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Environmental Effects of Oxygen on the Fading of Monochlorotriazinyl Reactive Dyes on Cotton Fabrics

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ABSTRACT

The environmental effects on the fading behavior of monochlorotriazinyl reactive dyes on dry cotton fabrics when exposed to an atmosphere of nitrogen, oxygen, and air were studied. Most dyes showed a two step fading behavior, i.e. an initial and then smaller subsequent fading. Many of the dyes examined underwent the largest fading in oxygen, but a phthalocyanine dye showed it in a nitrogen environment. With an increase in the concentration of oxygen, the initial fading of almost all of the dyes increased. On exposure in air, some dyes showed an initial oxidative fading followed by a reductive fading, while the fading for a phthalocyanine dye and for CI Reactive Blue 2 decreased in nitrogen, i.e. a suppressive effect of oxygen on reductive fading. © 1998 Elsevier Science Ltd

Keywords: cotton fabrics, monochlorotriazinyl reactive dye, photofading, environmental effect, oxidative fading, reductive fading.

INTRODUCTION

On exposure of reactive cellulose dyeings under dry and wet conditions, the potential photochemical properties of reactive dyes are manifested in the fading behavior on exposure in various aqueous solutions [1–4], although

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they are also influenced by the environmental conditions. On exposure of dry dyed cellulose, the rates of fading were considerably lowered, and some potential properties seemed to be lost. Some dyes on cotton fabrics underwent a large initial fading from the large surface of the fibers. With an increase in the dye concentration on dry cellulose, an improvement of light-fastness was observed, which was, to a large extent, explained by the filter effect, while the rate of fading for dyes with very high photosensitivity was, in contrast, increased [1].

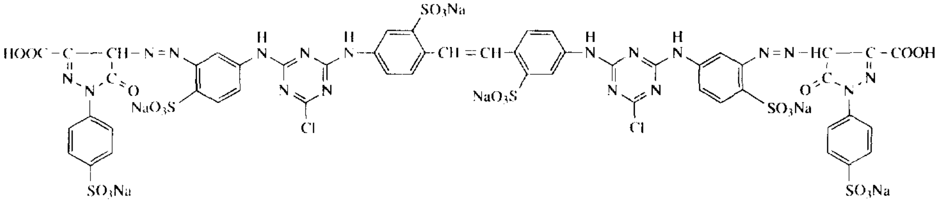
In the present study, the fading behavior of 10 MCT dyes on cotton fabrics was examined by exposure in the presence and absence of oxygen, in order to analyze how their potential properties materialize on exposure. Whether or not the initial fading of some of the dyes on cotton fabrics disappears on exposure in nitrogen atmosphere is also examined. On irradiating the dyes on cotton fabrics and cellulose films, differences in the fading behavior which appears as the initial and subsequent fading were analyzed in terms of their potential properties as examined previously [1–4].

EXPERIMENTAL

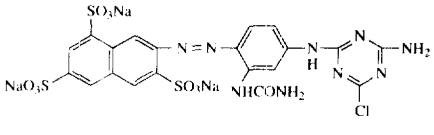
Materials

The 10 reactive MCT dyes used were the same as utilized in previous studies [1–4] and were supplied by Nippon Kayaku Co. Ltd. Their chemical structures are shown below:

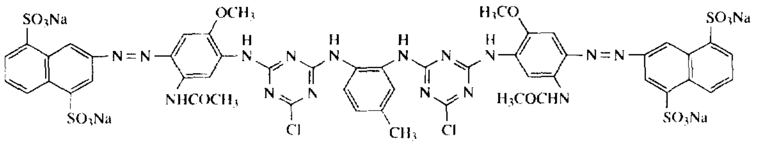
1. A stilbene pyrazolinyl disazo dye (Yellow)



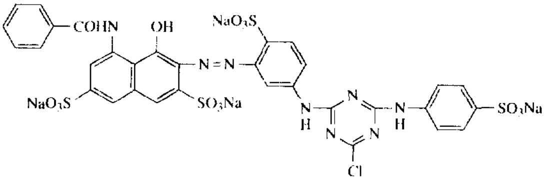
2. An o-ureidoazo dye (Yellow R)



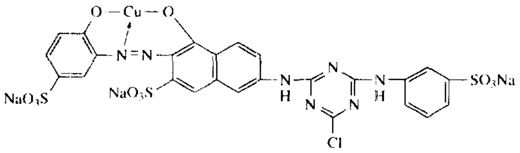
3. An *o*-phenylenediamine disazo dye (Orange)



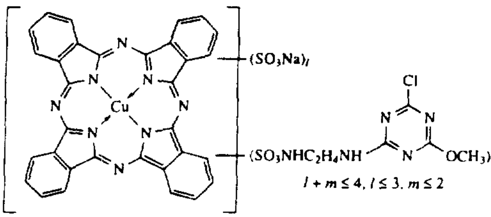
4. CI Reactive Red 4, CI 18105 (Red 4)



