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# Photosensitization and Simultaneous Reductive or Oxidative Fading of Monochlorotriazinyl Reactive Dyes on Cellulose under Wet Conditions

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*ABSTRACT*

*The photosensitivity of ten monochlorotriazinyl (MCT) reactive dyes (three monoazo, five disazo, a copper phthalocyanine, and an anthraquinone) was estimated by exposing the binary mixtures of each MCT dye and an aminopyrazolinyl azo dye on cellulose in aerated water. The ease with which MCT dyes were photo-oxidized was examined by use of Rose Bengal. MCT dyes on cellulose dyed in admixture underwent reductive or oxidative fading depending on the own properties and on the conditions of exposure, and sensitized the oxidative fading of the partner dyes at the same time. The concentration dependence of fading for two dyes on cellulose was examined under wet conditions.*

## 1 INTRODUCTION

The photofading of vinylsulfonyl (VS) reactive dyes on cellulose under wet conditions occurs via photo-oxidation by singlet oxygen.[1-5] However, some VS dyes on cellulose, such as C.I. Reactive Red 22 and Black 5, are

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photo-reduced on exposure in deaerated water, irrespective of the absence of substrate.[6] The fading of MCT dyes under wet conditions has been explained by Datyner *et al.*[7] in terms of a radical mechanism. In a previous paper,[8] it was reported that seven monochlorotriazinyl (MCT) reactive dyes were photo-reduced on exposure in deaerated water. On exposure of the MCT dyes in aerated water, four MCT dyes were photo-reduced, and the other three photo-oxidized. Thus, the chemical structure of the dyes, and the atmospheric conditions of the exposure, determine whether MCT dyes on cellulose undergo oxidative or reductive fading.[6,8]

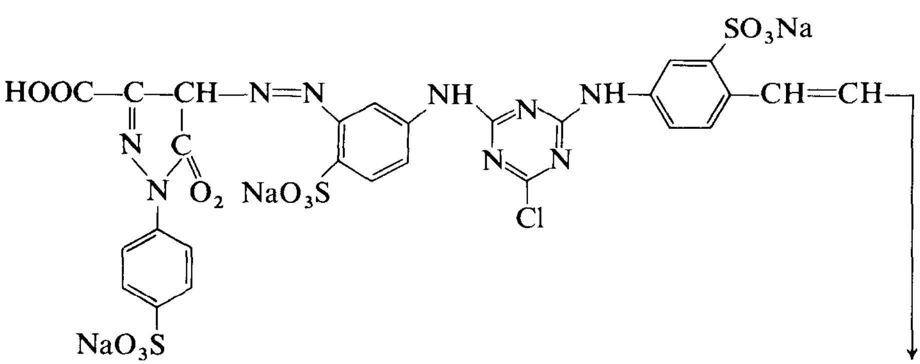
In the present paper, the fading behavior of ten MCT dyes is examined, to elucidate whether they sensitize the oxidative fading of their partner dyes on cellulose, whether dyed in admixture or not, when they undergo reductive or oxidative fading on exposure in aerated water. Since VS-Yellow undergoes only oxidative fading,[6] whether MCT dyes undergoing reductive fading on exposure in aerated water sensitize the oxidative fading, or not, can be clarified by examining the fading of VS-Yellow on cellulose dyed in admixture with MCT dyes. As in the case of VS dyes,[3] the photosensitivity, and the ease with which MCT dyes are oxidized, are estimated for these dyes. The fading behavior of MCT dyes on cellulose is discussed according to the fading mechanism examined in a previous study.[8]

