Dyes and Pigments, Vol. 35, No. 4, pp. 311–330, 1997
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PII: S0143-7208(96)00124-6 0143-7208/97 $17.00+0.00

Estimation of Potential Photochemical Properties for Monochlorotriazinyl Reactive Dyes and their Manifestations in the Fading of Dyed Cellulose

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(Received 2 October 1996; accepted 5 November 1996)

ABSTRACT

Cellulose films dyed with 10 monochlorotriazinyl reactive dyes were exposed to light in various aqueous solutions and the following potential photochemical reactivities of dyes estimated: (i) ease with which the dyes are photo-oxidized, (ii) ease with which dyes are photo-reduced, (iii) apparent photosensitivity, and (iv) the rates of fading in aerated water. On irradiating the dry reactive cotton dyeings, fading proceeded in two steps, viz. many dyes exhibited a considerable initial fading, accompanied by slow subsequent fading. On exposing the dry dyed cellulose films, little initial fading was observed. The fading behavior of some dyes could be explained by their potential properties, while other dyes underwent slow fading, probably due to a compensation between oxidative and reductive photofading processes even though the dyes had high photoreactivity. The concentration dependence on the fading behavior of dyed films could be explained by the filter effect with some exceptions, where dyes with high photosensitivity showed larger or similar fading in deep dyeings than that in the paler dyeings. © 1997 Elsevier Science Ltd

Keywords: fading, reactive dye, cotton fabrics, cellulose film, environmental effect.

INTRODUCTION

On exposure of reactive dyes on cellulose in aerated water, many vinylsulfonyl (VS) dyes undergo oxidative fading [1–4], while some monochlorotriazinyl (MCT) dyes undergo reductive or oxidative fading [5, 6]. Some MCT dyes on cellulose undergo reductive fading on exposure in deaerated water irrespective of non-addition of substrate [5]. In the presence of substrate, most reactive dyes on cellulose show reductive fading [1, 5]. Thus, whether reductive or oxidative fading of reactive dyes on cellulose occurs depends upon the chemical structure of the dyes and on the environmental conditions of exposure. The latter conditions may produce effects not only on the properties of the dye itself, such as azo–hydrazone tautomerism and the redox potential of the original dye and the semi-reduced intermediate, but also on the rates of photochemical reactions. In many cases, the conditions seem to determine whether oxidative or reductive fading occurs, if the dyes on cellulose have the potential property to undergo both these mechanisms. In general, however, dyes may show oxidative fading at the initial time of irradiation (if it occurs), and later they have a tendency to show reductive fading, although some dyes undergo oxidative fading throughout.

The photofading behavior of VS dyes on cellulose, or their potential fading properties can be easily elucidated by an accelerated testing method for the photostability of dyes [1], where the relative fading of VS dyes under defined conditions are examined.

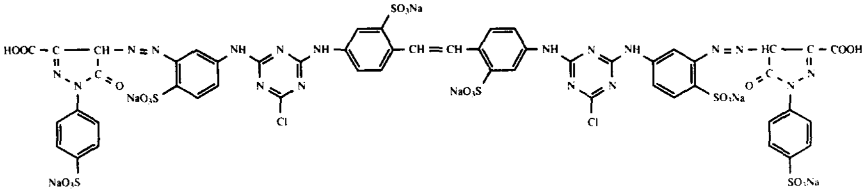
In the present study, the fading behavior of 10 MCT dyes on cellulose is examined by exposure in the presence of oxygen and substrate under wet conditions. Cotton fabrics and cellulose films dyed with these dyes were also irradiated under atmospheric dry conditions and the fading behavior was analyzed in terms of their potential photochemical properties. The effect of migration time in the exhaustion dyeing on the initial fading of dyed fabrics as well as the dye concentration effect of dyed films, are investigated. How these MCT dyes on cotton fabrics and cellulose films manifest a different fading behavior from that under wet conditions is also analyzed.

EXPERIMENTAL

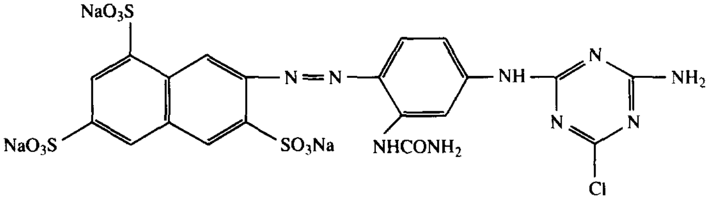
Materials

The 10 reactive MCT dyes used were these used in previous investigations [5–7] and were supplied by Nippon Kayaku Co. Ltd. In order to estimate the photosensitivity of MCT dyes, a VS aminopyrazolinyl azo dye, supplied by Sumitomo Chemical Co. Ltd. was used, as before [7, 8]. The structures of the dyes are shown below:

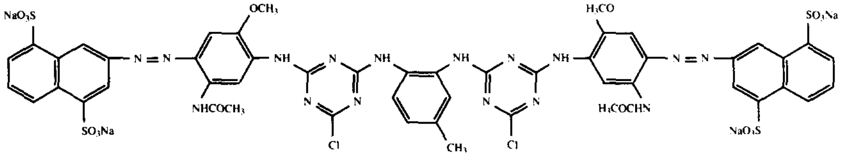
1. A stilbene pyrazolinyl disazo dye (Yellow)



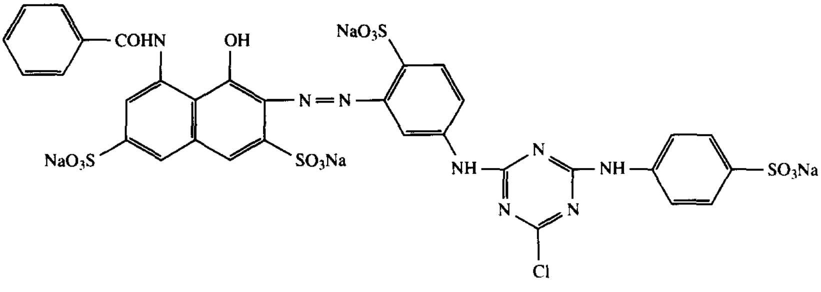
2. An *o*-ureidoazo dye (Yellow R)



