Dyes and Pigments **12** (1990) 197–211

Catalytic Fading of Vinylsulfonyl Reactive Dye Mixtures on Cellulose under Wet Conditions

Yasuyo Okada, Toshiko Kato

School of Domestic Science, Ohtsuma Women's University,
Sanbancho, Chiyoda-ku, Tokyo 102, Japan

Hiromi Motomura & Zenzo Morita

School of Engineering, Tokyo University of Agriculture and Technology,
Koganei, Tokyo 184, Japan

(Received 12 December 1988; accepted 6 February 1989)

ABSTRACT

*Vinylsulfonyl reactive dyes on cellulose, present as a mixture of an aminopyrazolinyl azo yellow dye (**1**) and a phthalocyanine blue dye (**2**) showed marked catalytic fading of dye **1** under wet conditions, but only a slight fading under dry conditions. The fading was almost completely suppressed in the absence of oxygen and considerably by the addition of the singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane. Dye **1** on cellophane showed catalytic fading by adsorbing Rose Bengal on the film under wet conditions. The photosensitized fading of dye **1** on cellophane dyed in a mixture was proved by exposing only dye **2** or Rose Bengal to light of wavelength above 520 nm, and was also confirmed to be due to the singlet oxygen mechanism by diagnostic tests. The phenyl groups of dye **1** were not split off from the substrate during the fading of the dye.*

1 INTRODUCTION

It is well known that the lightfastness of certain dyes applied alone to textile fibers is better than when applied in mixtures.[1–7] In the combinations where the lightfastness of mixture dyeings is lower than that of single dyeings, many yellow dyes sensitize the fading of blue dyes,[1–4] whilst a few blue, violet or reddish anthraquinone dyes sensitize that of yellow azo or anthraquinone dyes.[5-7] Such a phenomenon has been termed 'catalytic fading' and has been proved to be attributable to the action of singlet oxygen.[7-11]

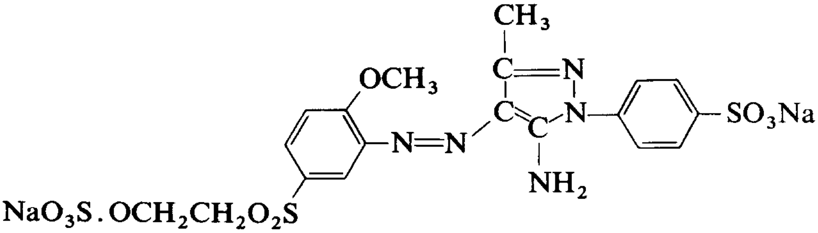
On the other hand, it is known that the lightfastness of dyes under wet conditions is in general lower than that under dry conditions.[12-16] In the case of monochlorotriazinyl reactive dyeings of cotton, Datyner *et al.* studied the mechanism of fading under wet conditions.[16]

With reactive dyes for cotton, some mixture dyeings of yellow and blue dyes are known to show anomalous fading only when wet. In this present study, mixture dyeings of an aminopyrazolinyl azo dye and a phthalocyanine dye are confirmed to show anomalous fading under wet conditions. The fading rates for single and mixture dyeings on cellulose film under dry and wet conditions are estimated. The fading mechanism is studied by use of anaerobic conditions and diagnostic tests.

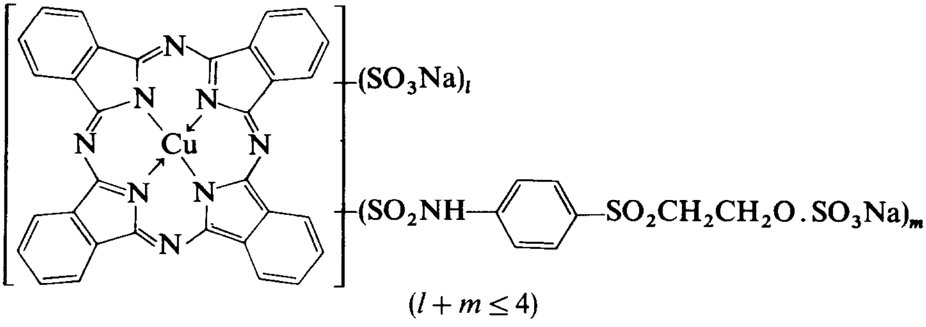
2 EXPERIMENTAL

2.1 Materials

The two vinylsulfonyl reactive dyes used, an aminopyrazolinyl azo yellow dye **1** and a phthalocyanine blue dye **2**, were supplied by Sumitomo Chemical



1



$(l + m \leq 4)$

2

Industries Ltd and were used without further purification for the dyeing of films. Dye **2** used for the measurement of absorption spectra in solution was purified using organic solvents.[17] The molar concentration of dye **1** was determined by use of the hydrolyzed species purified by the method of Robinson & Mills,[18] whilst for dye **2** the molar extinction coefficient in a 50% aqueous dimethylformamide (DMF) solution was assumed to be 10^6 at the wavelength of maximum absorption, since the liquid chromatogram of dye **2** was too complex to purify it. Dye **1** was hydrolyzed at 80°C for 2 h with 0·1M-sodium hydroxide and the purity of the hydrolyzed sample was checked by HPLC.