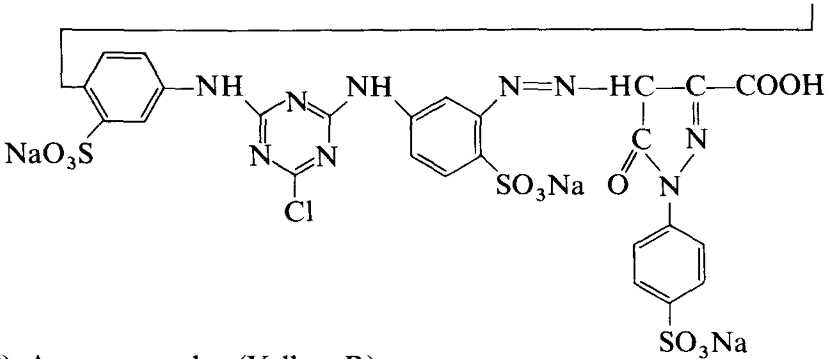
## 2 EXPERIMENTAL

### 2.1 Dyes used

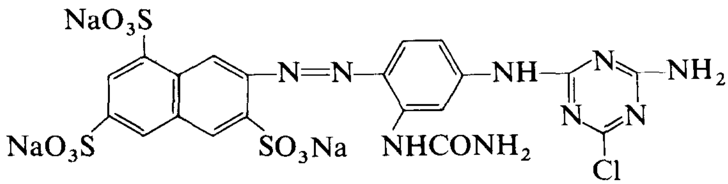
Ten MCT dyes, an aminopyrazolinyl VS dye and Rose Bengal (RB) were used. The chemical structure of the dyes used and the abbreviations used in the text are as follows:

(1) A stilbene pyrazolinyl disazo dye (Yellow)

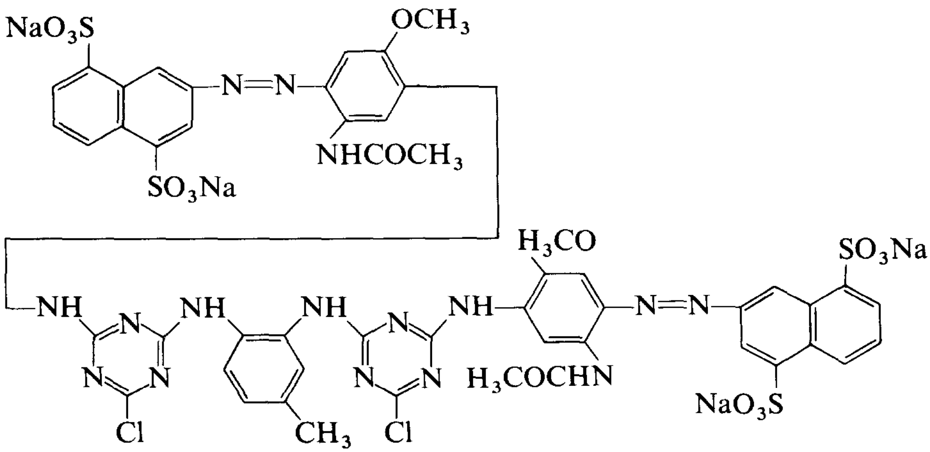




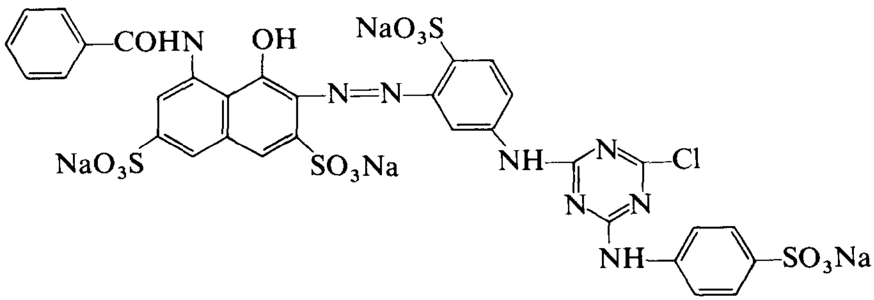

(2) A monoazo dye (Yellow R)



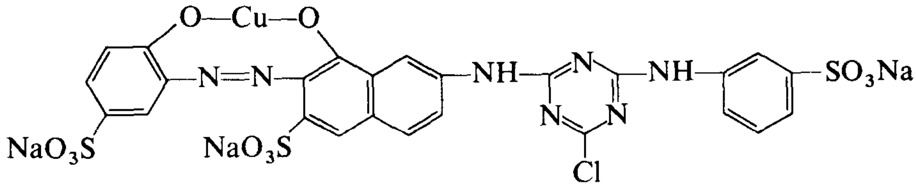

(3) An *o*-phenylenediamine disazo dye (Orange)



