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Photodegradation Behavior of Disperse Dyes in Solution

Nobuyuki Katsuda,[a]* Takashi Omura[a] & Toru Takagishi[b]

[a]Fine Chemicals Research Laboratory, Sumitomo Chemical Co., Ltd., Konohana,
Osaka 554, Japan
[b]Department of Applied Materials Science, College of Engineering, Osaka Prefecture University,
Sakai, Osaka 593, Japan

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ABSTRACT

The photodegradation behavior of some azo and anthraquinone disperse dyes was investigated in solution in the presence of polyester and compared with that on polyester fiber. Ethyl acetate as a solvent, a soluble polyester of low molecular weight as a typical model of polyester fiber, and monochromatic light of various wavelengths as light source were employed in the investigation. The influence of added polyester, dissolved oxygen, and of an ultraviolet absorber on the photodegradation of the dyes was studied to gain an insight into the nature of the photofading of the dyes on polyester fiber. It was found that the results obtained in polyester-containing solution correlated very well to those on polyester fiber. © *1997 Elsevier Science Ltd*

Keywords: photodegradation, disperse dye, spectroirradiator, wavelength, ethyl acetate, polyester.

INTRODUCTION

The mechanism of the photodegradation of dyes on fibers is complicated since the system involves many factors which act independently to, or overlap, each other [1, 2]. One of the most important factors involved is the kind of light source employed [3–5]. The light sources so far used are the carbon arc lamp, xenon arc lamp, high pressure mercury vapor lamp, and

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*Corresponding author: fax: +81-6-466-5457.

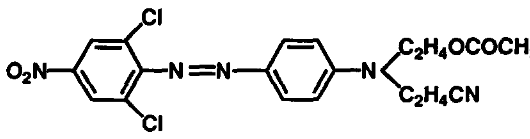
low pressure mercury vapor lamp. In order to standardize the light fastness of dyes on fibers in the field of automotive interiors, the xenon arc lamp has been chosen [6, 7]. Another important factor is the wavelength of the lamp. In previous papers, to avoid the complexity of the irradiation wavelength, a monochromatic light source divided into 20 distinct parts of monochromatic wavelength between 200 and 700 nm was used for studies on polyester, nylon, diacetate, triacetate or cotton fiber dyed with disperse dyes or reactive dyes [8, 9]. It was found that the fiber alone, and a dye on the fiber, underwent photodegradation at a wavelength specific for the fiber. For example, the wavelengths for polyester, nylon, diacetate, triacetate, and cotton fibers were 316, 372, 230, 259, and 259 nm, respectively. Another important factor is the environment which surrounds the dye molecules.

In this investigation, in order to clarify and simplify the system of dyed fiber, the photodegradation behavior of two types of disperse dyes (azo and anthraquinone) in solution was checked in the presence of a soluble polyester of low molecular weight as a typical model of polyester fiber, and also in the presence and absence of oxygen in the system. The effects of polyester and oxygen on the photofading of the disperse dyes were studied using monochromatic light of various wavelengths in order to evaluate the mode of action of the surroundings on the photodegradation of the dyes.