The cellophane sheets used (No. 300, Tokyo Cellophane Sheet Ltd) were cut 4·0 cm wide and 50 cm long and were scoured with distilled water for 3 h. They were dyed at 50°C so as to obtain level dyeings of various concentrations from a dyebath containing 1–2 g dye dm^{-3} and 5–50 g Na_2SO_4 dm^{-3} and by the addition of 20 g Na_2CO_3 dm^{-3}. The other chemicals used, DMF, Rose Bengal (RB), 1,4-diazabicyclo[2.2.2]octane (DABCO), deuterium oxide (D_2O) etc., were of reagent grade.

2.2 Exposure to light

In order to maintain constant experimental conditions during the exposure of the dyed cellophane, the film was set on the inner surface of a glass cell filled with an aqueous solution at 50°C. The upper end of the film was fixed with a Teflon cell stopper and the lower end with the weight of a small glass plate so as to stick the film on the inner surface of the front glass of the cell. The glass cell was fixed on a cell holder placed in a glass vessel as shown in Fig. 1 and was exposed to a carbon-arc lamp in a fadeometer Model FAL-3 (Suga Test Instruments Co.). The dyed film was exposed to light of wavelength longer than 290 nm. A Toshiba Y-51 filter (>520 nm) was set between two glass cells for the appropriate tests. The cell holder with which the glass vessel was equipped was made by modifying a sample holder for JIS L 0888.[19] A front glass cell filled with water was used to keep the temperature of the solution in the sample cell constant and not to raise that of the filter. The chamber temperature of the fadeometer during exposure was set at 40°C, and the black panel temperature was kept at 65°C. It was confirmed that these conditions maintained the solution temperature of the sample cell at 50 ± 2°C.

In the case of the exposure of dry films, glass cells, in one of which a dyed film was set, were used and silica gel was placed at the bottom of the glass vessel. In the case of tests at 100% relative humidity (RH), water was added in the vessel. The fadeometer was carefully cleaned before each exposure.

The absorption spectra of a dyed film before and after exposure were

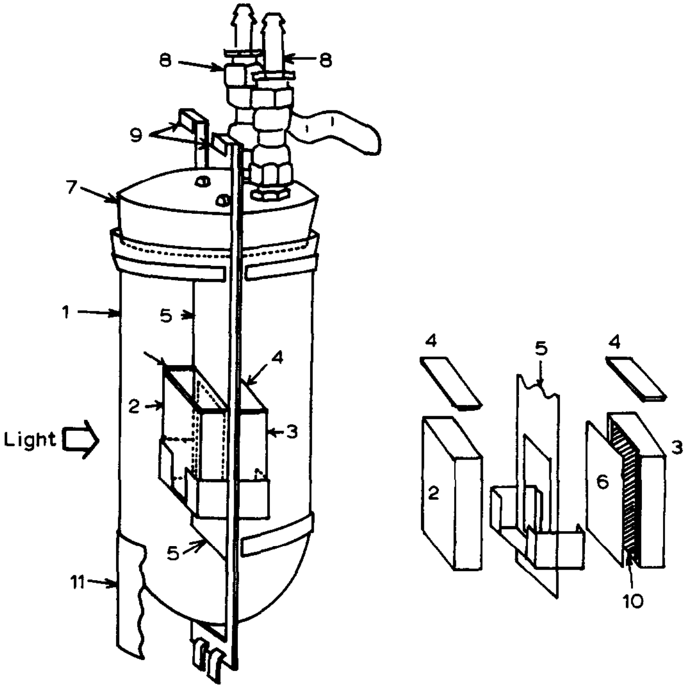


Fig. 1. Attachment of a fadeometer for the exposure of dyed cellophane in a glass cell set in a glass vessel. 1, Pyrex glass vessel (i.d. 70 mm); 2, front glass cell, 1 cm (optical path length) × 4 cm (height) × 4 cm (width); 3, glass cell for setting the dyed cellophane (the same size as the front cell); 4, Teflon stopper; 5, cell holder; 6, filter (when necessary); 7, silicone rubber stopper; 8, gas inlet or outlet pipe equipped with a cock; 9, part for attachment to the panel of fadeometer; 10, dyed cellophane (sample); 11, shading plate.

measured on a UVUDEC-505 recording spectrophotometer (Japan Spectroscopic Co. Ltd) or on a UV-190 spectrophotometer (Shimadzu Corporation) either dry or in aqueous DMF solution using a cell spacer. The rate of fading was determined by the absorbance measurements at the appropriate wavelength.

3 RESULTS AND DISCUSSION

3.1 Fading of dye 1 in single dyeings

The absorption spectra for the yellow dye **1** on cellophane before and after exposure under wet conditions were similar in shape showing that the dye faded at a similar rate over the wavelength range above 350 nm (Fig. 2).

