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# Photodegradation of a Disperse Dye on Polyester Fiber and in Solution

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## ABSTRACT

*The photodegradation behavior of dyes on fibers such as nylon, cotton fibers, and in particular, polyester, and in a solution has been investigated. The undyed and dyed fibers were irradiated with monochromatic light of various wavelengths. The light source was separated into 20 distinct wavelengths and the photodegradation behavior at each wavelength was examined. It was found that the most effective wavelength for the photodegradation of a disperse dye on polyester fiber was near 320 nm. The wavelength also affected the photodegradation of the fiber itself. Similar phenomena were observed for nylon fiber: light near 370 nm influenced significantly both the dye on the fiber and the fiber itself. With cotton, light at 260 nm was significant. To clarify these results, photodegradation of the dye in ethyl acetate containing dissolved polyester was also carried out. The same phenomena as those observed on the fiber were shown to be operative. Copyright © 1996 Elsevier Science Ltd*

## INTRODUCTION

Many studies concerning the photodegradation of dyes have been reported.[1–21] However, because the photodegradation of dyes involves many factors, its mechanism is not yet clear. For example the photodegradation behavior of dyes on fibers is not correlated with those in solution. In previous studies on the photodegradation of dyes, the light source used was a carbon or xenon arc lamp. These lamps cover all the wavelength regions from the ultraviolet to the visible. It is likely that this makes the photodegradation behavior more complex and diffuse.

In this investigation, the photodegradation of dyes on fibers and in solution has been measured using a monochromatic light source divided into 20 parts distinct monochromatic wavelengths between 201 and 701 nm. The photodegradation behavior at each wavelength was examined using principally a polyester fiber and an azo type disperse dye system, and nylon-disperse dye and cotton-reactive dye systems were also examined for comparison.

## EXPERIMENTAL

### Materials

Sumikaron Rubine SE-GL (C.I. Disperse Red 73, Sumitomo Chemical Co., Ltd) was used as a typical azo type disperse dye; the commercial grade dye was purified by column chromatography. As a reactive dye, Sumifix Supra Brilliant Red 3BF of commercial grade (C.I. Reactive Red 195, Sumitomo Chemical Co., Ltd) was employed and used without further purification for cotton fiber. The polyester (Tetron tropical, Toray Co., Ltd) and nylon (nylon jersey, Teijin Co., Ltd) fibers were utilized after scouring. Mercerized cotton fiber (cotton knit, Teijin Co., Ltd) was also used. For dyeing polyester, a commercial grade sample of anionic surfactant, Sumipon TF (Sumitomo Chemical Co., Ltd) was added. In order to clarify the photodegradation phenomena of the polyester-disperse dye system, such phenomena were also checked in a solution, using ethyl acetate as solvent and polyester with a low molecular weight of about 10 000.

### Dyeing of polyester

The dye bath (180 ml) was prepared with 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°C to 130°C.

### Dyeing of nylon

Nylon fiber was dyed by the same method as that used for the dyeing of polyester, but the dyeing temperature was 100°C.

## Dyeing of cotton

The dyebath (200 ml) was prepared at 80°C with the reactive dye and sodium sulfate (10 g), giving a neutral solution of pH 6.8. The dye concentration was calculated to correspond to a 1/1 shade (JIS). Cotton fiber (5 g) was immersed in the dyebath and dyed under the neutral condition for 20 min with stirring; sodium carbonate (4 g) was then added to make the solution alkaline (pH 11.5), and dyeing was continued for a further 60 min. The dyed cotton fiber was rinsed in cold water and then in boiling water to remove unfixed dye, and dried in an oven at 80°C.

## Apparatus

A spectroirradiator (CRM-FA, JASCO Co., Ltd) was used to irradiate monochromatic lights of various wavelengths. The outline of the apparatus is shown in Fig. 1. The light source was a xenon lamp of 2 kW (UXL-2003D, Ushiodenki Co., Ltd). The light irradiated by the lamp covers all wavelengths from 200 nm to 700 nm. The light is gathered by the mirror of $M_1$ and reaches the mirror of $M_2$ through the slit. The light reflected by $M_2$ is 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 the diffraction lattice. The light of each single wavelength irradiates the fibers or cells mounted in the 20 sample holders used.