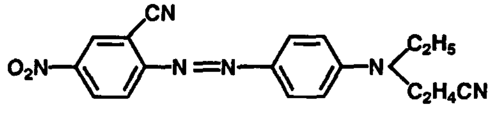
EXPERIMENTAL

Materials

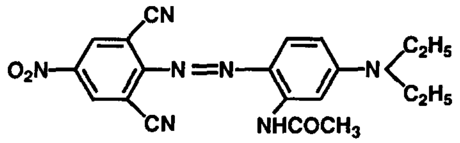
Sumikaron Yellow Brown S-2RL (C.I. Disperse Orange 30, Sumitomo Chemical Co., Ltd.), Sumikaron Rubine SE-GL (C.I. Disperse Red 73, Sumitomo Chemical Co., Ltd.), Sumikaron Blue S-BBL (C.I. Disperse Blue 165, Sumitomo Chemical Co., Ltd.), and Sumikaron Red E-FBL (C.I. Disperse Red 60, Sumitomo Chemical Co., Ltd.) were used as typical azo and anthraquinone type disperse dyes. These are of commercial grade and purified by column chromatography prior to use. The polyester fiber (Tetron tropical, Toray Co., Ltd.) was utilized after scouring, and for dyeing polyester, a commercial grade sample of an anionic surfactant, Sumipon TF (Sumitomo Chemical Co., Ltd.) was added. To investigate the photodegradation of the disperse dye in solution, ethyl acetate as a solvent, an ultraviolet absorber (Sumisorb 300, Sumitomo Chemical Co., Ltd.) as an additive, and a soluble polyester with a low molecular weight of about 10 000 as a model of polyester fiber were employed. The structures of the dyes and the ultraviolet absorber are shown in Fig. 1.



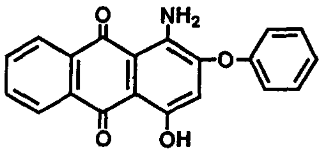
CI Disperse Orange 30



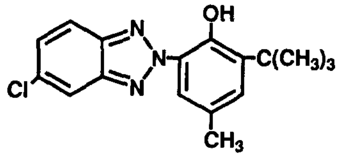
CI Disperse Red 73



CI Disperse Blue 165



CI Disperse Red 60



Ultraviolet absorber

Fig. 1. Structure of dyes and ultraviolet absorber used.

Dyeing of Polyester

The dyebath (180 ml) contained the disperse dye, anionic surfactant (0.2 g), and acetate buffer (0.2 g of sodium acetate and 0.05 g of acetic acid, pH 5). The dye concentration was calculated to correspond to a 1/1 shade (JIS). Polyester fiber (5 g) was immersed in the dyebath at 60°C and the temperature was raised from 60 to 130°C, and dyeing continued for 30 min at 130°C. The temperature was then lowered to 60°C, and rinsing was carried out.

Apparatus

The spectroirradiator (CRM-FA, JASCO Co., Ltd.) used was the same as that previously described, and the outline of the apparatus is presented there [8]. The light source was a xenon lamp of 2 kw (UXL-2003D, Ushiodenki Co., Ltd.) which covers all the wavelength regions from 200 to 700 nm. The light was divided into 20 single wavelengths of 201, 230, 259, 288, 316, 344, 372, 399, 426, 453, 479, 505, 531, 556, 581, 606, 630, 654, 678, and 701 nm by a diffraction lattice and the apparatus was equipped with 20 sample compartments. The fibers or cells mounted in the sample rooms were irradiated by monochromatic light of each wavelength.

Measurements of photodegradation

The coloration of dyed polyester was evaluated by color difference (ΔE) using a Macbeth Color-Eye 3000 (Sicomuc 20, Sumika Chemical Analysis Service Co., Ltd.). The extent of photodegradation of the disperse dye in ethyl acetate in the presence and absence of soluble polyester was measured using a UV-VIS spectrophotometer (UVPC-3101, Shimadzu Co., Ltd.). Dissolved oxygen in the solvent was removed by bubbling nitrogen gas through the solvent in the cell if necessary.

RESULTS AND DISCUSSION

In previous articles, the photodegradation behavior of disperse dyes on fibers such as nylon, diacetate, triacetate, and in particular polyester fibers, has been investigated [8, 9]. The photodegradation of the dyes was followed after spectroirradiation. The undyed and dyed fibers were irradiated with monochromatic light of various wavelengths. It was found that the most effective wavelength for the photodegradation of the disperse dyes on polyester fiber was near 316 nm, irrespective of the structure of the disperse dye. Polyester fiber alone, and any disperse dye on the fiber, underwent photodegradation at the wavelength specific for the fiber.

