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Fading of Vinylsulfonyl Reactive Dyes on Cellulose in Admixture under Wet Conditions

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ABSTRACT

The fading of vinylsulfonyl(VS) reactive dyes on cellulose in a binary mixture was investigated under wet conditions. Dyes with a high photosensitivity such as Rose Bengal, a copper phthalocyanine, C.I. Reactive Red 22 and Black 5, gave a positive concentration dependence on the fading of the partner dye or of its own, when the partner or itself was easily oxidized. A preferential surface fading model for reactive dyes on cellulose in a mixture is proposed to explain the fading behavior under wet conditions and the model was experimentally confirmed by the variation in the concentration profiles during the fading for both dyes on film dyed in admixture. A dye which underwent fading more readily when it was oxidized showed accelerated fading when present in a mixture with a dye having high fading sensitivity, compared with the fading of the single dyeing at the same concentration. A dye which faded with moderate ease, when present in a mixture with a dye which faded less readily, showed decreased fading.

1 INTRODUCTION

It is known that dyes on a substrate fade more rapidly when they are dyed in a mixture than when dyed singly. The present authors[1] have shown, for vinylsulfonyl(VS) reactive dyes on cellulose under wet conditions, that the ease with which dyes are oxidized and their photosensitivity vary with the dye structure and that the lightfastness of a dye is mainly dependent on the

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former property. The oxidation of dyes on cellulose takes place more rapidly under wet conditions than under dry conditions. Some thiazine, fluorone, phthalocyanine, anthraquinone and azo dyes are known to sensitize the fading of dyes on substrate.[2,3a,4] It has been previously shown[1] that a range of VS dyes, based on phthalocyanine, anthraquinone, monoazo, disazo and copper-complex azo dyes sensitized the fading of VS dyes on cellulose under wet conditions.

In the VS dyes thus studied, it was found[1] that the order of the ease with which the VS dyes were oxidized was:

$$\text{Yellow} \gg \text{Red 22} \gg \text{Blue-Cu} > \text{Black 5} > \text{Cu-Pc} > \text{Blue 19} \qquad (1)$$

and that the order of efficiency in sensitizing the fading of VS dyes was:

$$\text{Red 22} > \text{Cu-Pc} > \text{Blue 19} > \text{Black 5} > \text{Yellow} \sim \text{Blue-Cu} \qquad (2)$$

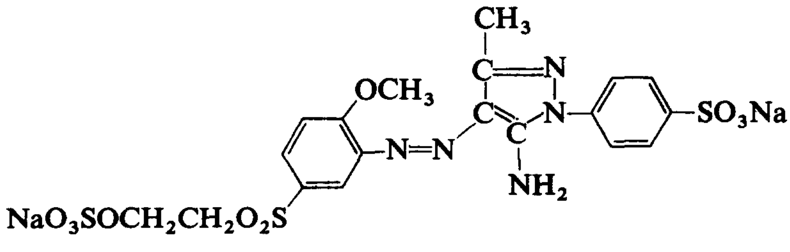
The rate of fading for Red 22 increased with an increase in the concentration on cellulose, in contrast to the other VS dyes examined.[1] Since the same mechanism of fading for Red 22 was shown to hold as that for the other VS dyes[1] and the rate of fading usually decreased with increase in the concentration, why this dye showed exceptional behaviour in having a 'positive' concentration dependence of fading could not be elucidated.

In this present paper, a model describing the fading behavior of reactive dyes is presented and is then evaluated experimentally. The concentration dependence of Rose Bengal(RB) on the fading of Yellow on cellulose is examined under wet conditions. The concentration effect of the partner dye on the fading of Yellow and Red 22 on cellulose dyed in a binary mixture is also investigated under wet conditions. From the rate of fading for Yellow in a mixture with RB and VS dyes, the values of the photosensitivity and the rate constants of the reaction with singlet oxygen are estimated.

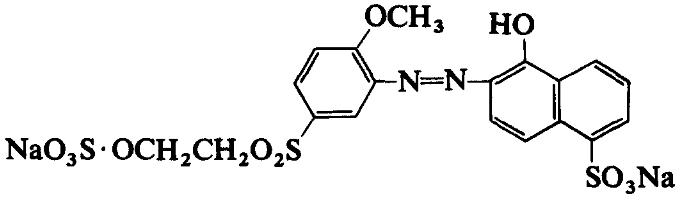
2 EXPERIMENTAL

Materials used, VS dyes and cellophane films, and the experimental methods were the same as previously described.[4] The structures of the dyes used are as follows:

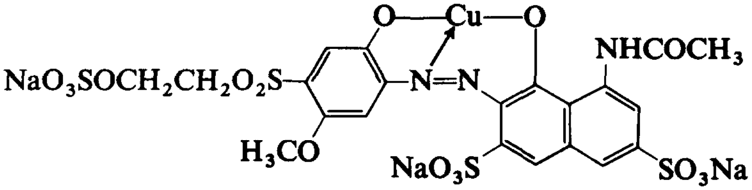
(1) An aminopyrazolinyl azo dye (Yellow)



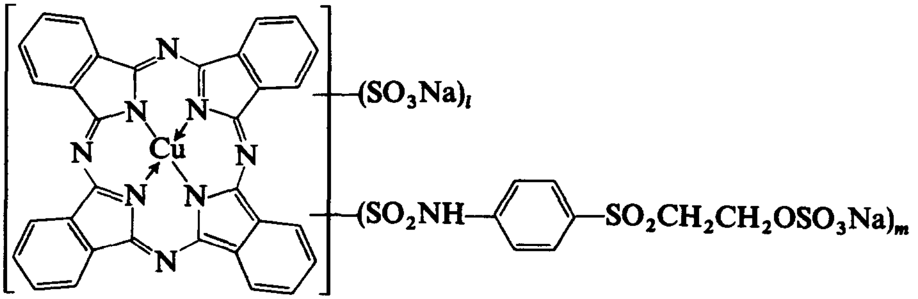
(2) C.I. Reactive Red 22 (Red 22)



(3) A copper-complex azo dye (Blue-Cu)

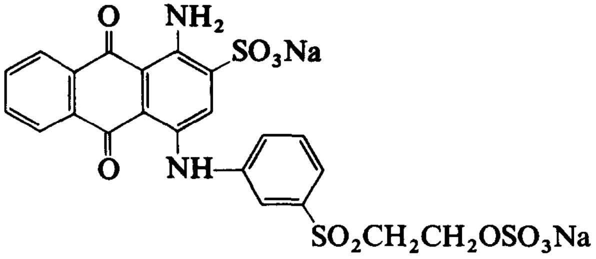


(4) A copper phthalocyanine dye (Cu-Pc)

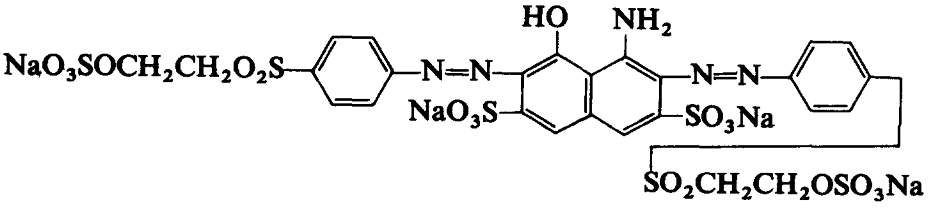


($l + m \leq 4$)

(5) C.I. Reactive Blue 19 (Blue 19)



(6) C.I. Reactive Black 5 (Black 5)



In the mixture dyeing, the superposition of the absorption spectra of the dyes used is inevitable. However, the filter effect of the partner dye may be made as small as possible by a use of combinations or dyes of different colors. In preliminary experiments, it was found that the filter effect of the partner dye on the fading of a dye was observed when the sum of absorbance was about 1·7. In this study, therefore, a sum of absorbance smaller than 1·5 and dye combinations of different colors were used.

