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Photofading, photosensitization and the effect of aggregation on the fading of triphenodioxazine and copper phthalocyanine dyes on cellulosic film

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Abstract

The photosensitized oxidation of four triphenodioxazine (TPDO) reactive dyes and a copper phthalocyanine (CuPc) reactive dye on cellulosic films by Rose Bengal (RB) was examined in aqueous solution under aerobic conditions. The rates of photo-oxidation of 4,11-bis(vinylsulfonyl)TPDO dyes were smaller than those obtained for 3,10-bis(disubstituted triazinyliminoethylimino)TPDO dyes. The rates of photofading of the four TPDO dyes and a CuPc dye on cellulose were similar in the order to the rates of the photosensitized oxidative fading with RB. Photo-oxidation left the aromatic residue from TPDO ring along with the reactive anchor bound to cellulose. No aggregation effect was observed on the fading of TPDO dyes and a CuPc dye on cellulose. The photosensitivity of the TPDO dyes was very small, this being estimated by the photosensitized fading of an aminopyrazolinylazo dye (Yellow dye) on cellulosic films dyed in admixture with TPDO dyes by use of a yellow filter to shield Yellow dye on exposure. It is concluded that the good light-fastness of the TPDO dyes on cellulosic substrate is attributed to the very small photosensitivity in spite of their relatively large ease with which they are oxidized. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Triphenodioxazine reactive dyes; Copper phthalocyanine reactive dye; Photo-oxidation; Photosensitivity; Fading mechanism; Aggregation effect on fading

1. Introduction

In a previous paper [1], the aggregation of triphenodioxazine (TPDO) dyes in aqueous solution in both the absence and presence of electrolyte as well as on a cellulosic substrate were examined. TPDO vinylsulfonyl (VS) dyes aggregate in aqueous solution especially in the presence of electrolyte as well as on cellulosic substrates. The aggregation tendency in aqueous solution is similar to that of typical ionic dyes with high aggregation propensity [2–5]. It was spectrophoto metrically proven that TPDO vinylsulfonyl dyes existed partially as dimers on cellulose and the swelling of

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dyed cellophane by water promoted aggregation [1]. A copper phthalocyanine (CuPc) VS dye did not undergo this particular behavior, although it also existed partially as dimers on cellulose [1,6].

Giles et al. [7–10] emphasized the role of aggregation in suppressing dye fading, although these workers considered the existence of large dye aggregates on a substrate, which might be observable with an electron microscope. The presence of such aggregates was not found in usual dyeing depth by the previous studies [1,6] and recent reviews [2–5]. In the case of reactive dyes such as CuPc and TPDO which have a high aggregation tendency, the dyes exist as a mixture of monomers and dimers on cellulose [1,6] and the monomers of CuPc dye are photo-oxidized faster than are the dimers [6]. We propose that dye concentration rather than dye aggregation is important in dye fading, since no one has yet elucidated the real effects of aggregation on fading.

The finding that the order of the reaction of the oxidation of TPDO dyes on cellulose by hypochlorite was reversed when compared to that by hydrogen peroxide (HP) [11] supports the suggestion that aggregation has little effect on the oxidation of dyes.

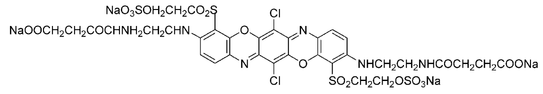
The present study aims to demonstrate that aggregation effect on photo-oxidative fading, we observe at first the fading behavior of four TPDO dyes and a CuPc dye at the three levels of concentration on cellophane films immersed in aerated water. We examine whether or not the monomer–dimer equilibriums of the dyes on water-swollen cellulose are changed with time of exposure. Thus, the absorption spectra of TPDO dyes with a high or low aggregation tendency as well as those of a CuPc dye on substrate are analyzed to estimate the effects of aggregation on the fading. The aggregation effects on the photo-oxidative fading are compared by use of spectral analysis. The absorption spectra of photo-decomposition products bound with cellulosic films are compared with the spectra of the products by thermal oxidation with hypochlorite and HP. The photosensitivity of TPDO dyes on mixture-dyed cellulose by use of an aminopyrazolinyl dye is also examined.

2. Experimental

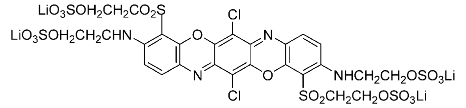
2.1. Dyes

The TPDO dyes used were the same as those employed in a previous study [1]. An aminopyrazolinyl azo dye, which was used for estimating the photosensitivity of TPDO dyes, was the same as that used in previous studies [6,12–14]. A CuPc VS dye, C.I. Reactive Blue 19, and a copper complex azo VS dye were supplied by DyStar Japan Ltd. The fastness of the TPDO dyes on cotton fabrics is listed in Table 1; the chemical structures of the dyes used are shown below.

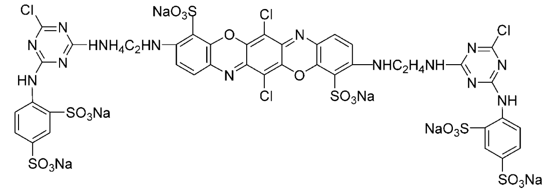
(1) A triphenodioxazine dye with two vinylsulfone anchors (VS-TPDO).



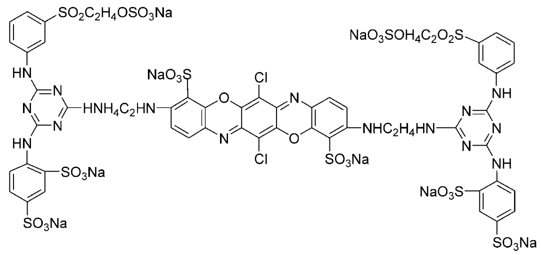
(2) A triphenodioxazine dye with two vinylsulfone anchors (PVS-TPDO).



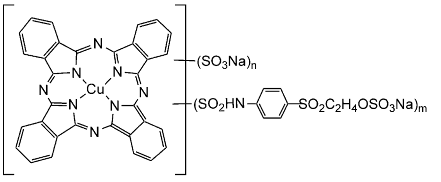
(3) A triphenodioxazine dye with two monochlorotriazine anchors (MCT-TPDO).



(4) A triphenodioxazine dye with two vinylsulfone anchors via a triazine ring (BF-TPDO).

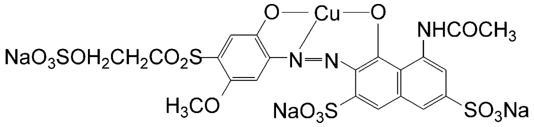


(5) A copper phthalocyanine VS dye (CuPc).

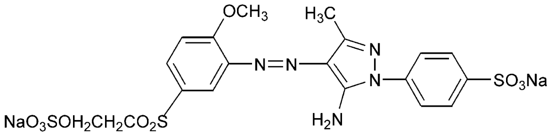


(m + n≦4, 1≦m≦2, 2≦n≦3)

(6) A copper complex azo VS dye (Blue-Cu).



(7) An aminopyrazolinyl azo dye (Pyr-Yellow).



All chemicals used were of reagent grade and were used without further purification.

2.2. Methods

2.2.1. Dyeing of cellophane films

The method of dyeing cellophane films is the same as before [1]. In order to obtain cellophane films on which VS- and PVS-TPDO have a low and a high degree of aggregation, dyeing conditions used a small and a large addition of electrolyte, respectively.

Dyeing by a small addition of electrolyte: dye, 0.50 g dm^{-3}; Na_2SO_4, 15 g dm^{-3}; $Na_2HPO_4 \cdot 12H_2O$, 10 g dm^{-3} (pH 9); temp., 60 °C; time, 3–4 h.

Dyeing by a large addition of electrolyte (alkali-shock method): adsorption: dye, 0.15 g dm^{-3}; Na_2SO_4, 180 g dm^{-3}; temp, 60 °C; time, >60 min; and the second bath for fixation: Na_2CO_3, 20 g dm^{-3}, Na_2SO_4, 180 g dm^{-3}; temp., 60 °C; time, >60 min.