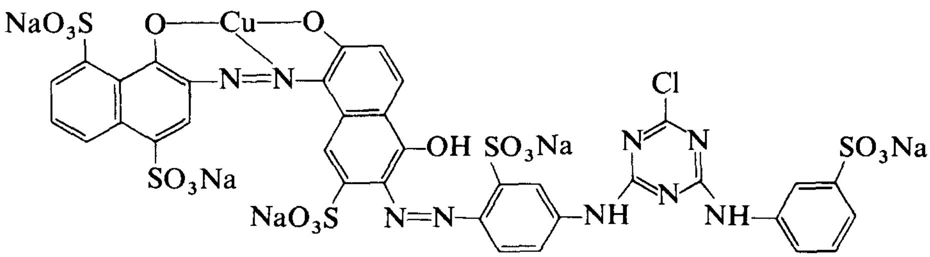

(4) C.I. Reactive Red 4; C.I. 18105 (Red 4)



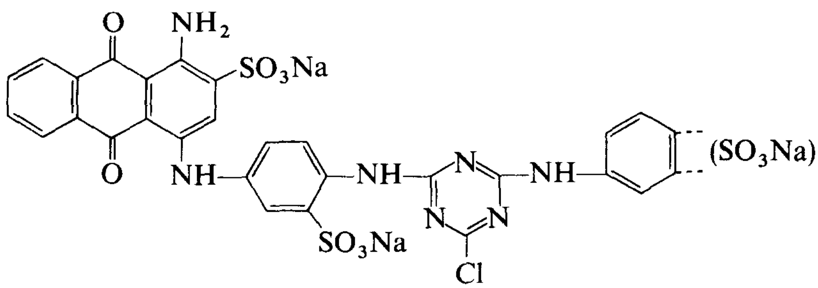
(5) C.I. Reactive Red 7; C.I. 17912 (red 7)



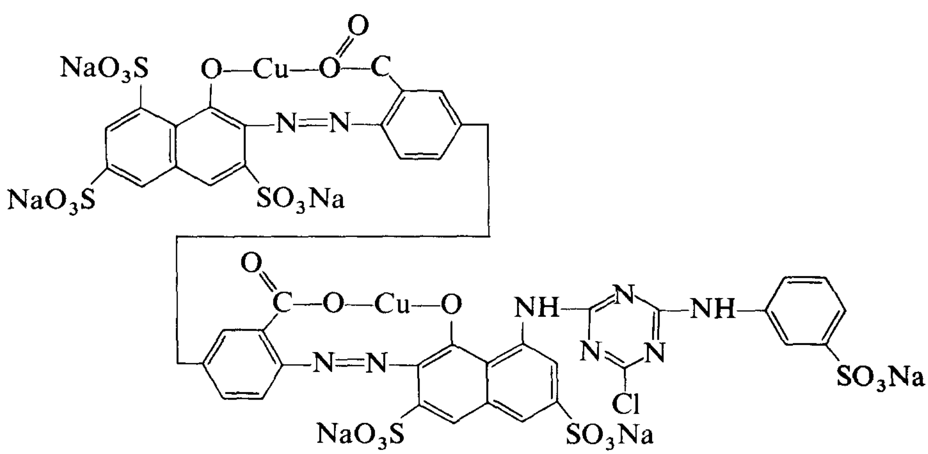

(6) A 1:1 Cu-complex disazo dye (Blue-Cu)



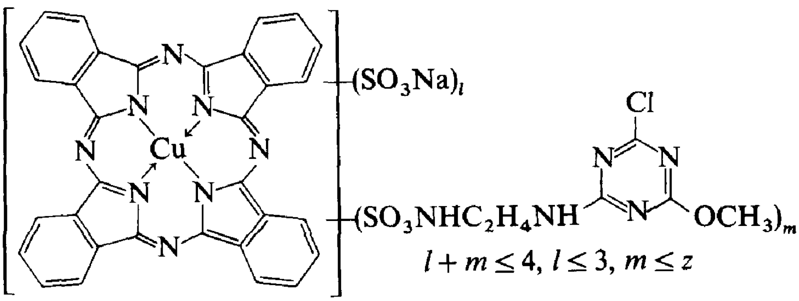

(7) C.I. Reactive Blue 2; C.I. 61211 (Blue 2)




(8) A 1:2 Cu-complex disazo dye (Blue-2Cu)