The relative fading (A/A_0) was estimated by measuring the absorption spectra of the dyed film before and after exposure; A and A_0 are the absorbance after and before an exposure at the wavelength of the maximum absorption (except for Cu-Pc, whose isosbestic point was used).

3 RESULTS AND DISCUSSION

3.1 A model of fading behavior of reactive dyes under wet conditions via a singlet oxygen mechanism

Textile fibers are often dyed in an order of 10^{-2} mol/kg and dyeings in an order of 10^{-3} mol/kg have a pale shade. The solubility of oxygen in water is *c.* 10 ppm at ambient temperature.[5,6] Reactive dyes are immobilized in the substrate and the molar concentration is about 20–100 times larger than that of oxygen in water. The penetration of oxygen is necessary in order to compensate for this consumption in the oxidative fading process of the dye.

In order to set up a model of fading, the variation in the concentration profiles was evaluated during fading. Three layers of cellophane dyed in a mixture of Yellow and Red 22 were tightly set in a glass cell by a plastic plate with a window (1·0 × 2·0 cm), through which oxygen could penetrate into the film from the rear side. (Care was taken so that no bubble was between layers.) The dyed film may be considered to be a water-swollen cellulose block, from the front of which light enters and only from the rear side of which oxygen can penetrate (cf. Fig. 1). In another case, light and oxygen were allowed to enter the film from the front side, by setting them inside the rear side of a glass cell (cf. Fig. 2).

The variations in the concentration profiles for Yellow and Red 22 during the exposure are shown in Figs 1 and 2. The concentration profiles for Yellow during fading showed preferential surface fading, whilst those for Red 22 were similar but slower than the Yellow. Little fading of Red 22 in the third layer, especially in case of entrance of light and oxygen from the front side, was observed within the experimental time. The diffusion of oxygen had little effect on the rate of fading far inside the substrate under wet

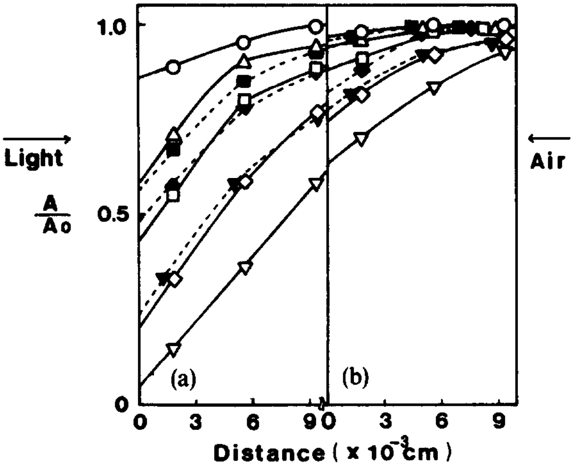


Fig. 1. Variations in the concentration profiles for (a) Yellow and (b) Red 22 in admixture during exposure for 1 h(○), 2 h(△), 4 h(□), 8 h(◇) and 16 h(▽) with exposure of both sides to light and oxygen (initial concentration of dye on the film = 1·01 × 10^{-2} mol/kg for Yellow (OD = 0·549) and Red 22 (OD = 0·383)), and in the profiles during exposure for 4 h(■), 8 h(◆) and 16 h (▼) using a Toshiba filter L-39S (>390 nm) (initial concentration ~9·12 × 10^{-3} mol/kg for Yellow (OD = 0·499) and 9·01 × 10^{-3} mol/kg for Red 22 (OD = 0·342)). (OD = optical density of a sheet of the dyed at λ_{max}.)

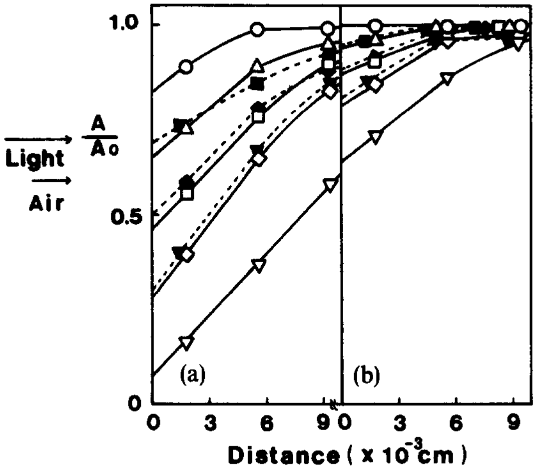


Fig. 2. Variations in the concentration profiles for (a) Yellow and (b) Red 22 during exposure for 1 h(○), 2 h(△), 4 h(□), 8 h(◇) and 16 h(▽) in the case of the one-side entrance (initial concentrations of dye on the film = 1·01 × 10^{-2} mol/kg for Yellow (OD = 0·552) and 1·00 × 10^{-2} mol/kg for Red 22 (OD = 0·380)), and those during exposure for 4 h(■), 8 h(◆) and 16 h (▼) using a Toshiba filter L-39S (>390 nm) (inital concentration ~ 1·02 × 10^{-2} mol/kg for Yellow (OD = 0·558) and 9·42 × 10^{-3} mol/kg for Red 22 (OD = 0·358)).

conditions. These fading behaviors show that the fading of dyes in cellophane is controlled by excitation by light absorption.

In order to confirm this picture and to examine the effect of the light source, the same experiments were carried out using a Toshiba filter L-39S (>390 nm) on the exposure. The concentration profiles for both the dyes during exposure are shown in Figs 1 and 2 (closed symbols). The exposure to visible light did not result in any influence on the concentration profiles during fading, except for the retardation effect. A decrease in the initial concentration seemed to result in a decrease in the slope of the concentration profiles.

In the water-swollen substrate dyed with reactive dyes, part of oxygen penetrated may be sensitized and converted into singlet oxygen $^1O_2$, which may diffuse and oxidize a dye molecule within its life time (a consumption of oxygen) or may revert to the ground state. The species which can diffuse is only oxygen, and the dye molecules which may sensitize oxygen or be oxidized are immobilized in the substrate. As the concentration profiles during fading show, the fading is controlled by the light absorption which occurs preferentially from the surface. Thus, there may be a specific preferential surface fading mechanism in the fading of reactive dyes on cellulose under wet conditions in the presence of sufficient oxygen. The life time ($2\,\mu s$[7]) of $^1O_2$ in water seems to be too short to homogenize the concentration of $^1O_2$ in the substrate. In the dyeing mixture, a dye which is more readily oxidized is preferentially faded and another dye which is less readily oxidised is subsequently faded. Since the concentration profiles of the dyes in cellulose during fading becomes steeper with an increase in the concentration, the preferential surface fading may become marked in the deep dyeing.