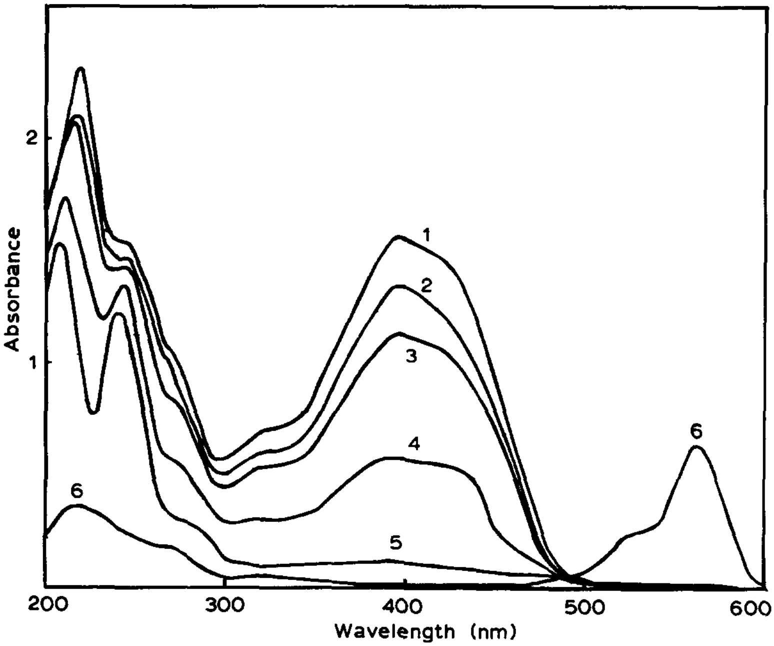


Fig. 2. Absorption spectra of dye **1** on singly dyed cellophane before and after the exposure, and of Rose Bengal on cellophane: 1, before exposure; 2, after exposure for 10 h in water; 3, 4 and 5, after exposure for 1, 2 and 3 h, respectively, in an aqueous solution containing RB ($3{\cdot}3 \times 10^{-5}$ mol dm^{-3}) and sodium sulfate (0·007 mol dm^{-3}); 6, RB ($2{\cdot}3 \times 10^{-3}$ mol kg^{-1}). The spectrum of dye **1** on the film after exposure for 20 h was almost the same as spectrum 3.

From the ratio of the optical density before (A_0) and after an exposure (A_t) for time t at the wavelength of maximum absorption on cellophane (395 nm), the relative rate of fading was obtained for various initial concentrations as shown in Fig. 3. Although the initial rate of fading for dye **1** showed considerable concentration dependence and was higher than the subsequent rate of fading, the latter rate showed small concentration dependence in the concentration range examined. The phenomenon in which dye **1** fades without being sensitized by another dye is referred to as 'self-fading'. Unlike the situation with dye **2**, dye **1** showed no evidence of aggregation on cellulose besides a shift of the main peak in aqueous DMF solution within the range of concentrations examined (cf. Section 3.2).

There was no difference in the shape of the absorption spectra after exposure under dry and wet conditions. The rates of fading under dry conditions and at 100% RH are shown in Fig. 4 and Table 1. The former was about one-fifth of the rate under wet conditions and the latter was about one-quarter of the wet rate. Thus, humidity or water increased the rate of fading.[12-16]

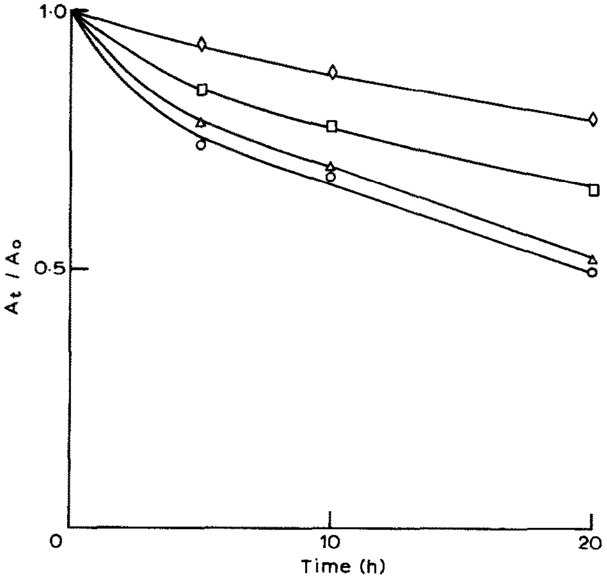


Fig. 3. Concentration dependence of fading of dye **1** on cellophane dyed singly at various concentrations when exposed under wet conditions. The concentrations of dye **1** on cellulose were (◇) $2{\cdot}74 \times 10^{-2}$, (□) $1{\cdot}90 \times 10^{-2}$, (△) $1{\cdot}10 \times 10^{-2}$ and (○) $6{\cdot}80 \times 10^{-3}$ mol kg^{-1}.

3.2 Aggregation and absorption spectra of dye 2

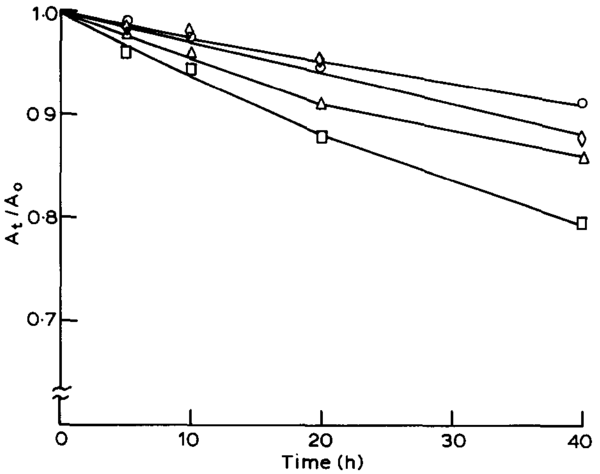
The absorption spectra of dye 2 in aqueous DMF and on cellophane show significant variations [Fig 5, (a) and (b)]. Spectra in aqueous DMF showed isosbestic points at 710 nm and at 646 nm between the main peak (λ_{max} = 673 nm) and a subpeak (λ = 603 nm) on varying the DMF–water composition. The ratios of absorbance at 603 and 673 nm were measured to