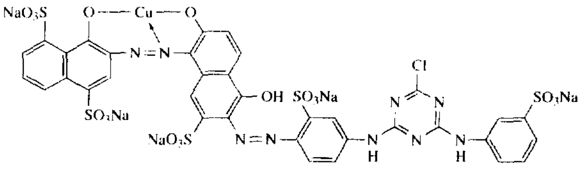
5. CI Reactive Red 7, CI 17912 (Red 7)



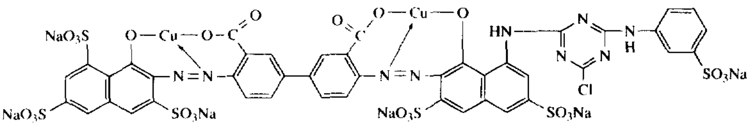
6. A copper-phthalocyanine dye (Cu-Pc)



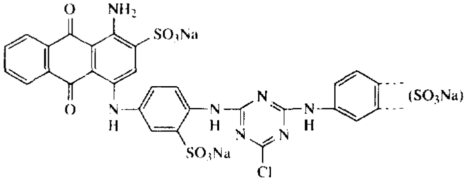
7. A 1:1 copper-complex azo dye (Blue-1Cu)



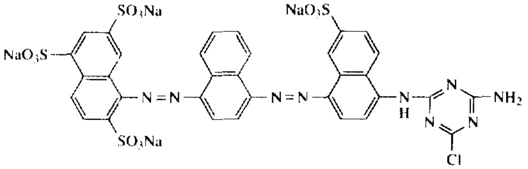
8. A 1:2 copper-complex azo dye (Blue-2Cu)



9. CI Reactive Blue 2, CI 61211 (Blue 2)



10. A brown disazo dye (Brown)



Dyeing and measurements

Cotton fabrics (calico) were dyed in a 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 case of Yellow (where a 60 min period was also examined), Yellow R, Orange, and Brown, and 30 min in case of the other dyes) and then treated for a further 60 min after adding 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 samples was carried out using the previously described apparatus [5,6]. Absorption spectra were measured on a Ubest V-560 spectrophotometer (Jasco Corp.) and reflection spectra by use of an equipped integrating sphere. The CIE tristimulus values were obtained under CIE illuminant and observer conditions of D65/10°.

In order to examine whether photo-oxidative or reductive fading occurred on irradiating the dry dyed cellulose in air, the same dyed cellophane as previously prepared with Yellow R, Orange and Brown [1], was irradiated for an extended length of time and the spectral analysis of the absorption spectra of irradiated film was performed using the same spectrophotometer.

RESULTS AND DISCUSSION

Yellow

The environmental effects of oxygen on the fading of cotton fabrics dyed with Yellow are shown in Fig. 1(a) and are summarized in Table 1. Compared

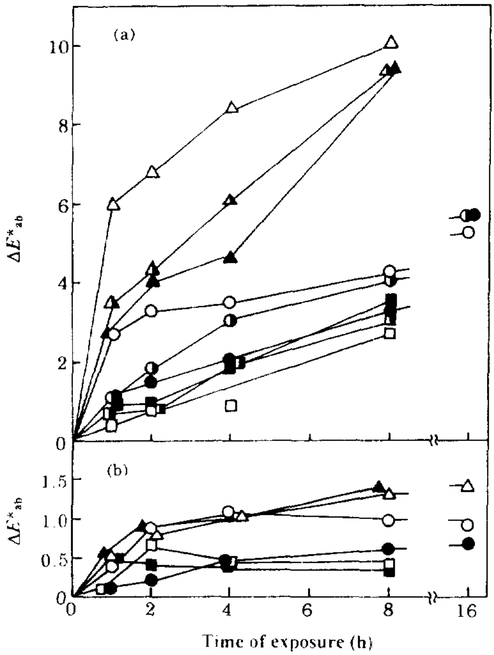


Fig. 1. (a) Relationship between color variation ΔE^*_{ab} after the exposure under different environmental conditions shown below and the time of exposure for cotton fabrics dyed with Yellow and the effect of migration time on the fading;

Migration time	*Symbol*			*Value of chromaticness*		
	In N_2	In air	In O_2	L^*_{ab}	a*	b*
30 min	□	○	△	87.12	−11.21	59.13
60 min	◨	◑	◭	86.74	−10.49	58.57
120 min	■	●	▲	85.84	−10.46	58.63

and (b) the same relationships for Brown.

Migration time	*Symbol*			*Value of chromaticness*		
	In N_2	In air	In O_2	L^*_{ab}	a*	b*
30 min	□	○	△	51.84	29.20	15.98
120 min	■	●	▲	52.27	28.34	14.27

The values of chromaticness for each sample before exposure are shown in the above tables.