In order to clarify and gain an insight into these phenomena, in this investigation the photodegradation behavior of disperse dyes in solution instead of on polyester fiber was studied in the presence of a soluble polyester of low molecular weight as a typical model of polyester fiber. In this experiment, four typical azo and anthraquinone type disperse dyes were employed, the structures of which are shown in Fig. 1. These dyes have orange, red, and blue hues. Ethyl acetate was used as a solvent due to the solubility of both the polyester and the dyes and stability to light. The solvent can dissolve both substrates. C.I. Disperse Orange 30, Red 73, Blue 165, and Red 60 exhibit a maximum wavelength at 475, 525, 620, and 520 nm, respectively in ethyl acetate.

The color difference (ΔE) between the original and the irradiated fibers, which gives an indication of the extent of photodegradation of the dye on polyester fiber by spectroirradiation, with respect to the irradiation wavelength, is shown in Figs 2–5. In these figures the degree of decomposition of the dye in ethyl acetate by spectroirradiation is also represented. With C.I. Disperse Orange 30 (Fig. 2) the maximum change in ΔE and the degree of decomposition appears at 316 nm, although the irradiation energy is not always the same on the polyester fiber and in the solution, suggesting that the largest effect on the photodegradation is specific for the irradiation wavelength, and that the dye undergoes photodegradation on the fiber and in the polyester-involving solution in a similar manner. Quite the same situation can be observed with C.I. Disperse Red 73, C.I. Disperse Blue 165, and C.I. Disperse Red 60 as shown in Figs 3–5, respectively, although these dyes have different maximum wavelengths. This implies that the dye is affected at 316 nm on the polyester fiber and also in the polyester-containing solution, regardless of the dye structure. The photodegradation behavior of the dye on the polyester fiber is strongly correlated to that of the dye in the solution in the presence of soluble polyester.

In order to obtain more detailed information concerning the photofading after spectroirradiation, light of wavelengths at 288, 316, 344, and 372 nm

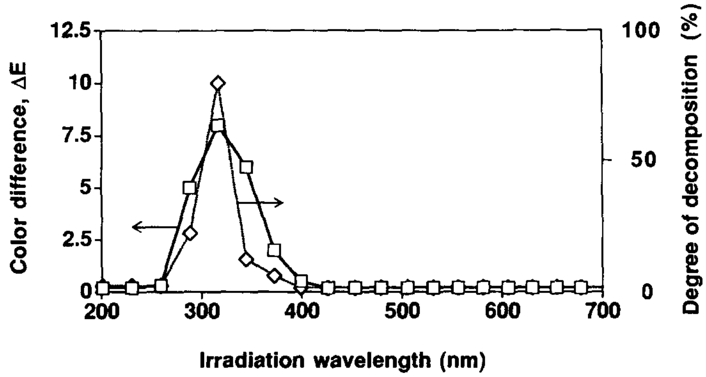


Fig. 2. Color change of polyester dyed with C.I. Disperse Orange 30 and degree of decomposition of the dye in ethyl acetate in the presence of soluble polyester by spectroirradiator: (□) color change of dyed polyester. Irradiation energy: 290 kj cm^{-2}; (◇) degree of decomposition in ethyl acetate. Irradiation time: 5 h.

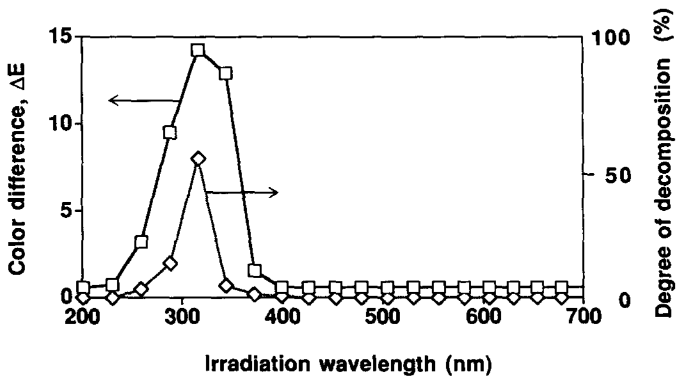


Fig. 3. Color change of polyester dyed with C.I. Disperse Red 73 and degree of decomposition of the dye in ethyl acetate in the presence of soluble polyester by spectroirradiator: (□) color change of dyed polyester. Irradiation energy: 290 kj cm^{-2}; (◇) degree of decomposition in ethyl acetate. Irradiation time: 5 h.