TABLE 1

Relative Rate of Fading (% min^{-1}) for Dyes **1** and **2** under Various Conditions[a]

Dye	*Period of fading*	*In dry*		*At 100% RH*		*In water*	
		Single	*Mixture*	*Single*	*Mixture*	*Single*	*Mixture*
1	Initial	0·0038	0·0075	0·0052	0·013	0·023	0·42
	Subsequent	0·0038	0·0042	0·0052	0·007	0·015	0·19
2	Initial	0·0022	0·0058	1×10^{-5}	0·010	0·009	0·058
	Subsequent	0·0013	0·0033	7×10^{-5}	0·003	0·002	0·058

[a] The concentrations on cellulose were $2{\cdot}7 \times 10^{-2}$ mol kg^{-1} for dye **1** and $7{\cdot}7 \times 10^{-3}$ mol kg^{-1} for dye **2**.



	In dry	*At* 100% *RH*
Single	○	◇
Mixture	△	□

Fig. 4. Fading of dye 1 on cellophane dyed singly or in admixture when exposed under dry conditions. Concentrations: $2{\cdot}7 \times 10^{-2}\,\mathrm{mol\,kg^{-1}}$ for dye **1** and $7{\cdot}7 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$ for dye **2**.

be 0·22 in DMF and 0·70 in water. The ratio of absorbance at 630 and 673 nm was also 0·20 in DMF, although there was no shoulder at 630 nm.

The absorption spectra of dye **2** on reactively-dyed cellophane measured in aqueous DMF gave the same isosbestic points at 710 nm and at 646 nm between the main peak and the shoulder ($\lambda = 630$ nm) on varying the water–DMF composition [Fig. 5, (b)]. The subpeak disappeared, but a shoulder ($\lambda = 630$ nm) appeared, whilst the main peak ($\lambda_{max} = 675$ nm) was shifted to longer wavelength. The spectrum of dye **2** on a dry film intersected also at the isosbestic points, if the swelling effect was taken into account. The ratios of the absorbance at 630 and 675 nm, however, showed complicated variations. For example, when a dyed film with a ratio of 0·67 (measured dry) was boiled in water for 20 min and then immersed in DMF, the ratio measured in DMF decreased to 0·37. When it was immersed in a 50% aqueous DMF after boiling in water for 20 min, the ratio was 0·51. It was estimated to be 0·67 on water-swollen cellophane, the same value as that on the dry film. A long immersion of the film in DMF solution without boiling gave the same result.

It is inferred that the absorption spectra of dye **2** on cellophane exhibited similar variations to those of a monomer–dimer equilibrium, as typically shown by the existence of isosbestic points and different variations from a dimer–tetramer equilibrium.[20] Thus, dye **2** may be present in the substrate as a mixture of monomer and dimer at most and not as a mixture of large aggregates.

This ratio corresponds to the *y*/*x*-ratio in previous studies.[21–24] An increase in the ratio has been attributed to an increase in aggregation of

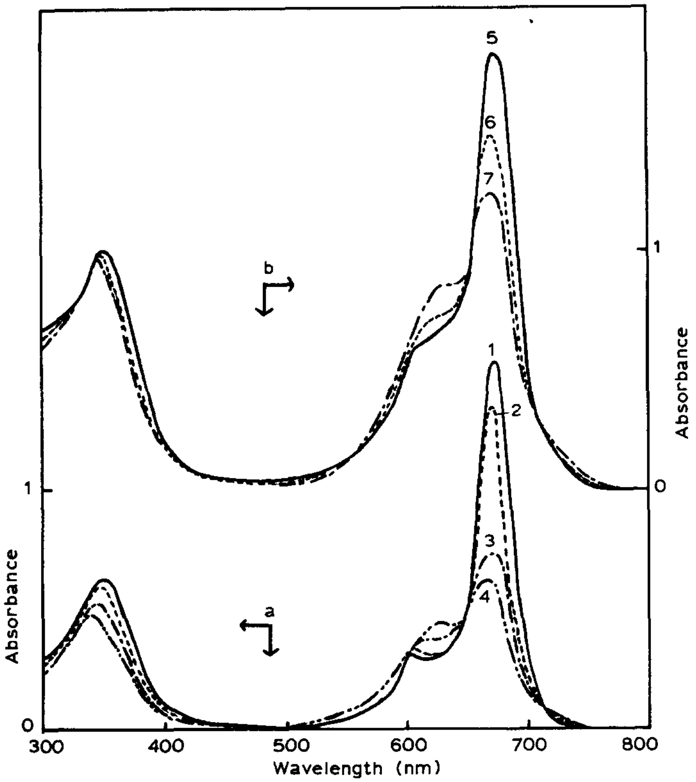


Fig. 5. Absorption spectra of dye **2**. (a) In aqueous DMF solutions ($0{\cdot}014\,g\,dm^{-3}$): 1, In 100% DMF; 2, in a 45% aqueous DMF solution; 3, in a 11% aqueous DMF solution; 4, in water. (b) On cellophane ($7{\cdot}7 \times 10^{-3}$ mol kg^{-1}) swollen by aqueous DMF solutions; it was boiled for 20 min in water and then immersed: 5, in 100% DMF; 6, in a 50% aqueous DMF solution; and 7, in water.

dye **2**.[24] Reactive dyes in cellulose may be in a metastable state which varies readily depending on the environment, although the substrate restricts the disaggregation even when the dyeings are immersed in DMF. Thus, dye **2** aggregates more in cellulose than in DMF, and less in cellulose than in water.