On the other hand, due to the lack of oxygen in cellulose in the case where a glass plate was placed on the rear side of the dyed film on exposing it in aerated water in the glass cell, the all over fading of the film was almost completely restrained and fading of the film occurred only from the edge of the glass plate.[1] In this case, the fading is controlled by the edgewise diffusion of oxygen from the external solution, due to the incomplete compensation of oxygen consumed in the substrate.

Since reactive dyes give different concentration profiles in the substrate depending on the dyeing method, the light fastness should be dependent on the dyeing method, as observed by Kissa.[8] The fact that the deeper the penetration of the dye, the better the light fastness, may also be explained by the model proposed.

Although all the behaviors which are further mentioned below may be explained in terms of this picture, a quantitative treatment of them is difficult.

3.2 Fading of Yellow sensitized by Rose Bengal

The concentration effect of the sensitizer on the fading of the Yellow dye was initially investigated. In a previous paper, one-tenth as much concentration of RB as the solubility of oxygen was used to sensitize the fading of Yellow on cellulose in aerated water.[4] In the present study, RB up to a concentration similar to the solubility of oxygen was used to sensitize the fading of Yellow.

The rate of fading for the Yellow sensitized by various concentrations of RB is shown in Fig. 3. Care was taken not to expose the dyed film in water to natural light. Not only the concentration effect of RB but also that of the Yellow, were observed on the rate of fading for the Yellow on cellulose under wet conditions. In order to clarify the concentration effect of RB on the fading of the Yellow, values of A/A_0 after exposure for 10 min were obtained over a wide concentration range of RB at three concentration levels of the Yellow (Fig. 4). RB in the water-swollen cellulose is partitioned between the aqueous phase in cellulose and the inner surface of the substrate.

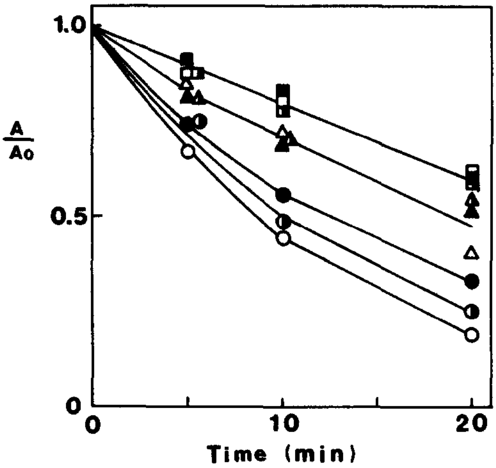


Fig. 3. Relative rate of fading for the Yellow on water-swollen cellophane on which Rose Bengal was adsorbed (in Na_2SO_4 0·05 mol/dm^3 soln).

Yellow	Rose Bengal
●: 7·50 × 10^{-3} mol/kg	5·47 × 10^{-4} mol/kg (3·3 × 10^{-5} mol/dm^3)
▲: 1·35 × 10^{-2} mol/kg	5·71 × 10^{-4} mol/kg (3·3 × 10^{-5} mol/dm^3)
■: 2·72 × 10^{-2} mol/kg	5·78 × 10^{-4} mol/kg (3·3 × 10^{-5} mol/dm^3)
◐: 8·23 × 10^{-3} mol/kg	8·40 × 10^{-4} mol/kg (8·2 × 10^{-5} mol/dm^3)
◭: 1·50 × 10^{-2} mol/kg	9·30 × 10^{-4} mol/kg (8·2 × 10^{-5} mol/dm^3)
◧: 2·92 × 10^{-2} mol/kg	8·61 × 10^{-4} mol/kg (8·2 × 10^{-5} mol/dm^3)
○: 7·13 × 10^{-3} mol/kg	2·76 × 10^{-3} mol/kg (3·3 × 10^{-4} mol/dm^3)
△: 1·46 × 10^{-2} mol/kg	2·63 × 10^{-3} mol/kg (3·3 × 10^{-4} mol/dm^3)
□: 2·96 × 10^{-2} mol/kg	2·53 × 10^{-3} mol/kg (3·3 × 10^{-4} mol/dm^3)

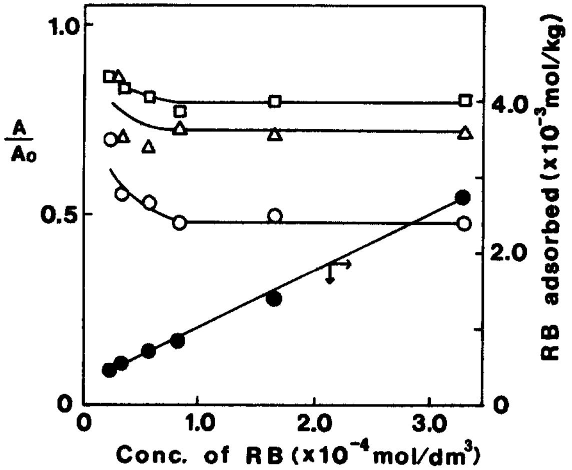


Fig. 4. Concentration effect of RB on the relative fading A/A_0 for the Yellow (○, $7{\cdot}62 \times 10^{-3}$ mol/kg; △, $1{\cdot}44 \times 10^{-2}$ mol/kg; □, $2{\cdot}87 \times 10^{-2}$ mol/kg) after an exposure for 10 min under wet conditions and the adsorption of RB (●) on cellulose (in Na_2SO_4 0·05 mol/dm³ soln).

The adsorption of RB on cellulose was linearly increased with an increase in the concentration of RB in the external solution. Since scattering of the adsorption of RB was observed with variation in the amount of the Yellow, within experimental errors (cf. the caption for Fig. 3), their average value was plotted against the concentration of the external solution. The decrease in the adsorption of RB by the fading during exposure may be negligible, because the concentration of the external solution was kept constant. Since the efficiency of RB to generate $^1O_2$ is much larger than that of the Yellow,[1] the self-sensitivity of the Yellow may be regarded as being negligible compared with the sensitivity of RB. The concentration effect of the Yellow on the fading of the Yellow seems to be larger than that of RB. RB showed an increasing effect on the rate of fading of the Yellow only in the lower concentration range examined. No decrease in the rate of fading for the Yellow was observed with an increase in the concentration of RB. This indicates that there is no quenching mechanism in the fading of the Yellow sensitized by RB.