In the case of the CuPc dye, the alkali-shock method yielded dyeings of low aggregation in spite of the large addition of electrolyte mode. However, dyeing using weakly alkaline all-in method ($Na_2HPO_4 \cdot 12H_2O$, 20 g dm^{-3}) provided cellulosic films of highly aggregated dyeings.

Table 1
Fastness of reactive TPDO and CuPc dyes (N/3)[a] on cotton fabrics

Dye	Light[b]	Perspiration-light[c]		Chlorinated water[d]
		Acid	Alkaline	
PVS-TPDO	5–6	4–5	4–5	2–3
VS-TPDO	5–6	4–5	4–5	2
MCT-TPDO	5	4–5	4–5	1
BF-TPDO	4–5	4–5	4–5	1
Blue 19[e]	6	4	4^{-}[f]	3
CuPc	4	2	2	2
Blue-Cu	5–6	1	1	4

[a] Concentration depth of a third of standard one.

[b] JIS L 0842 (carbon arc).

[c] JIS L 0888, in which the concentration of histidine in the artificial perspiration is 10 times larger than the established one.

[d] ISO 105/E03, available chlorine 20 mg dm^{-3}, pH 7.5, 27°C, 1 h, liquor ratio 1:100.

[e] C.I. Reactive.

[f] 4^{-} describes the ratings between (3–4) and 4.

At the end of dyeing, the dyed films were repeatedly rinsed in boiling water for less than 30 min to remove any unfixed dyes until no coloration of the rinsing water occurred. Apparently, the degree of aggregation for both the PVS- and VS-TPDO was lowered by the rinsing process as shown by the shade change from violet to royal blue.

2.2.2. Dyeing of cellophane in admixture using TPDO dyes and Pyr-Yellow

This was carried out as follows: for MCT- and BF-TPDO (alkali-shock method): adsorption: dye, 0.5 g dm^{-3}; Na_2SO_4, 25 g dm^{-3}; for 2 h; at 80 °C for MCT-TPDO and 60–70 °C for BF-TPDO, and the second bath for fixation: Na_2CO_3, 20 g dm^{-3}; Na_2SO_4, 50 g dm^{-3}; for 1 h; at 80 °C for MCT-TPDO and for 1–1.5 h at 50 °C for BF-TPDO. For VS- and PVS-TPDO (all-in method): dye, 0.5 g dm^{-3}; Na_2SO_4, 40 g dm^{-3} for VS-TPDO and 15 g dm^{-3} for PVS-TPDO; for 2 h; $Na_2B_4O_7 \cdot 10H_2O$, 11.7 g dm^{-3} (pH 9); for 1–1.5 h; at 50 °C. For Pyr-Yellow (alkali-shock method):

adsorption: dye, 0.5 g dm^{-3}; Na_2SO_4, 100 g dm^{-3}; for 2 h; at 50 °C; and the second bath for fixation: Na_2CO_3, 20 g dm^{-3}; Na_2SO_4, 100 g dm^{-3}; for 1 h; at 50 °C. At the end of dyeing, the dyed films were repeatedly rinsed in boiling water to remove unfixed dye. The concrete procedure to carry out the mixture dyeing by the alkali-shock method is shown in Diagram 1. In the case of the all-in method, the dyebath conditions of VS- and PVS-TPDO were prepared as being mentioned above and the dyeing depth was adjusted by changing the dyeing time. (Flow chart was partially changed to fulfill this procedure.) According to this diagram, the dyeing depths can be adjusted to be $\alpha_1 \pm |\beta_1|$ and $\alpha_2 \pm |\beta_2|$, respectively.

The influence of the order of dyeing on fading behavior was examined by using the following samples: Firstly, cellophane film was dyed with the Pyr-Yellow dye followed by each of the TPDO dyes. Secondarily, the Pyr-Yellow dye was applied to films which had previously been dyed with each of the TPDO dyes.

2.2.3. Photofading of dyes on water-swollen cellophane films

The relative fading, A/A_0 (the ratio of the absorbance of the initial and exposed dyed samples), at λ_{max} and at the isosbestic point (ip) for dyes with an aggregation tendency, was estimated by exposing the dyed films immersed in aerated water to carbon arc light. By exposing the dyed films when immersed in an aqueous Rose Bengal solution (3.3×10^{-4} mol dm^{-3} + 0.05 M Na_2SO_4), the ease with which the dyes were photo-oxidized was estimated [12–14]. The aqueous Rose Bengal solution was renewed every ten hours during exposure to maintain the concentration of Rose Bengal on the film constant.

2.2.4. Estimation of the photosensitivity of TPDO dyes

Film samples which had been dyed in admixture with the TPDO dye and Pyr-Yellow were exposed behind a Toshiba filter Y-51 (> 520 nm) to carbon arc light [6,12]. Using the same procedure, samples which had been dyed with Pyr-Yellow, C.I. Reactive Blue 19, and Blue-Cu, the admixture were exposed to determine the photosensitivity of the TPDO dyes.

Table 2
Values of the apparent photosensitivity, f and the rate constant, k_0 (dm^3 mol^{-1} s^{-1}), of the second-order reaction with $^1O_2$ for TPDO and the other reactive dyes[a] on cellulose immersed in aerated water

No.	Dyes	f	k_0	Ref.
1	Rose Bengal	0.76	–	[12,15,16]
2	VS-TPDO	0.0086	0.21	This study
3	PVS-TPDO	0.0072	0.12	This study
4	MCT-TPDO	0.0083	0.28	This study
5	BF-TPDO	0.0075	0.36	This study
6	Pyr-Yellow	0.015	6.9	[12]
7	Blue 19[b]	0.027	0.014	[12]
8	CuPc	0.095	0.081	[12]
9	Blue-Cu	0.015	0.28	[12]
10	Black 5[b]	0.025	0.24	[12]

[a] Dyes of Nos. 2, 3, 5–10 are VS reactive dyes.
[b] C.I. Reactive.

Here, we estimate the photosensitivity of TPDO dyes by use of Pyr-Yellow with very large ease of photo-oxidation and small photosensitivity. However, since TPDO dyes showed much smaller photosensitivity than Pyr-Yellow, the influence of the photosensitivity of Pyr-Yellow itself on the estimation for TPDO dyes may not be neglected, as mentioned below (Section 3.5). In order to minimize the influence, therefore, the absorbance of Pyr-Yellow at λ_{max} in the mixture dyeing with TPDO dyes was adjusted so as to be constant ratio (in this case; about a third of that for TPDO dyes) and a yellow filter was used to remove the effect of self-photosensitivity of Pyr-Yellow on fading. The values of absorbance for the samples examined are listed in Table 3.

3. Results and discussion

3.1. Photofading on water-swollen cellulose

The photofading of four TPDO dyes and the CuPc dye at three concentrations was determined by exposing the dyed cellulosic films immersed in aerated water to carbon arc light. The fading behaviour is shown in Figs. 1 and 2. The order of the rates of fading for these dyes at the highest concentration shown in Figs. 1 and 2 (the initial absorbance at λ_{max} was 0.95 for VS-TPDO, 1.00