In this present study, the isosbestic point at 646 nm was used to determine the concentration of dye **2** in the substrate and the y/x-ratio as a measure of the degree of aggregation.

3.3 Fading of dye 2 in single dyeings

The rate of fading for dye **2** on cellophane in water and the y/x-ratio showed concentration dependence (Fig. 6). The ratio of absorbance at 630 and 675 nm was slightly increased during exposure, as reported by Shah &

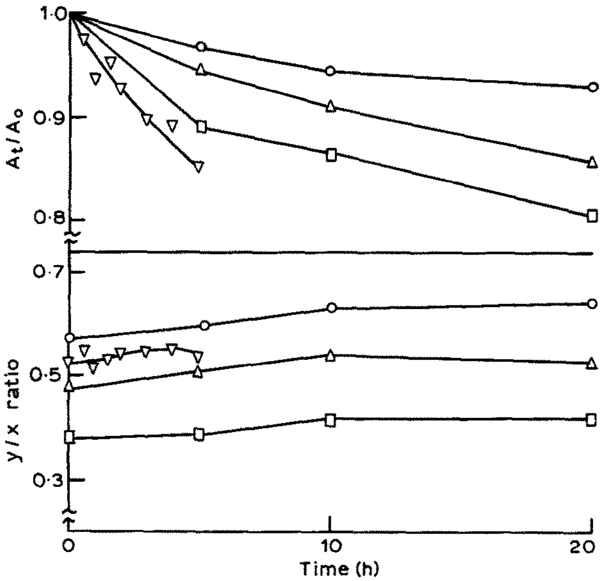


Fig. 6. Concentration dependence of fading for dye **2** on cellophane at various concentrations under wet conditions and variation of the y/x-ratio during fading. The concentrations of dye **2** were (○) $5{\cdot}5 \times 10^{-3}$, (△) $3{\cdot}4 \times 10^{-3}$, (□) $1{\cdot}8 \times 10^{-3}$ and (▽) $7{\cdot}7 \times 10^{-3}$ mol kg^{-1}. Concentration of dye **1** in admixture with **2** was (▽) $2{\cdot}7 \times 10^{-2}$ mol kg^{-1}.

Srinivasan.[24] Since smaller y/x-ratios for dye **2** gave a faster rate of fading, the concentration dependence of fading may be explained by the dye aggregation if the monomer of dye **2** was preferentially faded.

The rate of fading for dye **2** under wet conditions was larger than that under dry ones (Table 1). Thus, water increased the rate of fading as with dye **1**.

3.4 Fading of mixture dyeings under wet conditions

To obtain the green films, dye **1** was applied after dyeing with dye **2**, when a small amount of dye **2** was always desorbed. The absorption spectra of the green film before and after an exposure under wet conditions are shown in Fig. 7. The visible spectrum of the green film after fading resembled that of dye **2** with a trace of dye **1** being observed around 400 nm (cf. spectra 4 and 5), whilst the UV spectra were considerably different from those of dye **2**, confirming the presence of dye **1** (cf. Section 3.5). In order to calculate the rate of fading for dye **1**, the absorbance at 420 nm was used because of the overlap of the absorption spectra of the two dyes. The rates of fading for dye **1** on water-swollen cellophane reactively-dyed in admixture with dye **2** on exposure in various aqueous solutions are shown in Fig. 8 and Table 2.

