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Dyes and Pigments 45 (2000) 109–123

DYES and PIGMENTS

Photofading of monoazo disperse dyes on polyester and polyamide substrates

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Received 7 October 1998; accepted 15 November 1999

Abstract

Six monoazo disperse dyes were applied to nylon and polyester substrates and irradiated under aerobic and anaerobic conditions. The dyes underwent reductive fading under both sets of conditions, with few exceptions. Exposing nylon films containing disperse dyes and a vinylsulfonyl copper–phthalocyanine (CuPc) dye, when immersed in aerated or O_2-saturated water, led to a decrease in the rate of reductive fading compared with exposures involving disperse dyes without the CuPc dye. Singlet oxygen generated by the photosensitization of CuPc dye suppressed the reductive fading of disperse dyes. Nylon had a greater tendency to give light-induced reduction and oxidation of disperse dyes than polyester, depending upon the properties of the adsorbed dye. High lightfastness in disperse dyes requires $^1O_2$-suppressed reduction, due to self-photosensitization during exposures involving aerobic conditions.

Keywords: Azo disperse dye; Lightfastness; Reductive fading; Photosensitivity; Polyester; Nylon

1. Introduction

Improvements in the lightfastness of disperse dyes have made it possible to produce automotive upholstery composed of polyester (PET) fabric. While excellent reviews have been written on the development of disperse dyes [1–3], the relationship between chemical structure and lightfastness of disperse dyes has been covered to a lesser degree [4–6]. Consequently, a complete determination of the reaction mechanisms that characterize the photofading of disperse dyes on polyamide and PET substrates is still of interest.

Kuramoto and Kitao [7,8] investigated the light-induced reduction of phenylazonaphthols in alcohols as well as their photo-oxidation by singlet oxygen $^1O_2$. Albini et al. [9] investigated the wavelength-dependent photo-reduction of azobenzenes in various organic solvents, and Ascoria et al. reported the reductive fading of monoazo disperse dyes in amide solvents under N_2 [10] and on nylon films in the presence and absence of air [11]. Hashizume [5] suggested a photo-reductive pathway for the fading of azo and anthraquinone dyes on PET, and introduced electron-attracting groups into the parent dye structure to improve lightfastness. Freeman and Hsu [12] reported the reductive fading of a pair of monoazo dyes, along

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0143-7208/00/$ - see front matter
PII: S0143-7208(00)00009-7

with the photo-oxidative fading of an anthraquinone dye on PET and nylon in the presence of air.

In a series of papers involving the photo-fading of reactive dyes on cellulose, the present authors reported that the mechanisms of dye fading depends primarily on exposure conditions, including the physical form and properties of the dyed substrate and the presence of O_2 and water [13–19].

It has been reported that exposing dyes on cellulose under anaerobic conditions led to reductive fading [13–19]. Increasing O_2 concentration caused oxidative fading, depending on the dye employed. However, the absorption spectra of decomposition products of the azo disperse dyes on nylon and PET films could not be determined fully by spectral analysis, because some of the reaction products sublime during light exposures. Thus, unlike the case of reactive dyeings on cellulose, spectral analysis has not been too useful in determining the fading mechanism of disperse dyes.

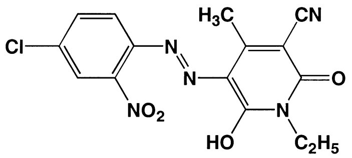
In the present study, six azo disperse dyes which possess high lightfastness on PET but very low lightfastness on nylon were exposed on nylon films and on nylon and PET fabrics under aerobic and anaerobic conditions. The objective was to determine the reason for their different stabilities to light on different substrates. The relationships between lightfastness and properties such as photo-reductivity, photosensitivity, and oxidizability are discussed. Based on the results of this study, the fading mechanisms observed on nylon and PET substrates, as exposure conditions were varied, are presented.

Disperse dyes used in this study are representative of those with high but not very high lightfastness on PET fabrics, except for the Violet dye. Their lightfastness on PET and nylon fabrics, as determined by ISO or JIS methods [20,21], is listed in Table 1. The dyes used were **1–7**.

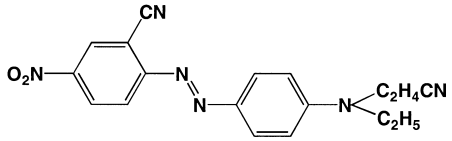
Table 1
Lightfastness of disperse dyes on polyester and nylon fabrics

No.	Dyes (CI generic name)	Lightfastness			
		Substrate	PET		Nylon
		Depth	1/5	1/10	1/5 and 1/10
1	CI Disperse Yellow 211		> 6	> 6	1
2	CI Disperse Red 73		> 6	> 6	1
3	CI Disperse Blue 79:1		4–5	4	1
4	CI Disperse Blue 165		> 6	> 6	1
5	CI Disperse Blue 291		4	3	1
6	A Disperse Violet dye		2	2	2–3

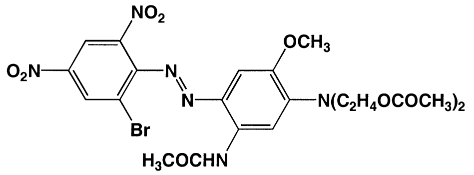
- **1** CI Disperse Yellow 211, CI 12755 (Yellow 211)



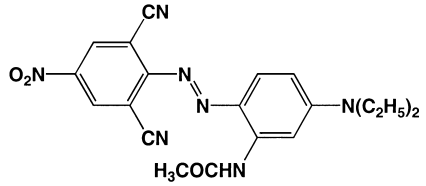
- **2** CI Disperse Red 73, CI 11116 (Red 73)



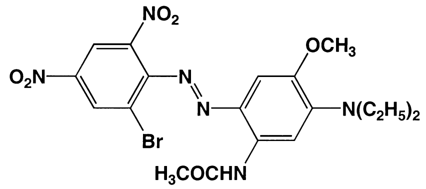
- **3** CI Disperse Blue 79:1, CI 11344 (Blue 79:1)



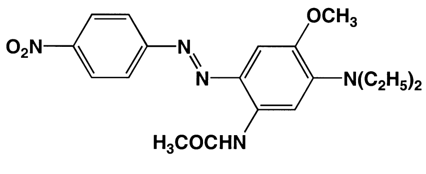
- **4** CI Disperse Blue 165, CI 11077 (Blue 165)



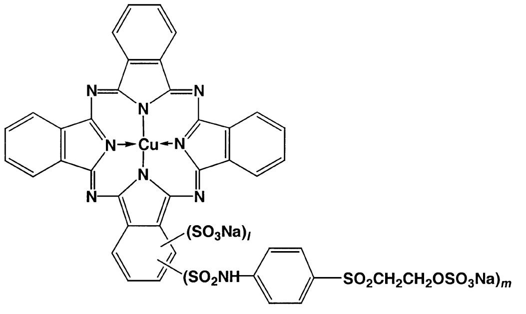
- **5** CI Disperse Blue 291 [22] (Blue 291)



- **6** A monoazo disperse violet dye (Violet dye)



- **7** A reactive copper phthalocyanine dye (CuPc dye)



$l + m \leq 4,\ l \leq 3,\ 1 \leq m \leq 2.$

2. Experimental

2.1. Materials

2.1.1. Dyes used

The disperse dyes and reactive dye were obtained from DyStar Japan Ltd.