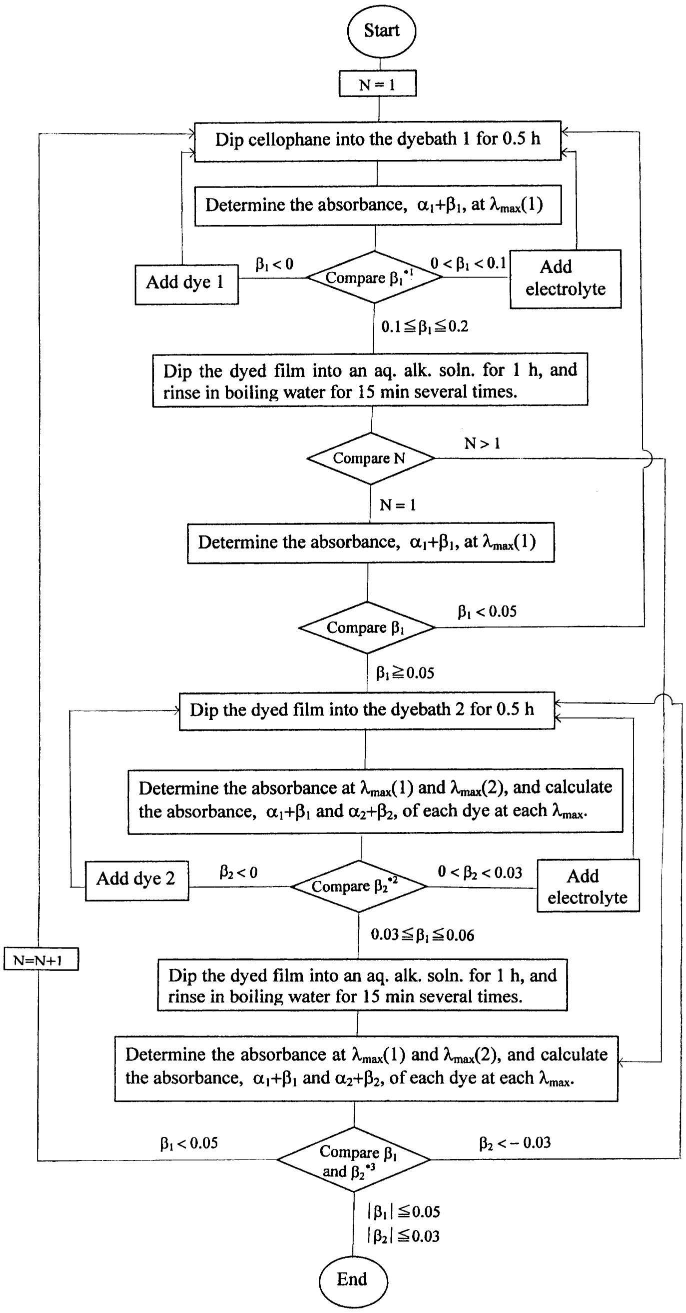


Diagram 1. Flow chart of mixture dyeing to dye cellophane film by the alkali-shock method initially with dye 1 at the absorbance of $\alpha_1 \pm |\beta_1|$ and secondarily with dye 2 at the absorbance of $\alpha_2 \pm |\beta_2|$. (Dyebaths 1 and 2 are prepared previously to contain dyes 1 and 2, respectively, and electrolyte of prescribed concentrations. cf. Section 2.2.2.)

*1Otherwise, the depth is too high. Restart after lowering the concentration of dye 1.

*2Otherwise, the depth is too high. Rinse the dyed film and dip again after lowering the concentration of dye 1.

*3Otherwise, the depth of dye 1 and/or dye 2 is too high. Restart after lowering the concentrations of dyes 1 and/or dye 2.

Table 3
Fading, A/A_0,[a] of TPDO dyes, Blue 19, Blue-Cu, and Pyr-Yellow on cellophane films dyed in admixture, and their mean rates of fading (min^{-1}) on exposure behind a Toshiba Y-51 filter on immersing in aerated water

Dyeings in admixture	A_0[b] at $\lambda_{\max}$	A/A_0[b] after exposure for			Mean rate of fading
		10 h	20 h	40 h	
Pyr-Yellow	0.265 (0.294)	0.979 (0.993)	0.963 (0.982)	0.942 (0.946)	2.5×10^{-5}
VS-TPDO	0.821 (1.045)	0.980 (0.979)	0.962 (0.969)	0.946 (0.959)	2.1×10^{-5}
Pyr-Yellow	0.323 (0.384)	0.993 (0.984)	0.978 (0.969)	0.957 (0.943)	2.1×10^{-5}
PVS-TPDO	0.830 (0.884)	0.970 (0.979)	0.948 (0.976)	0.946 (0.975)	1.7×10^{-5}
Pyr-Yellow	0.294 (0.330)	1.0 (0.988)	0.973 (0.964)	0.953 (0.936)	2.4×10^{-5}
MCT-TPDO	0.962 (0.972)	0.923 (0.944)	0.879 (0.919)	0.835 (0.872)	5.8×10^{-5}
Pyr-Yellow	0.341 (0.268)	0.979 (1.0)	0.967 (0.972)	0.952 (0.948)	2.2×10^{-5}
BF-TPDO	1.129 (0.979)	0.930 (0.962)	0.918 (0.952)	0.911 (0.923)	2.5×10^{-5}
Pyr-Yellow	0.389	0.910	0.850	0.790	7.7×10^{-5}
Blue 19	0.833	0.934	0.931	0.930	$<10^{-6}$
Pyr-Yellow	0.338	0.914	0.899	0.837	4.4×10^{-5}
Blue-Cu	0.709	0.925	0.911	0.877	3.0×10^{-5}

[a] A/A_0 at isosbestic point for VS- and PVS-TPDO and at $\lambda_{\max}$ for Pyr-Yellow, MCT- and BF-TPDO.

[b] Data of the sample dyed later with Pyr-Yellow are shown in the parentheses.

for PVS-TPDO, 1.07 for MCT-TPDO, 0.91 for BF-TPDO, and 1.04 for CuPc) was as follows:

$$\text{CuPc} > \text{BF-TPDO} \geqslant \text{MCT-TPDO} >> \text{VS-TPDO} \geqslant \text{PVS-TPDO} \tag{1}$$

This order coincides well with the lightfastness of the TPDO dyes on dry cotton fabrics (cf. Table 1). As discussed later, the order was also similar to that of the ease with which the dyes were oxidized except for CuPc. Thus, the differences in the rate of fading between the TPDO dyes on dry and wet cellulose may be attributed to the differences in the ease with which they are oxidized.

3.2. Oxidative fading by photosensitization with Rose Bengal

The fading behaviour of dyed cellophane which had been immersed in aqueous aerobic Rose Bengal solution and exposed to carbon arc light is shown in Fig. 3. The cellophane films were dyed so that their absorbance was 0.95±0.04 at $\lambda_{\max}$ on dry cellulosic film. The order of the rate of oxidative fading for the TPDO dyes at the absorbance was:

$$\text{MCT-TPDO} \risingdotseq \text{BF-TPDO} \gg \text{PVS-TPDO} \geqslant \text{VS-TPDO} > \text{CuPc} \tag{2}$$

This order is similar to that [the order (1)] with the exception of the CuPc dye.

The values of the apparent second-order rate constant, k_0 ($\mathrm{dm^3\ mol^{-1}\ s^{-1}}$), of the reaction with singlet molecular oxygen were calculated using the method described earlier [12]. However, as the concentration effects on the rate of fading differ for different dyes, care should be taken in estimating the intrinsic values of the rate constant of the reaction. Two examples of the concentration dependence of fading behavior for the PVS- and MCT-TPDO dyes are shown in Fig. 3. The existence of a similar concentration dependence was also found for the other dyes used. From the photosensitized fading of the four TPDO dyes and the CuPc dye or samples which had been dyed at low concentrations (initial absorbance at $\lambda_{\max}$ PVS-TPDO 0.303, VS-TPDO 0.377, MCT-TPDO 0.367 and BF-TPDO 0.458), the values of k_0 were obtained (Table 2), together with the values for some reactive dyes [12,13]. The rates of photosensitized fading by Rose Bengal for CuPc and C.I. Reactive Black 5 were used as the "reference"