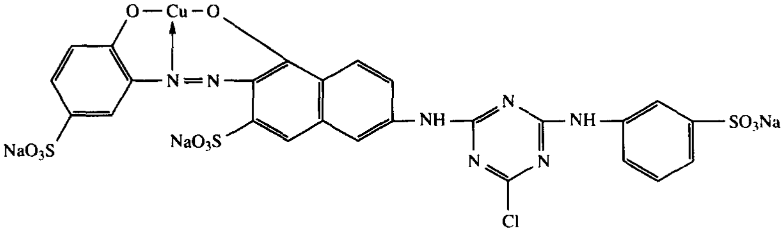
3. An *o*-phenylenediamine disazo dye (Orange)



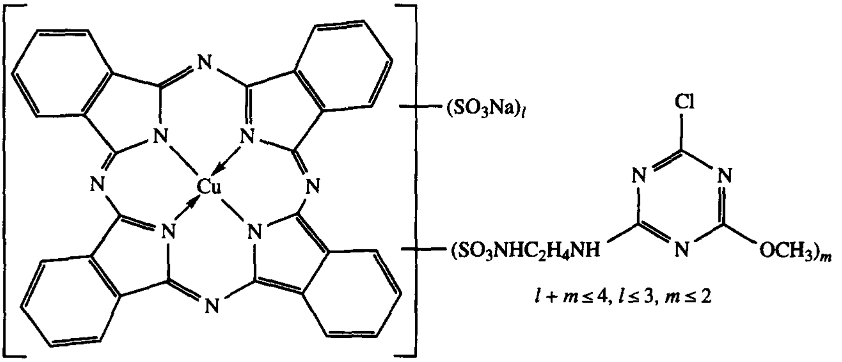
4. CI Reactive Red 4, CI 18105 (Red 4)



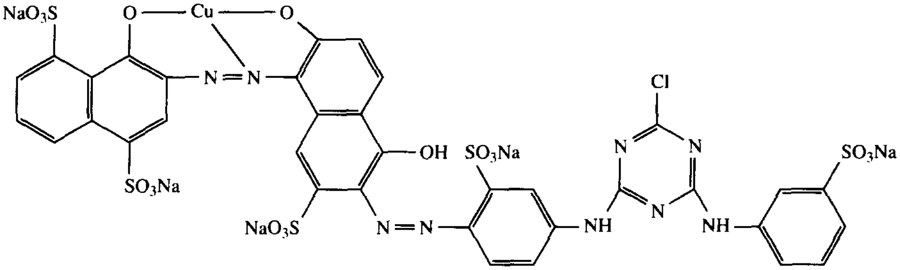
5. CI Reactive Red 7, CI 17912 (Red 7)



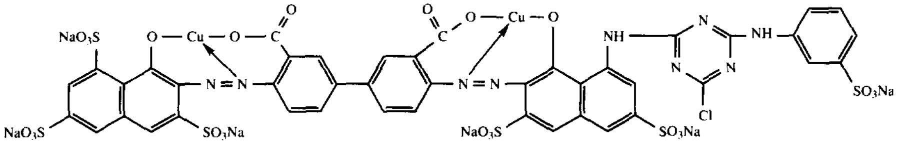
6. A copper–phthalocyanine dye (Cu-Pc)



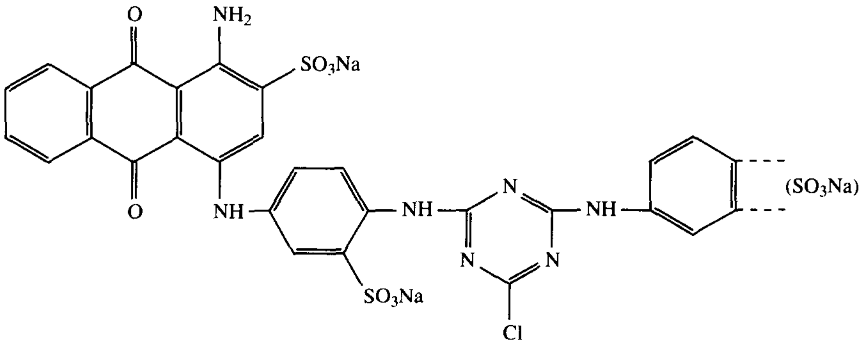
7. A 1:1 copper–complex azo dye (Blue-1Cu)



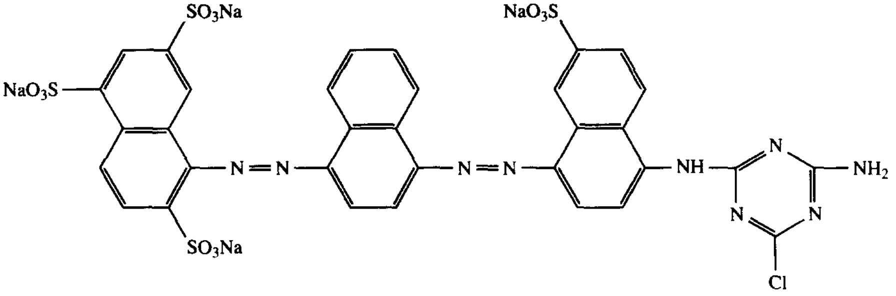
8. A 1:2 copper–complex azo dye (Blue-2Cu)



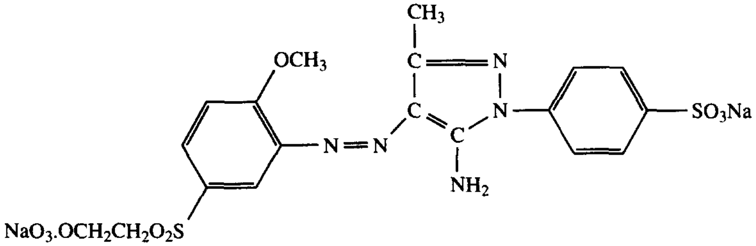
9. CI Reactive Blue 2, CI 612 11 (Blue 2)