Plots of $\ln(A/A_0)$ versus time gave a straight line when $A_0 \leq 8{\cdot}2 \times 10^{-3}$ mol/kg, implying a pseudo-first-order reaction mechanism, whilst those of A/A_0 versus time gave a straight line when $A_0 \geq 2{\cdot}7 \times 10^{-2}$ mol/kg (cf. Fig. 3). Since no increase was observed in the rate of fading for the Yellow with an increase in the concentration of RB, this shows that oxygen is almost completely converted into the singlet state by RB, and the concentration of $^1O_2$ may be regarded as being equal to the solubility of oxygen in water at the temperature used. The rate constant k_0 of the second-

TABLE 1

Values of the Apparent Photosensitivity $f(-)$ and the Rate Constant k_0 (dm^3/mol s) of the Second-order Reaction with $^1O_2$ of VS Dyes on Cellulose under Wet Conditions, and the Quantum Yield ϕ $(-)$ for the Formation of $^1O_2$

	RB	*Yellow*	*Red 22*	*Blue-Cu*	*Cu-Pc*	*Blue 19*	*Black 5*
k_0	—	6·9	0·66	0·28	0·081	0·014	0·24
f	0·7$_6$	(0·01$_5$)	0·1$_1$	0·01$_5$	0·09$_5$	0·02$_7$	0·02$_5$
ϕ[9]	0·5		0·0048			0·017	

Subscript numbers = second significant figures.

order reaction of the Yellow with $^1O_2$ was estimated to be 6·9 dm^3/mol s from the slope of the plots of $\ln(A/A_0)$ and time, and from the solubility (1·96 × 10^{-4} mol/dm^3)[5] of oxygen at 50°C and under 1 atm of air.

Since the plots of A/A_0 versus time for the other VS dyes on exposure in a RB solution gave a straight line, the values of k_0 for the other VS dyes could be estimated by comparing the value for the Yellow with their values of A/A_0 after exposure for 4 h in the aerated RB solution, as shown in Table 2 in a previous paper.[1] The values of k_0 for various VS dyes are shown in Table 1. The value of k_0 for the Yellow is 500 times larger than that for Blue 19 and those for the other VS dyes are in between them.

3.3 Concentration effect of VS dyes on the fading of the Yellow under wet conditions

3.3.1 Effect of Red 22

The concentration dependence of the values of A/A_0 for VS dyes after exposure for 8 h under wet conditions, estimated in previous papers,[1,4] are summarized in Fig. 5. Although the values of A/A_0 for all the VS dyes examined depend on the concentration, only Red 22 shows a 'positive' concentration dependence. In order to examine further the mechanism of fading mentioned above, films dyed with a mixture of the Yellow and the other VS dyes were exposed in water (Figs 6 and 7). Red 22 gave a profound 'positive' concentration dependence on the fading of the Yellow, i.e. the higher the concentration of Red 22, the larger the rate of the fading for the Yellow dye at a nearly similar concentration. When the concentration of Red 22 was kept constant, the rate of fading of the Yellow decreased with an increase in the concentration of the Yellow (Fig. 6). In particular, the initial rate of fading for the Yellow increased with an increase in the concentration of Red 22, whilst the subsequent rate of fading became constant independent of the concentration of Red 22.

In order to more exactly compare the fading of the mixture dyeing with

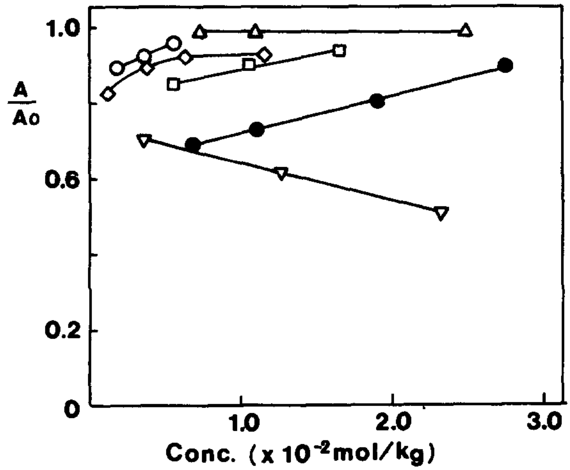


Fig. 5. Concentration dependence of the relative fading A/A_0 for VS dyes on cellulose after exposure for 8 h under wet conditions (●, Yellow; ▽, Red 22; □, Blue-Cu; ○, Cu-Pc; △, Blue 19; ◇, Black 5).

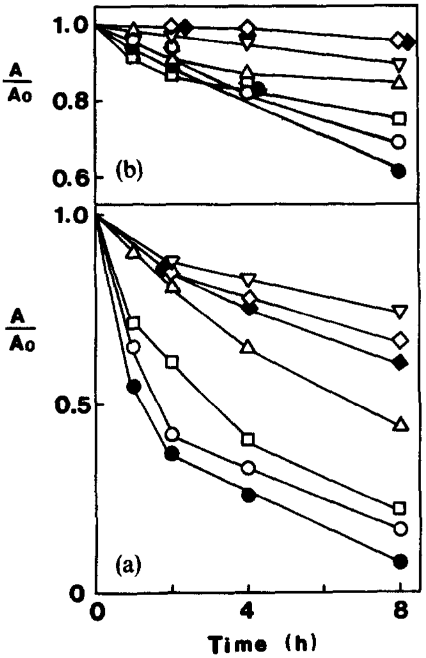


Fig. 6. (a) Relative rate of fading for the Yellow on water-swollen cellophane dyed in admixture with Red 22 or Black 5; (b) that for Red 22 or Black 5 on the same cellophane.

Yellow	Partner dyes (Conc.)
○: 1·99 × 10^{-2} mol/kg	Red 22 (1·97 × 10^{-2} mol/kg)
●: 6·58 × 10^{-3} mol/kg	Red 22 (2·09 × 10^{-2} mol/kg)
□: 1·77 × 10^{-2} mol/kg	Red 22 (1·22 × 10^{-2} mol/kg)
△: 1·77 × 10^{-2} mol/kg	Red 22 (4·26 × 10^{-3} mol/kg)
◇: 1·84 × 10^{-2} mol/kg	Black 5 (5·62 × 10^{-3} mol/kg)
◆: 7·18 × 10^{-3} mol/kg	Black 5 (5·66 × 10^{-3} mol/kg)
▽: 1·73 × 10^{-2} mol/kg	Black 5 (2·97 × 10^{-3} mol/kg)

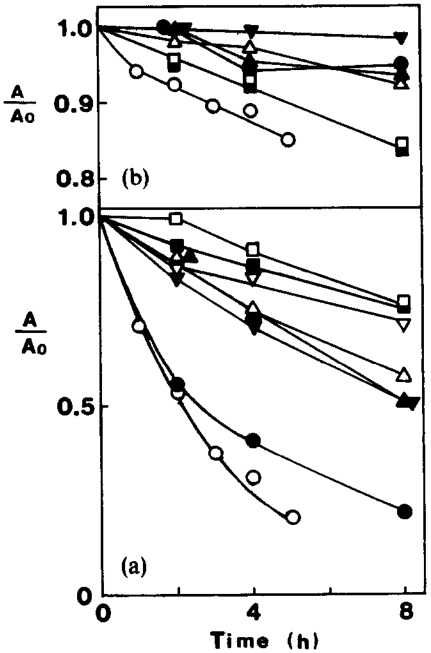


Fig. 7. (a) Relative rate of fading for the Yellow on water-swollen cellophane dyed in admixture with Blue-Cu, Blue 19, or Cu-Pc and (b) that for Blue-Cu, Blue 19 and Cu-Pc on the same cellophane.