2.1.2. Substrates

Nylon films are Emblem products (Unitica Ltd., thickness = 25 μm) made of nylon 6. Nylon 6 fabrics (taffetas) utilized as adjacent fabrics in the JIS test method [23], and PET fabrics (tropical, manufactured by Toray Ind., Inc.) were used.

2.2. Methods

2.2.1. Dyeing

Nylon films were dyed for 2–5 h at 80°C from aqueous dyebath containing disperse dyes without a dispersing agent. CI Disperse Blue 79:1 and Blue 291 were applied over 5 h, while the other dyes were applied over 2 h, to obtain the desired shade depth. Nylon fabrics were also dyed at 2.0% shade depth, at 30:1 liquor ratio, and at 90°C for 40 min. PET fabrics were dyed (1/10 of standard depth) at 130°C for 1 h. Dye concentrations are provided in the captions for Tables 2 and 3 and Figs. 2–7.

In other experiments, nylon films were pre-dyed with CuPc dye by the alkali shock method, after equilibrium absorption at a predetermined depth

Table 2
Relative fading, A/A_0, of combinations of disperse dye and a CuPc vinylsulfonyl dye on nylon film following exposure in aerated water

Dyes (Conc: abs., at w.l.)	Component of mixture	Time of exposure (h)		
		1.0	2.0	5.0
CuPc dye	CuPc alone	0.60	0.35	0.27
(A_0 = 1.077, 676 nm)				
Yellow 211 + CuPc dye	Yellow 211 alone	0.74	0.50	0.25
(A_0 = 0.291, 455 nm)	Yellow 211 with CuPc dye	0.68	0.43	0.18
(A_0 = 0.851, 676 nm)	CuPc dye with Yellow 211	0.79	0.67	0.43
Red 73 + CuPc dye	Red 73 alone	0.91	0.79	0.68
(A_0 = 0.313, 532 nm)	Red 73 with CuPc dye	0.94	0.83	0.69
(A_0 = 0.713, 676 nm)	CuPc dye with Red 73	0.75	0.55	0.46
Blue 79:1 + CuPc dye	Blue 79:1 alone	0.86	0.66	0.41
(A_0 = 0.261, 618 nm)	Blue 79:1 with CuPc dye	0.90	0.69	0.40
(A_0 = 0.899, 676 nm)	CuPc dye with Blue 79	0.77	0.57	0.43
Blue 165 + CuPc dye	Blue 165 alone	0.65	0.44	0.17
(A_0 = 0.332, 630 nm)	Blue 165 with CuPc dye	0.73	0.47	0.20
(A_0 = 0.873, 676 nm)	CuPc dye with Blue 165	0.78	0.60	0.43
Blue 291 + CuPc dye	Blue 291 alone	0.90	0.80	0.58
(A_0 = 0.314, 645 nm)	Blue 291 with CuPc dye	0.95	0.84	0.52
(A_0 = 0.958, 676 nm)	CuPc dye with Blue 291	0.75	0.63	0.42
Violet dye + CuPc dye	Violet dye alone	0.95	0.84	0.72
(A_0 = 0.279, 570 nm)	Violet dye with CuPc dye	0.97	0.91	0.64
(A_0 = 0.959, 676 nm)	CuPc dye with Violet dye	0.72	0.60	0.40

Table 3
Relative fading, A/A_0, of combinations of disperse dyes and a CuPc vinylsulfonyl dye on nylon film following exposure in O_2-saturated water

Dyes (Conc: abs., at w.l.)	Component of mixture	Time of exposure (h)		
		1.0	2.0	5.0
CuPc dye	CuPc dye alone	0.75	0.63	0.32
A_0= 1.077, 676 nm)				
Yellow 211+ CuPc dye	Yellow 211 alone	0.71	0.46	0.29
(A_0= 0.291, 455 nm)	Yellow 211 with CuPc dye	0.61	0.38	0.19
(A_0= 0.851, 676 nm)	CuPc dye with Yellow 211	0.81	0.65	0.53
Red 73+CuPc dye	Red 73 alone	0.92	0.86	0.68
(A_0= 0.313, 532 nm)	Red 73 with CuPc dye	0.95	0.89	0.73
(A_0= 0.713, 676 nm)	CuPc dye with Red 73	0.73	0.54	0.48
Blue 79:1+CuPc dye	Blue 79:1 alone	0.86	0.69	0.47
(A_0= 0.261, 618 nm)	Blue 79:1 with CuPc dye	0.97	0.79	0.52
(A_0= 0.899, 676 nm)	CuPc dye with Blue 79	0.79	0.72	0.56
Blue 165+CuPc dye	Blue 165 alone	0.82	0.64	0.20
(A_0= 0.332, 630 nm)	Blue 165 with CuPc dye	0.89	0.70	0.41
(A_0= 0.873, 676 nm)	CuPc dye with Blue 165	0.79	0.66	0.42
Blue 291+CuPc dye	Blue 291 alone	0.90	0.81	0.60
(A_0= 0.314, 645 nm)	Blue 291 with CuPc dye	0.92	0.83	0.58
(A_0= 0.958, 676 nm)	CuPc dye with Blue 291	0.74	0.57	0.49
Violet dye+CuPc dye	Violet dye alone	0.87	0.79	0.60
(A_0= 0.279, 570 nm)	Violet dye with CuPc dye	0.93	0.84	0.61
(A_0= 0.959, 676 nm)	CuPc dye with Violet dye	0.73	0.71	0.50

at pH 3.5. The pre-dyed films were then dyed with the disperse dyes.

2.2.2. Light exposures

Light-induced fading studies employed the carbon-arc based test method JIS L 0888, which was modified as reported previously [19]. Oxygen, air or nitrogen was enclosed in the glass vessel used in the test chamber and was refreshed every day, unless air was employed. Silica gel was added to the bottom of the glass vessel in cases involving dry air and nitrogen, water in case of 100% RH, and an oxygen absorber in case of anaerobic exposure. Conditioning at 40°C was conducted for 1 week under anaerobic conditions before the exposure and for 1 day under aerobic conditions. Color variations on PET and nylon fabrics after exposures were assessed from chromaticity (L^*, a^*, and b^*) values.

The color variations of CI Disperse Blue 165 on nylon fabrics under all exposure conditions were as follows: $L_0^*=45.83$, $a_0^*=-11.40$, $b_0^*=-26.66$; $L_5^*=49.40$, $a_5^*=6.64$, $b_5^*=-17.92$ in the presence of N_2, $L_5^*=48.74$, $a_5^*=5.58$, $b_5^*=-21.37$ in air, and $L_5^*=48.02$, $a_5^*=6.78$, $b_5^*=-20.98$ in the presence of O_2 (100% RH) (see Fig. 5). The color variations on PET fabrics were negligible because of the low level of fading. The influences on A/A_0 caused by color variation on nylon films were negligible, due to the use of λ_{max}.