10. A brown disazo dye (Brown)



11. A VS aminopyrazolinyl azo dye (VS-Yellow)



Dyeing and measurements

Cellophane sheets (# 300, Futamura Kagaku Kogyo K.K.) were cut 4 cm wide and 50 cm long and were scoured in boiling distilled water for more than 3 h. They were dyed with each MCT dye to have an equilibrium adsorption at 80°C from a dyebath containing an appropriate concentration of dye and 50 g dm^{-3} of sodium sulfate. After the equilibrium adsorption, the films were dipped in an aqueous solution of sodium carbonate (20 g dm^{-3}) and sodium sulfate (100 g dm^{-3}) at 80°C to fix the adsorbed dye, and then washed to remove completely the unfixed species. The dyeing method of VS-Yellow was the same as that previously noted [7],[8].

Cotton fabrics (calico) were dyed from the dyebath (liquor ratio 1:30, dye 1.0% o.w.f., sodium sulfate 50 g dm^{-3}) at 80°C for a prescribed time (30 min and 2 h in the cases of Yellow, Yellow R, Orange, and Brown, and 30 min in the cases of the other dyes) and then treated for a further 60 min after addition of sodium carbonate (20 g dm^{-3}). After fixation, the dyed fabrics were washed in boiling water to remove the unfixed dyes.

Exposure of the dyed sample was carried out using the same apparatus as described before [8]. Measurements of absorption spectra were made with a

V-560 spectrophotometer (Jasco Corp.), and the reflection spectra by use of an integrating sphere; the calculation of chromaticity values for the C light source were effected using approporiate color calculation softwear.

RESULTS AND DISCUSSION

Test methods to estimate the essential properties of dyes under wet conditions

In order to elucidate the photofading behavior of MCT dyes on cellulose, their relative rates of fading on exposure in various aqueous substrate solutions were examined as shown in Table 1, where the relative rates of fading on exposure in aerated water and in an aerated aqueous Rose Bengal solution, estimated in a previous paper [3], are also presented. Using the absorption spectra of the photodecomposition products for MCT dyes on cellulose after exposure, it could be determined whether oxidative or reductive fading occurred [1]. Since most MCT dyes undergo multi-step photodecomposition in the presence of oxygen and substrate, it was too complex to analyze the simultaneous oxidative and reductive fading by spectral analysis [5, 6].

From the results of Table 1, various properties for the MCT dyes examined are summarized as follows:

1. rates of fading in aerated water: [5, 6]
   (a) $$\begin{aligned}&\mathrm{Red7} \geq (\mathrm{Blue}-2\mathrm{Cu}) > \mathrm{Blue}-1\mathrm{Cu} > \mathrm{Cu}-\mathrm{Pc} > \mathrm{Red4}\\ &> \mathrm{Yellow} > (\mathrm{Brown}) > (\mathrm{YellowR}) \approx (\mathrm{Orange}) > \mathrm{Blue2}\end{aligned} \quad (1)$$
   (b) where dyes in parentheses underwent reductive fading.
2. ease with which dyes are oxidized [7]:
   (a) $$\begin{aligned}&\mathrm{Blue}-1\mathrm{Cu} > \mathrm{Red7} \gg \mathrm{Red4} > \mathrm{Blue}-2\mathrm{Cu} > \mathrm{Yellow}\\ &> \mathrm{Brown} > \mathrm{Cu}-\mathrm{Pc} > \mathrm{YellowR} > \mathrm{Orange} > \mathrm{Blue2}\end{aligned} \quad (2)$$
3. apparent photosensitivity to the fading of VS-Yellow [7]:
   $$\begin{aligned}&(\mathrm{a})\ \mathrm{Cu}-\mathrm{Pc} > (\mathrm{Blue}-2\mathrm{Cu}) > \mathrm{Red4} > (\mathrm{YellowR}) > \mathrm{Yellow}\\ &> \mathrm{Blue}-1\mathrm{Cu} > (\mathrm{Brown}) > \mathrm{Red\,7} \approx (\mathrm{Orange}) > \mathrm{Blue\,2} > \mathrm{VS}-\mathrm{Yellow}\end{aligned} \quad (3)$$
   (b) MCT dyes in parentheses undergo reductive fading on exposure in aerated water and at the same time sensitize the oxidative fading of the partner dye which has an ability to undergo oxidative fading.
4. ease with which dyes are photo-reduced or the rates of fading in an anaerobic DL-mandelate solution [3]:

$$\begin{aligned}\text{(a)}\quad & \text{Blue} - 2\text{Cu} > \text{Red7} > \text{Blue} - 1\text{Cu} \gg \text{Brown} > \text{Red4} \\ & > \text{YellowR} > \text{Cu} - \text{Pc} > \text{Orange} > \text{Yellow} > \text{Blue2}\end{aligned} \tag{4}$$

According to Griffiths and Kramer et al. [9–12] singlet oxygen oxidizes the hydrazone-form of an azo dye and breaks the azo group, i.e. oxidative fading. Photoreduction of azo dyes may also occur via the azo-configuration [13], although it has not yet been established whether the hydrazone-form is also photo-reduced, or not. When the 'azo group' in a dye exists predominantly as the hydrazone-form, the dye may show low resistance to oxidative fading and high fastness to reductive fading as shown by VS-Yellow as a typical example [1]. Dyes can generally be considered to have an opposite relationship between reductive and oxidative fading, but this relationship seems to hold only in the fading of a limited number of dyes. Thus, Yellow and VS-Yellow, which are concluded to exist considerably or exclusively as the hydrazone-form have low light fastness to oxidative fading, while Yellow R, Orange and Brown, in the azo-form have the reverse tendency. Many dyes seem to exist as a mixture of azo- and hydrazone-forms.