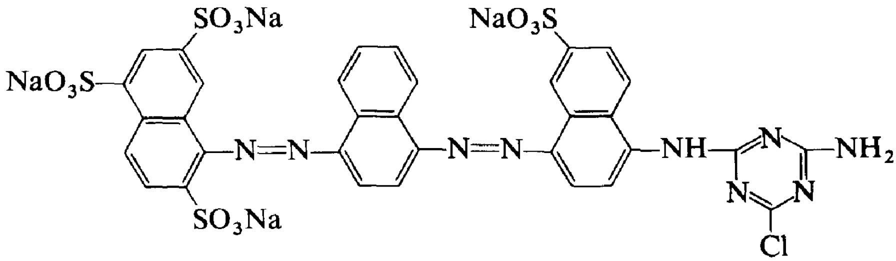


(9) A copper phthalocyanine dye (Cu-Pc)

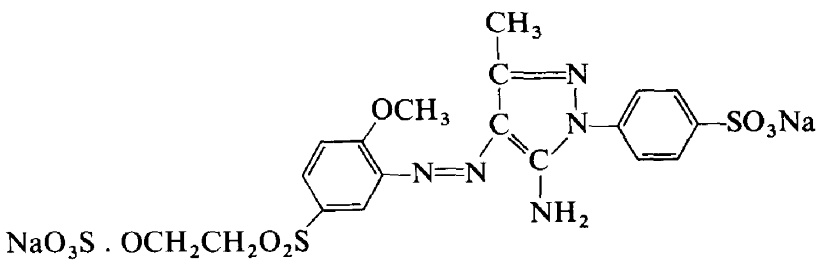



$l+m \leq 4$, $l \leq 3$, $m \leq z$

(10) A disazo dye (Brown)




(11) An aminopyrazolinyl azo dye (VS-Yellow)




MCT dyes used were supplied by Nippon Kayaku Co. Ltd, Tokyo, and VS-Yellow by Sumitomo Chemical Co. Ltd, Osaka. Red 7 was a commercial product manufactured by Ciba-Geigy Corp. They were the same as those used in previous studies,[8,9] and were used without further purification.

## 2.2 Dyeing and exposure

Cellophane films (# 300, manufactured by Tokyo Cellophane Sheet Co. Ltd, Tokyo) were dyed by the method reported previously.[8] In the case of Blue-Cu and Cu-Pc, the exhaustion was lower than 80%, although it was adjusted by the addition of sodium sulfate (≤75 g $dm^{-3}$). Sodium carbonate (20 g $dm^{-3}$) was added to obtain fixation. After dyeing, the dyed films were scoured with 10% aqueous dimethylformamide (DMF) solution at 60°C until no coloration of the solution occurred, and they were then scoured in boiling water containing non-ionic surfactant (2 g $dm^{-3}$) to remove DMF. The method of exposure and the apparatus used were the same as previously described;[1,2] Other chemicals used were of reagent grade.

## 3 RESULTS AND DISCUSSION

### 3.1 Fading of single dyeings

Some VS dyes,[1,2] and many other dyes[10] show on cellulose a concentration dependence on the rate of fading. But dyes having both a high photosensitivity and a high ease with which they are oxidized may have the possibility to exhibit a positive or unusual concentration dependence of fading under wet conditions, as in the case of C.I. Reactive Red 22.[2,3] The fading properties are discussed later, but in the MCT dyes examined, Red 7, Blue-Cu and Cu-Pc may have the possibility of showing such

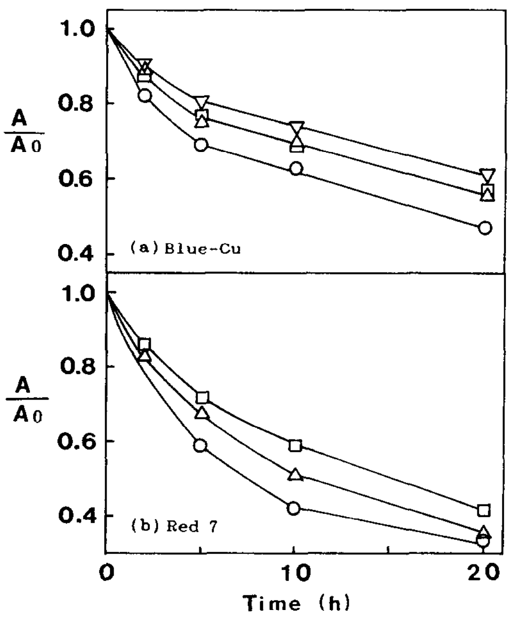



**Fig. 1.** Concentration dependence of fading for (a) Blue-Cu and (b) Red 7 on cellophane dyed singly at various concentrations when exposed under wet conditions. Concentrations of Blue-Cu on cellulose were (○) $3{\cdot}87 \times 10^{-3}$, (Δ) $7{\cdot}91 \times 10^{-3}$, (□) $1{\cdot}38 \times 10^{-2}$, and (∇) $1{\cdot}98 \times 10^{-2}$ mol/kg, and those for Red 7 were (○) $2{\cdot}96 \times 10^{-3}$, (Δ) $6{\cdot}80 \times 10^{-3}$ and (□) $1{\cdot}21 \times 10^{-2}$ mol/kg.