Yellow	Partner dyes (Conc.)
▽: $1{\cdot}65 \times 10^{-2}$ mol/kg	none
□: $1{\cdot}49 \times 10^{-2}$ mol/kg	Blue-Cu ($1{\cdot}09 \times 10^{-2}$ mol/kg)
■: $6{\cdot}52 \times 10^{-3}$ mol/kg	Blue-Cu ($1{\cdot}07 \times 10^{-2}$ mol/kg)
△: $1{\cdot}88 \times 10^{-2}$ mol/kg	Blue 19 ($1{\cdot}19 \times 10^{-2}$ mol/kg)
▲: $2{\cdot}17 \times 10^{-2}$ mol/kg	Blue 19 ($5{\cdot}93 \times 10^{-3}$ mol/kg)
▼: $6{\cdot}85 \times 10^{-3}$ mol/kg	Blue 19 ($1{\cdot}33 \times 10^{-2}$ mol/kg)
○: $2{\cdot}70 \times 10^{-2}$ mol/kg	Cu-Pc ($7{\cdot}70 \times 10^{-3}$ mol/kg)
●: $6{\cdot}16 \times 10^{-3}$ mol/kg	Cu-Pc ($5{\cdot}28 \times 10^{-3}$ mol/kg)

that of the single dyeing, the same plots as those of Fig. 5 were made as shown in Figs 8 and 9. Although plots of A/A_0 against time for some dyes was not linear, comparisons between dyes are possible. The rate of fading for the Yellow in the mixture dyeing is much larger than that of the single dyeing at the same concentration (cf. Fig. 5), whilst in contrast, that for Red 22 is smaller. The rate of fading for the Yellow and Red 22 in their mixture dyeing is dependent only on the concentration of Red 22, although the values of A/A_0 for the Yellow in Fig. 9 showed small scattering which corresponds to the concentration effect of the Yellow on the rate of fading. Since no decrease in the rate of fading (quenching) occurs in the fading of the Yellow, irrespective of the increase in the concentration of Yellow in the substrate as

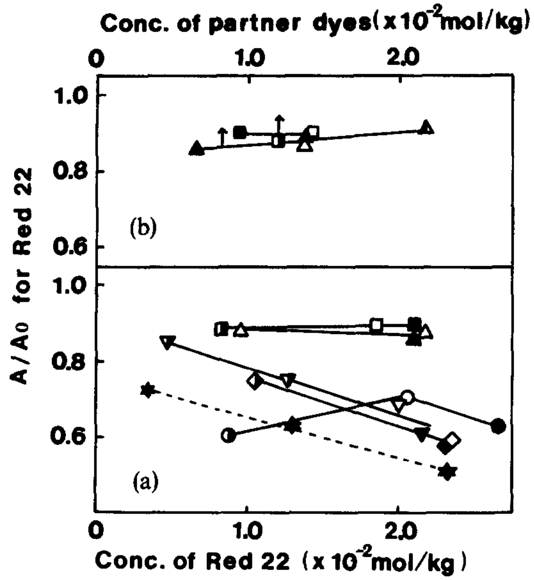


Fig. 8. (a) Concentration dependence of the relative fading A/A_0 for Red 22 on cellulose dyed in admixture with Yellow (▼, 0·658; ⧩, 1·77; ▽, 1·99 × 10^{-2} mol/kg); Blue-Cu (■, 0·951; ◧, 1·21; □, 1·42 × 10^{-2} mol/kg), Cu-Pc (●, 2·92; ◑, 3·81; ○, 9·07 × 10^{-3} mol/kg), Blue 19 (▲, 0·651; △, 1·37 × 10^{-2} mol/kg), and Black 5 (◆, 2·49; ◇, 4·66; ⬖, 5·21 × 10^{-3} mol/kg), that for Red 22 in the single dyeing (★) on the concentration of Red 22 after exposure for 8 h under wet conditions; (b) that for Red 22 on the concentration of the partner dye: Blue-Cu at the concentration of Red 22 (■, 2·08; ◧, 0·824; □, 1·86 × 10^{-2} mol/kg) and Blue 19 at the concentration of Red 22 (▲, 2·11; ◭, 0·961; △, 2·17; ◭, 3·21 × 10^{-2} mol/kg) (cf. Figs 6 and 11–13).

shown above (cf. Section 3.2), the photosensitivity of Red 22 may act predominantly compared with that of Yellow in the fading of a mixture of the Yellow and Red 22, and accelerate the fading of the Yellow. The fading of Red 22 is suppressed probably by the preferential consumption of oxygen by the Yellow, because there is a limited amount of $^1O_2$.

The fading behavior of two dyes in a mixture can be analyzed using the molar ratio, *Y*/*R*, of the Yellow faded during the interval of exposure to Red 22 (Table 2). The absorbance, or the concentration measured, corresponds to the mean value in a film examined. Since no homogenization of the fixed species occurs in the substrate, the local rate of fading for each component varies with time, depending on their concentration profiles. Both the dyes were faded at different rates, depending on the molar ratio in the substrate and on the concentration profiles of the Yellow and Red 22, which might change with the time of fading. The analyses were experimentally supported by the variation in the concentration profiles for both the dyes during exposure (cf. Table 2 and Figs 1 and 2). The high initial rate of fading

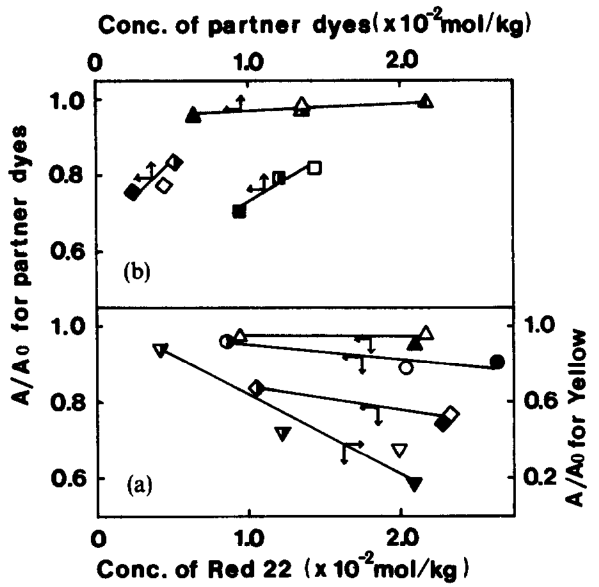


Fig. 9. (a) Dependence of the relative fading A/A_0 for the partner dyes on cellulose dyes in admixture with Red 22 on the concentration of Red 22 after exposure for 8 h under wet conditions, (Yellow ▼, 0·658; ⧨, 1·77; ▽, 1·99 × 10^{-2} mol/kg; Cu-Pc ●, 2·92; ◑, 3·81; ○, 9·07 × 10^{-3} mol/kg; Blue 19 ▲, 0·651; △, 1·37 × 10^{-2} mol/kg; and Black 5 ◆, 2·49; ◇, 4·66; ⬖, 5·21 × 10^{-3} mol/kg); (b) that for the partner dyes in admixture with Red 22 on the concentration of the partner dyes: Blue-Cu at the concentrations of Red 22: 0·824(◨), 1·86(□), 2·08(■) × 10^{-2} mol/kg; Blue 19 at those of Red 22: 0·961(◭), 2·11(▲), 2·17(△), 3·21(◭) × 10^{-2} mol/kg; and Black 5 at those of Red 22: 1·04(⬖), 2·29(◆), 2·32(◇) × 10^{-2} mol/kg (cf. Figs 6 and 11–13).