was employed for the spectroirradiation of the sample solution. These wavelengths were chosen so that the dye was not decomposed by light above 400 nm, as shown in Figs 2–5, and since light below 260 nm is not involved in natural light. The photodegradation behavior of C.I. Disperse Orange 30 in ethyl acetate under various conditions is illustrated in Fig. 6, in which the percentage of residual dye in the solution is plotted against the irradiation time at 288, 316, 344, and 372 nm. In this experiment the irradiation time was changed at a given wavelength. Thus the level of irradiation energy should be different at each wavelength in the experimental system used. In order to eliminate such influence, in the previous study the irradiation energy at each wavelength was kept constant by adding supplemental energy [8]. However,

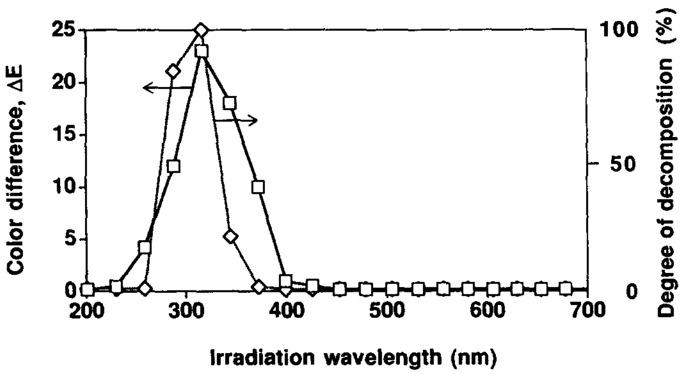


Fig. 4. Color change in polyester dyed with C.I. Disperse Blue 165 and degree of decomposition of the dye in ethyl acetate in the presence of spectroirradiator: (□) color change of dyed polyester. Irradiation energy: 290 kj cm^{-2}; (◇) degree of decomposition in ethyl acetate. Irradiation time: 5 h.

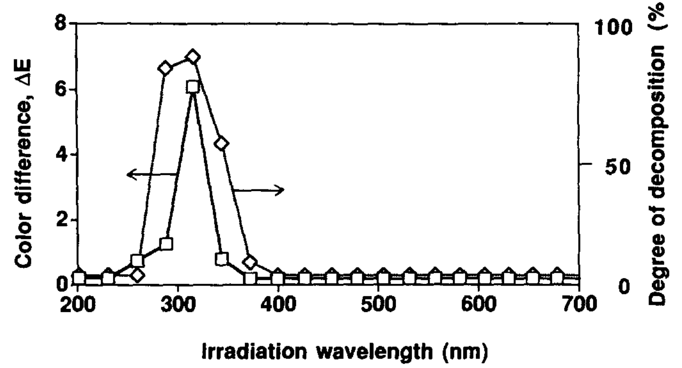


Fig. 5. Color change of polyester dyed with C.I. Disperse Red 60 and degree of decomposition of the dye in ethyl acetate in the presence of soluble polyester by spectroirradiator: (□) color change of dyed polyester. Irradiation energy: 290 kj cm^{-2}; (◇) degree of decomposition in ethyl acetate. Irradiation time: 5 h.

it was found that the photodegradation was almost the same, in spite of a constant or inconstant irradiation energy level at each wavelength.