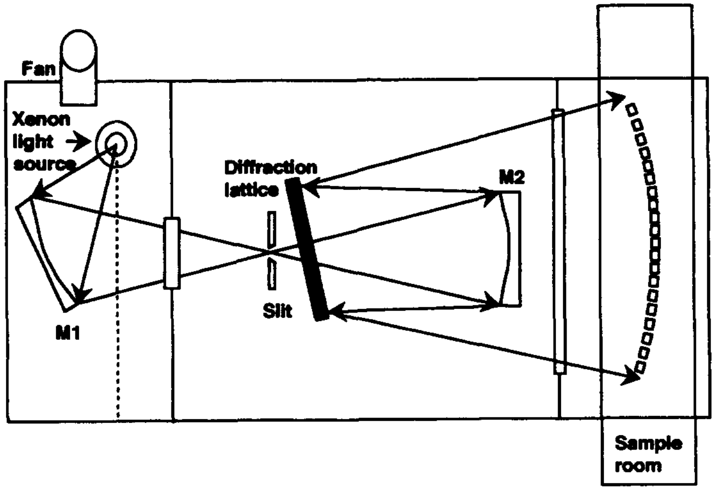

**Fig. 1.** Diagram of spectroirradiator system used.

## Measurements of photodegradation

The photodegradation of the disperse dye in solution was measured using a UV-VIS spectrophotometer (UVPC-3101, Shimadzu Co., Ltd). The photodegradation of polyester, nylon or cotton fiber dyed and undyed was assessed by color difference (ΔE) using a Macbeth Color-Eye 3000 (Sicomuc 20, Sumika Analysis Center Co., Ltd).

## RESULTS AND DISCUSSION

Polyester and dyed polyester fibers were irradiated by the spectroirradiator. The changes in color of the fiber itself and of the dyed fiber are shown in Fig. 2. It was found that with longer irradiation time, the fiber became more yellow, and the dyed fiber more faded. The regions indicated by mesh in Fig. 2 (A) and (B) represent the color change of the fiber itself or the fading of the dyed fiber. The gradations in Fig. 2 show the extent of color change qualitatively. From the results obtained in Fig. 2 it is apparent that the color change or fading is dependent on the irradiation wavelength. The fiber itself or the dye molecule on the fiber is decomposed only by light of a specific wavelength.

In order to express these results quantitatively, the color difference between the original and the irradiated fibers was measured. The color

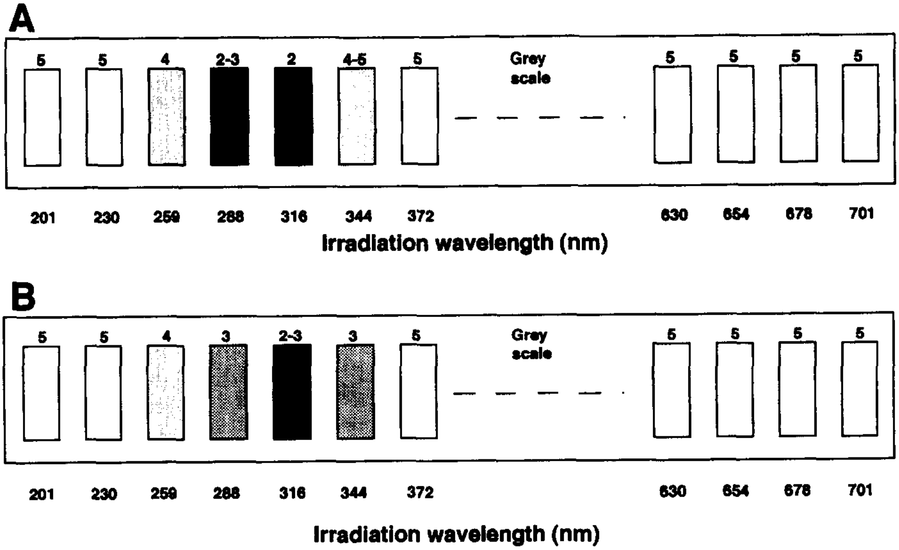

**Fig. 2.** Color change and fading by spectroirradiator: (A) Color change of undyed polyester fiber, (B) Color change and fading of dyed polyester fiber. Irradiation energy; 290 kJ/cm$^2$.