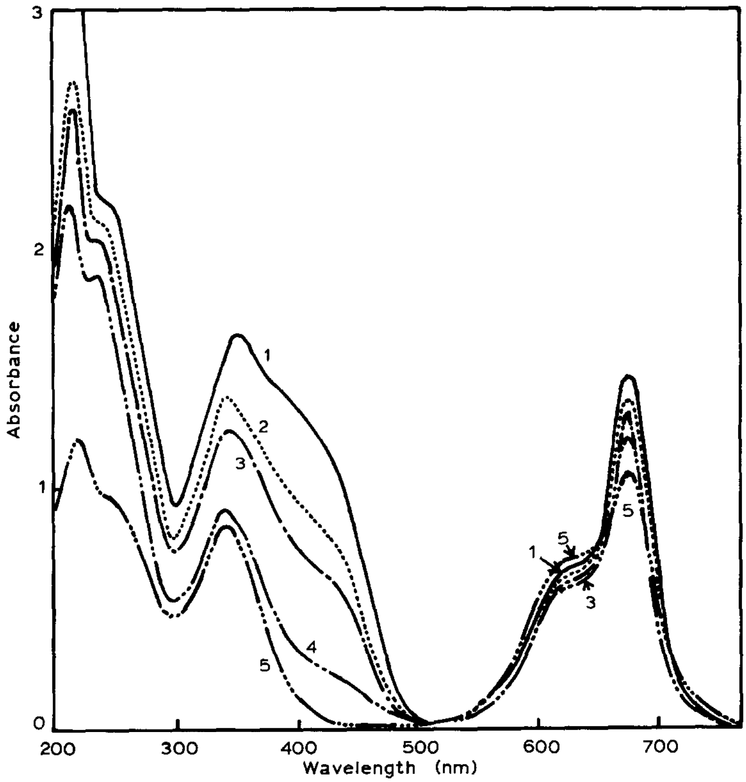


Fig. 7. Absorption spectra of reactive dye mixtures on cellophane before and after exposure in water, and spectrum of dye **2** on the film. The concentrations on cellulose were $2{\cdot}7 \times 10^{-2}$ mol kg^{-1} for dye **1** and $7{\cdot}7 \times 10^{-3}$ mol kg^{-1} for dye **2**. 1, Before exposure; 2, 3 and 4, after exposure for 1, 2 and 5 h, respectively; 5, dye **2** on the film dyed singly (before exposure).

TABLE 2

Initial Rate of Fading for Dye **1** on Cellophane Reactively-Dyed in Mixture with Dye **2** on Exposure to the Carbon-Arc Lamp of a Fadeometer under Various Conditions at 50°C[a]

Conditions	*Initial rate of fading* (% *min*$^{-1}$)	
	Without filter	*With filter*
In aerated water	0·42	0·21
In water saturated with oxygen	2·17	—[b]
In water saturated with nitrogen	0·003	—[b]
In aerated deuterium oxide	0·50	—[b]
In aerated DABCO soln (0·1 mol dm^{-3})	0·22	—[b]

[a] The concentrations on cellulose were $2{\cdot}7 \times 10^{-2}$ mol kg^{-1} for dye **1** and $7{\cdot}7 \times 10^{-3}$ mol kg^{-1} for dye **2**.

[b] Not determined.

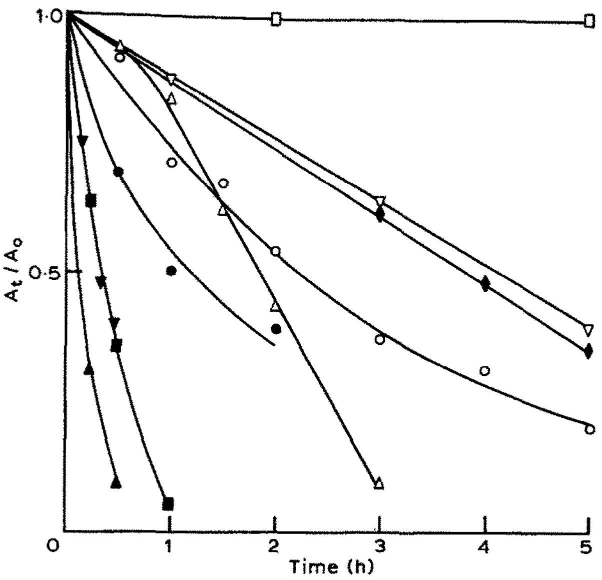


Fig. 8. Fading of dye **1** on water-swollen cellophane reactively-dyed in mixture with dye **2** on exposure under various conditions, and effect of Rose Bengal on the fading of dye **1** on singly dyed cellophane. The concentrations on cellulose were $2{\cdot}7 \times 10^{-2}$ mol kg^{-1} for dye **1** and $7{\cdot}7 \times 10^{-3}$ mol kg^{-1} for dye **2**. ○, In aerated water; ●, in aerated deuterium oxide; ■, in water saturated with O_2; ◆, in DABCO (0·1M) soln; □, in degassed water under a nitrogen atmosphere; △, in water containing RB ($3{\cdot}3 \times 10^{-5}$ mol dm^{-3}) and Na_2SO_4 (0·007M); ▲, in water containing RB and Na_2SO_4 (0·05M); ▽, in aerated water on exposure through a Toshiba Y-51 filter; ▼, in water containing RB and Na_2SO_4 (0·05M) on exposure through a Toshiba Y-51 filter.

Under dry conditions, the rate of fading of dye **1** on the green film was 1·5 times higher than that of dye **1** on cellophane dyed singly, while at 100% RH it was twice as high. Under wet conditions the rate of fading for dye **1** on the green film was ten times higher than that of single dyeing and about 100 times higher than the rate of fading of dye **1** alone under dry conditions. There is thus a marked anomalous fading in the mixture dyeings with dyes **1** and **2** under wet conditions and a slight fading under dry conditions. The anomalous fading may not be a problem in practice under dry conditions, since the rate of fading of dye **1** is similar to that of a single dyeing, except in the initial rate of fading.

The fading of dye **2** on the green film was difficult to evaluate for the following reasons. The *y*/*x*-ratios of dye **2** on cellophane dyed in admixture with dye **1** were always smaller than those in the single dyeings, as the spectra in Fig. 7 show, even when dye **1** was applied after dye **2**. Thus, the reactive dyeings with dye **1** decreased the degree of aggregation of dye **2**. This means that the fading of dye **2** in the single and mixture dyeings may not be directly compared with each other.

The rate of fading for dye **2** in the mixture dyeings was faster than that in the single dyeings under both dry and wet conditions, whilst fading rates under wet conditions were higher than those under dry conditions in both the mixture and single dyeings (Table 1). The difference in the rate of fading between the mixture and single dyeings in dry and wet conditions may be attributed to the aggregation effect reported by Shah & Srinivasan,[24] as noted above, where the presence of dimers as aggregates is suggested. However, Fig. 6 shows also that the y/x-ratio is not sufficient to explain the fading behavior of dye **2** on the green film.