Discussions in the the present paper, however, are continued on the assumption that the hydrazone-form is the species which is preferentially photo-oxidized and the azo-form is the species which is photo-reduced, although this assumption can result in some problems as yet unresolved.

In general, on exposure under aerobic conditions, reactive azo dyes which exist exclusively as the azo-form on cellulose have higher lightfastness than

TABLE 1

Relative Fading, A/A_0 (—), of Monochlorotriazinyl Dyes on Cellophane in Aqueous DL-Mandelate Solution after Exposure for 4 h, in Aerated Water for 8 h, and in Aerated Aqueous Rose Bengal (RB) Solution (1.0×10^{-5} mol dm^{-3} + 0.5 M Na_2SO_4) for 4 h.

Dyes	*Conc. on cellulose (mol kg^{-1})*	*Water in air (for 8 h)*	*Aq. RB in air (for 4 h)*	*Aq. sodium* DL-*mandelate (0.05 mol dm^{-3}, for 4 h)*		
				in N_2	*in air*	*in O_2*
Yellow	0.00651	0.861	0.708	0.961	0.977	0.904
Yellow R	0.0186	0.974	0.900	0.799	0.937	0.931
Orange	0.0136	0.975	0.939	0.910	0.952	0.963
Red 4[a]	0.0103	0.846	0.436	0.540	0.637	0.589
Red 7[a]	0.0105	0.628	0.099	0.029	0.704	0.539
Cu-Pc	0.00258	0.825	0.849	0.805	0.815	0.855
Blue-1Cu	0.0143	0.723	0.042	0.090	0.839	0.748
Blue-2Cu	0.0103	0.628	0.507	0.014	0.815	0.918
Blue 2[a]	0.0259	0.995	0.977	0.998	0.973	0.997
Brown	0.00796	0.898	0.785	0.450	0.660	0.753

[a] CI Reactive generic name.

those which exist mainly as the hydrazone-form. The first principle, therefore, for high lightfastness, is that azo dyes should exist exclusively as the azo-form. Since all dyes on cellulose sensitize the oxidative fading of partner dyes dyed in admixture, they should preferably show lower photosensitivity.

From comparison between the orders of fading (1) and (4) above, the fading for Yellow R and Brown was promoted by the addition of substrate, while that for Yellow was suppressed. This fact implies that Yellow R and Brown exist mainly in the azo-form of the azo–hydrazone tautomerism and Yellow in the hydrazone-form [3], as mentioned above. As the second principle, dyes should have a low capacity to be photo-reduced, although the necessay blocks for this still remain to be elucidated.

Analysis of the results on the effect of O_2 on the fading of dyed film

Monotonical suppression with an increase in the concentration of O_2

All the dyes examined so far sensitize by generating singlet oxygen, although the photosensitivity or quantum yield for such generation of singlet oxygen varies between dyes. Singlet oxygen may be consumed in oxidizing the hydrazone-form of azo dyes, or the semi-reduced product of the azo-form, on exposure. If dyes exist exclusively in the azo-form, singlet oxygen may oxidize the semi-reduced azo-form to regenerate the azo-form, i.e. an inhibition of reductive fading. This can be observed on the exposure of Orange and Brown on cellulose in an aerated or oxygen-saturated solution of substrate. Although it is not an azo dye, Cu-Pc showed similar fading behavior. Thus, with an increase in the concentration of oxygen, fading of Orange, Blue-2Cu, Cu-Pc, and Brown was decreased on exposure in DL-mandelate solution. Since Blue-2Cu has two kinds of azo groups showing high photoreactivity, the suppression effect by oxygen is complex but profound.

Since the fading of Yellow R in an oxygen-saturated DL-mandelate solution was almost similar to that in the aerated solution, the content of the hydrazoneform for Yellow R may be very low, even if this dye exists as a mixture of the two forms.

Suppression and promotion effects of oxygen on fading

With an increase in the concentration of oxygen, the fading of Yellow, CI Reactive Red 4, CI Reactive Red 7, and Blue-1Cu was suppressed, and was then promoted again by oxygen, unlike Orange, Brown, Blue-2Cu, and Cu-Pc. Yellow has a symmetric structure and may contain a considerable amount of the hydrazone-form, since pyrazolinyl azo dyes are known to exist mainly in the hydrazone-form [14–16]. The fading behavior noted above for

CI Reactive Red 4 and Red 7 implies that they exist as a mixture of the two forms.

In general, reactive dyes on cellulose have the potential properties to undergo oxidative and/or reductive fading, depending on their chemical structure. However, whether they show oxidative or reductive attack on exposure may also be significantly influenced by the environmental conditions. Thus, when cellulose is the environment of the reactive dyes, it may show in its character, and promote or suppress both the fading mechanisms. Thus, when cellulose absorbs water, which promotes the diffusion of oxygen, enhancement of oxidative fading and/or suppression of reductive fading may be observed [1]. When cellulose absorbs a substrate, reductive fading may be promoted.

Fading behavior of dry dyed cotton fabrics

Two step photofading in air

In the above discussion based on a series of studies [1–7], the potential properties of MCT dyes on cellulose were elucidated under wet conditions. In this section, the changes in the color differences of dry cotton fabrics dyed with these MCT dyes on exposure were measured. The features of the fading behavior on dry fabrics were evaluated in terms of the potential properties of the dyes, by taking into consideration the environmental effects which may result from the types of, or the form of, the substrate.

