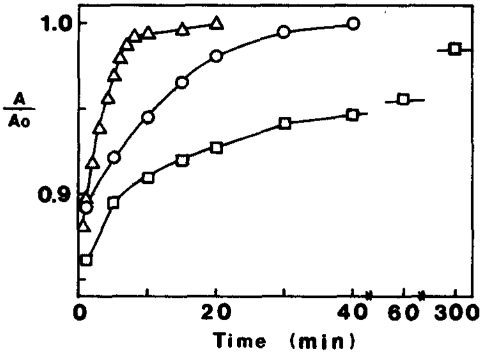

Fig. 8. Variation of the optical density under atmospheric conditions for dye **1** and **2** on cellophane after exposure for 30 min (□, **1** ($1{\cdot}50 \times 10^{-2}$ mol kg^{-1}) at 26°C and 46% RH; ○, **2** ($1{\cdot}77 \times 10^{-2}$ mol kg^{-1}) at 26°C and 46% RH; △, **2** ($1{\cdot}69 \times 10^{-2}$ mol kg^{-1}) at 24·5°C and 75% RH.

function of the medium viscosity.[21] The *cis–trans* isomerization of reactive azo dyes in cellulose, therefore, would be restrained in the substrate even at ambient temperature. This may be the case for dye **1** and for dye **2**, the *cis*-isomer of which was preserved after exposure under dry conditions.

The azo–hydrazone tautomerism of azo dyes has been extensively studied by a use of solvatochromism, NMR, IR and Raman spectroscopy,[13,22,23] but only a few methods have been applied to estimate the equilibrium constant for the tautomerism. The role of the solvent and temperature in determining the extent of the azo–hydrazone tautomeric equilibrium is known to be quite significant. It has been reported that polar and aprotic solvents tend to favor the more polar hydrazone form of *p*-hydroxyazo compounds,[22–26] and that the content of the azo form increases with an increase in temperature.[27–29]

Dye **1**, a derivative of 1-aryl-4-arylazopyrazoline,[30,31] and dye **2**, a derivative of 2-arylazo-1-naphthol, are inferred to exist predominantly as the hydrazone form[26–28] which is promoted further by the *o*-methoxy group.[13,21] The extent of the blue shift may show that the relative content of azo form for dye **1** is larger than that for dye **2** (cf. Figs 7 and 8).

The reason why the increase in humidity of the substrate or swelling by water relaxed the restraint in the *cis*-isomer may be a decrease in the medium viscosity and/or an increase in the content of the hydrazone tautomer.

3.5.2 Fading of VS dyes in admixture

The fading behavior of dye **1** on cellulose dyed in admixture with VS dyes under dry conditions is shown in Fig. 6. The concentrations of the two components were obtained by solving the two simultaneous linear equations describing the absorbance at the wavelength of maximum absorption of each component. The rate of fading for dye **1** of the mixture dyeing was larger than that of the single dyeing in the case of admixture with dyes **2** and **4**, smaller in the case of admixture with dyes **3** and **6**, and similar in the case of admixture with dye **5**, when they were compared at the same concentration. The efficiency of VS dyes to sensitize the fading of dye **1** on cellulose dyed in mixtures was in the following order, under dry conditions:

$$\mathbf{2} > \mathbf{4} \sim \mathbf{5} > \mathbf{6} \qquad (5)$$

This is the same order as that under wet conditions and implies that the fading is due to a singlet oxygen mechanism. An anomalous fading is also observed under dry conditions, but it is considerably smaller than that under wet conditions.

In the mixture dyeings with dye **1**, the relative rate of fading for the partner dye, except for dyes **2** and **5**, was nearly the same as that for the single dyeing, when compared at the same concentration. The rate of fading for dye **2** became a little less than that for the single dyeing and that for dye **5** became slightly less.

4 SUMMARY

The fading of VS dyes under wet conditions is caused by a singlet oxygen mechanism. All the VS dyes examined have a photosensitivity which varies with the dye structure. The oxidizability also varied widely. The latter property mainly determines the rate of fading under wet conditions.

In the mixture dyeing, dyes with a higher oxidizability are more rapidly faded by the photosensitization of the partner dye and also by self-sensitization, especially under wet conditions. This behavior is observed as an anomalous fading.

Under dry conditions, the rate of fading is considerably diminished compared with that under wet conditions. The photosensitized fading of VS dyes is also observed under dry conditions. The fading behavior implies that the singlet oxygen mechanism holds also under dry conditions. The azo–hydrazone tautomerism also influences the fading behavior under dry conditions.

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