The color variations of CI Disperse Blue 291 on nylon fabrics under all exposure conditions were as follows: $L_0^*=47.49$, $a_0^*=-16.85$, $b_0^*=-20.00$; $L_5^*=48.87$, $a_5^*=-8.26$, $b_5^*=-15.52$ in the presence of N_2, $L_5^*=51.75$, $a_5^*=-7.45$, $b_5^*=-15.00$ in air, and $L_5^*=47.49$, $a_5^*=-8.36$, $b_5^*=-16.56$ in the presence of O_2 (100% RH). Variations on PET fabrics under all conditions were as follows: $L_0^*=64.37$, $a_0^*=-15.61$, $b_0^*=-22.02$; $L_{40}^*=65.98$, $a_{40}^*=-14.76$, $b_{40}^*=-20.94$ in the presence of N_2, $L_{40}^*=67.43$, $a_{40}^*=-14.14$, $b_{40}^*=-20.49$ in air, and $L_{40}^*=67.53$, $a_{40}^*=-13.99$, $b_{40}^*=-20.35$ in the presence of O_2 (100% RH) (cf. Fig. 6).

2.2.3. Fading in aqueous NaClO

Aqueous NaClO (available chlorine = 0.20 g dm^{-3}) was prepared and NaH_2PO_4 (0.01 M) was added to adjust the pH to 6.77. Available chlorine was determined by iodometry with the aid of $Na_2S_2O_3$ [24].

3. Results and discussion

3.1. Dye degradation on nylon films in aqueous NaClO

The ease with which dyes are photo-oxidized may be estimated from a rates of NaClO bleaching on a substrate. When nylon films dyed with disperse dyes were immersed in aqueous NaClO, absorbance at the wavelength of the maximum absorption (λ_{max}) decreased almost linearly with time of immersion (see Fig. 1). The bleaching rate for the six disperse dyes on nylon films was quite high, with the order of bleaching (oxidizability) as follows:

$$\text{Violet dye} > \text{Blue 291} > \text{Blue 79} > \text{Blue 165} > \text{Red 73} > \text{Yellow 211}$$

3.2. Exposure of disperse dye–CuPc combinations

In order to examine the photosensitivity of individual dyes and to elucidate the mechanism of O_2-suppressed reduction, nylon films dyed with a mixture of disperse dye and CuPc dye were exposed under aerobic conditions. In these combinations, the disperse dye was applied at one-third the absorbance of CuPc dye, to minimize the filter effects of the disperse dye.

The concentrations of the dyes in the mixture were determined from the absorbances at two wavelengths that were separated as much as possible from each other. Normally, the concentration of CuPc dye could be determined at the wavelength of the isosbestic point for the monomer–dimer equilibrium [25]. This point could not be used in our case, due to overlapping spectra. Consequently, the absorbance at 676 nm for CuPc dye and the λ_{max} of the disperse dyes were used to evaluate dye concentrations. For fadings in aerated water, it was assumed that the CuPc dye monomer–dimer equilibrium on nylon film in the presence and absence of disperse dye was the same, if the relative fading was unchanged. Thus, the absorption spectra of CuPc dye with essentially the same initial absorbance and the same relative fading were used as reference spectra, to calculate dye concentrations in mixtures. Subtracting the spectrum of the disperse dye from the combined spectra after each exposure confirmed the overlap for every calculation. This adjustment was not needed for fadings in O_2-saturated water, because no change in the shape of the absorption spectrum of CuPc dye was observed as disperse dye fading occurred.

The results of fading disperse dye/CuPc dye combinations in aerated and O_2-saturated water are summarized in Tables 2 and 3, respectively, together with results from the exposure of disperse dyes in the absence of CuPc dye. Since the fading behavior of disperse dyes in combination with CuPc dye varied with time of exposure, relative fading during the initial period of exposure (1 or 2 h) was mainly used to study the effects of the second dye and conditions of exposure. Since fading can occur heterogeneously or preferentially from the film surface, complete analysis of our system comprises future work.

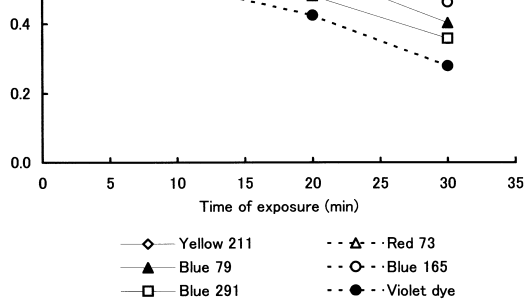


Fig. 1. Rate of fading (A/A_0) of six disperse dyes on nylon film immersed in aqueous NaClO (available chlorine: 0.20 g dm^{-3}) at pH 6.77 (0.01 M NaH_2PO_4) and at 25°C.

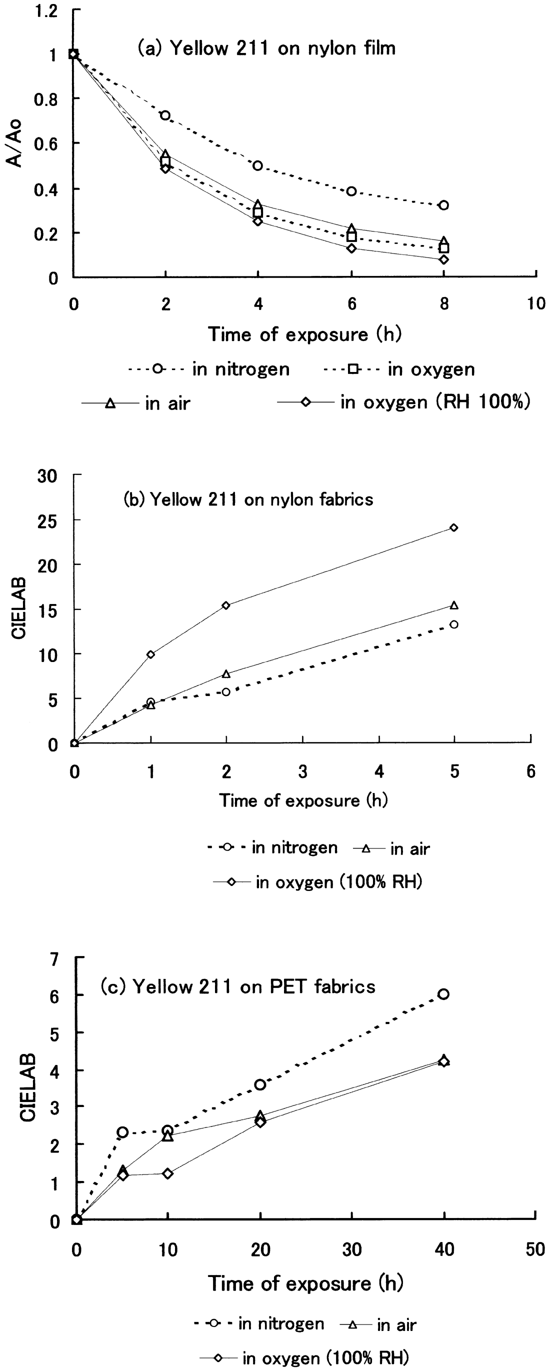


Fig. 2. Relationship between the fading of CI Disperse Yellow 211 (a) on nylon film ($A_0 = 0.783$), (b) on nylon fabric ($X_0 = 35.71$, $Y_0 = 35.70$, $Z_0 = 14.31$), and (c) on PET fabric ($X_0 = 61.45$, $Y_0 = 68.52$, $Z_0 = 23.55$) and the time of exposure, under various conditions.