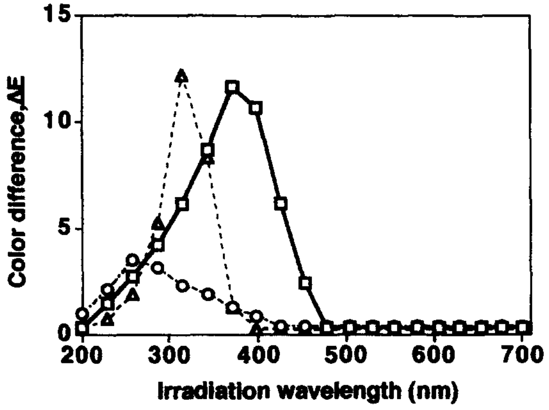

Fig. 3. Color change of fiber by spectroirradiation: (□) Undyed nylon, (○) Undyed cotton, (△) Undyed polyester.

difference of the undyed polyester, nylon or cotton fiber is shown in Fig. 3. It is evident that the extent of color change for any fiber depends on the irradiation wavelength. The maximum change appears at 316 nm for polyester, 372 nm for nylon, and 259 nm for cotton fiber, suggesting that the largest effect on the photodegradation is a specific fiber-wavelength combination.

Figure 4 shows the extent of color change of undyed nylon and fiber dyed with C.I. Disperse Red 73. The maximum effect of photodegradation is observed at the same wavelength of irradiation, namely, 372 nm for both dyed and undyed nylon. Figure 5 depicts the photodegradation behavior of cotton which is undyed or dyed with C.I. Reactive Red 195. As apparent in

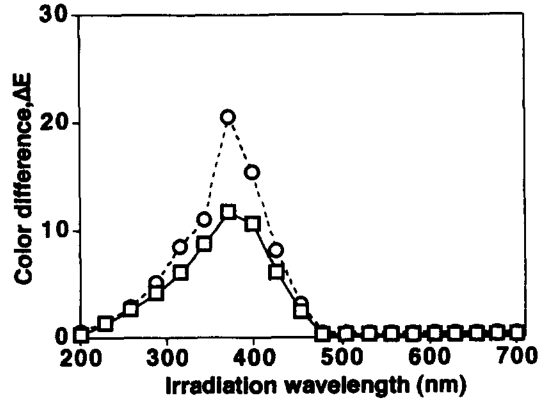

Fig. 4. Color change of undyed and dyed nylon fibers by spectroirradiation: (□) Undyed nylon, (○) Nylon dyed with C.I. Disperse Red 73.

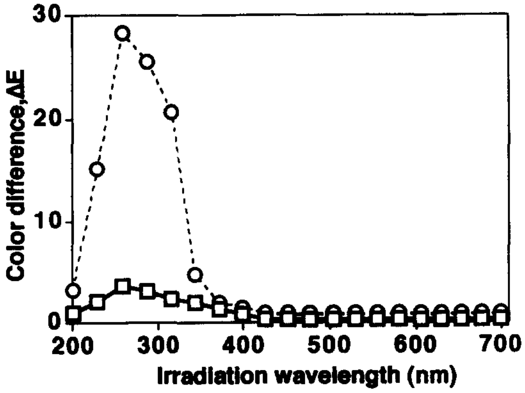

**Fig. 5.** Color change of undyed and dyed cotton fibers by spectroirradiation: (□) Undyed cotton, (○) Cotton dyed with C.I. Reactive Red 195.

Fig. 5, the extent of fading of dyed cotton is much larger than the color change of undyed cotton. This might be due to structural properties of the reactive dye. However, the undyed and dyed fibers are influenced maximally at 259 nm. The situation observed for cotton is similar to that for nylon shown in Fig. 4. Figure 6 represents the case of polyester fiber. With the polyester fiber the same tendency as that of nylon or cotton was also recognized. Accordingly, it is likely that photodegradation of C.I. Disperse Red 73 takes place at a different wavelength on nylon and polyester fibers, and is strongly dependent on the nature of the fiber itself.

When light of each wavelength is irradiated for a given time, the level of irradiation energy should be different at each wavelength in the experimental system used. In order to eliminate such an influence, the irradiation energy at

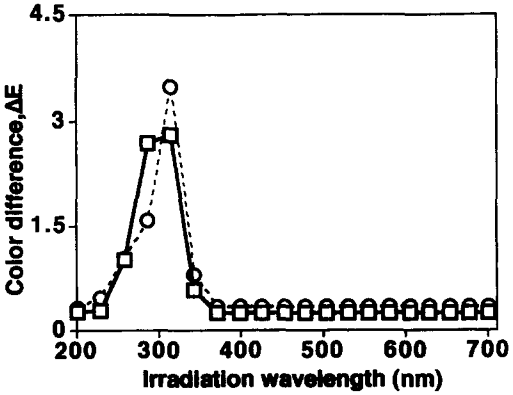

**Fig. 6.** Color change of undyed and dyed polyester fibers by spectroirradiation: (□) Undyed polyester, (○) Polyester dyed with C.I. Disperse Red 73.