3.5 Diagnostic test for singlet oxygen mechanism

In order to elucidate the mechanism operative in the anomalous fading, various diagnostic tests were used (Fig. 8 and Table 2).

When a green film in degassed water was exposed to light under anaerobic conditions, i.e. under a nitrogen atmosphere, the photofading of both the dyes **1** and **2** was completely suppressed. If a green film was exposed in water saturated with oxygen, a marked increase in the fading of dye **1** was observed.

According to Merkel *et al.*,[25,26] deuterium oxide (D_2O), which extends the lifetime of singlet oxygen by a factor of ten, is a good diagnostic chemical to test the singlet oxygen mechanism. Since a deuterium exchange of dyed cellulose must occur gradually when immersed in D_2O, a green film was immersed overnight in deuterium oxide prior to an exposure. As shown in Fig. 8 and Table 2, the treatment in D_2O accelerated the photofading of dye **1**. Immersion for 2 h prior to an exposure, however, gave the same rate of fading.

In order to confirm the formation of singlet oxygen in dyed cellulose, Rose Bengal (RB) was added to an aqueous solution in which a film dyed with dye **1** was exposed[27] (Fig. 8 and Table 3). Addition of RB and of an insufficient amount of sodium sulphate to the immersing solution retarded the photofading of dye **1**, because singlet oxygen was generated outside the substrate due to no adsorption of RB on cellulose. Addition of a sufficient amount of sodium sulphate to the solution or an adsorption of RB on cellulose both resulted in marked photofading of dye **1**.

The absorption spectra of cellophane dyed with dye **1** after exposure in water containing RB and sodium sulphate are shown in Fig. 2. The visible spectra indicate a small adsorption of RB on cellulose as well as a marked fading of dye **1**. On the other hand, the UV spectra (<300 nm) imply the presence of a phenyl group in the cellulose after complete or partial fading of dye **1** by RB and Fig. 7 supports this. Although it has been presumed that reactive dyes fade after fission from the substrate,[28] these results indicate

TABLE 3

Effect of Rose Bengal Added to an Aqueous Solution on the Fading of Dye **1** on Cellophane[a]

Additives to aerated water	*Initial rate of fading (% min^{-1})*	
	Without filter	*With filter*
Rose Bengal ($3{\cdot}3 \times 10^{-5}$ mol dm^{-3}) and Na_2SO_4 ($0{\cdot}05$ mol dm^{-3})	4·67	2·17
Rose Bengal ($3{\cdot}3 \times 10^{-5}$ mol dm^{-3}) and Na_2SO_4 ($7{\cdot}04 \times 10^{-3}$ mol dm^{-3})	0·59[b]	—

[a] Concentration of dye **1** on cellophane = $2{\cdot}7 \times 10^{-2}$ mol kg^{-1}.

[b] Subsequent rate of fading.

[c] Not determined.

that the vinylsulfonyl groups were not split off from the substrate during exposure. According to Griffiths & Hawkins,[29,30] singlet oxygen oxidizes the hydrazone form of an azo dye, breaking the azo group and this may result in an aminopyrazolinyl compound being split off and a vinylsulfonylmethoxyphenyl compound being bound to cellulose.[29]

Another effective diagnostic chemical is the singlet oxygen quencher, DABCO, which is expected to suppress the sensitization of photo-oxidation.[31,32] Addition of DABCO to an aqueous solution in which a dyed film was immersed gave a suppression effect on the fading of dye **1** (Fig. 8 and Table 2).

In this present study it was demonstrated under wet conditions that singlet oxygen plays an important role in the photofading of dye **1** on a mixture-dyed green film because of sensitization by dye **2** or RB. However, the acceleration effect of water on the fading of dye **1** may be attributed not only to the accelerated diffusion of singlet oxygen in water-swollen cellulose but also to the water-enhanced sensitivity of dye **1** to singlet oxygen.

3.6 Photosensitization by dye 2 or Rose Bengal

In order to confirm the photosensitization effect of dye **2** on the fading of dye **1**, a green film was exposed to light of wavelength above 520 nm using a Toshiba Y-51 filter. This filter diminished the rate of fading of dye **1** under wet conditions (Fig. 8). Only the photosensitized fading by dye 2 would occur and the self-fading of dye **1** would disappear. The lowering effect of the filter was much larger than the self-fading of dye **1**. (No correction was made for the imperfect transmission (84%) for light of wavelength above 520 nm.)

An exposure of cellophane dyed with dye **1** in an aqueous solution containing RB to filtered light (>520 nm) also showed the photosensitized fading of dye **1** to be accompanied by a reduction in the rate of fading (Fig. 8 and Table 3).

These results imply a singlet oxygen mechanism in the fading, especially in the anomalous fading. The fact that no fading occurred under anaerobic conditions shows that only singlet oxygen acts as an oxidizer of the dyes.

4 CONCLUSION

The photofading of two vinylsulfonyl reactive dyes, an aminopyrazolinyl yellow dye **1** and a phthalocyanine blue dye **2**, on cellulose was investigated by exposure to carbon-arc light of wavelength above 290 nm of a fadeometer under wet conditions.