for the Yellow may be caused by the preferential surface fading of the Yellow as shown in Figs 1 and 2. In the case of low concentrations of Red 22, the values of Y/R were greatly increased within the experimental conditions examined, as the fading proceeded. An increase in the Y/R ratios at the intermediate interval for the fading of the first to third layers (*b in Table 2) is attributed to the delayed fading of Red 22 in the second layer compared with that of the Yellow. When a layer of film is used, these complex behaviors may be observed in the fading of dyes occurring with less ease than with which they are oxidized within the initial period of fading than when more than one layer is examined (cf. Red 22 in Fig. 6).

3.3.2 *Effect of Blue 19*

Although the effect of Blue 19 on the fading of the Yellow was smaller than that of Red 22, Blue 19 accelerated the fading of the Yellow compared with its fading in the single dyeing at the same concentration, whilst the fading of Blue 19 was slightly accelerated by the Yellow (Fig. 7). The higher the

TABLE 2

Fading Behaviors of Yellow and Red 22 on Cellulose Dyed in Mixture under Wet Conditions, Shown by the Molar Ratio Y/R of the Dye Faded during the Interval of Exposure for the Yellow to that for Red 22, and the Relative Degree of Fading A/A_0 for both the dyes after an Exposure for 8 h.

	Conc. × 10^2		*Y/R for time interval of exposure (h)*			*A/A_0 for 8 h*	
	Yellow (mol/kg)	*Red 22*	*0–2*	*2–4*	*4–8*	*Yellow*	*Red 22*
	2·0	2·0	9·8	1·2	1·2	0·168	0·691
	1·8	0·43	8·2	26	53	0·437	0·852
	1·8	1·2	4·7	6·3	3·5	0·218	0·747
	0·66	2·1	1·7	0·56	0·26	0·083	0·611
*a	1·0	1·0	4·5	4·7	2·2	0·328	0·815
*b	1·0	1·0	6·5	16·1	2·1	0·486	0·883

*a: the first layer in Fig. 1(a).
*b: the first to third layers in Fig. 1(a).

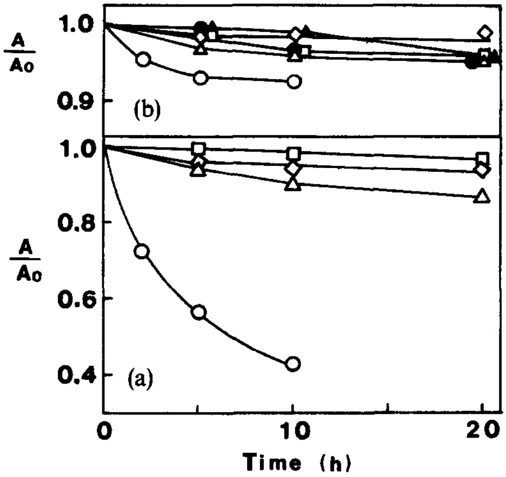


Fig. 10. (a) Relative rate of fading for the Yellow on water-swollen cellophane dyed singly and in admixture with other VS dyes; (b) that for the partner dye on the same cellophane on exposure through a Toshiba R-60 filter (>600 nm).

	Yellow	Partner dyes (Conc.)
●:	—	Cu-Pc (5·84 × 10^{-3} mol/kg)
▲:	—	Blue 19 (1·20 × 10^{-2} mol/kg)
□:	1·86 × 10^{-2} mol/kg	Blue-Cu (1·04 × 10^{-2} mol/kg)
○:	1·40 × 10^{-2} mol/kg	Cu-Pc (4·60 × 10^{-3} mol/kg)
△:	1·93 × 10^{-2} mol/kg	Blue 19 (1·18 × 10^{-2} mol/kg)
◇:	1·59 × 10^{-2} mol/kg	Black 5 (5·53 × 10^{-3} mol/kg)

concentration of the Yellow, the larger was the rate of fading of Blue 19. The acceleration effect of the Yellow was also observed in exposures with a Toshiba R-60 filter (>600 nm) (Fig. 10). In spite of the shielding of the Yellow, the fading of Blue 19 was slightly 'sensitized' by the Yellow. This is probably due to the increase in oxygen consumption by the Yellow, giving increased opportunities of collisions between oxygen and Blue 19.

Blue 19, when dyed on cellulose in admixture with the Yellow, gave no concentration dependence on the fading of the Yellow, although Red 22, Cu-Pc and Black 5 showed a 'positive' dependence (cf. Section 3.3.3). The reasons for the concentration effect of Blue 19 on the fading of Yellow are not clear (Fig. 7).

3.3.3 Effect of the other dyes

The concentration effect of Cu-Pc on the fading of the Yellow was similar to that of Red 22 (Fig. 7). The rate of fading for Cu-Pc was slightly accelerated by the Yellow as previously shown[4] (cf. Section 3.4).

In the case of a mixture of the Yellow with Black 5, the concentration effect of Black 5 on the fading of the Yellow was similar to, but smaller than, that of Red 22 (Fig. 6). It is noteworthy that Black 5 gave the positive concentration dependence on the fading of the Yellow, whilst the rate of fading for Black 5 became smaller with increase in the concentration of Black 5. The fading of Black 5 was suppressed by the presence of the Yellow when compared at the same concentration.

In the case of Blue-Cu, no concentration effect of Blue-Cu on the fading of the Yellow was observed (Fig. 7), since Blue-Cu and the Yellow have similar properties. But, as in the case of Blue 19, the fading of Blue-Cu was slightly increased by the Yellow, compared with the single dyeing.

Dyes with a high photosensitivity, such as RB, Red 22, Cu-Pc and Black 5, seem to give a positive concentration effect on the sensitized fading of a partner dye which is easily oxidized or on the self-fading in the case of Red 22. Thus, 'positive' concentration dependence of fading is a common behavior observed in fading under wet conditions, although it depends on the nature of the dyes.

In spite of the marked concentration effect of the sensitizer on the fading of the Yellow, the order for the rate of photosensitized fading for the Yellow in the mixture dyeings was as follows:

$$\text{RB} > \text{Red 22} > \text{Cu-Pc} > \text{Blue 19} > \text{Black 5} > \text{Blue-Cu} \tag{3}$$

This order describes the efficiency of VS dyes in sensitizing the fading of the Yellow and is the same as the order (2) above. The rate of fading for the Yellow sensitized by VS dyes on exposure using a filter (Toshiba R-60, >600 nm) showed the same order (Fig. 10).