TABLE 1
Comparison of the Fading Behavior for Yellow on Cotton Fabrics under Various Environmental Conditions [cf. Figure 1(a)]

Environmental conditions	*Effect of t_m[a] on the rate of fading*	*Effect of environmental conditions on the rate of fading*
In nitrogen	$0.5\,h < 1.0\,h \leqq 2.0\,h$	In $O_2 \gg$ in air $\geqq$ in N_2
In air	$0.5\,h > 1.0\,h > 2.0\,h$	Subsequently,
In oxygen	$0.5\,h \gg 1.0\,h > 2.0\,h$	in $O_2 \gg$ in $N_2 \geqq$ in air

[a] t_m = migration time in the adsorption of reactive dye.

with exposure in air, exposure in oxygen promoted the initial fading and the rate of subsequent fading. Removal of oxygen eliminated the initial fading due to photo-oxidation, and revealed a reductive fading. The promotion effects of oxygen on the initial oxidative fading, as well as on the subsequent fading, show that Yellow has a high facility to be photo-oxidized. On exposure in a nitrogen atmosphere, little initial fading was observed, but the rate of fading was not so small. On exposure in air, the magnitude of the initial fading was in between those in nitrogen and oxygen, while the rate of subsequent fading became similar to, or rather smaller than, that in nitrogen. By decreasing the content of oxygen by a factor of a fifth, the initial fading was lowered by a factor of about a half. The fact that the period showing initial fading depended upon the state of the surface dyeing implies that fading occurs from the surface. Then, the fading behavior, and as a result the fading mechanism, is influenced by the state of the dyes in the substrate. From the observation that the rate of subsequent fading in air was somewhat lower than that in nitrogen, an O_2-suppressive reductive fading was inferred to occur. Although Yellow on cellophane immersed in aerated water underwent only oxidative fading [2], the fading mechanism in air may be changed to be photo-reduction suppressed by oxygen, since the supply of air into the inner part of the fiber where fading occurs mainly will diminish after dye fading at the outer part progresses. The fading mechanism of this dye on dry cellulose under different environmental conditions is summarized as shown in Table 2.

The fact that Yellow on fabrics dyed with prolonged migration showed a considerable decrease in the initial fading may arise from the same behavior as a decrease in the initial fading with a decrease in the concentration of oxygen. It is notable that surface dyeing results in an improvement in the fading property of this dye on cotton fabrics on exposure under anaerobic conditions. The fading behavior of this dye with change of environmental conditions is relatable to the property of this dye, as listed in Table 2. Thus, Yellow has the basic properties to be easily photo-oxidized and to be fairly readily photo-reduced. If the photo-oxidation of azo dyes occurs via their hydrazone form [7–10], Yellow may exist predominantly as the hydrazone form.

TABLE 2
Fading Mechanism of MCT Dyes on Cotton Fabrics under Different Environmental Conditions

Dye	*Fading in* N_2	*Fading in air*	*Fading in* O_2	*Fading of dyed film in aerated water* [2]
Yellow	Reduction	Initial oxidation → reduction[a]	Oxidation	Oxidation
Yellow R	Reduction	Initial oxidation → reduction	Oxidation	Reduction
Orange	Reduction	O_2-suppressive reduction	Oxidation	Reduction
Red 4	Reduction	Initial oxidation → reduction[a]	Oxidation	Oxidation
Red 7	Reduction	Initial oxidation → reduction[a]	Initial oxidation → reduction	Reduction
Cu-Pc	Reduction	O_2-suppressive reduction	Oxidation	Reduction
Blue-1Cu	Reduction	Initial oxidation → reduction[a]	Initial oxidation → reduction	Oxidation
Blue-2Cu	Reduction	Initial oxidation → reduction[a]	Initial oxidation → reduction	Oxidation
Blue 2	Reduction	O_2-suppressive reduction	Oxidation	Oxidation
Brown	Reduction	Initial oxidation → reduction	Oxidation	Reduction

[a] Little or a small rate of subsequent fading.

Brown

Brown has the opposite photochemical reactivity to that of Yellow; this dye can be photo-oxidized with a medium level of ease, and has not so high a resistance to photo-reductive attack in absence of oxygen on exposure under wet conditions [2].

The fading behavior on exposure of dry cotton dyeings under various environmental conditions is shown in Fig. 1(b) and Table 3. Spectral analysis of dry dyed cellophane irradiated in air for 200 h showed that oxidative fading mainly occurred in air, as shown in Fig. 2(a), although the differences in the form of substrate must be taken into consideration. In the case of dry cotton fabrics, initial oxidative fading is enhanced due to the large surface area, and subsequent reductive fading is suppressed. The relationship between ΔE^*_{ab} and the time of exposure is complicated because of their superposition and the small differences in their fading behavior, but the effect of the environmental conditions on the relationships is apparent. The rates of initial fading were observed to be in the order: in $O_2 >$ in air $>$ in N_2. On exposure in an anaerobic atmosphere, the fading of this dye was the lowest compared with that in other environments. Thus, in absence of oxygen, Brown on dry cellulose undergoes only slow reductive fading due to the weak action of dry cellulose as substrate.