Figure 6(A) indicates the effect of the irradiation wavelength on the photodegradation of the dye in solution without polyester and in the presence of oxygen, while Fig. 6(B) illustrates the effect of added polyester on the photodegradation of the dye. From the results shown in Fig. 6(A) and (B), it is apparent that the dye tends to be decomposed maximally and specifically at 316 nm in the presence of polyester while the dye is degraded by light at 288 nm and is scarcely affected by light of longer wavelengths (316, 344, and 372 nm) in the absence of polyester. This tendency in the presence of polyester is the same as that observed on polyester fiber [8, 9]. Such peculiar

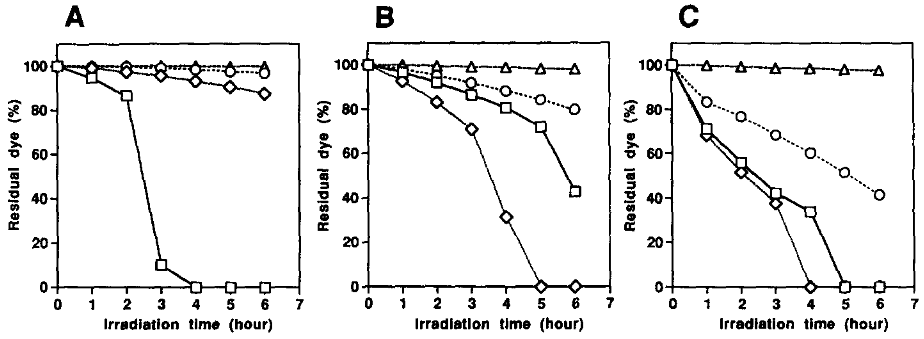


Fig. 6. Effect of irradiation wavelength on decomposition of C.I. Disperse Orange 30 in ethyl acetate: (A) with oxygen and without soluble polyester, (B) with oxygen and soluble polyester, (C) without oxygen and with soluble polyester: (□) 288 nm, (◇) 316 nm, (○) 344 nm, (△) 372 nm.

photodegradation behavior of dyes on various kinds of fibers has been already reported and discussed in detail in previous articles [8–9]. The absorbed energy characteristic of polyester fiber and/or degradation products of the fiber formed at the characteristic wavelength (316 nm) play a significant role in the photodegradation of dyes on the fiber. In the absence of polyester [Fig. 6(A)], the shorter the wavelength, the greater the photofading, although the photofading is very slight over 316 nm. This phenomenon is generally recognized and is attributable to the higher energy level at shorter wavelength.

Figure 6(C) demonstrates the photofading of C.I. Disperse Orange 30 in the oxygen-free solution involving polyester. When the results of Fig. 6(B) and Fig. 6(C) are compared, it is obvious that the photodegradation of the dye is enhanced and accelerated in the absence of oxygen. C.I. Disperse Orange 30 is an azo type disperse dye. It is well known that the principal photodegradation of an azo type dye proceeds via a reductive reaction [10, 11]. Accordingly, it is reasonable that C.I. Disperse Orange 30 should be decomposed increasingly without oxygen, although the decomposition of polyester itself and thus the influence of the degradation products of polyester produced at the specific wavelength of 316 nm should be depressed in an oxygen-free atmosphere. A similar situation can be observed for the other two dyes, C.I. Disperse Red 73 and C.I. Disperse Blue 165, which are also azo dyes as indicated in Figs 7(C) and 8(C).

With C.I. Disperse Red 60 an anthraquinone dye [Fig. 9(A) and (B)], the photodegradation behavior is quite similar to that of the azo type dyes C.I. Disperse Orange 30, C.I. Disperse Red 73, and C.I. Disperse Blue 165, in the presence and absence of polyester when oxygen is present in the system. In marked contrast, as is apparent in Fig. 9 (B) and (C), the photodegradation of C.I. Disperse Red 60 is suppressed in the absence of oxygen. In particular,