a fading behaviour. The oxidative fading for Yellow, Red 4, Red 7, Blue-Cu, Cu-Pc, and Blue 2 on cellulose in aerated water was confirmed by the absorption spectra of the photodecomposition products after exposure in aerated water, and the reductive fading for Yellow R, Orange, Brown, and Blue-2Cu has been previously reported.[8,9]

The relative rates of fading on water-swollen cellulose for Blue-Cu and Red 7 were initially examined at various concentrations. The results are shown in Fig. 1, in which the ratios of absorbance ($A/A_0$; $A_0$ & $A$: absorbance at the wavelength $\lambda_{max}$ of the maximum absorption before and after the exposure for a given time) are used to evaluate the rate of fading. The concentration dependence of the rate of fading for Cu-Pc has been elsewhere reported.[9] Three dyes, including Cu-Pc, showed a usual concentration dependence of fading.

Although the relative rates of fading decreased with increase in the dye concentration on cellulose, the order of the relative rates of fading for the MCT dyes on cellulose on exposure in aerated water can be estimated over a range of concentrations in which the individual dye shows a smaller concentration dependence on the rate of fading. Cellophane films were dyed by individual MCT dyes so as to give an absorbance of 0·8–1·1 at $\lambda_{max}$. The rates of fading for ten MCT dyes at a given concentration in aerated water are shown in Fig. 2. In order to clarify the order of the rate of fading, the $A/A_0$ values were measured for exposure in aerated water for 8 h (Table 1). The order of the rate of fading was as follows:

Red 7 > Blue-Cu = VS-Yellow > (Blue-2Cu) > Cu-Pc > Red 4 >
Yellow > (Brown) > (Orange) > (Yellow R) > Blue 2 (1)

The dyes in parentheses undergo reductive fading on exposure in aerated water, and the others oxidative fading.[8,9] It is noted, however, that the lightfastness of reactive dyes is not determined solely by the fading mechanism, i.e., whether oxidative or reductive fading occurs.

On the other hand, on exposure in deaerated water in a nitrogen atmosphere, no fading of Blue-Cu, Blue 2, and Cu-Pc was observed[9] as in the case of VS-Yellow and some other VS dyes,[1,2] while the other dyes examined showed reductive fading.[6,8]

### 3.2 Sensitized fading by Rose Bengal

The ease with which MCT dyes were oxidized was examined by exposing the dyes on cellulose in aqueous RB solution. The values of $A/A_0$ after exposure for 4 h are summarized in Table 1. The fading behavior

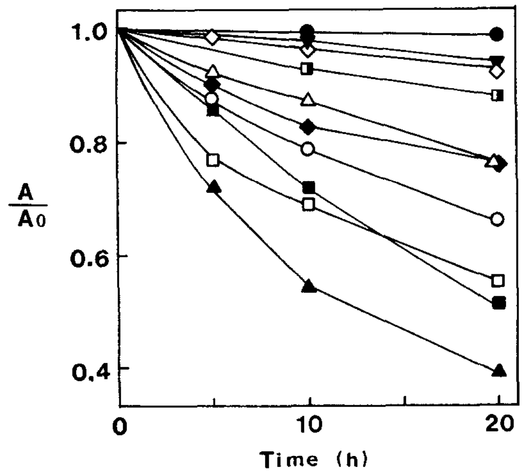



**Fig. 2.** Relative fading for VS dyes on cellophane under wet conditions. The concentrations (mol/kg) on cellulose were (●) $3{\cdot}87 \times 10^{-2}$ for Blue 2, (▼) $1{\cdot}86 \times 10^{-2}$ for Yellow R, (◇) $1{\cdot}39 \times 10^{-2}$ for Orange, (◨) $9{\cdot}24 \times 10^{-3}$ for Brown, (Δ) $5{\cdot}06 \times 10^{-3}$ for Yellow, (♦) $1{\cdot}08 \times 10^{-2}$ for Red 4, (O) $5{\cdot}17 \times 10^{-3}$ for Cu-Pc, (□) $1{\cdot}38 \times 10^{-2}$ for Blue-Cu, (■) $9{\cdot}73 \times 10^{-3}$ for Blue-2Cu, and (▲) $1{\cdot}21 \times 10^{-2}$ for Red 7, respectively.