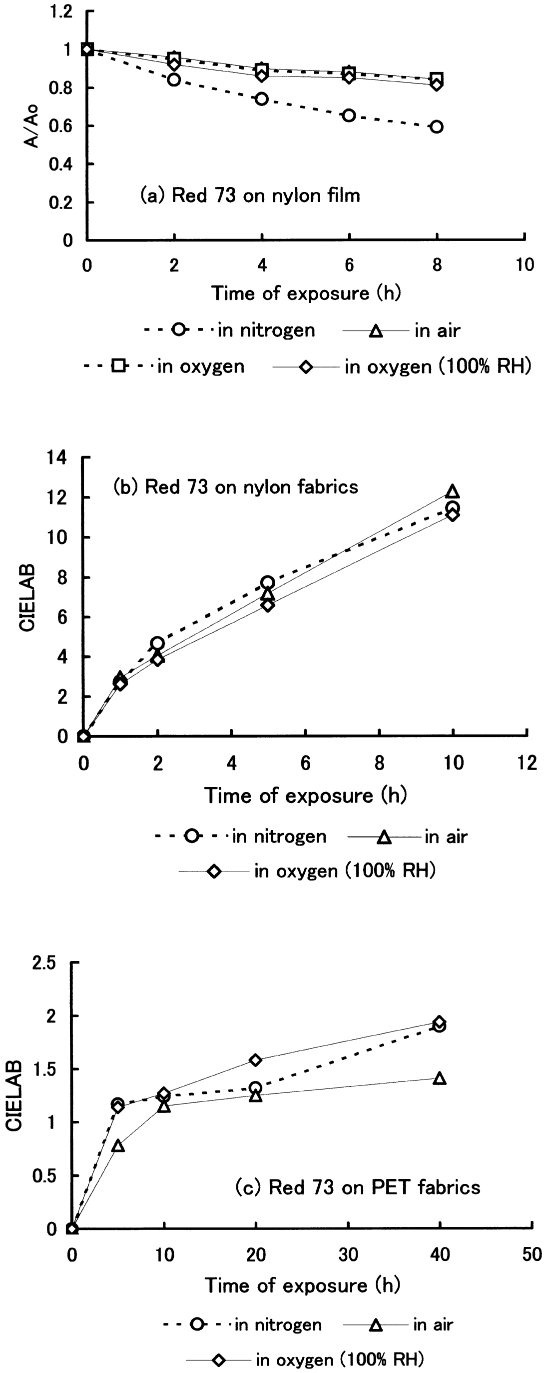


Fig. 3. Relationship between the fading of CI Disperse Red 73 (a) on nylon film ($A_0 = 1.538$), (b) on nylon fabric ($X_0 = 10.27$, $Y_0 = 6.81$, $Z_0 = 9.20$), and (c) on PET fabric ($X_0 = 37.66$, $Y_0 = 27.94$, $Z_0 = 30.54$) and the time of exposure, under various conditions.

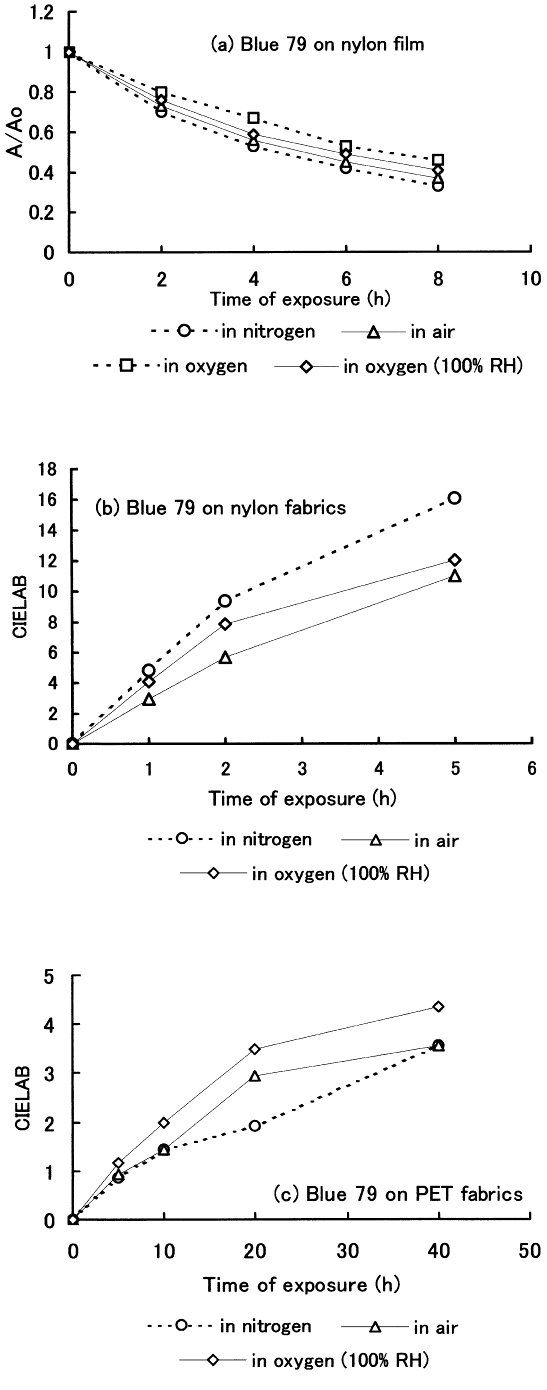


Fig. 4. Relationship between the fading of CI Disperse Blue 79:1 (a) on nylon film ($A_0 = 0.802$), (b) on nylon fabric ($X_0 = 9.60$, $Y_0 = 10.74$, $Z_0 = 21.82$), and (c) on PET fabric ($X_0 = 24.48$, $Y_0 = 27.56$, $Z_0 = 49.75$) and the time of exposure, under various conditions.