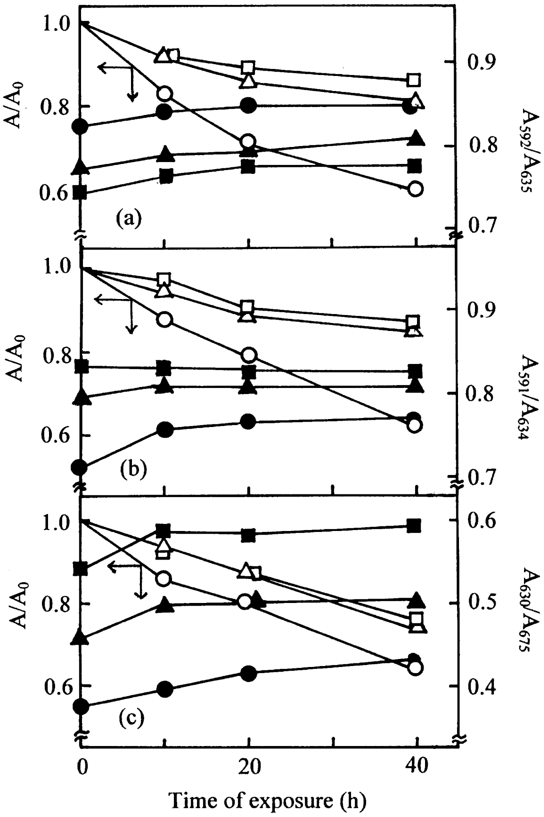


Fig. 1. Relationship between relative fading, A/A_0, measured at ip and the time of exposure for (a) VS-TPDO: ○, 0.42 (initial absorbance at λ_{max}, 635 nm), 0.33 (initial absorbance at ip, 601 nm); △, 0.73, 0.58; □, 0.95, 0.79; (b) PVS-TPDO: ○, 0.30 (initial absorbance at λ_{max}, 634 nm), 0.23 (initial absorbance at ip, 601 nm); △, 0.71, 0.58; □, 1.00, 0.84; and (c) CuPc: ○, 0.45 (initial absorbance at λ_{max}, 675 nm), 0.19 (initial absorbance at ip, 646 nm); △, 0.75, 0.36; □, 1.04, 0.58; on cellophane immersed in aerated water on exposure to carbon arc light, and the same relationship of A_d/A_m (ratio of absorbance at λ_{max} for dimer and monomer bands; the wavelengths are shown in the subscript), plotted with the same closed symbols. The absorbance of dyes was measured on dry films.

for the TPDO dyes [12]. The values of k_0 obtained for the TPDO dyes using the two reference values were virtually the same.

The order of the k_0-values for the four TPDO dyes was:

$$\text{BF-TPDO} > \text{MCT-TPDO} > \text{VS-TPDO} > \text{PVS-TPDO} \quad (3)$$

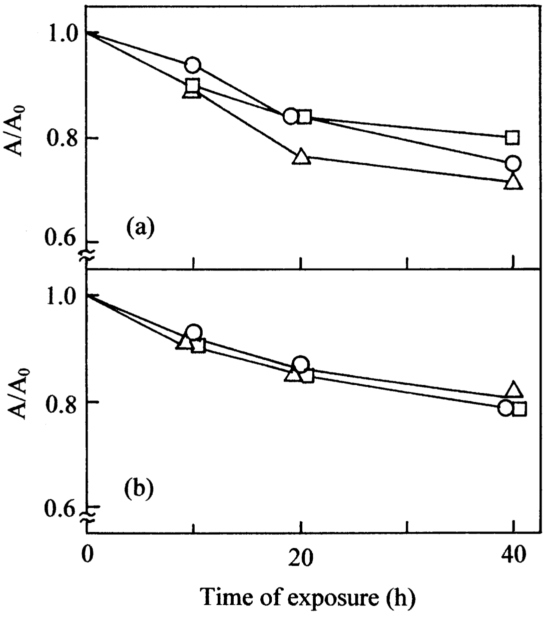


Fig. 2. Relationship between relative fading, A/A_0, measured at λ_{max} and the time of exposure for (a) MCT-TPDO: ○, 0.37 (initial absorbance at λ_{max}, 644 nm); △, 0.68; □, 1.07; and (b) BF-TPDO: ○, 0.42 (initial absorbance at λ_{max}, 649 nm); △, 0.67; □, 0.91; on cellophane immersed in aerated water on exposure to carbon arc light. □ The absorbance of dyes was measured on dry films.

While the relation between the BF- and the MCT-TPDO varied in the order, the order of the ease with which the dyes were photo-oxidized could be determined as order (3) of the k_0 values from the concentration dependence of the rates of photo-oxidation. The order (3) was almost the same as that of the hypochlorite bleaching and the reverse order of that of hydrogen peroxide bleaching for the TPDO dyes [11] with the exception of the relationship between BF- and MCT-TPDO. The observation for the TPDO dyes may be explainable, because HClO and singlet molecular oxygen attack the same position in the dye, namely that where the electron density of the HOMO is largest [17] and the order of nucleophilic reaction with hydrogen peroxide may often be the reverse to that of electrophilic reaction. The relationship between the BF- and the MCT-TPDO dye in the k_0-values and their reactivity to HClO may be attributed to the biradical character of $^1O_2$, although both $^1O_2$ and HClO act also as electrophiles.

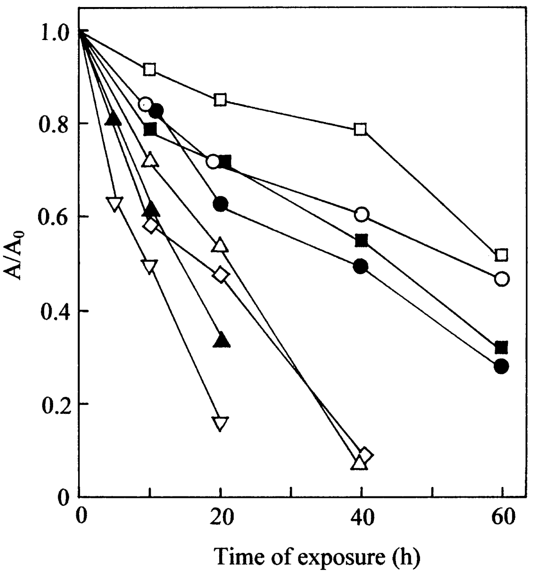


Fig. 3. Relationship between relative fading, A/A$_0$, measured at ip (for VS- and PVS-TPDO) or λ_{max} for MCT- and BF-TPDO) and the time of exposure for TPDO dyes: VS-TPDO: ○, 0.98 (initial absorbance at λ_{max}, 635 nm), 0.81 (initial absorbance at ip, 601 nm); PVS-TPDO: □, 1.09 (initial absorbance at λ_{max}, 634 nm), 0.93 (initial absorbance at ip, 601 nm); ■, 0.91, 0.82; ●, 0.47, 0.38; MCT-TPDO: △, 0.99 (initial absorbance at λ_{max}, 644 nm); ▲, 0.65; ▽, 0.37; and BF-TPDO: ◇, 0.92(initial absorbance at λ_{max}, 649 nm); on cellophane on exposure in aerated aqueous Rose Bengal (3.3×10^{-4} mol dm^{-3} + 0.050 mol dm^{-3} Na_2SO_4) solution. The absorbance of dyes was measured on dry films.

The light stability of the dyes on cellulose is frequently related to the ease of photo-oxidation of the dye and the quantum yield, f(-), of singlet oxygen generation or photosensitivity [18–21]. The low light stability of CuPc can be attributed to its high photosensitivity, irrespective of the smaller ease of its photo-oxidation compared to the TPDO dyes (Table 2). The stability of dyes on cellulose to photo-oxidative attack may depend upon the product of the values of k_0 and f, and the environmental conditions under which the substrate exists.

3.3. Effects of aggregation and concentration on fading

3.3.1. Aggregation of dyes on cellulose

The TPDO dyes exhibited different degrees of aggregation on cellulose, even when applied at similar concentration [1]. In addition to the CuPc dye, the PVS- and the VS-TPDO dyes are two other representatives of dyes that are spectrophotometrically confirmed to exist as a mixture of monomer and dimer on cellulose [1,6]. The degree of aggregation depends upon the compounds itself, its concentration, the medium in which the dyes exist, the presence of additives and their concentration, etc. [2–5]. In the case of a cellulosic substrate, the degree of aggregation may depend also, to a minor degree, on the dyeing methods used. An example of the dye combination between which the largest interaction exists has been known to be C.I. Direct Yellow 12 and C.I. Direct Blue 1 [22–24]. According to Horiki et al. [23,24], even in the case where Yellow 12 and Blue 1 mostly exist as 1:1 and 2:1 complex in the dyebath at high temperature, the adsorption of the complex to cellulosic substrate is small. In general, stability constant of homo-dimer is smaller than that of mixed dimer [25]. Since the number of sulfonate groups in the dimer or complex is larger than that of monomer, the adsorption of the complex or dimer should be small [24].