The rate of photofading for dyes **1** and **2** under wet conditions was higher than that under dry conditions. Reactive dyeings on cellulose using a mixture of dyes **1** and **2** showed anomalous or catalytic fading of dye **1** under wet conditions. The use of a filter demonstrated the photosensitized fading of dye **1** by dye **2** or Rose Bengal. The photofading of dye **1** was suppressed by exposure under anaerobic conditions and was accelerated by a factor of five under an oxygen atmosphere. A slight anomalous fading of dye **1** in mixture dyeings with dyes **1** and **2** was observed under dry conditions. The results show that the fading of dye **1** is due to a singlet oxygen mechanism. The anomalous fading of the reactive dye–cellulose system under wet conditions occurs by the singlet oxygen mechanism. Under dry conditions, it is inferred that the same situation holds.

ACKNOWLEDGEMENT

The authors thank Sumitomo Chemical Co. Ltd for their assistance in the preparation of this paper.

REFERENCES

1. Asquith, A. S. & Ingham, P., *J. Soc. Dyers Colour.*, **89** (1973) 81.
2. Fiebig, D. & Metwally, S. A., *Melliand Textilber.*, **56** (1975) 637.
3. Scholefield, F. & Goodyear, E. H., *Melliand Textilber.*, **11** (1929) 867.
4. Kramer, H. E. A. & Maute, A., *Photochem. Photobiol.*, **17** (1973) 413.
5. Fiebig, D., *Textil-Praxis*, **35** (1980) 443.
6. Rembold, M. W. & Kramer, H. E. A., *J. Soc. Dyers Colour.*, **94** (1978) 12.
7. Zweig, A. & Henderson, W. A., Jr, *J. Polym. Sci., Polym. Chem. Ed.*, **13** (1975) 717.

8. Egerton, G. S. & Morgan, A. G., *J. Soc. Dyers Colour.*, **86** (1970) 242.
9. Oda, H., Kuramoto, N. & Kitao, T., *J. Soc. Dyers Colour.*, **97** (1981) 462.
10. Kuramoto, N. & Kitao, T., *J. Soc. Dyers Colour.*, **98** (1982) 334.
11. Kuramoto, N. & Kitao, T., *J. Chem. Tech. Biotech.*, **30** (1980) 129.
12. McLaren, K., *J. Soc. Dyers Colour.*, **72** (1956) 527.
13. Giles, C. H. & McKay, R. B., *Text. Res. J.*, **33**, (1963) 527.
14. Giles, C. H., Shah, C. D., Johari, D. P. & Sinclair, R. S., *J. Soc. Dyers Colour.*, **88** (1972) 59.
15. Cunliffe, P. W., *J. Soc. Dyers Colour.*, **72** (1956) 330.
16. Datyner, A., Nicholls, C. H & Pailthorpe, M. T., *J. Soc. Dyers Colour.*, **93** (1977) 213.
17. Mehta, H. U., Ravikrishnan, M. R. & Chitale, A. G., *J. Soc. Dyers Colour.*, **78** (1962) 552.
18. Robinson, C. & Mills, H. A. T., *Proc. Roy. Soc.*, **131A** (1931) 576.
19. Japanese Industrial Standards Committee, JIS L 0888-1977 *Testing Method for Colour Fastness to Light and Perspiration* (reaffirmed 1982).
20. Schnabel, E., Noether, H. & Kuhn, H., *Recent Progress in the Natural and Synthetic Coloring Matters and Related Fields*, ed. T. S. Gore, B. S. Joshi, S. V. Sunthankar & B. V. Tilak. Academic Press, New York, 1962, p. 561.
21. Bach, H., Pfeil, E., Philippar, W. & Reich, M., *Angew. Chem.*, **75** (1963) 407.
22. McKay, R. B. & Hillson, P. J., *Trans. Faraday. Soc.*, **61** (1965) 1800, *idem, ibid.*, **63** (1967) 777.
23. Blander, M. J., Brivati, J. A., Fox, M. F., Symons, M. C. R. & Varma, C. S. P., *Trans. Faraday Soc.*, **63** (1967) 1850.
24. Shah, C. D. & Srinivasan, R., *J. Appl. Chem. Biotech.*, **25** (1975) 615.
25. Merkel, P. B., Nilsson, R. & Kearns, D. R., *J. Am. Chem. Soc.*, **94** (1972) 1030.
26. Monroe, B. M. In *Singlet O_2*, Vol. I, ed. A. A. Frimer, CRC Press, Florida, USA, 1985, Chapter 5, pp. 177–224.
27. Rosenthal, I. In *Singlet O_2*, Vol. I, ed. A. A. Frimer, CRC Press, Florida, USA, 1985, Chapter 2, pp. 13–38.
28. Calin, C., Rosenberg, S. & Mihai, A., *Textil-Praxis*, **29** (1974) 342–7.
29. Griffiths, J. & Hawkins, C., *J. Chem. Soc., Perkin 2*, (1977) 747.
30. Griffiths, J. & Hawkins, C., *J. Appl. Chem. Biotech.*, **27** (1977) 558.
31. Ouannes, C. & Wilson, T., *J. Am. Chem. Soc.*, **90** (1968) 6527.
32. Smith, W. F., Jr, *J. Am. Chem. Soc.*, **94** (1972) 186.