of MCT dyes on cellulose in aerated RB solution has been reported elsewhere[8,9] in order to examine their oxidative fading. The rates of fading for MCT dyes on cellulose on which RB was adsorbed during the exposure, were in the order:

VS-Yellow > Red 7 > Blue-Cu > Blue-2Cu > Red 4 ≑ Yellow >
Brown > Yellow R > Cu-Pc > Orange > Blue 2 (2)

Although the value of $A/A_0$ for Blue-Cu after exposure for 4 h in RB solution was smaller than that for Red 7, the values for a short time were the reverse. From the absorption spectra of the photodecomposition products for the MCT dyes examined on exposure in an aerated RB solution, all the fading in RB solution was confirmed as being due to photo-oxidation.[8,9] Although Yellow R, Orange, Blue-2Cu, and Brown undergo reductive fading on cellulose on exposure in aerated water, an increase in the concentration of singlet oxygen generated by RB almost completely inhibited the reductive fading and caused an oxidative fading.

The second-order rate constants ($k_0$) of the reaction for MCT dyes with singlet oxygen were estimated by the method as described earlier[3] from the values of $A/A_0$ on exposure in an aerated RB solution (Table 1). Compared with the values for other VS dyes (0·66 for C.I. Reactive Red 22 and 0·24 for Black 5), the values for Red 7, Blue-Cu, and Blue-2Cu are very large and show a low stability to oxidative fading, although VS-Yellow has the largest value of $k_0$.[3]

TABLE 1
Relative Fading, $A/A_0(-)$, of Monochlorotriazinyl Dyes on Cellophane on Exposure in Aerated Water for 8 h and in Aerated Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm$^{-3}$ + 0·5 mol dm$^{-3}$ $Na_2SO_4$) Solution for 4 h, the Rate Constant, $k_0$ (dm$^3$ mol$^{-1}$ s$^{-1}$), of the Reaction with Singlet Oxygen and the Apparent Photosensitivity, f(−)

| *Dyes* | *Conc. (mol/kg)* | *$A/A_0$ on exposure in* | | *$k_0$* | *f* |
|---|---|---|---|---|---|
| | | *aerated water for 8 h* | *aerated RB soln for 4 h* | | |
| Yellow | $5{\cdot}89 \times 10^{-3}$ | 0·880 | 0·708 | 0·28 | $0{\cdot}05_3$ |
| Yellow R | $2{\cdot}32 \times 10^{-2}$ | (0·980)[a] | 0·945 | 0·053 | $0{\cdot}07_6$ |
| Orange | $1{\cdot}41 \times 10^{-2}$ | (0·975)[a] | 0·972 | 0·027 | $0{\cdot}02_2$ |
| Red 4 | $1{\cdot}53 \times 10^{-2}$ | 0·860 | 0·705 | 0·28 | $0{\cdot}08_8$ |
| Red 7 | $7{\cdot}13 \times 10^{-3}$ | 0·552 | 0·099[c] | 3·7 | $0{\cdot}01_7$ |
| Blue-Cu | $1{\cdot}41 \times 10^{-2}$ | 0·723 | 0·042[d] | 3·2 | $0{\cdot}03_7$ |
| Blue 2 | $2{\cdot}59 \times 10^{-2}$ | 0·988 | 0·985 | 0·014 | $0{\cdot}01_6$ |
| Blue-2Cu | $7{\cdot}13 \times 10^{-3}$ | (0·773)[a] | 0·507 | 0·48 | $0{\cdot}1_6$ |
| Cu-Pc | $2{\cdot}46 \times 10^{-3}$ | 0·825 | 0·960 | 0·038 | $0{\cdot}1_9$ |
| Brown | $5{\cdot}92 \times 10^{-3}$ | (0·940)[a] | 0·915 | 0·082 | $0{\cdot}03_1$ |
| VS-Yellow | $1{\cdot}56 \times 10^{-2}$ | —[b] | —[e] | 6·9 | $0{\cdot}01_5$ |