On the other hand, on exposure in oxygen, the largest rate of initial fading was observed compared with the rates in air and nitrogen. During the exposure in oxygen, the rate of subsequent fading was strongly suppressed, as in the case of a nitrogen atmosphere. There thus exists some quenching mechanism for the suppression in the subsequent fading. A probable mechanism may be the suppression of reductive fading by oxygen, or the oxidation of a reductive intermediate by oxygen. Similar situations were observed on exposure in air, although the rate of initial fading was smaller than that in oxygen. But since the same suppression in the subsequent fading may act as in the case of exposure in nitrogen, competition of reductive and oxidative reactions is improbable. The mechanism of fading in air and oxygen

TABLE 3
Comparison of the Fading Behavior for Brown on Cotton Fabrics under Various Environmental Conditions [cf. Figure 1(b)]

Environmental conditions	*Effect of t_m* [a] *on the rate of fading*	*Effect of environmental conditions on the rate of fading*
In nitrogen	$0.5\,h \approx 2.0\,h$	
In air	$0.5\,h > 2.0\,h$	In $O_2 >$ in air $>$ in N_2
In oxygen	$0.5\,h \approx 2.0\,h$	

[a] t_m = migration time in the adsorption of reactive dye.

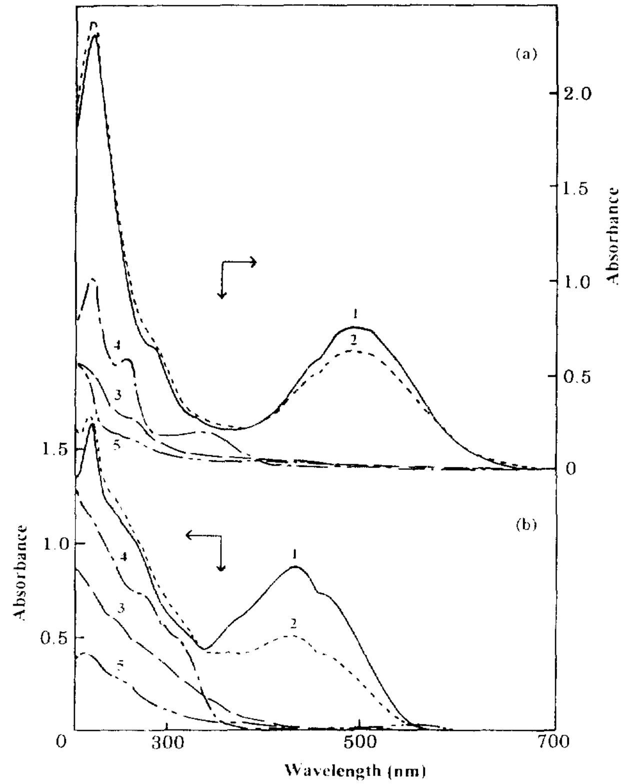


Fig. 2. Absorption spectra of the photo-decomposed product of Brown (a) and Orange (b) on the deeply dyed cellophane [1]. (1, Original as dyed; 2, exposed for 200 h in dry air; 3, difference spectrum of 1 and 2; 4, photo-reduction product exposed in anaerobic aqueous DL-mandelate; 5, photo-oxidation product exposed in aerobic Rose Bengal aqueous solution).

was presumed to be oxidative, but from the viewpoint of the properties of Brown, a competitive mechanism may be probable. The fading behavior of Brown under different environmental conditions is summarized as shown in Table 2.

A decrease in the surface dyeing resulted in a small fading on exposure under all the environmental conditions examined. But on exposure in oxygen, cotton fabrics with extensive surface dyeing underwent the largest rate of subsequent fading, although the initial fading was the same as that of fabrics in which no surface dyeing existed. This dye shows a considerable resistance to photo-oxidative attack and its high lightfastness on dry cotton fabrics may be attributed to the decrease in the rate of subsequent fading. The photochemical properties of Brown may be partially manifested on exposure of dyed cotton fabrics, depending on the environmental conditions if their behavior is analyzed as above.

Orange

Results of the fading of Orange on cotton fabrics in oxygen and nitrogen atmosphere, together with those in air [1], are shown in Fig. 3(a) and are

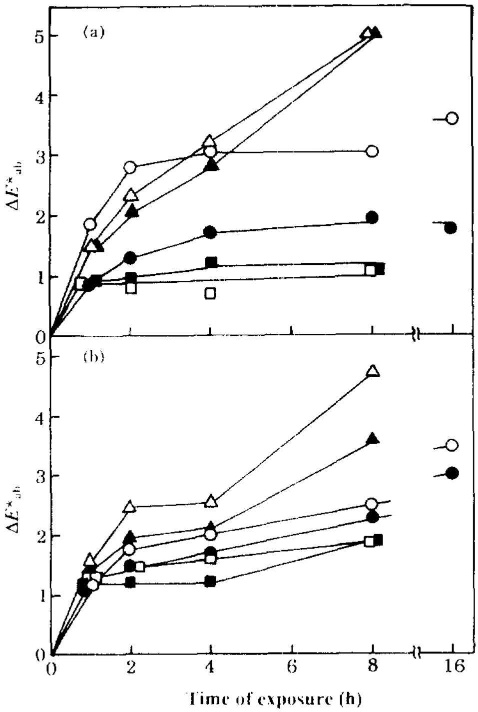


Fig. 3. (a) Relationship between color variation ΔE^*_{ab} after the exposure under different environmental conditions shown below and the time of exposure for cotton fabrics dyed with Orange and the effect of migration time on the fading;

Migration time	*Symbol*			*Value of chromaticness*		
	In N_2	In air	In O_2	L^*_{ab}	a*	b*
30 min	□	○	△	75.81	17.99	60.20
120 min	■	●	▲	73.72	19.36	58.85

and (b) the same relationships for Yellow R.