The values of the color differences, $\Delta E_{ab}{}^*$, of dyed cotton fabrics by exposure were initially determined as a function of the time of exposure, as shown in Fig. 1. The results showed that fading of the dyed fabrics occurred by two steps, viz. initial and subsequent fading. The chromaticness of the dyed fabrics before the exposure are listed in the figure captions. The fading behavior observed is summarized as follows:

1. the order of the magnitude for the initial fading,

$$\begin{aligned}&\text{Yellow} > \text{Orange} > \text{Red4} > \text{Yellow } R > \text{Red 7}\\ &> Cu - Pc \approx \text{Brown} \approx \text{Blue } - 1Cu \approx \text{Blue} - 2Cu \approx \text{Blue 2}\end{aligned} \tag{5}$$

2. the order of the rates for subsequent fading,

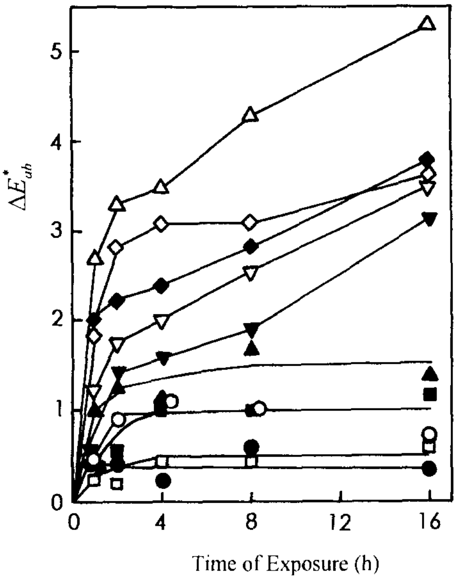
$$\begin{aligned}&\text{Yellow} \approx Cu - Pc \approx \text{Yellow } R \approx \text{Red 4} > \text{Orange} \approx \text{Red 7}\\ &\geq \text{Brown} \approx \text{Blue} - 1Cu \approx \text{Blue} - 2Cu \approx \text{Blue 2}\end{aligned} \tag{6}$$

3. the order of the magnitude for the final fading,

$$\begin{aligned}&\text{Yellow} \gg \text{Red 4} \approx \text{Orange} \approx \text{Yellow } R > Cu - Pc \gg \text{Red 7}\\ &> \text{Blue } - 2Cu \approx \text{Brown} > \text{Blue} - 1Cu > \text{Blue 2}\end{aligned} \tag{7}$$

The order of final fading seems to be determined mainly by that of the initial fading in case of the exposure for 16 h, and the magnitudes of the final fading depended upon both the factors, given by the orders (5) and (6), with some exceptions as shown in Fig. 1.

These results on the order of initial fading are considered to reflect the ease with which the dyes are photo-oxidized. However, they might be influenced by other factors since the order of the ease of oxidation was partially different from the order of initial fading. The large differences between the order (5) for initial fading and the order (2) for the ease with which the dyes were photo-oxidized were observed for CI Reactive Red 7, Blue-1Cu, Blue-2Cu, Yellow, Yellow R, and Orange. The former three dyes showed a smaller initial fading than that expected from the potential properties (2), while in contrast, the latter three dyes showed a larger initial fading. The other four dyes, i.e. CI Reactive Red 4, Brown, Cu-Pc, and CI Reactive Blue 2, underwent fading as expected. The reasons for such differences are discussed below (cf. Sections 3.2.2 and 3.4).



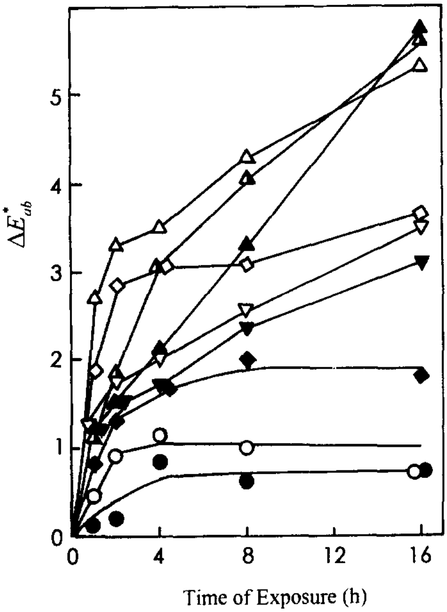
Dye	Yellow	Yellow R	Orange	Red 4	Red 7	Blue-1Cu	Blue-2Cu	Cu-Pc	Blue 2	Brown
Symbol	△	▽	◇	◆	▲	□	■	▼	●	○
L^*_{ab}	87.12	81.88	75.81	61.30	52.16	52.80	46.84	64.47	62.22	51.84
a^*	−11.21	3.17	17.99	47.45	43.64	11.16	9.77	−24.66	−10.34	29.20
b^*	59.13	53.97	60.20	−4.46	−6.03	−26.10	−30.92	−28.84	−20.74	15.98

Fig. 1. Relationship between color variation ΔE_{ab}^* after exposure and the time of exposure for cotton fabrics dyed with monochlorotriazinyl reactive dyes. The values of chromaticness for each sample before exposure are shown.

As mentioned above, the magnitude of initial fading does not always seem to be dependent upon the potential properties of these dyes. Since the testing method for the light fastness examines the color differences of test fabrics by comparing with the blue scale after exposure for a given time, the results may approximate the initial and/or final fading, as in the case of the present study, and may not always reflect the potential properties of these dyes. Compared with the fading on cellulose films, that on cotton fabrics may be strongly affected by the surface, since the fabrics have a much larger surface area than films (cf. Section 3.3).

Effect of surface dyeing of dyed fabrics on the fading

In order to investigate why the initial fading occurred prominently on the dyed fabrics, the effects on the fading of migration time, and of the duration



Dye	Migration time	L^*_{ab}	a*	b*	Symbols
Yellow	60 min	86.74	−10.49	58.57	◭
Yellow	120 min	85.84	−10.46	58.63	▲
Yellow R	120 min	82.20	3.26	50.86	▼
Orange	120 min	73.72	19.36	58.85	◆
Brown	120 min	52.27	28.34	14.27	●

Fig. 2. Effect of migration time on the relationship between color variation ΔE_{ab}^* after exposure and the time of exposure for cotton fabrics dyed with monochlorotriazinyl reactive dyes. The chromaticness values of each sample before exposure are shown above. (The same symbols are used for the same four dyes, whose migration time is for 30 min, as those in Fig. 1.)

of neutral exhaustion dyeing before the fixation, which may be a measure of surface dyeing, were measured. The cotton fabrics were dyed in a beaker (1 liter) at 80°C by circulating the dye liquor with a glass rod without using a dyeing machine. Especially for fabrics dyed with dyes of higher substantivity, surface dyeing may occur in the initial period of dyeing. In this section, Yellow, Yellow R, Orange, and Brown were used to examine the effect of surface dyeing by changing the migration time. The results, which are shown in Fig. 2, may be analyzed as follows:

Yellow
With prolongation of migration, the initial fading was still apparent, but decreased, while the rate of subsequent fading was increased, giving, as a result almost unchanged final fading. A decrease in the surface dyeing of this dye resulted in a noticeable decrease in the initial fading but little influence on the final fading.