It is, therefore, virtually impossible to dye cellulosic films with reactive dyes to a prescribed degree of aggregation and a prescribed concentration. No systematic comparison of the effect of aggregation on the rate of fading among TPDO dyes is thus possible. As high additions of neutral electrolyte may result in cellulosic dyeings with reactive dyes of apparently high aggregation, during subsequent rinsing or wash-off processes, the apparent high degree of aggregation will be considerably lowered, since no dimer of a reactive dye is able to react with cellulose.

In the case of the CuPc dye, the alkali-shock dyeing method resulted in dyeings with a low degree of aggregation despite the large addition of electrolyte, while the all-in dyeing method at pH 9 yielded a high degree of aggregation despite a low electrolyte addition. High alkalinity may lower the degree of aggregation of the CuPc on cellulose in the fixation stage. In order to examine the aggregation effect on the fading, however, one must estimate accurately the degree of aggregation of dyes on cellulose before and after the exposure to light.

Except for the case of dyed cellulosic films with small absorbance, however, the filter effects are inevitable on exposure. According to Rabek [26], the filter effect becomes negligible at absorbance below 0.05. Since dyes at the absorbance much greater than 0.05 nearer the film surface of light incidence become the excited states at higher degrees, the distribution of excited dye molecules is far from homogeneous. It causes preferential surface fading that results in a heterogeneous distribution of dye in the substrate called filter effects. Lowering the concentration of dyes by fading may reduce the degree of aggregation preferentially from the direction of exposure, if the monomer-dimer equilibrium is dynamic.

To investigate the effect of aggregation on fading, the equilibrium should move during exposure and measurement by keeping the amount of dimer constant, if the monomer is preferentially faded. This situation may be fulfilled in the case of CuPc vinylsulfonyl dyes on cellulose [6]. But, in the case of TPDO dyes, the quasi-equilibrium may break or the degree of aggregation may diminish following a reduction in dye concentration especially near the textile surface as a result of fading.

Thus, one can find no suitable dye with which the effect of aggregation of dyes on fading can be enunciated. However, the four TPDO dyes used previously [1,11] may form a series of dyes with different aggregation tendency. By using the aggregation tendency of TPDO dyes as well as a typical dye with high aggregation tendency, namely CuPc, it may be possible to analyze the effects of aggregation on fading.

3.3.2. Concentration effect on the rate of fading under wet conditions

Since the absorption spectra of the four TPDO dyes were similar to each other in the visible region but differed below 320 nm, then similar filter effects may emerge in the fading, if they were compared at the same absorbance at λ_{max}. The same situation may hold for CuPc dyes. However, the difference in absorption at a wavelength below 320 nm may not contribute to fading, because carbon-arc light of wavelength greater than 290 nm was used.

As mentioned before, CuPc, VS- and PVS-TPDO dyes aggregate, while MCT- and BF-TPDO dyes have no aggregation tendency [1,6]. Initially, the concentration effects on the rate of fading for four TPDO dyes and a CuPc dye on cellulosic films when applied at three concentrations were examined. The fading behavior on wet cellulose (Figs. 1 and 2) reveals some differences in the concentration dependence of fading rates. VS- and PVS-TPDO and CuPc showed simple concentration dependence, in so far as the rate of fading decreased with increase in dye concentration. MCT-TPDO exhibited no concentration dependence whereas BF-TPDO showed intermediate behavior.

Comparing the fading behavior of the dyes at three concentrations, it is clear that dyes of marked aggregation tendency showed similar concentration dependence which differed to that displayed by MCT- and BF-TPDO dyes which have little aggregation tendency. However, the fading behavior of the former three dyes did not correlate well with aggregation tendency.

3.3.3. Aggregation effect on fading and the variation of monomer–dimer equilibrium during fading

Since the absorption spectra of the monomers and dimers in the cases of PVS-TPDO and CuPc overlap each other [1,6,27], the ratios of the absorbance, A_d/A_m, at λ_{max} for the dimer and monomer bands, are not equal to the ratios of the dye concentrations. In the case of CuPc, the situation is more complex in that many isomers are present, each of which consists of various combinations of sulfonate solubilizing groups and vinylsulfonyl reactive groups. While the dimer of CuPc may be a mixture of complexes that consist of two phthalocyanine nuclei having different combinations of solubilizing and reactive groups, the A_d/A_m ratios may reflect, qualitatively, the changes in the concentration ratios of the monomer and dimer.

The values of A_d/A_m for the dimer and monomer bands for VS- or PVS-TPDO as well as CuPc are plotted as a function of time of exposure in Fig. 1(a)–(c). The A_d/A_m ratio for the three dyes showed a small increase with progress of fading but aggregation did not suppress the rate fading. Fig. 1 shows a larger extent of fading of monomer species (or a small increase in A_d/A_m) for VS-TPDO and CuPc than for PVS-TPDO. This suggests that there is little effect of aggregation on fading.

To confirm whether or not the relative concentrations of monomers and dimers in the TPDO dyes change upon fading, as in case of CuPc [6], samples were prepared having different relative concentrations of monomers and dimers of PVS-TPDO, by adding small and large additions of electrolyte to the dyebath and were examined spectrophotometrically before and after exposure in aqueous Rose Bengal solution. Since swelling in water promotes aggregation of PVS-TPDO [1], the absorption spectra of the dyes were measured on dry and wet films [Fig. 4(a)–(d) for PVS-TPDO, and those on dry films in Fig. 5(a)–(c) for CuPc and in Fig. 6(a)–(c) for VS-, MCT- and BF-TPDO]. The absorption spectra on wet films are shown only for PVS-TPDO, since no variation in the spectra was observed except for PVS- and VS-TPDO.

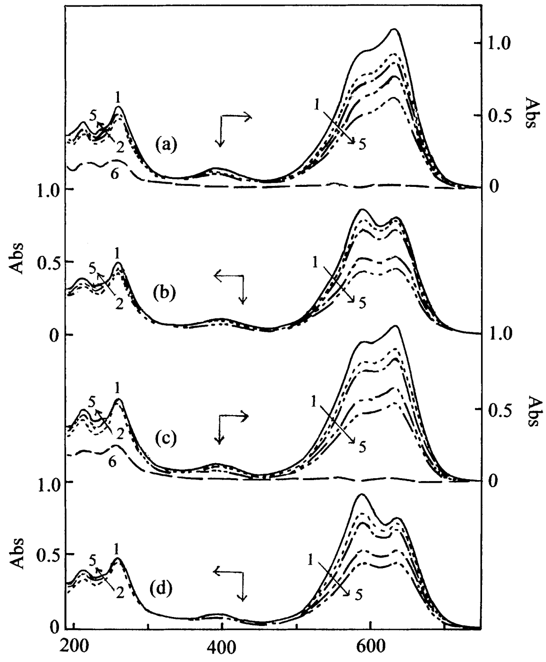


Fig. 4. Absorption spectra of (a) PVS-TPDO dyed by usual method on dry cellophane, (b) PVS-TPDO dyed by usual method on water-swollen cellophane, (c) PVS-TPDO dyed by large addition of Na_2SO_4, on dry cellophane, and (d) PVS-TPDO dyed by large addition of Na_2SO_4, on water-swollen cellophane, on exposure in aerated Rose Bengal (3.3×10^{-4} mol dm^{-3} + 0.050 mol dm^{-3} Na_2SO_4) solution for 0 h (1), 10 h (2), 20 h (3), 40 h (4), and 60 h (5), and the spectra of the decomposition products (6) on dry film. (For dyeing conditions, see Section 2.2.1. After exposure, RB adsorbed on the film was extracted by 50% aqueous DMF solution at room temperature for 30 min.)

In the case of PVS-TPDO the A_d/A_m values showed that varying addition of electrolyte gave varying aggregation. CuPc displayed low and high degree of aggregation depending upon the dyeing method used (Fig. 5).