Migration time	*Symbol*			*Value of chromaticness*		
	In N_2	In air	In O_2	L^*_{ab}	a*	b*
30 min	□	○	△	81.50	3.76	53.88
120 min	■	●	▲	82.20	3.26	50.86

The values of chromaticness for each sample before exposure are shown in the above tables.

summarized in Table 4. Spectral analysis of the dry dyed cellophane irradiated in air for a long period indicated that the fading was essentially photoreductive [Fig. 2(b)]. Low absorption in the near UV region suggests the existence of monoazo intermediates in the photo-decomposition. The slow rate of subsequent fading in air is attributed to the O_2-suppressive reductive fading. In a previous paper [1], this dye was shown to undergo initial oxidative fading followed by reductive fading on exposure in air.

In the fading behavior of dyed cotton fabrics in oxygen and air, a very large difference was observed between the rates of subsequent fading, although their initial fading was not so different. Exposure in oxygen promoted the initial fading as well as the rate of subsequent fading, although exposure in air suppressed the rate of subsequent fading. It should be noted that the existence of an excess amount of oxygen does not suppress the reductive fading, but promotes oxidative fading. But a comparison of the fading behavior under three environmental conditions implies that the initial fading in air is oxidative. The very large surface area of cotton fabrics results in oxidative fading.

On exposure in a nitrogen atmosphere, a small initial fading and a very slow subsequent fading were observed. Although the effect of surface dyeing was prominent when they were irradiated in air [1], little effect was noticed on the fading in nitrogen and oxygen. Then, on exposing the dyed fabrics in air, a decrease in surface dyeing resulted in an improvement in the lightfastness ratings because of a reduction in initial fading.

Whether or not oxidative fading was completely suppressed could not be elucidated on exposure in dry air; the fading of Orange on dry cotton fabrics is as shown in Table 2. The potential photochemical properties of Orange become apparent on exposure of dyed cellulose depending upon the environmental conditions.

Yellow R

The environmental effects on the fading behavior of this dye are very apparent, as shown in Fig. 3(b) and in Table 5: the initial fading is independent

TABLE 4
Comparison of the Fading Behavior for Orange on Cotton Fabrics under Various Environmental Conditions [cf. Figure 3(a)]

Environmental conditions	*Effect of $t_m{}^a$ on the rate of fading*	*Effect of environmental conditions on the rate of fading*
In nitrogen	$0.5\,h \approx 2.0\,h$	
In air	$0.5\,h \gg 2.0\,h$	In $O_2 \gg$ in air $>$ in N_2
In oxygen	$0.5\,h \approx 2.0\,h$	

[a] t_m = migration time in the adsorption of reactive dye.

TABLE 5
Comparison of the Fading Behavior for Yellow R on Cotton Fabrics under Various Environmental Conditions [cf. Figure 3(b)]

Environmental conditions	*Effect of t_m[a] on the rate of fading*	*Effect of environmental conditions on the rate of fading*
In nitrogen	0.5 h $\geqq$ 2.0 h	
In air	0.5 h $>$ 2.0 h	In O_2 > in air > in N_2
In oxygen	0.5 h $\gg$ 2.0 h	

[a] t_m = migration time in the adsorption of reactive dye.

of the environmental conditions, and an increase in the rate of fading occurs with an increase in the concentration of oxygen. The notable features are the effects of surface dyeing on the initial fading on the exposure in oxygen: the surface dyeing promoted the initial fading but had little effect on the subsequent fading.

Spectral analysis of dyed film irradiated in dry air for long time showed that both oxidative and reductive fading occurred.

On exposure in air, this dye may initially undergo oxidative fading on dry cotton fabrics, and subsequently reductive fading, since the rate of fading in air was larger than that in nitrogen and was smaller than that in oxygen. The fading behavior of this dye under different environmental conditions is shown in Table 2.

Cu-Pc

The fading behavior of Cu-Pc is clearer than that of Yellow R, as shown in Fig. 4 and Table 6. This dye has very high photosensitivity and undergoes both oxidative and reductive fading [1]. But since this dye has a high ease with which it is photo-reduced, the presence of oxygen suppresses the reductive fading, and that of substrate such as textile resin or histidine promoted the reductive fading [2,11]. Since the magnitude of the initial fading and the rate of subsequent fading on exposure in air is smaller than that in nitrogen and oxygen, the mechanism of fading in air is of an oxygen-suppressed reduction. However, little variation in color of this dye was observed during exposure in air. The fading behavior of this dye under different environmental conditions is summarized in Table 2.