Orange and Brown
The initial and final fading for the dyed fabrics over a longer migration time were decreased, i.e. an increase in the lightfastness. A decrease of initial fading caused a smaller final fading and the subsequent fading of these dyes was practically suppressed. The fading of dyes which have a potential property to undergo reductive fading on dry cellulose may thus be suppressed after the initial fading at the surface. An even distribution of Orange in cellulose, or removal of the surface dyeing, made a large improvement to the lightfastness.

Yellow R
Since Yellow R, a monoazo dye, has a high leveling property, unlike the disazo dyes (Yellow, Orange, and Brown) the increase of migration seems to give a small improvement on the fading.

Thus, the effects of larger surface area may become apparent in the initial period of exposure, since the large area promotes the oxidative fading and give stronger exposure of the dye which exists near the surface of the substrate. In the fading behavior, only the potential properties of the dye was manifested, but these may be modified by various environmental factors and by the distribution state of the dye in the substrate. From the results of the four dyes which were dyed with a migration time of 2 h (Fig. 2), the differences in the initial fading among the dyes examined became inconspicuous, and the order of the magnitude for the final fading was:

$$\begin{gathered}\text{Yellow} \gg \text{Red 4} > \text{Yellow } R \approx Cu - Pc \gg \text{Orange} > \text{Red 7} \\ > \text{Blue} - 2\text{Cu} \approx \text{Brown} > \text{Blue} - 1\text{Cu} > \text{Blue 2}\end{gathered} \tag{8}$$

In order to examine these phenomena, the surface effects of substrate on fading were than further investigated by exposure of cellophane dyed with these dyes.

PHOTOFADING OF DYED CELLULOSE FILMS IN AIR

The fading behavior of MCT dyes on cellophane films is shown in Figs 3 and 4 as a function of the time of exposure. The influence of dye concentration on the fading may be observed by comparing the fading behavior of the dyes on films dyed at higher dye concentration (Fig. 4) relative to pale dyeing (Fig. 3). The order of the magnitude for the rates of fading for 10 MCT dyes on cellulose films dyed in pale and deep shades is as follows:

1. Fading in pale shade (Fig. 3),

$$\begin{gathered}\text{Yellow} > \text{Yellow } R > Cu - Pc > \text{Red4} > \text{Orange} > \text{Blue} \\ -2Cu > \text{Blue} - 1Cu \approx \text{Red } 7 \gg \text{Brown} > \text{Blue } 2\end{gathered} \tag{9}$$

2. Fading in deep shade (Fig. 4),

$$\begin{gathered}\text{Yellow} > \text{Blue} - 2Cu > Cu - Pc > \text{Yellow } R > \text{Orange} > \text{Red } 4 \\ > \text{Blue} - 1Cu \approx Red\,7 \approx \text{Brown} > \text{Blue } 2\end{gathered} \tag{10}$$

In general, MCT dyes on dry films show a slower fading than that on dry fabrics and wet films, and no or smaller initial fading compared to dry fabrics. The small fading of the dyed films may be attributed to the relatively smaller surface or to the more closed structure of the substrate.

Comparison of the order (9) on dry films with the order (8) on dry fabrics, shows agreement, with the exception of CI Reactive Red 4 and Red 7, if the small differences in their order are neglected. CI Reactive Red 4 and Red 7 showed larger fading on dry fabrics than that on dry films, which may be attributed to the relatively larger initial fading on dry fabrics than that on films. CI Reactive Red 4 and Red 7, as well as Brown, near the surface of cellulose of cotton fabrics may suffer oxidative fading in the initial period of exposure due to the very large surface area.

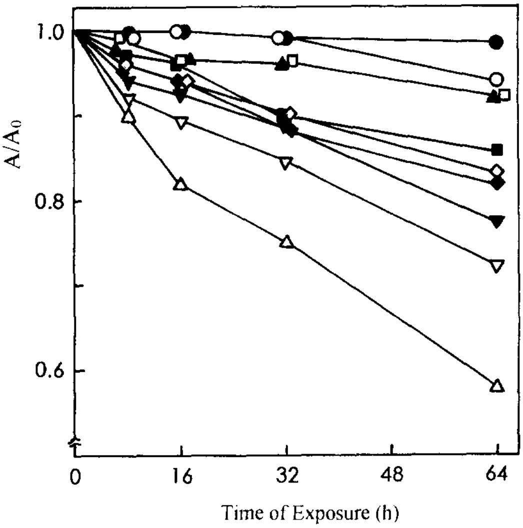
The general features of fading on cellulose are not influenced by the form (fabrics or films) of the substrate, but show some relative effects.

Effect of concentration on the rate of fading of dyed film in air

In order to evaluate the concentration effect on fading, the fading behavior on films dyed in different shades is summarized, for the initial and final fading, in Table 2. Judging from the fact that the time of exposure for the final fading is eight times as long as that for initial fading, Table 2 shows that little initial fading exists in the case of films. Thus, only the final fading can be compared among the dyes examined.