Dzhanashvili *et al.*[9] estimated the quantum yield ϕ of generation of $^1O_2$ for some VS dyes (cf. Table 1). As reference value, they used 0·5 for the ϕ of RB in water. The quantum yield of singlet oxygen formation for RB, however, was estimated to be 0·76 in methanol.[10,11] By use of the highest initial rate of fading for the Yellow on cellulose dyed in mixture with the other VS dyes, the apparent photosensitivity (f) of VS dyes could be estimated from Figs 6 and 7, as shown in Table 1. The value of 0·76 was used as the reference of f for RB in the present study.

The calculation of f values is based on the following propositions:

(1) The absorbance of the dyed film at the wavelength of the maximum absorption is in the range between 0·7 and 0·8. Thus, the photon absorption per unit time may be regarded as being nearly constant.

(2) The value of k_0 for Yellow is much larger than those for the other VS dyes. Therefore, the contribution of fading from the partner dyes in the calculation of f values may be neglected.

Since the initial rate of fading for the Yellow in admixture with Black 5 was considerably larger than the subsequent fading, and the subsequent fading in admixture with Blue 19 was larger than that in admixture with Black 5, the sensitivity for Blue 19 seemed to be larger than that for Black 5, although their f values were very similar. Since the Yellow and Blue-Cu have similar sensitivity, described above (cf. Section 3.3.3), the f value for Yellow was estimated to be the same as that of Blue-Cu. The f value for Blue 19 was in agreement with the value of ϕ which Dzhanashvili *et al.*[9] obtained if 0·5 was used as the reference of f for RB. The value for Red 22 was not in agreement. Griffiths has expressed some doubt about the values for azo dyes.[3b] The value of ϕ for Blue 19, however, may be accurate, because it causes little reaction with $^1O_2$ as examined by the present study. On the basis of these factors, the f values obtained in the present study may be reasonable, in spite of the use of a carbon-arc as the light source and may quantitatively, though approximately, describe the photosensitivity of VS dyes.

The order for the rate of fading for the partner dye in a mixture with the Yellow was as follows:

$$\text{Red 22} > \text{Cu-Pc} > \text{Blue-Cu} > \text{Blue 19} > \text{Black 5} \qquad (4)$$

Comparing this order with the order (1), it is noticed that the fading of Cu-Pc and Blue 19 is accelerated by mixture dyeing with the Yellow. Although the order is not affected, that of Red 22 and Black 5 is suppressed, and that of Blue-Cu is slightly accelerated.

3.4 Concentration effect of VS dyes on fading of Red 22 under wet conditions

The rate of fading for Red 22 on cellulose dyed in admixture with the other VS dyes was also examined in aerated water. The results are shown in

Figs 11, 12 and 13, and the values of A/A_0 for Red 22 and the partner dyes on the exposure for 8 h in Figs 8 and 9. In the fading behavior of VS dyes in a mixture with Red 22, the following concentration effects of fading were noted:

(1) The fading of Red 22 was suppressed by the Yellow and by Black 5 with a 'positive' dependence of fading on the concentration of Red 22.
(2) The fading of Red 22 was considerably suppressed by Blue 19 with a 'negative' dependence of fading on the concentration of Blue 19 and with no dependence on that of Red 22.
(3) The fading of Red 22 was considerably suppressed by Blue-Cu with a small 'negative' dependence of fading on the concentration of Red 22 and with no dependence on that of Blue-Cu.
(4) The fading of Yellow, Cu-Pc and Black 5 was considerably accelerated by Red 22 with a 'positive' dependence of fading on the concentration of Red 22.
(5) The fading of Black 5 and of Blue-Cu was considerably accelerated

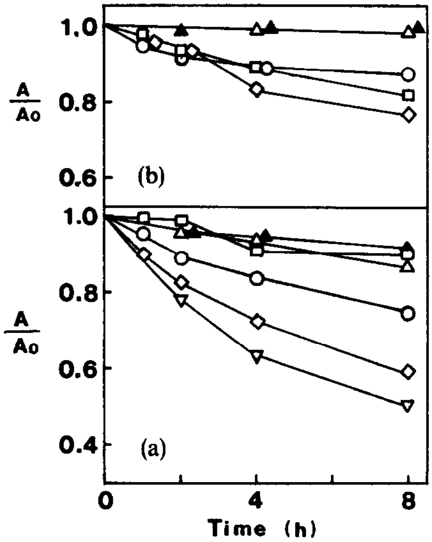


Fig. 11. (a) Relative rate of fading for Red 22 on water-swollen cellophane dyed singly and in admixture with other VS dyes; (b) that for the partner dye on the same cellophane.

Red 22	Partner dyes (Conc.)
▽: 2·32 × 10^{-2} mol/kg	none
□: 1·86 × 10^{-2} mol/kg	Blue-Cu (1·42 × 10^{-2} mol/kg)
○: 2·02 × 10^{-2} mol/kg	Cu-Pc (9·07 × 10^{-3} mol/kg)
△: 2·17 × 10^{-2} mol/kg	Blue 19 (1·37 × 10^{-2} mol/kg)
▲: 3·21 × 10^{-2} mol/kg	Blue 19 (2·18 × 10^{-2} mol/kg)
◇: 2·32 × 10^{-2} mol/kg	Black 5 (4·66 × 10^{-3} mol/kg)

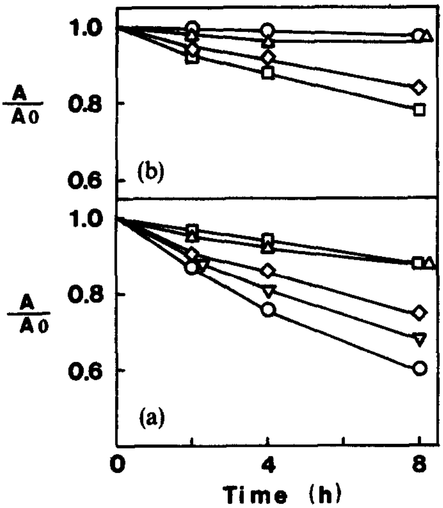


Fig. 12. (a) Relative rate of fading for Red 22 on water-swollen cellophane dyed singly and in admixture with other VS dyes; (b) that for the partner dye on the same cellophane.

Red 22	Partner dyes (Conc.)
▽: $8{\cdot}00 \times 10^{-3}$ mol/kg	none
□: $8{\cdot}24 \times 10^{-3}$ mol/kg	Blue-Cu ($1{\cdot}21 \times 10^{-2}$ mol/kg)
○: $8{\cdot}45 \times 10^{-3}$ mol/kg	Cu-Pc ($3{\cdot}81 \times 10^{-3}$ mol/kg)
△: $9{\cdot}61 \times 10^{-3}$ mol/kg	Blue 19 ($1{\cdot}37 \times 10^{-2}$ mol/kg)
◇: $1{\cdot}04 \times 10^{-2}$ mol/kg	Black 5 ($5{\cdot}21 \times 10^{-3}$ mol/kg)

by Red 22, with a large 'negative' dependence of the concentration of Black 5 or Blue-Cu.