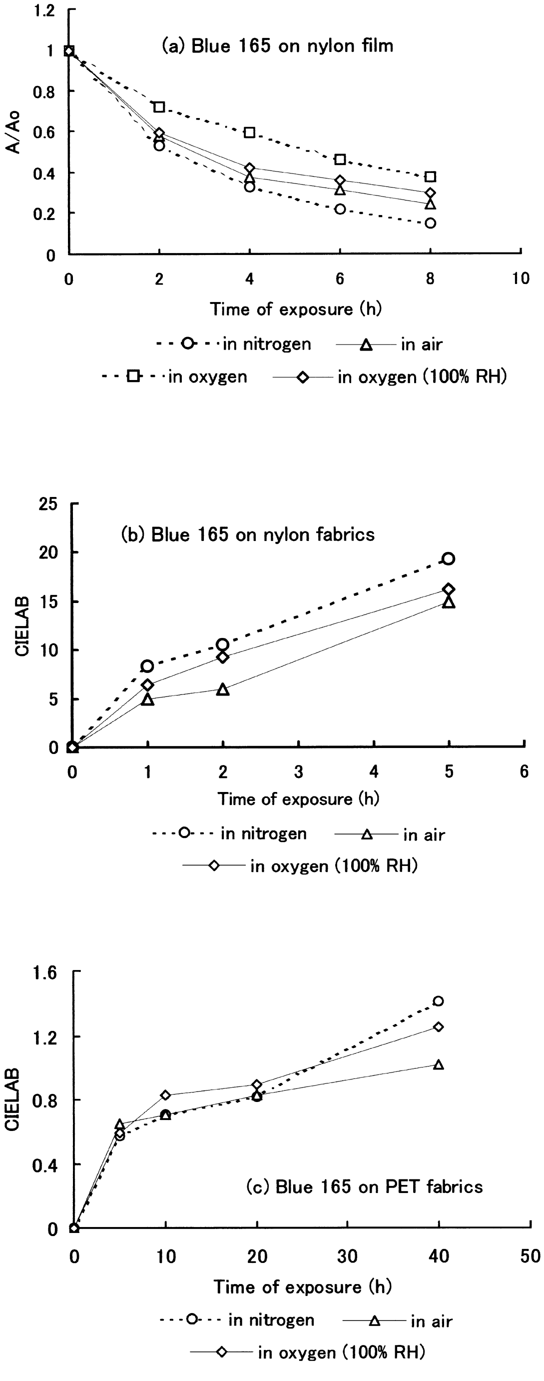


Fig. 5. Relationship between the fading of CI Disperse Blue 165 (a) on nylon film ($A_0 = 0.848$), (b) on nylon fabric ($X_0 = 12.59$, $Y_0 = 15.14$, $Z_0 = 31.75$), and (c) on PET fabric ($X_0 = 27.08$, $Y_0 = 31.73$, $Z_0 = 62.75$) and the time of exposure, under various conditions.

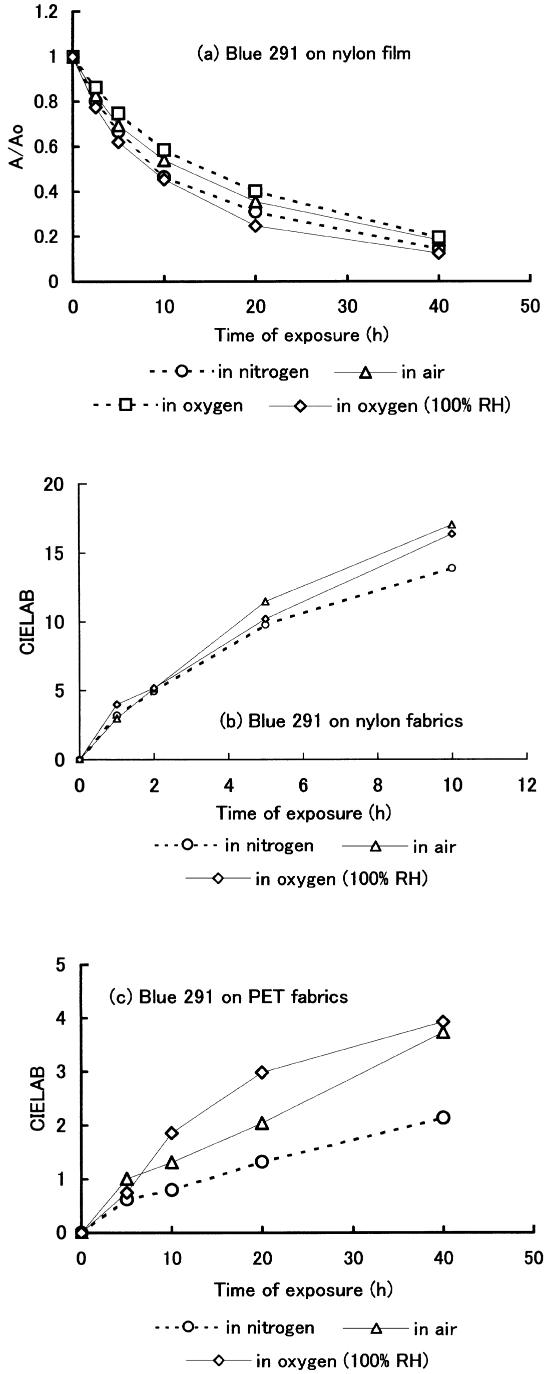


Fig. 6. Relationship between the fading of CI Disperse Blue 291 (a) on nylon film ($A_0=0.930$), (b) on nylon fabric ($X_0=12.85$, $Y_0=16.40$, $Z_0=29.12$), and (c) on PET fabric ($X_0=27.46$, $Y_0=33.26$, $Z_0=55.57$) and the time of exposure, under various conditions.

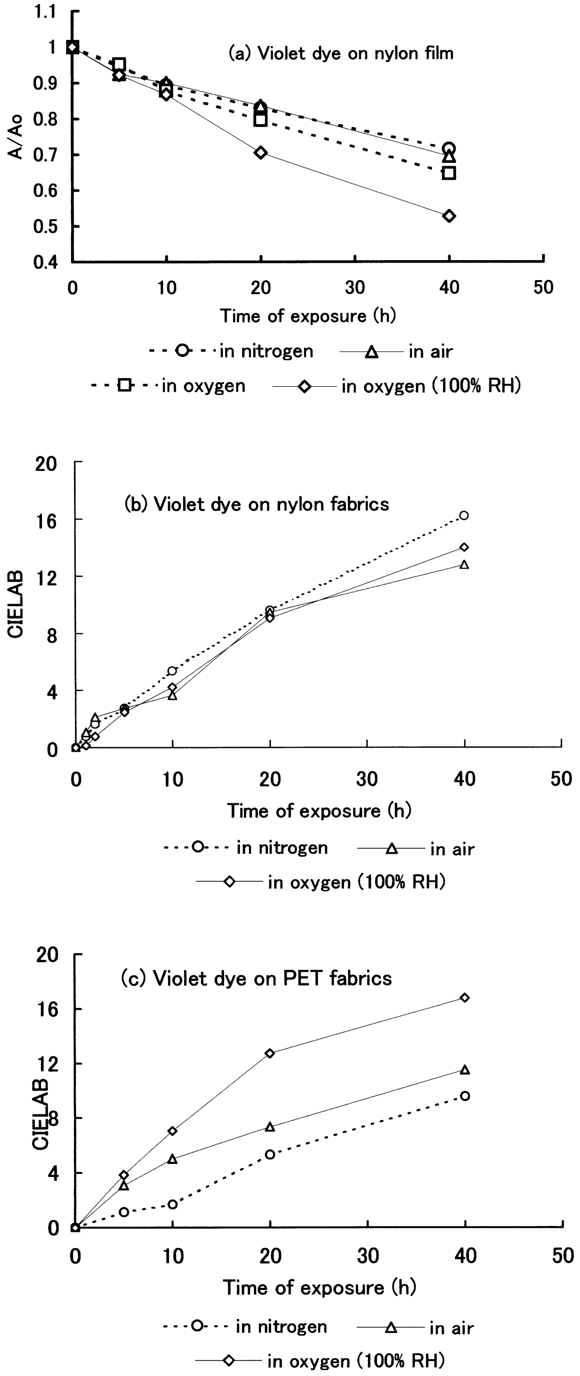


Fig. 7. Relationship between the fading of Violet dye (a) on nylon film ($A_0=0.799$), (b) on nylon fabric ($X_0=13.00$, $Y_0=10.36$, $Z_0=26.28$), and (c) on PET fabric ($X_0=24.91$, $Y_0=21.24$, $Z_0=42.08$) and the time of exposure, under various conditions.