Using the samples of different degrees of aggregation, the rates of fading of PVS-TPDO as well as CuPc and the variations of the A_d/A_m ratio on exposure in aerated water and in aerated aqueous RB solution (only for the former dye) were investigated to determine the effect of aggregation on fading. The results are shown in Fig. 7(a) and (b) for PVS-TPDO and in Fig. 8 for CuPc. PVS-TPDO and CuPc, with marked larger aggregation tendency, showed no reduced rate of fading. The A_d/A_m ratio showed no preferential fading of monomer species and little change in the ratio. A decrease in the ratio was observed in the case of

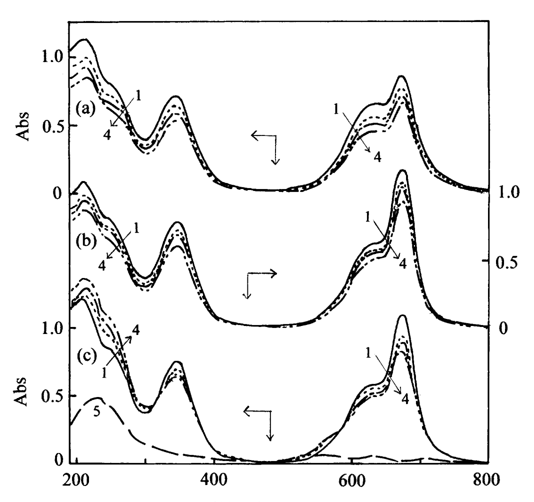


Fig. 5. Absorption spectra of (a) CuPc with higher degree of aggregation, and (b) CuPc with lower degree of aggregation on dry cellophane after exposure in aerated water for 0 h (1), 10 h (2), 20 h (3), and 40 h (4), and those of (c) CuPc on dry cellophane after exposure in aerated Rose Bengal (3.3 $\times10^{-4}$ mol dm^{-3} + 0.050 mol dm^{-3} Na_2SO_4) solution for 0 h (1), 5 h (2), 10 h (3), and 20 h (4), and the spectra of the decomposition products (5). (For dyeing conditions, see Section 2.2.1. After exposure, RB adsorbed on the film was extracted by 50% aqueous DMF solution at room temperature for 30 min.)

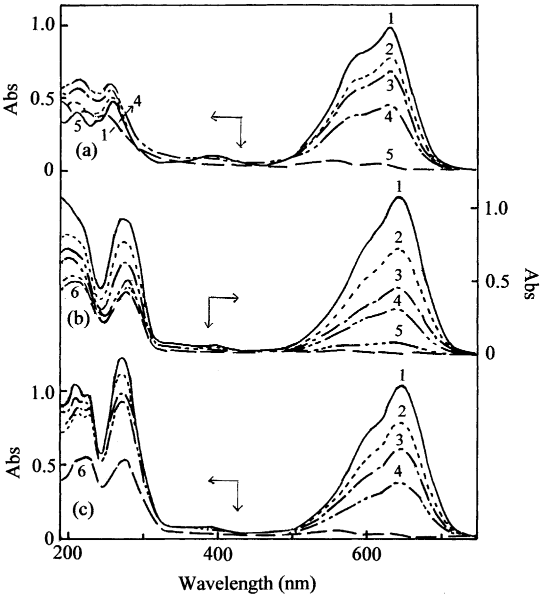


Fig. 6. Absorption spectra of (a) VS-TPDO on dry cellophane after exposure in aerated Rose Bengal (3.3×10^{-4} mol dm^{-3} + 0.050 mol dm^{-3} Na_2SO_4) solution for 0 h (1), 10 h (2), 20 h (3), and 60 h (4), and the spectra of the decomposition products (5), and those of (b) MCT-TPDO, and (c) BF-TPDO on dry cellophane after exposure in the same solution for 0 h (1), 5 h (2), 10 h (3), 20 h (4), and 40 h (5), and the spectra of the decomposition products (6). (After exposure, RB adsorbed on the film was extracted by 50% aqueous DMF solution at room temperature for 30 min.) (Spectrum 6 for BF-TPDO = (spectrum 4)–0.37×(spectrum 1).)

PVS-TPDO at high degrees of aggregation [Fig. 7(b)]. Thus, it can be concluded that aggregation of the dyes has little effect on the rates of fading for PVS-TPDO and CuPc on cellulose under wet conditions.

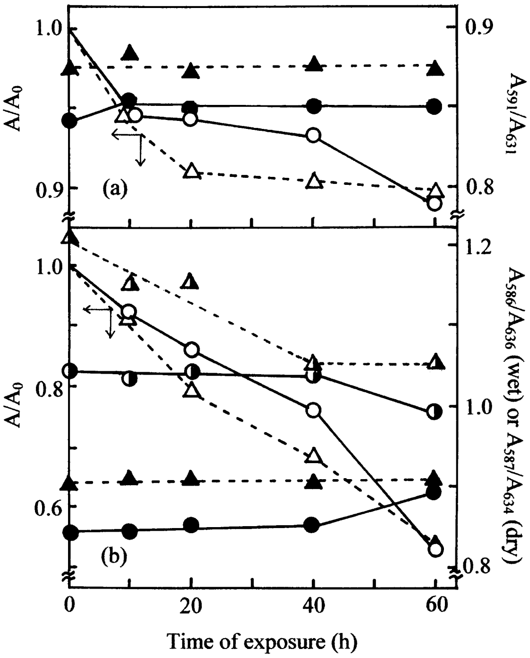


Fig. 7. Relationship between relative fading, A/A_0, measured at ip and the time of exposure for (a) PVS-TPDO on cellophane dyed by small addition of Na_2SO_4: ○, 1.08 (initial absorbance at λ_{max}) and 0.93 (initial absorbance at ip, 601 nm); and by large addition of Na_2SO_4: △, 1.06 and 0.94 on cellophane films immersed in aerated water and (b) PVS-TPDO on the same samples immersed in aerated Rose Bengal (3.3×10^{-4} mol dm^{-3} + 0.050 mol dm^{-3} Na_2SO_4) solution on exposure to carbon arc and the same relationship of A_d/A_m (ratios of absorbance at λ_{max} for dimer and monomer bands; the wavelengths are shown in the subscript), illustrated by the same closed symbols. (A_d/A_m estimated from absorbance on wet films dyed by small (◑) and large (▲) additions. For dyeing conditions, see Section 2.2.1.)

When a film sample in a glass vessel was exposed to carbon arc light in a fade-ometer, the temperature of the aqueous solution in which the films were immersed being kept at 50 °C, resulted in decreased dye aggregation. A large amount of electrolyte was needed to minimize the difference in adsorption of RB on cellulosic films, resulting in a large increase in aggregation. (Since the TPDO dyes used have differing numbers of sulfonate groups, the dyed films may show different co-ion exclusion effects on the adsorption of RB in the case of the small addition of electrolyte.) Exposure of PVS-TPDO films in RB solution where higher aggregation existed, revealed neither effect of aggregation on the rate of fading nor variation in the A_d/A_m ratio. Since the latter ratio variation was small, no absorption spectra corresponding to Fig. 7(a) are shown.

To conclude, in terms of the effect of aggregation on dye fading, only the dye concentration affected the fading.

3.4. Decomposition products of photo-oxidative fading

The decomposition products of TPDO dyes produced as a result of photo-oxidative fading were

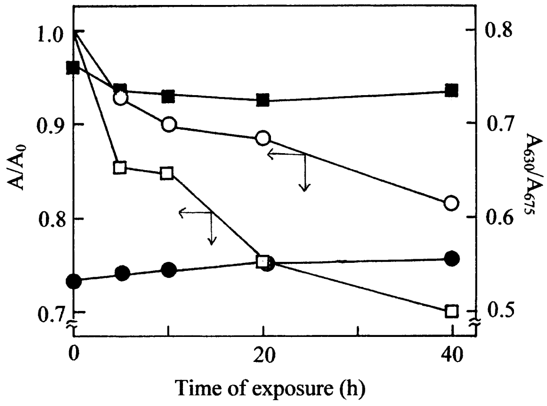


Fig. 8. Relationship between relative fading, A/A_0, measured at ip and the time of exposure for CuPc of high aggregation on cellulosic film dyed by weakly alkaline all-in method: □, 0.9 (initial absorbance at λ_{max}= 675 nm), 0.19 (initial absorbance at ip, 646 nm) and for CuPc dyed by alkali-shock method: ○, 1.15 (initial absorbance at λ_{max}) and 0.96 (initial absorbance at ip); on cellophane films immersed in aerated water on exposure to carbon arc and the same relationship of A_d/A_m (ratio of absorbance at λ_{max} for dimer and monomer bands; the wavelengths are shown in the subscript), illustrated by the same closed symbols. (Dyeing conditions: Section 2.2.1.)

examined from the absorption spectra of irradiated samples (Figs. 4–6). RB which was adsorbed on films dyed with TPDO dyes and a CuPc dye during exposure in aqueous RB solution was not completely removed by immersing the films in boiling water. It was however thoroughly extracted by 50% aqueous dimethylformamide (DMF) solution at room temperature.