[a] The values in parentheses show the relative rates of reductive fading.
[b] The values of $A/A_0$ for VS-Yellow were 0·868 for 2 h, 0·834 for 3 h, and 0·722 for 8 h, respectively.
[c] Those for Red 7 were 0·839 for 10 min, 0·702 for 20 min, and 0·497 for 40 min, respectively.
[d] Those for Blue-Cu were 0·884 for 10 min, 0·720 for 20 min, and 0·488 for 40 min, respectively.
[e] The values of $A/A_0$ for VS-Yellow were 0·851 for 5 min and 0·712 for 10 min, respectively.
The values of $A_0$ were in the range of 0·8 to 1·1.
Subscript numbers = second significant figures.

### 3.3 Fading in mixture dyeing

Since the differences between the order of (1) and (2) may be attributed to differences in the photosensitivity between the individual dyes and RB, the fading of MCT dyes dyed in admixture on cellulose was examined in order to elucidate the photosensitivity of MCT dyes under wet conditions. The fading behaviour for Blue-Cu on cellulose dyed in admixture with MCT dyes, as well as that for the partner dyes on exposure in aerated water has been reported elsewhere.[10] The photosensitivity of the MCT dyes to the fading of Blue-Cu was in the following order:

$$\text{Cu-Pc} \gg \text{Yellow} \fallingdotseq \text{Orange} > \text{Blue-Cu} \quad (3)$$

The fading of Blue-Cu was accelerated by the partner MCT dyes, whilst that of the partner dyes was almost unchanged by Blue-Cu, compared with the single dyeing at the same concentration.[10] Since Orange itself undergoes reductive fading on exposure in aerated water,[8] it sensitizes the fading of Blue-Cu dyed in admixture with Orange at the same time. Although the consumption of singlet oxygen by the partner dye may diminish the suppression effect on the reductive fading by oxygen, little effect on the rates of fading for MCT dyes was noted.

Blue-Cu may be anomalously faded, especially under wet conditions, if it is dyed in a mixture with dyes having a high efficiency to generate singlet oxygen such as Cu-Pc.

The fading of VS-Yellow photosensitized by these MCT dyes is examined in detail in this present paper. Since VS-Yellow is the most readily oxidized of the VS dyes examined, and has a low efficiency to generate singlet oxygen[2,3] and the absorption spectrum of Blue-Cu is superimposable on that of some MCT dyes, it is appropriate to use VS-Yellow to examine the photosensitivity of MCT dyes. VS-Yellow undergoes no reductive fading, even in the presence of substrate under anaerobic conditions.[4] Thus, VS-Yellow shows only oxidative fading whenever it is faded. The fading behaviour for VS-Yellow on cellulose dyed in admixture with MCT dyes is shown in Fig. 3. The order of the photosensitivity for the MCT dyes to the fading of VS-Yellow was as follows:

$$\text{Cu-Pc} > (\text{Blue-2Cu}) > \text{Red 4} > (\text{Yellow R}) > \text{Yellow} > \text{Blue-Cu} > (\text{Brown}) > (\text{Orange}) \doteqdot \text{Red 7} \doteqdot \text{Blue 2} \doteqdot \text{VS-Yellow} \quad (4)$$

Since the dyes in parentheses undergo reductive fading in aerated water, Yellow R, Orange, Blue-2Cu, and Brown sensitize the oxidative fading of VS-Yellow during their own reductive fading. The order (4) coincides with the order (3), except for Blue-Cu which gave a larger initial rate of fading for VS-Yellow than the subsequent rate of fading. Red 4 and Blue-2Cu were confirmed to have a high photosensitivity, similar to that of Cu-Pc. The apparent photosensitivity (f), which corresponds to the quantum yield, ($\phi$) in the generation of singlet oxygen for the MCT dyes, was estimated by the same method as that used for VS dyes,[3] from the values of $A/A_0$ for VS-Yellow (whose optical densities on a sheet of cellophane at $\lambda_{max}$ were about 0·3) on cellulose dyed in admixture with MCT dyes (Table 1). The value of $\phi$ for RB(0·76)[11,12] was used as the reference of f in the present study.