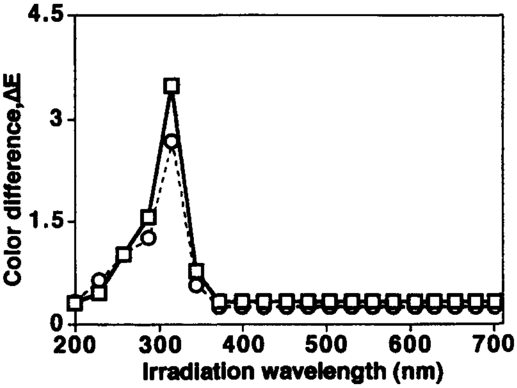

**Fig. 7.** Color change of polyester fiber by spectroirradiation: (□) Polyester dyed with C.I. Disperse Red 73 (the same irradiation time), (○) Polyester dyed with C.I. Disperse Red 73 (the same irradiation energy).

each wavelength was kept constant by adding supplemental energy. A typical result for dyed polyester is shown in Fig. 7. As is evident in Fig. 7, the situation is the same and the maximum effect appears at 316 nm in spite of a constant or inconstant irradiation energy level at each wavelength. In any event, although the xenon lamp and also sunlight cover a wide range of wavelengths for which an uneven energy level is involved, maximum fading of the dye on nylon, cotton or polyester takes place at the wavelength at which each individual fiber is affected by the light.

In order to clarify the above phenomena, the photodegradation behavior of the disperse dye in solution was also investigated in the presence of a soluble polyester of low molecular weight as a typical model of polyester fiber. The molecular weight of the polyester used was about 10000. Ethyl acetate was used as a solvent because this solvent is stable to light and can dissolve both the polymer and the dye (C.I. Disperse Red 73). The photodegradation of the dye was followed after spectroirradiation. It was found that the dye was not decomposed by light above 400 nm. Light below 260 nm is not involved in natural light. Thus, in this experment, light of wavelengths at 288, 316, 344, and 372 nm was employed for the spectroirradiation of the sample solution. The photodegradation behavior of the dye under various conditions is shown in Fig. 8, in which the percent of residual dye in the solution is plotted against the irradiation time. Figure 8 (A) indicates the effect of irradiation wavelength on the photodegradation of the dye in the solution without polyester. Figure 8 (B) depicts the effect of the polyester on the photodegradation of the dye. It is evident from Fig. 8 (A) that the dye is decomposed by the light at 288 nm and is hardly influenced by light of longer wavelength, namely, 316, 344, or 372 nm. The dye never undergoes

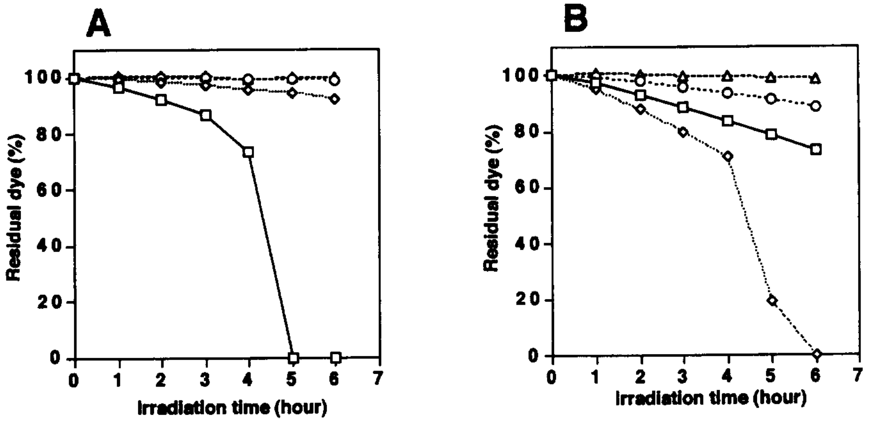

**Fig. 8.** Effect of irradiation wavelength on decomposition of C.I. Disperse Red 73 in ethyl acetate: (A) Without polyester, (B) With polyester, (□) 288 nm, (◇) 316 nm, (○) 344 nm, (△) 372 nm.