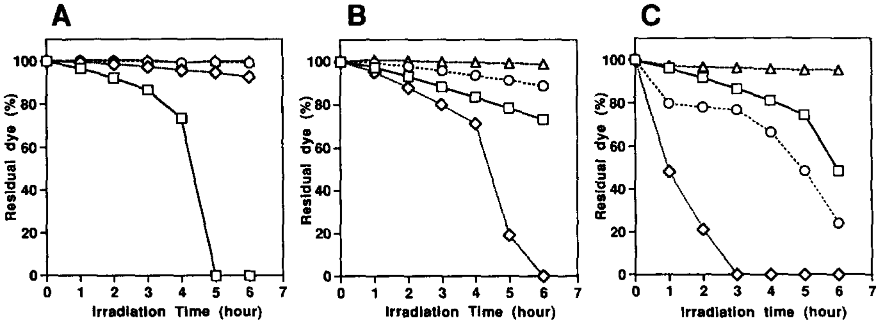


Fig. 7. Effect of irradiation wavelength on decomposition of C.I. Disperse Red 73 in ethyl acetate: (A) with oxygen and without soluble polyester, (B) with oxygen and soluble polyester, (C) without oxygen and with soluble polyester: (□) 288 nm,(◇) 316 nm,(○) 344 nm, (△) 372 nm.

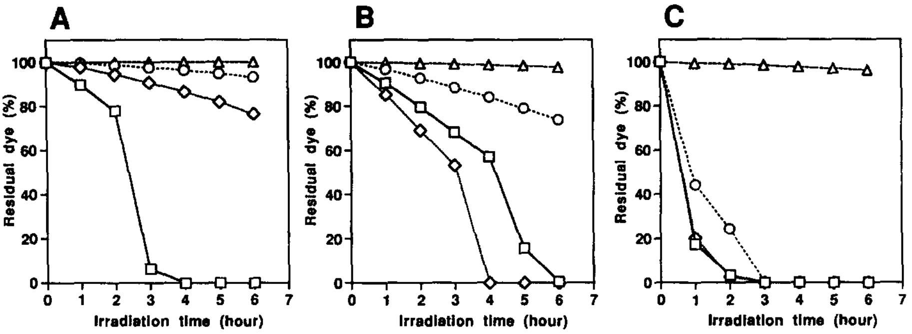


Fig. 8. Effect of irradiation wavelength on decomposition of C.I. Disperse Blue 165 in ethyl acetate: (A) with oxygen and without soluble polyester, (B) with oxygen and soluble polyester, (C) without oxygen and with soluble polyester: (□) 288 nm, (◇) 316 nm, (○) 344 nm, (△) 372 nm.

the photodegradation at 316 nm is remarkably improved when oxygen is absent in the system. The fading curve at 288 nm, where the influence of added polyester should be small, as shown in Fig. 9(A) and (B), retards slightly in the absence of oxygen [Fig. 9(C)] compared with that in the presence of oxygen [Fig. 9(B)]. The results of the anthraquinone dye strongly demonstrate that this type of dye is decomposed by light through an oxidative reaction. In the absence of oxygen the photodegradation of the polyester matrix itself should be depressed, and hence degradation products induced at 316 nm must be decreased. Therefore, in the case of Fig. 9(C), that is, the anthraquinone dye without oxygen, the photodegradation of the dye at 316 nm is significantly decreased. This implies that the photodegradation of the dye on the fiber is attributed mainly to the degradation products of the fiber formed at the characteristic wavelength.