The main absorption band of the TPDO dyes in visible region decreased with time of exposure. However, as the UV spectra of VS- and PVS-TPDO show, TPDO nuclei have an absorption band below 350 nm, while the MCT- and BF-TPDO dyes with aromatic reactive anchor systems have similar absorption that is larger than that of the former two dyes. The absorption of BF-TPDO less than 350 nm was larger than that of MCT-TPDO, since the former dye has a larger aromatic anchor system. As photodecomposition progressed, a compensation effect was observed between a decrease in absorption due to the TPDO nucleus and an increase in absorption due to the aromatic residue from the TPDO nucleus. CuPc has a phenyl nucleus, MCT-TPDO a phenyl nucleus with a triazinyl nucleus, and BF-TPDO two phenyl nuclei and a triazinyl nucleus as the reactive anchor group system. When there was an aromatic residue bound to a reactive anchor group system in TPDO or phthalocyanine (Pc) nucleus, the absorption spectra corresponded to the aromatic residue bound with the anchor system may be observed, which may change with a progress of fading.

The absorption spectra obtained for the decomposition products with little absorption in the visible region, which are illustrated in Fig. 4 (spectrum 6) for PVS-TPDO, in Fig. 5(c) (spectrum 5) for CuPc, in Fig. 6(a) (spectrum 5) for VS-TPDO and in Fig. 6(b) (spectrum 6) for MCT-TPDO, support this tendency. The greater the number of aromatic nuclei the dye has in its anchor group system, the larger was the absorption lower than 350 nm. This situation held for BF-TPDO for which the absorption spectra of the decomposition product are shown in Fig. 6(c) (spectrum 6) for BF-TPDO. The absorption spectra of the decomposition products obtained for MCT- and BF-TPDO were obtained by subtracting the visible spectra of original dyed film of corresponding concentration from the spectra of the dyed film exposed to carbon arc light. In case of MCT-TPDO, since the effect of the original dye on the spectra of the decomposition product was very small, the tendency was easily confirmed. However, in the case of BF-TPDO, if the corresponding absorption spectra with about half of dyes left undecomposed were converted to the complete decomposition by subtracting the spectrum of undecomposed species of corresponding concentration, it is confirmed that the relation also holds.

When the absorption spectra of dyed films exposed to carbon arc light were compared with those of dyed films which had been immersed in aqueous hypochlorite and HP solutions, reported previously [11], clear differences were found in the UV region. The fading of TPDO dyes on cellulose by the photosensitization with RB as well as the thermo-chemical attacks with hypochlorite and HP solutions may decompose the TPDO nucleus on cellulose [11]. Singlet molecular oxygen may not decompose completely the TPDO and Pc rings to leave the reactive anchor system and some aromatic residues bound with cellulose, while oxidizing bleaching agent left only the anchor system without aromatic fragment of chromophore. From the spectral changes, it is also supposed that oxazine rings in TPDO nuclei are split into two fragments during the photodecomposition.

It is also noted that the present discussion on the photodecomposition of TPDO and Pc nuclei is based on the results by use of Rose Bengal. When TPDO dyes on cellulose are exposed in aerated water, exposure of a long time was necessary to decompose TPDO nuclei due to the low photosensitivity (Section 3.5), which resulted in further decomposition of aromatic fragments to give a little smaller absorption in UV region.

3.5. Estimation of photosensitivity for TPDO dyes

3.5.1. Fading of TPDO dyes and Pyr-Yellow on mixture-dyed cellulose

The photosensitivity of TPDO dyes on cellulose following dyeing with an admixture of TPDO and Pyr-Yellow was estimated according to a previously reported method [6,12,13]. Because Pyr-Yellow has the lowest photosensitivity and the greatest ease of photo-oxidation among the approximately 20 reactive dyes thus far examined (Table 2), one can expect to neglect the influence of the photosensitivity of Pyr-Yellow on the photosensitivity of the partner dyes on cellulose.

Initially, the mixture-dyed film was exposed to carbon arc light. The results are shown in Fig. 9. Surprisingly, the fading of Pyr-Yellow was suppressed, while that of TPDO dyes was promoted, compared with the fading on singly-dyed film, implying that Pyr-Yellow accelerates the fading of TPDO dyes. These results clearly showed that TPDO dyes have even lower photosensitivity than Pyr-Yellow. For this reason, there is no direct exposure method that can be used to estimate the photosensitivity of TPDO dyes on cellulose dyed in admixture with Pyr-Yellow; rather, a yellow filter should be used to remove the influence of the self-photosensitivity of Pyr-Yellow itself.

3.5.2. Photosensitization of TPDO dyes to the fading of Pyr-Yellow under wet conditions

By shielding Pyr-Yellow with a yellow filter and exposing TPDO dyes to carbon arc light to minimize the effect of self-photosensitization by Pyr-Yellow, the rate of fading was estimated for both dyes on mixture-dyed cellulose in aerated water. The results are summarized in Table 3. When five dyes were compared with respect to the rates of fading in the presence and absence of a filter, the fading of Pyr-Yellow on cellulosic films dyed in admixture was found to be considerably suppressed by the filter, while that of the four TPDO dyes was only slightly suppressed. The relative rates of fading of each of the TPDO dyes were larger than 0.9 within the 40 h exposure period. The rates of fading were similar to each other in

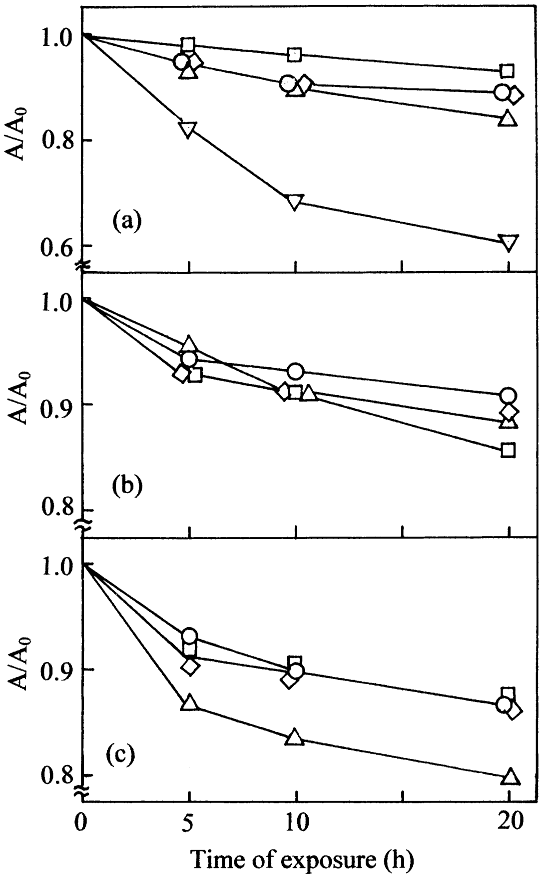


Fig. 9. Relationship between relative fading, A/A_0, and the time of exposure to carbon arc (a) for VS-TPDO (○), PVS-TPDO (□), MCT-TPDO (△), BF-TPDO (◇), and Pyr-Yellow (□) in the single dyeing, (b) for Pyr-Yellow in the mixture dyeing with these TPDO dyes (the same symbols used), and (c) for TPDO dyes in the mixture dyeing with Pyr-Yellow on cellulosic films immersed in aerated water. (Dyeing conditions: Section 2.2.2 and Table 3 for the absorbance of samples.)

the first significant order and different in the second one. From the viewpoint of experimental accuracy, it is possible to compare only the order of magnitude in the photosensitivity among TPDO dyes.