(6) The fading of Blue 19 was slightly accelerated by Red 22 with a 'negative' dependence of the concentration of Blue 19 and with no dependence on that of Red 22.

The rate of fading for Red 22 in the mixture was lower than that of the single dyeing at the same concentration, except in the case of a mixture of Cu-Pc and Red 22 at lower concentration. The fading of Blue-Cu, Cu-Pc and Black 5 was considerably accelerated by Red 22, whilst that of Blue 19 was slightly increased. Blue 19 and Blue-Cu have the property to suppress self-fading, as well as the fading of the partner dye. The fading in admixture with Cu-Pc is discussed in the next section.

3.5 Fading of VS dues in admixtures with Cu-Pc

The rate of fading of Cu-Pc was accelerated by Red 22 compared with that in the single dyeing at the same concentration, whilst that for Red 22 was suppressed, except in a mixture of Red 22 of low concentration.

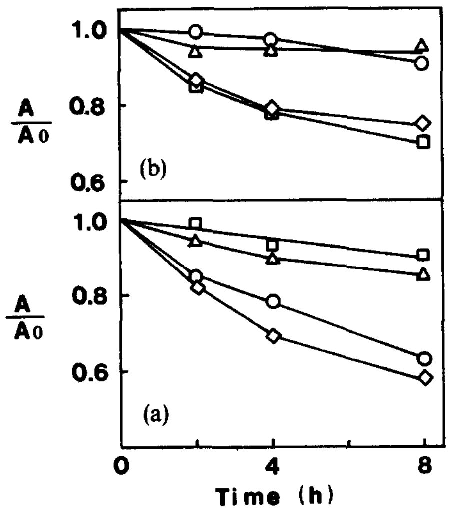


Fig. 13. (a) Relative rate of fading for Red 22 on water-swollen cellophane dyed singly and in admixture with other VS dyes; (b) that for the partner dye on the same cellophane.

Red 22	Partner dyes (Conc.)
□: 2·08 × 10^{-2} mol/kg	Blue-Cu (9·51 × 10^{-3} mol/kg)
○: 2·62 × 10^{-2} mol/kg	Cu-Pc (2·92 × 10^{-3} mol/kg)
△: 2·11 × 10^{-2} mol/kg	Blue 19 (6·51 × 10^{-3} mol/kg)
◇: 2·29 × 10^{-2} mol/kg	Black 5 (2·49 × 10^{-3} mol/kg)

The fading behaviors of Red 22 and Cu-Pc in their binary mixture showed the complicated concentration effects of both dyes. The rate of fading for Cu-Pc was roughly proportional to the concentration of Red 22, a 'positive' concentration dependence, but was not dependent on that of Cu-Pc.

Cu-Pc is known to be present in the substrate as a mixture of monomer and dimer, depending on the dyeing conditions.[4,12] The state of aggregation can be described by the y/x ratios. As shown in Fig. 14, the y/x values for Cu-Pc in a mixture with Red 22 were proportional to the total concentration of both dyes in cellulose and not to the concentration of Cu-Pc only. The y/x values increased with time of exposure, although a maximum of y/x values was observed in the case of the dyeings with Cu-Pc of the largest y/x value. Consideration of the relationship between the y/x values and the rate of fading for Cu-Pc and Red 22 showed that the larger the y/x values, the larger was the rate of fading for Cu-Pc (Fig. 14). In contrast, the larger the y/x values, the smaller was the rate of fading for Red 22. This implies that the aggregation of Cu-Pc in cellulose accelerates the fading of Cu-Pc and suppresses the fading of Red 22. The opposite, more normal situation was observed in the fading of Cu-Pc in admixture with the Yellow.[4]

In fact, the aggregation of Cu-Pc seemed to show some reverse effects on

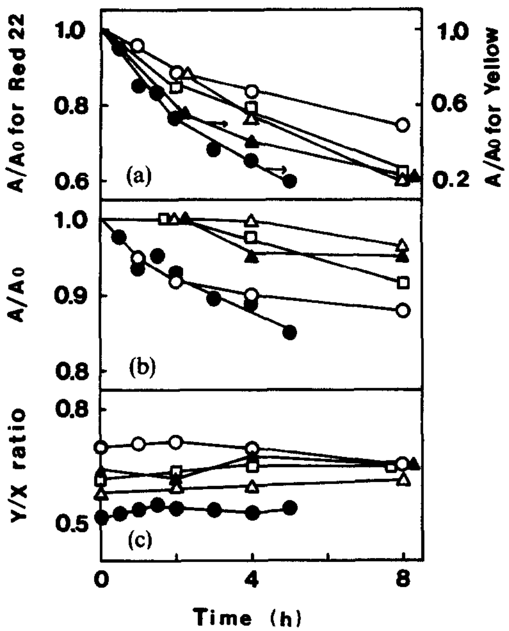


Fig. 14. Comparisons of the relative rate of fading for Red 22 or the Yellow (a) and Cu-Pc (b) with the y/x ratios (c) (= the ratios of the absorbance at 630 nm to that at 675 nm) for Cu-Pc in a mixture of Cu-Pc and Red 22 or the Yellow during exposure under wet conditions.

Cu-Pc	Partner dyes (conc.)
●: 7·70 × 10^{-3} mol/kg	Yellow (2·70 × 10^{-2} mol/kg)
▲: 5·28 × 10^{-3} mol/kg	Yellow (6·16 × 10^{-3} mol/kg)
○: 9·07 × 10^{-3} mol/kg	Red 22 (2·02 × 10^{-2} mol/kg)
△: 3·81 × 10^{-3} mol/kg	Red 22 (8·45 × 10^{-3} mol/kg)
□: 2·92 × 10^{-3} mol/kg	Red 22 (2·62 × 10^{-2} mol/kg)

the fading of Red 22 and Cu-Pc in their mixture to the fading model proposed so far,[13] but why this is so remains to be studied.

4 SUMMARY

The photosensitivity of VS dyes and the ease with which they were oxidized were quantitatively estimated from the rate of fading for VS dyes by RB and from that for the Yellow in mixture with VS dyes, respectively.

The preferential surface fading model in the fading of VS dyes on cellulose under wet conditions was experimentally demonstrated by the variation in the concentration profiles during fading.

The concentration effect of some dyes on the fading of VS dyes was examined. Dyes with a high photosensitivity such as RB, Red 22, Cu-Pc and

Black 5 gave a positive concentration dependence on the fading of the partner dye or of its own fading, when the partner dye or itself was easily oxidized.

When a dye faded with more ease than with which it was oxidized (such as the Yellow), occurring in a mixture with a dye having high sensitivity (such as Red 22, Cu-Pc, Blue 19 and Black 5), the fading was accelerated compared with the fading of a single dyeing at the same concentration. The fading of a dye with a moderate fading rate (such as Red 22) was suppressed in admixture with a dye which faded less readily.

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