3.2.1. Fading of films containing a single dye

For dyeings involving a single dye, an increase in O_2-concentration suppressed the fading of CI Disperse Blue 165 and CuPc dye considerably, but had little effect on the fading of Red 73, Blue 79:1 and Blue 291. On the other hand, extensive fading of Yellow 211 and the Violet dye occurred. These results suggest a reductive fading mechanism for all dyes except Yellow 211 and the Violet dye, and show the large photosensitivity of the individual dyes. A large reduction in fading in the presence of O_2 may be attributed to the large sensitivity of dyes.

In the case of the Violet dye, an increase in O_2 concentration accelerated fading. Moreover, the fading of this dye on nylon film containing CuPc dye was reduced during exposures in aerated and O_2-saturated water, versus fading in the absence of the CuPc dye (see Section 3.2.2). This suggests that the Violet dye undergoes oxidative fading under aerobic conditions. In the presence of the CuPc dye, the concentration of oxygen in nylon is lowered. In this case the CuPc dye may consume oxygen during the fading process. It is also possible that CuPc dye exerts a filter effect on the fading of the Violet dye, as the mechanism of reduced fading.

CI Disperse Blue 165 acquired a reddish hue as fading progressed. The color change was greater in aerated water than in O_2-saturated water, and was greater in the absence of the CuPc dye. This color change may arise from the reduction of the nitro group without reduction of the azo bond.

3.2.2. Effects of disperse dyes on CuPc dye

The rate of reductive fading of CuPc dye was suppressed by disperse dyes and the magnitude of the reduction in aerated water varied with the disperse dye employed. The relative order of fading reduction was as follows:

- Yellow 211 > Blue 165 > Blue 79:1 > Red 73≑Blue 291 > Violet dye

In O_2-saturated water, disperse dye suppression of CuPc dye fading during the initial period of exposure was observed in mixtures involving Yellow 211, Blue 165, Blue 79:1 and Violet dye, while Red 73 and Blue 291 had an accelerating effect. The reductive fading of the CuPc dye in the absence of disperse dye was suppressed by an increase in O_2 concentration. Fade reductions caused by Red 73 and Blue 291 were mainly observed after an initial 1–2 h exposure. Although disperse dyes may exert a filter effect, some cause an increase in O_2 concentration. It is proposed that the oxidation of CuPc dye near the substrate surface is promoted by an increase in O_2, and that reduction is suppressed in the substrate interior. In O_2-saturated water, the order of the magnitude of fade reduction was as follows:

- Yellow 211 > Blue 165 > Blue 79:1 > Blue 291 > Violet dye≑Red 73.

3.2.3. Effects of CuPc dye on the fading of individual disperse dyes

- *CI Disperse Yellow 211:* This dye had the lowest oxidizability and the highest photosensitivity. The latter property led to the largest suppression of the reductive fading of CuPc dye. However, a synergistic action arising from the photosensitivity of both dyes accelerated the oxidative fading of Yellow 211 in combination with CuPc dye, and an increase in O_2 concentration further accelerated fading.
- *CI Disperse Red 73, Blue 79:1, and Blue 165:* CuPc dye decreased the fading of these dyes in aerated and O_2-saturated water. Increasing O_2 concentration decreased fading. The significant effect of CuPc dye on the stability of these dyes suggests that CuPc dye-induced $^1O_2$ plays a role in the O_2-suppressed fading process.
- *CI Disperse Blue 291 and Violet dye:* CuPc dye seemed to suppress the fading of Blue 291 and Violet dye, especially during the initial period of exposure. This effect was smaller in O_2-saturated water than in aerated water. It is suggested that a decrease in O_2 concentration caused by CuPc dye O_2 consumption accounts for the reduction in Violet dye fading. Since Blue 291 has an oxidizability similar to the Violet dye, fading of this dye may follow the same mechanism.

3.3. Fading of individual dyes on dry nylon film

Nylon films dyed with disperse dyes were exposed to carbon-arc radiation under various conditions. The fading behavior for six dyes,

Table 4
Relative fading, A/A_0, for some disperse dyes on nylon film, and their fading, ΔE^*_{ab}, on Nylon and PET fabrics in air

Dye (CI Disperse)	A/A_0 of dyes on nylon film					ΔE^*_{ab} of dyed fabrics		
	Exposure				Immersion in NaClO	Exposure in air		
	In air	In N_2	In aerated water			Nylon	PET	
	2 h	2 h	1 h	2 h	30 min	5 h	10 h	40 h
Yellow 211	0.545	0.725	0.759	0.528	0.739	15.4	2.3	4.3
Red 73	0.959	0.850	0.922	0.821	0.656	7.2	1.2	1.4
Blue 79:1	0.721	0.697	0.876	0.707	0.404	12.7	1.4	3.6
Blue 165	0.561	0.533	0.671	0.476	0.463	14.9	0.7	1.0
Blue 291	0.870	0.840	0.904	0.808	0.359	11.5	1.3	3.7
Violet dye	0.970	0.975	0.958	0.854	0.279	2.8	5.0	11.5

shown as the ratios of absorbance at the λ_{max}, is illustrated in part (a) of Figs. 2–7. The fading rates on nylon films under various conditions are summarized in Table 4. Although environmental effects on fading rates varied from dye to dye, the relationships between fading rates and environmental conditions could be defined by the patterns shown in Table 5.

Based on the fading behavior of the dyes examined, it can be concluded that CI Disperse Red 73, Blue 79:1, Blue 165, and Blue 291 undergo reductive fading in air, while Yellow 211 undergoes oxidation, and the Violet dye undergoes both processes. The rates of reductive fading for these dyes decreased with increased O_2 concentration and reductive fading was suppressed by O_2.

Reddening associated with the fading of CI Disperse Blue 165 increased with decreased O_2 concentration. While the rates of reduction of the azo group (fading) and nitro group (reddening) seemed to be dependent upon the environmental conditions, they did not change with the time of exposure. Since the species produced by reduction of the nitro group had a low fading rate, color variation seemed to occur mainly during the latter stages of light exposures.

- *CI Disperse Yellow 211:* The rates of fading were proportional to O_2 concentration, implying oxidative fading on nylon under aerobic conditions, while the fading rate in N_2 was quite high. The latter observation indicates reductive fading under anaerobic conditions. This combination of fading behaviors is consistent with a high level of photosensitivity and photo-reductivity, although this dye had the lowest oxidizability.
- *CI Disperse Red 73:* The relatively low rate of reductive fading was substantially suppressed by air, but exposure in O_2 did not further suppress reductive fading. The latter

Table 5
Effects of exposure conditions on fading rate on dry nylon film, and primary mechanism of fading

CI generic name	Order of fading rates	Primary mechanism of fading on dry nylon films[a]
CI Disperse Yellow 211	O_2 (100% RH) > O_2 > air > N_2	Oxidation under aerobic conditions and reduction in N_2
CI Disperse Red 73	N_2 > air = O_2 (100% RH) = O_2	Reduction in N_2 and O_2-suppressed reduction under aerobic conditions
CI Disperse Blue 79:1	N_2 > air > O_2 (100% RH) > O_2	Reduction in N_2 and O_2-suppressed reduction under aerobic conditions
CI Disperse Blue 165	N_2 > air > O_2 (100% RH) > O_2	Reduction in N_2 and O_2-suppressed reduction under aerobic conditions
CI Disperse Blue 291	O_2 (100% RH) > N_2 > air > O_2	Reduction in N_2, O_2-suppressed reduction in air and O_2, and oxidation in O_2(100% RH)
Disperse Violet dye	O_2 (100% RH) > O_2 > air = N_2	Oxidation under aerobic conditions and reduction in N_2

[a] Deduced from Figs. 2–7 and Tables 2 and 3.