CI Reactive Blue 2

The fading behavior of this dye on dry cotton fabrics is shown in Fig. 4 and summarized in Tables 2 and 6. CI Reactive Blue 2 is a dye which has low photoreactivity to oxidative and reductive attacks [1]. It underwent some

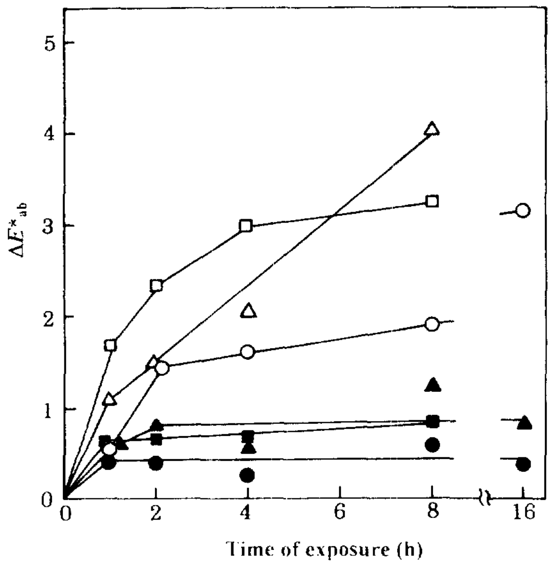


Fig. 4. Relationship between color variation ΔE^*_{ab} after the exposure under different environmental conditions shown below and the time of exposure for cotton fabrics dyed with CI Reactive Blue 2 and Cu-Pc. The values of chromaticness for each sample before exposure are shown below.

Dye	*Symbol*			*Value of chromaticness*		
	In N_2	In air	In O_2	L^*_{ab}	a*	b*
Cu-Pc	□	○	△	64.47	−24.66	−28.84
Blue 2	■	●	▲	62.22	−10.34	−20.74

fading in presence of oxygen. It may suffer oxidative fading in oxygen because the rate of fading in air is smaller than that in nitrogen, a suppression effect of air on the reductive fading. The photo-reduction intermediate has a life time long enough to react with oxygen. The rate of fading for this dye was promoted by the presence of substrate, as for Cu-Pc: essentially,

TABLE 6

Comparison of the Fading Behavior for CI Reactive Red 4, CI Reactive Red 7, CI Reactive Blue 2, Cu-Pc, Blue-1Cu, and Blue-2Cu on Cotton Fabrics under Various Environmental Conditions [cf. Figs 4–6)

Dye	*Effect of environmental conditions on the rate of fading*
CI Reactive Red 4	In O_2 > in air > in N_2
CI Reactive Red 7	In O_2 > in air > in N_2
CI Reactive Blue 2	In O_2 ≈ in N_2 > in air
Cu-Pc	In N_2 > in O_2 > in air
Blue-1Cu	In O_2 > in air ≈ in N_2
Blue-2Cu	In O_2 > in air ≈ in N_2

they have the same properties in photoreactivity, although their degree is different.

CI Reactive Red 4 and CI Reactive Red 7

Since these dyes resembles Yellow in their fading behavior, their behavior is compared in this section. On exposure of dry cotton fabrics, the environmental effects on the fading behavior of CI Reactive Red 4, CI Reactive Red 7, and Yellow were similar to one another as shown in Fig. 5 and Tables 2 and 6. However, the rates of subsequent reductive fading for these dyes in a nitrogen atmosphere were of the following order: Yellow > CI Reactive Red 4 > CI Reactive Red 7, and those of oxidative fading in oxygen were:

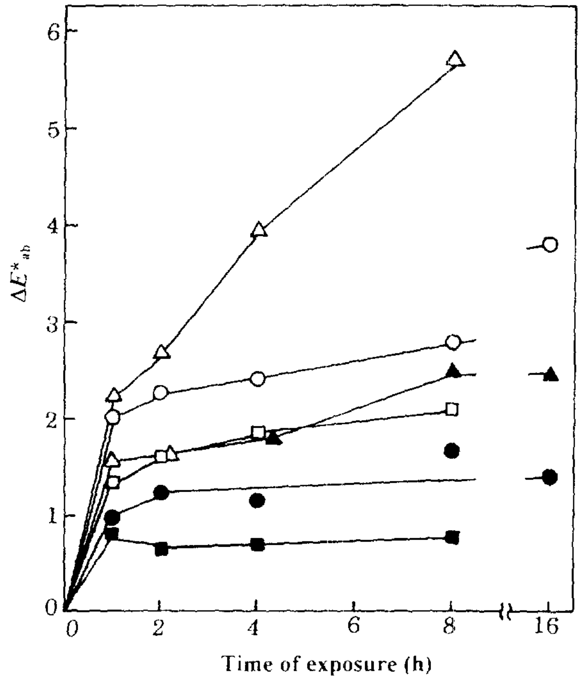


Fig. 5. Relationship between color variation ΔE^*_{ab} after the exposure under different environmental conditions shown below and the time of exposure for cotton fabrics dyed with CI Reactive Red 4 and Red 7. The values of chromaticness for each sample before exposure are shown below.