Except for Blue-2Cu and Cu-Pc, the orders (9) and (10) were very similar to each other. As in the case of Fig. 1, Yellow showed the largest rate of fading, while Blue 2 and Brown and Blue-l Cu showed the smallest fading. The rates of fading for the other dyes were in between these. The exceptional behavior of Blue-2Cu and Cu-Pc may be attributed to the very high photosensitivity shown by the order (3). These dyes at higher concentration thus generate a larger amount of singlet oxygen to promote self-fading, as in the case of CI Reactive Red 22 [4]. Thus, Blue-2Cu of 4 times higher concentration promoted fading by a factor of 1.6, while Cu-Pc of 5 times higher concentration gave the same fading, compared to the fading of pale dyeings. Since there must be a filter effect in deeply dyed films, promotion more than is actually observed may influence the fading of these dyes. The fading of films dyed by the other dyes in deeper shades was, in general, slower than that in pale shade. This may be attributed to the filter effect, although this explanation is only qualitative.

As noted above, the 10 MCT dyes manifested their potential photo-chemical properties in their fading behavior depending upon the environmental



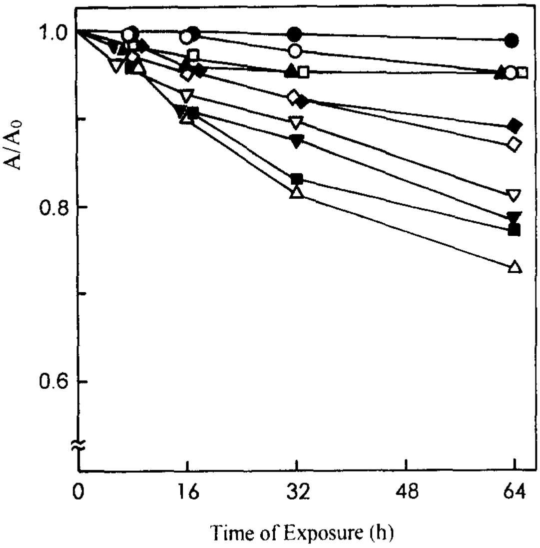
Dye	Yellow	Yellow R	Orange	Red 4	Red 7	Blue-1Cu	Blue-2Cu	Cu-Pc	Blue 2	Brown
Symbol	△	▽	◇	◆	▲	□	■	▼	●	○

Fig. 3. Relationship between A/A_0 and the time of exposure for monochlorotriazinyl reactive dyes on cellulose films dyed in pale shade (cf. Table 2).

conditions. The fading of dyes on substrate, therefore, may be explained in terms of photochemistry of the dyes, whose triplet state may interact with the substrate, or oxygen, etc. The presence of water has a profound influence on their interaction.

The observation on the fading behavior for the 10 MCT dyes on cotton fabrics and cellophane films, and their analyses in this present study, is almost completely contradictory with the aggregation theory of photofading proposed by Giles et al. [17–20] as discussed below. In many cases, these authors carried out fading experiments on dyed films whose absorbance were larger than 0.2. Rabek [21] has suggested, that the exposure of dyed films whose absorbance is larger than 0.05 has a filter effect. The excited states of dyes have a concentration profile within an absorbing medium depending on the absorbance values. Thus, in the case of absorbance >0.05, the fading should occur preferentially from the incident surface of the medium. Since factors other than the filter effect may also influence their fading rates, the contribution of the filter effect must be taken into consideration in the analysis of fading rates, a factor which Giles et al. [18–20] seemed to neglect.

The photofading of dyes on various substrates, therefore, may be explained by photochemistry of the dye themselves. The reason why these dyes show such fading behavior is discussed in Section 3.4.



Dye	Yellow	Yellow R	Orange	Red 4	Red 7	Blue-1Cu	Blue-2Cu	Cu-Pc	Blue-2	Brown
Symbol	△	▽	◇	◆	▲	□	■	▼	●	○

Fig. 4. Relationship between A/A_0 and the time of exposure for monochlorotriazinyl reactive dyes on cellulose films dyed in deeper shade (cf. Table 2).

RELATION BETWEEN THE FADING ON DRY CELLULOSE AND THEIR POTENTIAL PROPERTIES

Yellow

On exposing the dyed films in an anaerobic DL-mandelate solution, Yellow underwent a small reductive fading, while on exposure in aerobic solution, reductive fading was was a little suppressed, and an increase in the concentration of oxygen resulted in oxidative fading, with an increase in the overall rate of fading (Table 1). Thus, Yellow has a large ability to be photo-oxidized, and a small one to be photo-reduced. The former property is promoted by oxygen, and the latter one suppressed by it. Since the photooxidation on dyed fabrics may be manifested on the initial irradiation and a decrease in the surface area diminishes the initial fading, Yellow undergoes such a fading behavior, as shown in Figs 1–3.

CI Reactive Blue 2

As shown by the orders (1)–(6), CI Reactive Blue 2 has the highest resistance to photo-oxidation and reduction. Besides the small molar extinction coefficient, the reason why this dye has such low photoreactivity has not yet been elucidated, but it is interesting that a dye with such parameters does exist.

TABLE 2

Initial and Final Relative Fading,[a,b] A_8/A_0 and A_f/A_0, of Monochlorotriazinyl Reactive Dyes on Cellulose Films Dyed in Pale and Deep Shades

	Dyed in pale shade			*Dyed in deep shade*		
Reactive dyes	A_0 at λ_{max}	A_8/A_0	A_f/A_0	A_0 at λ_{max}	A_8/A_0	A_f/A_0
Yellow	0.262	0.898	0.581	0.606	0.958	0.727
Yellow R	0.253	0.919	0.723	0.838	0.957	0.810
Orange	0.190	0.962	0.831	0.831	0.976	0.869
Red 4[c]	0.216	0.947	0.824	0.902	0.984	0.893
Red 7[c]	0.173	0.976	0.922	0.795	0.982	0.950
Blue-1Cu	0.203	0.990	0.923	0.991	0.986	0.948
Blue-2Cu	0.254	0.970	0.859	0.932	0.954	0.768
Cu-Pc	0.103[d]	0.953	0.775	0.496[d]	0.977	0.782
Blue 2[c]	0.267	0.996	0.985	0.863	0.998	0.985
Brown	0.181	0.988	0.928	0.844	0.996	0.948

[a] Initial relative fading = A_8/A_0 (—), where A_0 and A_8 are the absorbance before and after exposure for 8 h, respectively.