The fading of Pyr-Yellow on cellulosic films dyed in admixture with TPDO dyes was smaller than the fading on the substrate dyed in admixture with C.I. Reactive Blue 19 and Blue-Cu. These dyes were selected as reference dyes because they have a blue color and small *f*-value (Table 2) identical to those of the TPDO dyes. In the previous papers [12,13], Rose Bengal was used as the reference dye to determine the *f*-values of reactive dyes on cellulosic substrate. In spite of their low photosensitivities, C.I. Reactive Blue 19 and Blue-Cu promoted the rate of fading for Pyr-Yellow, as distinct from the TPDO dyes, which did not. As a first approximation, we neglected the differences in the fading of C.I. Reactive Blue 19 and Blue-Cu in the mixture dyeing with Pyr-Yellow. The *f*-values of TPDO dyes were determined from the fading of Pyr-Yellow in the mixture dyeing. Mean values of the rates of fading for two kinds of samples (different order of dyeing; 2.2.2) were used for the calculation of *f*-values. The results are listed in Table 2. The *f*-values of TPDO dyes were about one-third to one-fourth those for C.I. Reactive Blue 19, Blue-Cu, and Pyr-Yellow. The order of the *f*-values for the six dyes was as follows:

$$\text{Blue 19} > \text{Blue-Cu} > \text{VS-TPDO} > \text{MCT-TPDO} > \text{BF-TPDO} > \text{PVS-TPDO} \tag{4}$$

This order of photosensitivity did not seem to be correlated with the above orders (1), (2), and (3). This matter is discussed below.

3.6. Photochemical properties of TPDO dyes

Among reactive dyes, TPDO dyes are characterized by their ease of photo-oxidation and their low photosensitivity, which is less than that of Pyr-Yellow (Table 2). Despite their high photooxidizability, TPDO dyes have fair lightfastness on dry and wet cellulose due to their low photosensitivity. However, if TPDO dyes are used singly or in admixture with dyes having very small photosensitivity, they exhibit high lightfastness.

This behavior may be primarily attributable to the small quantum yield needed to form both the excited triplet state and the high quantum yield (nearly unity) of internal conversion. Because these dyes require a large molecular extinction coefficient to reach the excited singlet state, they should have effective photophysical deactivation processes occurring via the internal conversion of $S_1 \rightarrow S_0$ [28–30]. This could be supported by the photophysical property that these TPDO dyes emit no fluorescence. Despite the intensive studies that have been carried out to date, it is impossible to predict the efficiencies of the photophysical processes [31–40]. Numerous workers, including Nijegorodov [33–35], Becker [36], Lin [37], and Biczók [38] and their colleagues, have examined the relationship between the photophysical processes and the chemical structures of organic compounds but have arrived at no conclusions which might explain this relationship.

For even simple organic compounds, all the factors contribute to the phenomenon of the photophysical processes. Because even the subtlest structural change can result in an unpredictable change in the efficiencies, it remains impossible to predict the quantum yields for these processes. Mama [39] enumerated the characteristics of molecular structure for potentially fluorescent chromophores as follows: high rigidity, high planarity of the π-electron system, an absence of groups which cause steric crowding, an absence of nitro and azo groups, an absence of halogens with large atomic weight (chlorine is usually okay), an absence of chelating metal atoms, and an absence of pendant phenyl groups, especially on N and O atoms. Although they almost completely satisfied these criteria, the royal blue TPDO dyes examined here had no fluorescence (in previous studies, however, TPDO with no substituent has been shown to have a rose color with green fluorescence in organic solvents [41,42] and 6-methyl-13-isopropyl-TPDO has exhibited an orange-red color with strong green fluorescence [43]). The absorption of longer wavelength in the visible region diminishes the fluorescence. The decrease in S_1–S_0 energy interval may increase the rate of internal conversion, which is a general energy gap law in photochemistry [31,38, 44,45]. The chemical structure with high rigidity, planarity, and symmetry, and high degeneracy of vibrational modes of TPDO dyes may result in effective isoenergetic internal conversion of TPDO dyes of S_1 state into a highly excited vibrational state of S_0, followed by very rapid vibrational relaxation to the ground vibrational state of S_0. On the whole, TPDO dyes exhibit an internal conversion of high quantum yield (almost unity). This property may also endow TPDO dyes with a low quantum yield of photo-reduction as a result of the low quantum yield of intersystem crossing, $S_1 \rightarrow T_1$ (better perspiration-lightfastness in Table 1). Generally, it is known that certain procedures decrease the ease of oxidation through a substitution effect. If this could be accomplished without decreasing the quantum yield of internal conversion and without increasing the quantum yield of intersystem crossing, then TPDO dyes with higher lightfastness on dry and wet cellulose could be composed.

Among TPDO dyes, the order (4) of photosensitivity does not correspond to the order (3) of the stability to photo-oxidative attacks. The differences in photosensitivity among TPDO dyes may be too small to result in an observable difference in the photo-oxidative property. The latter property may depend upon the ease with which the dyes are oxidized, although the photosensitivity also plays an important role in the photo-oxidation. The importance of photosensitivity in the photo-oxidation may be explained by comparing the lightfastness of TPDO dyes with that of CuPc. Since CuPc possesses a considerably larger value of f and a smaller value of k_0 than do the TPDO dyes, CuPc has less lightfastness than TPDO dyes. Since C.I. Reactive Blue 19 has a slightly larger value of f but a considerably smaller value of k_0 compared to the TPDO dyes, it must have a slightly greater lightfastness than TPDO dyes. The low photosensitivity may play an important role in the lightfastness of TPDO dyes, i.e. the low ease of oxidation in the case of C.I. Reactive Blue 19, and the large photosensitivity in the case of CuPc. Under aerobic conditions, the lightfastness of reactive dyes on cellulosic substrate is dependent upon these two factors.

4. Summary

TPDO dyes used have a common large ring structure but different substituents on the same positions of the TPDO ring and different aggregation tendency. The photofading for four TPDO dyes and a CuPc dye on cellulosic films was examined by exposing the dyed films immersed in aerated water and in aerated RB solution. From the rates of oxidative fading using the photosensitization of RB, the ease with which the dye was photo-oxidized was estimated. The photostability of TPDO dyes on cellulosic substrate was proportional to this ease. It was also confirmed that the lightfastness of TPDO dyes on dry and wet cellulose has a close connection with the ease of photo-oxidation.

The photofading of all the dyes examined showed concentration dependence on the rate of fading. The effects of aggregation on the fading of the dyes having high aggregation tendency were investigated by preparing the dyed samples on which the dyes existed in a state of high or low degree of aggregation. It was confirmed that the aggregation of dyes on cellulosic substrate had little effect on the rate of fading.

By the photo-oxidative attacks, TPDO nuclei were decomposed to leave aromatic fragments connected with reactive anchor system, which bound with cellulose.

The photosensitivity of TPDO dyes was determined by photosensitized fading of Pyr-Yellow on cellulosic films dyed in admixture with TPDO dyes by exposing only TPDO dyes and shielding Pyr-Yellow by use of a yellow filter. The photosensitivity of the TPDO dyes is very small and determines the high lightfastness of TPDO dyes, but the differences in the lightfastness of TPDO dyes are controlled by the ease with which the dye is photo-oxidized. The photostability of dyes on cellulosic substrate is dependent upon the ease of photo-oxidation and the photosensitivity.

The photofading behavior of the TPDO dyes is attributed to the low quantum yield of the excited triplet state as well as to the high quantum yield of quenching of excited singlet state into ground state by internal conversion.

In general, the lightfastness of dyes on substrate is dependent upon the chemical structure that determines the photophysical and photochemical properties of dye itself but not upon the aggregation tendency, although the filter effect or concentration effect on the rate of fading exists always.

Acknowledgements

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