Dye	*Symbol*			*Value of chromaticness*		
	In N_2	In air	In O_2	L^*_{ab}	a*	b*
Red 4	□	○	△	61.30	47.45	−4.46
Red 7	■	●	▲	52.16	43.64	−6.03

Yellow > CI Reactive Red 4 > CI Reactive Red 7. The magnitudes of initial fading and the rates of subsequent fading on exposure in air were of the order: Yellow ≧ CI Reactive Red 4 > CI Reactive Red 7. Thus, on dry cotton fabrics, CI Reactive Red 4 has a larger ease with which it is photo-oxidized and reduced than CI Reactive Red 7.

In the case of the fading on cellulose films under wet conditions [1,2], on the other hand, CI Reactive Red 7 was photo-oxidized with much greater ease than CI Reactive Red 4 and Yellow. The rates of reductive fading for the two red dyes on cellophane on exposure in anaerobic aqueous DL-mandelate were larger than that for Yellow. The fading behavior on cotton fabrics did not correspond to that on film under wet conditions; water appears to remove the quenching mechanism of CI Reactive Red 7 on dry fabrics.

The photoreactivity properties may not always be apparent, due to a 'cancelling' effect between photo-oxidation and reduction, especially for CI Reactive Red 7 and CI Reactive Red 4 on dry cotton fabrics. On exposure of dry fabrics under different environmental conditions, initial fading, the extent of which was proportional to the concentration of oxygen, was observed in all cases. Moreover, since oxygen promoted the rates of subsequent fading, these dyes retain their essential photochemical reactivity.

Blue-1Cu and Blue-2Cu

These Cu-complex azo dyes had very high lightfastness on dry cotton fabrics on exposure even in an oxygen atmosphere, as shown in Fig. 6 and Tables 2 and 6, but they showed very high photo-reactivity for photo-oxidation and reduction under wet conditions [1,2]. As in the case of CI Reactive Red 7, Blue-1Cu and Blue-2Cu have antagonistical actions to photo-oxidation and reduction on exposure of dry cotton fabrics and lose those actions under wet conditions.

Blue-1Cu is very easily photo-oxidized and has a low photosensitivity [4], while Blue-2Cu has a very high photosensitivity [4]. The copper atoms in these dyes quench the singlet oxygen by the heavy atom effect, but this may become null under wet conditions. Their potential photochemical properties, apparent under wet conditions, were not manifested on dry fabrics. Their canceling or antagonistical action has not so far been studied, but it is now suggested that it is attributable to the oxidation of the photo-reductive intermediate, whose lifetime is long enough for it to be oxidized.

Probably due to the action of copper atoms, the initial photo-oxidative fading of these dyes is considerably lowered. The rates of subsequent fading for these dyes were practically suppressed. In the case of Blue-1Cu, the magnitude of the initial fading on exposure in oxygen was larger than those in nitrogen and air; the deactivation by copper atoms is sufficient to suppress the initial fading almost completely.

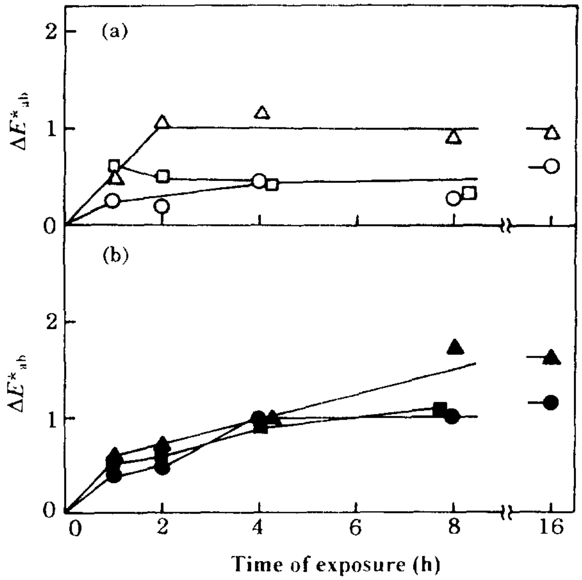


Fig. 6. Relationship between color variation ΔE^*_{ab} after the exposure under different environmental conditions shown below and the time of exposure for cotton fabrics dyed with Blue-1Cu and Blue-2Cu. The values of chromaticness for each sample before exposure are shown below.

Dye	*Symbol*			*Value of chromaticness*		
	In N_2	In air	In O_2	L^*_{ab}	a*	b*
Blue-1Cu	□	○	△	52.80	11.16	−26.10
Blue-2Cu	■	●	▲	46.84	9.77	−30.92

General fading behavior of MCT dyes on dry cotton fabrics

In general, the dyes on cotton fabrics underwent a larger initial fading than in the case of film, because the fabrics have a relatively larger surface area. The manifestation of surface effects on the fading behavior becomes smaller as the fading of dyes near the surface progresses.