Table 6
Effects of environmental conditions on fading rates for disperse dyes on polyester and nylon fabrics, and their mechanism of fading

Dye (CI Disperse)	Order of fading rates		Mechanism of fading	
	PET for 40 h	Nylon for 5 h	On PET fabric	On nylon fabric
Yellow 211	$N_2 > air \approx O_2$(100% RH)	O_2(100% RH) > air > N_2	Reduction in N_2 and O_2-suppressed reduction under aerobic conditions	Oxidation under aerobic conditions and reduction in N_2
Red 73	$N_2 \approx O_2$(100% RH) > air	N_2 > air > O_2(100% RH)	Reduction in N_2 and O_2-suppressed reduction under aerobic conditions	Reduction in N_2, and O_2-suppressed reduction under aerobic conditions
Blue 79:1	O_2(100% RH) > air $\approx N_2$	$N_2 >$ O_2(100% RH) > air	Oxidation in O_2(100% RH), reduction in N_2, and O_2-suppressed reduction in air	Oxidation in O_2(100% RH), reduction in N_2, and O_2-suppressed reduction in air
Blue 165	$N_2 > O_2$(100% RH) > air	$N_2 > O_2$(100% RH) > air	Reduction in N_2 and O_2-suppressed reduction under aerobic conditions	Reduction in N_2, and O_2-suppressed reduction under aerobic conditions
Blue 291	O_2(100% RH) > air > N_2	O_2(100% RH) $\approx$ air > N_2	Oxidation under aerobic conditions and reduction in N_2	Oxidation under aerobic conditions and reduction in N_2
Violet dye	O_2(100% RH) > air > N_2	N_2 > air $\approx O_2$(100% RH)[a]	Oxidation under aerobic conditions and reduction in N_2	Reduction in N_2, and O_2-suppressed reduction under aerobic conditions

[a] Comparison for 40 h.

phenomenon was also observed during the exposure of this dye in combination with CuPc dye. While this dye underwent less fading than the three blue dyes, its lightfastness rating was 1, on a scale of 1 (poor) to 8 (excellent) (cf Section 3.2.3).

- *CI Disperse Blue 79:1 and Blue 165:* Since the fading rates for Blue 79:1 and Blue 165 were lower in O_2 than in air, the ease with which both dyes were reduced seemed to be too great to be suppressed by air to give satisfactory lightfastness on nylon.
- *CI Disperse Blue 291:* The fading of this dye on nylon was faster under anaerobic conditions than under aerobic conditions, except when O_2 was used at 100% RH. In the latter case, fading was decreased by an increase in O_2 concentration, implying O_2-suppressed reductive fading except for the case of O_2 at 100% RH. When irradiating nylon films immersed in aerated and O_2-saturated water, this dye underwent oxidative fading. Since Blue 291 is easily oxidized, moisture promotes the rate of oxidative fading.
- *Violet dye:* Environmental effects on the fading behavior of this dye on nylon were different from that of Blue 291, although the dye showed higher oxidizability than Blue 291 (see Fig. 1 and Table 4). The rate of fading increased with increasing O_2 concentration, indicating oxidative fading under aerobic conditions.
- The Violet dye and CI Disperse Yellow 211 exhibited the same fading behavior, although former had the highest oxidizability and the latter had the highest photosensitivity.

3.4. Mechanism of $^1O_2$-suppressed reductive fading

Except for the reduction of nitro groups to amino groups in CI Disperse Blue 165 and Blue 291, the fading of disperse dyes on nylon films can be summarized as follows:

1. The dyes undergo reductive fading on nylon. Exceptions are Yellow 211 and Violet dye under all aerobic conditions, and Blue 291 in O_2-saturated water (see Table 5).
2. The mechanism of reductive fading is described by:

$$^{1}\mathrm{D} + h\nu \rightarrow {}^{1}\mathrm{D}^{*} \rightarrow {}^{3}\mathrm{D}^{*} \quad (1)$$

$$^{3}\mathrm{D}^{*} + [\mathrm{H}] \rightarrow \text{(semi-reduced radical)} \quad (2a)$$

$$\text{(semi-reduced radical)} + [\mathrm{H}] \rightarrow \text{(hydrazine intermediate)} \quad (2b)$$

$$\text{(hydrazine intermediate)} + [\mathrm{H}] \rightarrow \text{amines} \quad (2c)$$

where [H] denotes hydrogen atoms that are abstracted from the substrate by dye triplet. This mechanism characterizes the exposure of all azo dyes in an N_2 atmosphere.

3. The mechanism of O_2-suppressed reduction under aerobic conditions leading to regenerated starting dye is described by Eqs (3a) and (3b).

$$^{3}\mathrm{D}^{*} + {}^{3}\mathrm{O}_2 \rightarrow {}^{1}\mathrm{D} + {}^{1}\mathrm{O}_2 \quad (3a)$$

$$^{1}\mathrm{O}_2 + \text{(semi-reduced radical) or (hydrazine intermediate)} \rightarrow {}^{1}\mathrm{D} \quad (3b)$$

Since the larger the dye photosensitivity the more effectively reductive fading was suppressed, $^{1}O_2$ seems to play a role in the mechanism. Thus, in dye combinations involving CuPc dye, the high photosensitivity of the CuPc dye has a marked effect on O_2-suppressed reductive fading of disperse dyes. Also, disperse dyes of high photosensitivity exhibit greater suppression on the reductive fading of CuPc dye. When suppression is highly efficient, the disperse dye has enhanced lightfastness.

4. The mechanism of oxidative fading after the generation of $^{1}O_2$ in step (3a) is described by Eq. (4a):

$$^{1}\mathrm{D} + {}^{1}\mathrm{O}_2 \rightarrow \text{(photo-oxidized fragments)} \quad (4a)$$

For exposures under aerobic conditions, Yellow 211 and the Violet dye undergo this type fading on nylon film (cf. Table 5).

3.5. Fading of disperse dyes on PET and nylon fabrics

The fading behaviors of six disperse dyes on nylon and PET fabrics were also examined under various conditions. The results are reported in terms of the relationships between color differences, type of exposure, and the time of exposure, in parts (b) and (c) of Figs. 2–7. The fading behavior on PET fabric was analyzed to infer the fading mechanism, by comparing the data with results on nylon. To compare the fading behavior of individual dyes, the relative fading values for a given time of exposure under various conditions are summarized in Table 4. The environmental effects of exposures on the fading rates for disperse dyes on PET fabric are summarized in Table 6. Although fading on fabrics is more complex than on nylon films, the fading behavior could be explained on the basis of mechanism outlined in Section 3.4.