When the values of $k_0$ and f for Blue 2 and Cu-Pc are compared with those for corresponding VS dyes having similar chemical structure, C.I. Reactive Blue 19 and a VS phthalocyanine dye (Cu-Pc) has a $k_0$ value

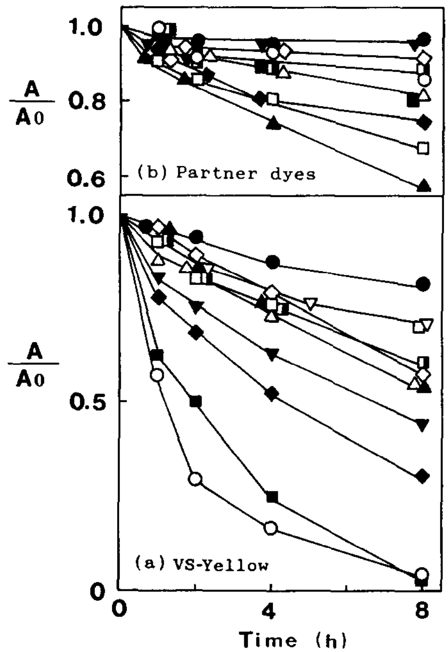



**Fig. 3.** **(a)** Relative rate of fading for VS-Yellow and (b) that for the partner MCT dyes on cellulose dyed in admixture on exposure in aerated water.

| | VS-Yellow | Partner dyes | |
|---|---|---|---|
| ∇: | $4{\cdot}80 \times 10^{-3}$ mol/kg | — | |
| ●: | $2{\cdot}68 \times 10^{-3}$ mol/kg | Blue 2 | $1{\cdot}98 \times 10^{-2}$ mol/kg |
| ▼: | $5{\cdot}19 \times 10^{-3}$ mol/kg | Yellow R | $1{\cdot}87 \times 10^{-2}$ mol/kg |
| ◇: | $6{\cdot}60 \times 10^{-3}$ mol/kg | Orange | $1{\cdot}39 \times 10^{-2}$ mol/kg |
| ◨: | $6{\cdot}14 \times 10^{-3}$ mol/kg | Brown | $4{\cdot}90 \times 10^{-3}$ mol/kg |
| Δ: | $2{\cdot}60 \times 10^{-3}$ mol/kg | Yellow | $5{\cdot}63 \times 10^{-3}$ mol/kg |
| ♦: | $3{\cdot}56 \times 10^{-3}$ mol/kg | Red 4 | $1{\cdot}64 \times 10^{-2}$ mol/kg |
| ○: | $6{\cdot}18 \times 10^{-3}$ mol/kg | Cu-Pc | $5{\cdot}16 \times 10^{-3}$ mol/kg |
| □: | $3{\cdot}51 \times 10^{-3}$ mol/kg | Blue-Cu | $8{\cdot}69 \times 10^{-3}$ mol/kg |
| ■: | $3{\cdot}11 \times 10^{-3}$ mol/kg | Blue-2Cu | $8{\cdot}03 \times 10^{-3}$ mol/kg |
| ▲: | $4{\cdot}37 \times 10^{-3}$ mol/kg | Red 7 | $5{\cdot}93 \times 10^{-3}$ mol/kg |

half that of, and an f value twice that of the corresponding VS dye, whilst Blue 2 has a value of $k_0$ similar to, and a value of f smaller than that for Blue 19.[3] The effect of the triazine ring in the dye may not be simple with respect to improvement of lightfastness.

Considering the high sensitivity for Red 4 and Cu-Pc and the low sensitivity for VS-Yellow, the differences in the order of (1) and (2) can be rationalised. The fading of Red 4 and Cu-Pc, with high sensitivity, may be promoted by their own photosensitivity on exposure in aerated water. The lightfastness of MCT dyes showing oxidative fading under wet conditions depends, therefore, mainly upon the ease with which they are oxidized or with which they abstract hydrogen from the substrate, but it may also be affected by self-photosensitivity. Catalytic fading may be observed in the dyeings of Red 7, Blue-Cu, and Blue-2Cu dyed in admixture with Yellow R, Red 4, Blue-2Cu, and Cu-Pc under wet conditions.

## 4 SUMMARY

The MCT dyes examined showed a wide variation in fading behaviour, as described by the values of $k_0$ and f, which was essentially similar to that of VS dyes. The lightfastness of MCT dyes is in general determined by the ease with which they are oxidised or with which they abstract hydrogen from the substrate. MCT dyes always sensitize the oxidative fading of partner dyes on cellulose dyed in admixture, irrespective of their own fading mechanism.

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