[b] Final relative fading = A_f/A_0 (—), where A_f is the absorbance after exposure for 64 h.

[c] CI reactive generic name.

[d] Absorbance at isosbestic point.

Brown

Brown has a photochemical reactivity exactly opposite to that of Yellow, although it has potentially a medium ease with which it is photo-oxidized, it has not so high resistance [5] to photo-reductive attack in the absence of oxygen (Figs 1–3). Since the azo groups further away from the MCT groups have a larger ease to be photo-oxidized than the azo groups nearer to the MCT groups [5], Brown also has a tendency to be photo-oxidized, as shown by the order (2) although it suffered reductive fading on exposure in aerobic water [7]. An increase in the concentration of oxygen in aqueous mandelate suppressed the rate of reductive fading (cf. Section 3.3 1 and Table 1). A decrease in the surface dyeing gave noticeable improvement in the initial fading on cotton fabrics, that is why this dye on cotton fabrics shows a fair initial fading, and a small rate of subsequent fading.

Yellow R and Orange

From the orders (1) and (2), these dyes have a similar small susceptibility for photo-oxidation. However, they showed considerable initial (probably oxidative) fading on cotton fabrics and slow rates of subsequent (probably reductive) fading (Fig. 1). Their initial fading disappeared in the case of cellulose film, resulting in their improved lightfastness on film compared with fabrics. Because the photo-reductivity of Orange was smaller than that of Yellow R (cf. Table 1), the lightfastness of Orange on films is higher than that of Yellow R (Figs 3 and 4). When Orange was dyed under conditions so that the surface dyeing was small, the lightfastness was improved (Fig. 2).

Cu-Pc

This dye suffers considerable fading by both photo-oxidative and reductive attacks. Probably due to the very high photosensitivity, it undergoes photo-oxidative fading on exposure in aerated water, while on exposure in DL-mandelate solution, the rate of reductive fading is decreased with an increase in the oxygen concentration. But the initial fading on dyed fabrics was not large due to the low photoreactivity to oxidative attack, although the initial fading was the same. The dye showed considerable rates of subsequent fading. Thus, the lightfastness, of Cu-Pc on cotton fabrics is moderate, and is improved on films.

CI Reactive Red 4, CI Reactive Red 7, Blue-1Cu, and Blue-2Cu

As shown in Table 1, CI Reactive Red 7, Blue-1Cu, and Blue-2Cu have very high photochemical reactivity to both oxidative and reductive attack. Blue-

2Cu suffered reductive fading on exposure even in aerated water, like Yellow R, Orange, and Brown [5–7]. On exposure in DL-mandelate solution, the rates of reductive fading for two Cu-complex dyes were astonishingly suppressed by aerating the solution, and the rate for Blue-2Cu was further decreased with an increase in the concentration of oxygen, but the rates of (probably oxidative) fading for CI Reactive Red 7 and Blue-1Cu were promoted again by such an increase.

On the other hand, CI Reactive Red 4 also has high reactivity to both the oxidative and reductive attack, though not so high as CI Reactive Red 7. This dye showed similar fading behavior to that of CI Reactive Red 7, but these two red dyes showed a large initial fading, unlike the two Cu–complex dyes.

In spite of the extraordinarily high reactivity to both oxidative and reductive attacks under wet conditions, these four dyes have ordinary rates of fading on dry cellulose, an antagonism between oxidative and reductive fading. Their lightfastness is fair but not ideal, because they have low fastness to the compound effects of light and water or substrate.

The photo-oxidation of the two Cu–complex azo dyes may be partially suppressed by the introduction of copper atom [22, 23]. However, the copper atoms in these dyes can be easily abstracted by immersing the dyed cellulose in aqueous histidine and EDTA [24]. The fading behavior of the two dyes whose copper atoms were abstracted has been examined elsewhere [25]. It was observed that the initial fading and the rates of subsequent fading for the Cu–complex dyes were a little lower than those for the original dyes. Thus, Cu–complex formation has been confirmed to be not so effective in improving lightfastness, since the parent dyes have only fair lightfastness [22] (cf. Table 1).

SUMMARY

On exposure of cellulose film dyed with reactive dyes in various aqueous solutions, oxidative and/or reductive fading occurred depending firstly upon the chemical structure of dyes and secondly upon the environmental conditions. The addition of substrate promoted reductive fading or suppressed oxidative fading, while an increase in the concentration of oxygen gave the reverse effects, the promotion of oxidative fading and the suppression of reductive fading. However, the potential photochemical properties of reactive dyes were manifested in the fading behavior on exposing in various aqueous solutions, although they were influenced by the environmental conditions.

On exposure of dry dyed cellulose, the rates of fading were considerably lowered and some potential properties seemed not to be operative. Some dyes on cotton fabrics suffered a large initial fading from the large surface and of the fibers. With an increase in the dye concentration on dry cellulose, an improvement of lightfastness was observed, which was almost explained by the filter effect, while the rates of fading for the dyes with very high photosensitivity was in contrast, increased. Some dyes with high photoreactivity showed slow fading, probably due to the compensation effect of conflicting properties.

Thus, by analyzing the fading behavior of 10 MCT dyes on dry cellulose, it was shown that some dye properties were very operative in the fading behavior. But the increase in lightfastness by the compensation effect may not be desirable, because the fading of dyes may be severely influenced by the change of environmental conditions.

Thus, reactive dyes have potentially diverse properties which are sometimes contradictory to each other and suffer various kinds of photodecomposition on cellulose. The photofading of dyes on cellulose must, therefore, be considered in the chemistry of dyes and their interaction with the surroundings.

ACKNOWLEDGEMENTS

The authors thank Nippon Kayaku Co. Ltd for their cooperation in the preparation of this paper. This work is supported by a Grant-in-Aid for Scientific Research (C) by the Minister of Education, Science and Culture, Japan, to whom our thanks are due.

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