When the potential photochemical properties for many MCT dyes on dry cotton fabrics were analyzed in terms of the magnitude of initial fading and the rates of subsequent fading, all the dyes manifested their potential properties depending upon the environmental conditions, mainly the concentration of oxygen in the environment (cf. Tables 2 and 6). The magnitudes of initial fading for all the dyes increased with an increase in the concentration of oxygen in the environment, as well as the rates of subsequent fading for most dyes. The mechanism of fading on the dry fabrics was almost photo-oxidative in oxygen and photo-reductive in nitrogen.

On exposure in air, many dyes such as Yellow R, Orange, CI Reactive Red 4, CI Reactive Red 7, Cu-Pc, Blue-1Cu, Blue-2Cu, CI Reactive Blue 2, and Brown showed little or a small rate of subsequent fading where an O_2-suppressive reductive fading might occur, although they underwent considerable initial fading. These dyes have a photo-reductive intermediate whose lifetime is long enough to allow oxidation. But in cases where dyes such as CI Reactive Red 4, CI Reactive Red 7, Blue-1Cu, and Blue-2Cu have a high photo-reactivity, the lifetime becomes shorter under wet conditions, although the reason why these dyes show such behavior remains to be examined.

In order to prepare dyes with high lightfastness, the dyes should have properties showing reductive fading on exposure in air, but the reductive fading should not progress on exposure in an aerobic atmosphere, as in the case of Orange, Brown, CI Reactive Blue 2, and, though not ideal, Yellow R. The relationship between chemical structure and photochemical properties will be evaluated in future studies.

There may, however be other principles to attain high lightfastness, viz., the aggregation theory [12–15]. But in previously reported results [1–4] together with results from this present study, no proof has been found to support the theory.

SUMMARY

On exposure of cellulose film dyed with reactive dyes in various aqueous solutions, oxidative and/or reductive fading occurred depending upon the chemical structure of dyes and primarily upon the environmental conditions. The addition of substrate promoted reductive fading or suppressed oxidative fading, while an increase in the concentration of oxygen gave reverse effects viz., the promotion of oxidative fading and the suppression of reductive fading. Thus, reactive dyes have potentially diverse properties which are sometimes contradictory to each other and suffer various kinds of photodecomposition on cellulose. The form of cellulose, film or fabrics, also has effects on the fading behavior of the dyes.

On exposing the MCT dyes on dry cotton fabrics, the dyes exhibited their potential properties depending upon the environmental conditions, although some dyes seemed to lose the properties which were apparent under wet conditions. On exposure in air many MCT dyes had high lightfastness, probably due to the O_2-suppressive photo-reductive fading, where such properties were inherent, although they showed poor lightfastness under wet conditions. Some dyes showed high lightfastness even under wet conditions.

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REFERENCES

1. Okada, Y., Fukuoka, F. and Morita, Z., Estimation of potential photo-chemical properties for monochlorotriazinyl reactive dyes and their manifestation in the fading of dyed cellulose, *Dyes and Pigments*, 1997, **35**, 311–330.
2. Okada, Y., Satoh, E., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1992, **19**, 1–19.
3. Okada, Y., Orikasa, K., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1992, **19**, 203–214.
4. Okada, Y., Kato, T., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1992, **20**, 123–135.
5. Okada, Y., Murata, J. and Morita, Z., *Sen'i Seihin Shohi Kagaku*, 1993, **34**, 678–685.
6. Okada, Y., Murata, J. and Morita, Z., *Sen'i Seihin Shohi Kagaku*, 1994, **35**, 34–40.
7. Griffiths, J. and Hawkins, C., *Journal of Chemical Society, Chemical Communications*, 1972, 463–464.
8. Griffiths, J. and Hawkins, C., *Journal Chemical Society, Perkin II*, 1977, 747–752.
9. Griffiths, J. and Hawkins, C., *Journal of Applied Chemistry and Biotechnology*, 1977, **27**, 558–564.
10. Rembold, M. W. and Kramer, H. E. A., *Journal of the Society of Dyers and Colourists*, 1978, **94**, 12–17.
11. Ingamells, W., *Journal of the Society of Dyers and Colourists*, 1963, **79**, 651–660.
12. Giles, C. H. and Forrester, S. D., *Photochemistry of Dyed and Pigmented Polymers*, ed. by N. S. Allen and J. F. McKellar, Applied Science Publishers Ltd., London, 1980, Ch. 2, pp. 51–91.
13. Baxter, G., Giles, C. H., McKee, M. N. and Macaulay, N., *Journal of the Society of Dyers and Colourists*, 1955, **71**, 218–235.
14. Baxter, G., Giles, C. H. and Lewington, W. J., *Journal of the Society of Dyers and Colourists*, 1957, **73**, 386–392.
15. Giles, C. H., Walsh, D. J. and Sinclair, R. S., *Journal of the Society of Dyers and Colourists*, 1977, **93**, 348–352.