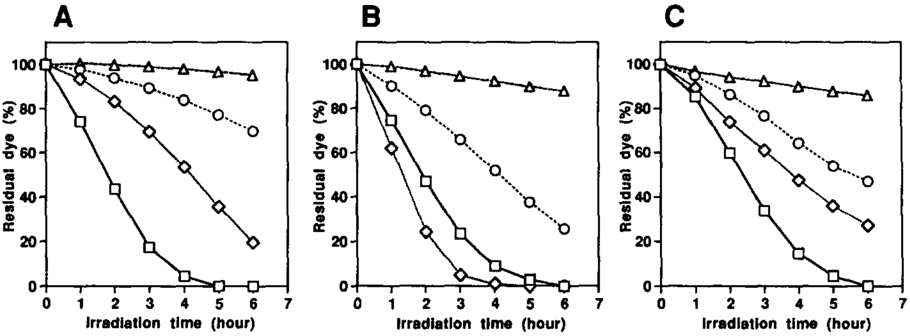


Fig. 9. Effect of irradiation wavelength on decomposition of C.I. Disperse Red 60 in ethyl acetate: (A) with oxygen and without soluble polyester, (B) with oxygen and soluble polyester, (C) without oxygen and with soluble polyester: (□) 288 nm, (◇) 316 nm, (○) 344 nm, (△) 372 nm.

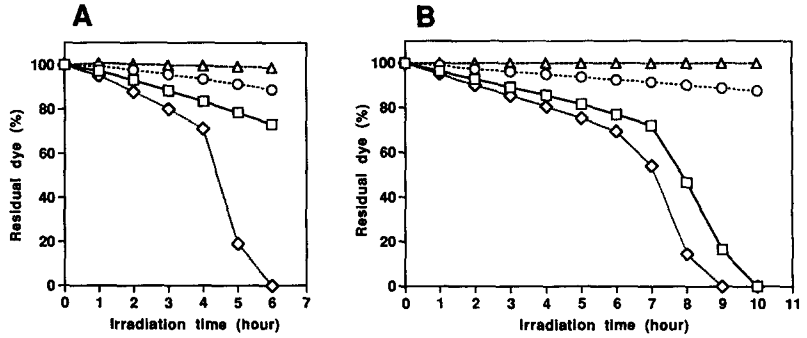


Fig. 10. Effect of irradiation wavelength on decomposition of C.I. Disperse Red 73 in ethyl acetate with oxygen and soluble polyester: (A) without ultraviolet absorber, (B) with ultraviolet absorber: (□) 288 nm, (◇) 316 nm, (○) 344 nm, (△) 372 nm.

Finally, the effect of an ultraviolet absorber on the photofading was investigated in ethyl acetate solution. The structure of the ultraviolet absorber is given in Fig. 1. The results are shown in Fig. 10(A) and (B). In this case, a benzotriazole type ultraviolet absorber was employed because this absorber is soluble in ethyl acetate and has been shown to be effective for improving the light fastness of disperse dyes on polyester [12]. As is evident in Fig. 10, the photofading can be retarded significantly by the added ultraviolet absorber.

CONCLUSION

This paper reports the development of an experimental system for the photodegradation of dyes, in which the photofading behavior of disperse dyes in polyester-containing solution is investigated using ethyl acetate as solvent, monochromatic light of various wavelengths as light source, and a soluble polyester of low molecular weight as a typical model of polyester fiber. Four disperse dyes of the azo and anthraquinone types, viz. C.I. Disperse Orange 30, C.I. Disperse Red 73, C.I. Disperse Blue 165, and C.I. Disperse Red 60, in ethyl acetate involving the soluble polyester were influenced maximally and specifically by spectroirradiation at 316 nm, irrespective of the different chemical structures and colors of the dyes. The largest effects on the photodegradation is a specific fiber-wavelength combination. The results in polyester-involving solution are consistent with those on polyester fiber. The photofading was also checked in solution in the presence and absence of oxygen. It was observed that the principal photodegradation of the azo dyes, i.e. C.I. Disperse Orange 30, C.I. Disperse Red 73, and C.I. Disperse Blue 165, proceeds via a reductive reaction. In contrast the anthraquinone dye, C.I. Disperse Red 60 was decomposed strongly by light through an oxidative reaction. With C.I. Disperse Red 60, the photofading at 316 nm was improved significantly in the oxygen-free atmosphere, because the photodegradation of polyester itself at this wavelength is suppressed and the formation of the degradation products of polyester at this wavelength are decreased. It was also shown that addition of an ultraviolet absorber strongly retarded the photofading of the dye in polyester-containing solution at 316 nm.

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