3.5.1. Fading of CI Disperse Yellow 211

The effects of O_2 on the fading of this dye on PET fabric were opposite of what we found on nylon fabric (Table 6). However, fading on nylon fabric was similar to the fading observed on nylon film (Tables 5 and 6). Under anaerobic conditions, the rate of reductive fading on nylon fabric was much greater than that on PET fabric (Fig. 2). Thus, reductive fading on PET might be suppressed by O_2, while no suppression of reductive and oxidative fading occurred on nylon under aerobic conditions. The rate of oxidative fading on nylon under aerobic conditions was greater than the rate of reductive fading in N_2. On the other hand, oxidative fading on nylon with increased with increased O_2 concentration. This dye was more easily reduced and oxidized on nylon than on PET. Although Yellow 211 had the lowest oxidizability of the dyes examined, under aerobic conditions its high photosensitivity caused oxidative fading on nylon and suppressed reductive fading on PET. Therefore, it exhibited lower lightfastness on nylon than on PET. The fading mechanisms for Yellow 211 on PET and nylon fabrics are summarized in Table 6.

3.5.2. Fading of CI Disperse Red 73

The fading behavior of Red 73 on PET and nylon fabrics is summarized in Table 6. The rate of reductive fading for Red 73 on nylon films and fabrics in an N_2 environment was the lowest of the dyes examined, except for the Violet dye. O_2 suppressed reductive fading on nylon and PET was distinct but small. An increase in O_2 concentration suppressed fading on nylon film and on PET and nylon fabrics. The rate of reductive fading for Red 73 was considerably but not perfectly suppressed by O_2, giving high lightfastness. Thus, as shown in Tables 2 and 3, combinations with CuPc dye showed less fading than when Red 73 was exposed alone.

3.5.3. Fading of CI Disperse Blue 79:1

The fading behavior of Blue 79:1 on PET and nylon fabric is summarized in Table 6. The rate of fading for this dye on nylon fabric in air was lower than that for Blue 165 and higher than that for Red 73. However, the fading rate on PET fabric was higher. This observation correlates well with the lightfastness of these dyes on PET fabric (see Table 1). Reductive fading on nylon fabric was suppressed considerably by air and slightly by O_2. Fading on PET fabric was accelerated by an increase in O_2 concentration, implying oxidative fading under aerobic conditions. The O_2-suppressed reduction mechanism may apply to nylon substrates but is less applicable to PET fabric (see Tables 2, 3 and 5). The fading of this dye on nylon film dyed in combination with the CuPc dye was suppressed by CuPc dye. The rate of reductive fading on PET fabric was only slightly reduced by exposure in air but was enhanced in O_2, implying oxidative fading. It may not be possible to balance the photosensitive and O_2-suppressed fading of this dye on PET to get high lightfastness. The antagonistic action for this dye on PET fabrics to give high fastness may be less perfect than for Blue 165.

3.5.4. Fading of CI Disperse Blue 165

The fading behavior of Blue 165 on PET and nylon fabrics is summarized in Table 6. O_2 had similar effects on the fading of Blue 165 on both fabrics. The exposure of this dye on nylon fabric under anaerobic conditions gave extensive fading, and air only slightly suppresses fading. The fading of this dye on nylon film dyed in combination with the CuPc dye decreased with increased O_2 concentration, implying O_2-suppressed reductive fading. Reddening of this dye on nylon fabric as fading progressed is consistent with the proposed fading mechanism.

On nylon this dye is easily reduced (see Section 3.6). On PET fabric, however, the dye showed the same fading behavior as observed on nylon fabric, but the rate of fading on PET was much lower than on nylon fabric (see Table 4).

3.5.5. Fading of CI Disperse Blue 291

The fading behavior of Blue 291 on PET and nylon fabrics is also summarized in Table 6. The fading behaviors of this dye on both the fabrics were quite similar. The fading of nylon films dyed in combination with the CuPc dye was consistent with an O_2-suppressed effect (Tables 2 and 3). The fading of this dye on nylon and PET fabrics, however, was accelerated by an increase in O_2 concentration, probably due to the ease with which the dye is oxidized and the larger surface area of fabric versus film.

On fabric, this dye exhibited a color shift from blue to red as fading progressed, probably due to the reduction of a nitro group. This color variation was not observed on nylon film. In order to improve its lightfastness, the ease with which this dye is oxidized must be decreased.

3.5.6. Fading of Disperse Violet dye

The fading of the Violet dye on PET and nylon fabrics is summarized in Table 6. The rates of reductive fading for this dye and Blue 165 were quite different on the two fabrics.

Despite oxidative fading under aerobic conditions, the fading of Violet dye on nylon film dyed in combination with CuPc dye was less than the level observed when this dye was exposed alone on nylon in aerated and O_2-saturated water. The rate of fading on PET fabric was the highest among the dyes examined. Clearly, the Violet dye is too easily oxidized and too difficultly reduced to afford acceptable lightfastness. The latter property is significant if O_2-suppressed reduction is critical in exposures involving PET fabric in air.

On nylon fabric, this dye showed the lowest rate of fading among the dyes examined, but the level of fading was still too great to give good lightfastness.

3.6. Fading behavior of nylon and PET fabrics under anaerobic conditions

As mentioned above, $^1O_2$-suppressed reduction was observed during the exposure of disperse dyes under aerobic conditions, giving enhanced lightfastness. In order to fully analyze the photochemical properties of disperse dyes on nylon and PET fabrics, fading under anaerobic conditions is worth comparing. Under aerobic conditions these properties are hidden.

The rates of reductive fading on PET fabrics in a nitorgen environment were in the following order:

- Violet dye > Yellow 211 > Blue 79 > Blue 291 > Red 73 > Blue 165

Inspecting the fading behavior of these dyes on PET fabric revealed fast initial fading followed by slow subsequent fading, for Red 73 and Blue 165, although the reason was not clear. This behavior was not observed with the other dyes.

The rates of reductive fading on nylon fabric in the presence of nitrogen were in the following order:

- Blue 165 > Blue 79 > Yellow 211 > Blue 291 > Red 73 > Violet dye

This order correlates well with the order of the fading rates on nylon films in the presence of nitrogen (see Table 4).

When the ratios of the rates of fading on nylon and PET fabrics were calculated, Blue 165 (the highest) and Violet dye (the lowest) were atypical. All other dyes had similar ratios and were comparable in ranking on the two substrates. We expected the ratios to be nearly constant for the different dyes, when examining their fading behavior on nylon by an accelerated testing method. In reality, Blue 165 afforded a very large ratio and high lightfastness on PET and very low lightfastness on nylon. Violet dye afforded a ratio near 1, low lightfastness on PET, and a lightfastness rating of 2–3 on nylon. No uncharacteristic properties were apparent for the Violet dye and Blue 165, from the summary provided in Tables 4–6. Despite the absence of a correlation between fading behavior on PET and nylon, nylon proved to be a useful substrate for assessing the photochemical properties of disperse dyes.

4. Summary

The monoazo disperse dyes examined in this study have a tendency to undergo reductive fading on PET when exposed in air. To attain high lightfastness, they should be re-designed such that reductive fading is inhibited as completely as possible in air. Since this inhibition is caused by the photosensitivity of the dye, a counteracting mechanism should take place in the substrate. When a dye has a low rate of photo-reduction, the mechanism of fading exists at a boundary between reduction and oxidation, giving a dye that is highly sensitive to exposure conditions and possesses low lightfastness.

On nylon substrates, the disperse dyes in this study showed fading behavior similar to that observed on PET. However, since the rates of photo-reductive and oxidative fading on nylon are larger than on PET, no antagonism between photo-oxidative and reductive fading occurs for the six dyes, giving very low lightfastness. This means that disperse dyes with high lightfastness on nylon should be engineered differently from disperse dyes for PET.

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