breakdown at 344 and 372 nm. This is due to the higher energy level at shorter wavelength. The effects of added polyester on the photodegradation of the dye were then evaluated in order to compare with the photofading of the dye on polyester alone. The results are shown in Fig. 8 (B). When polyester is present in the system, the dye tends to be decomposed significantly at 316 nm, namely, different from the result in the absence of the polymer, which shows maximum decomposition at 288 nm [Fig. 8 (A)]. In Fig. 9 the percent of residual dye in the solution is shown at each wavelength in the presence and absence of polyester. While at 288 nm the curve in the absence of the polyester decreases significantly, at 316 nm the curve in the presence of the polymer falls. As already shown in Fig. 6, polyester fiber itself is affected most strongly at 316 nm. Thus the results obtained in solution in the presence of polyester are consistent with those on the polyester fiber. In the absence of polyester in the solution, the dye is susceptible to light of shorter wavelength, i.e. of higher energy. In contrast, when polyester is present in the system, the dye tends to be decomposed by the light at 316 nm, at which wavelength of irradiation polyester undergoes photodegradation significantly. These results suggest that the energy absorbed by the polyester at 316 nm accelerates the photodegradation of the polyester itself to give degradation products. It is likely that the absorbed light at 316 nm and/or the reaction products would subsequently exert significant effects on the dye molecules on the fiber and cause photodegradation of the dye. In other words, it was found from the results of the spectroirradiation that in the wavelength region within which the fiber itself is not influenced, the dye on the fiber is scarcely affected. These factors are masked when the entire

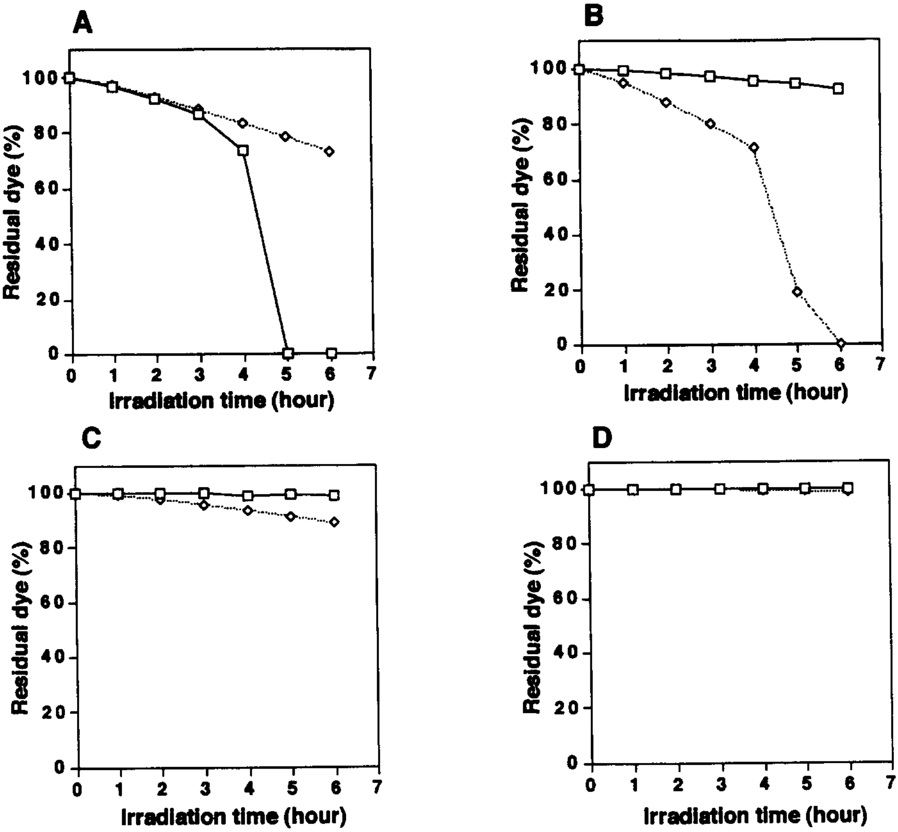

**Fig. 9.** Effect of polyester on decomposition of C.I. Disperse Red 73 in ethyl acetate: (A) 288 nm, (B) 316 nm, (C) 344 nm, (D) 372 nm, (□) Without polyester, (◇) With polyester.

wavelength from the ultraviolet to the visible are employed, i.e. as in more conventional methods for the photoirradiation of dyed fibers. This finding plays an important role in the clarification of the photofading of dyed fibers, and in the development of ultraviolet absorbers for dyed fibers. Further studies are in progress.

## CONCLUSIONS

It was found that polyester fiber alone, and a disperse dye on the fiber, undergo photodegradation at a wavelength specific for the fiber. The wavelength for polyester fiber was *ca.* 316 nm. A similar situation was observed for nylon-disperse dye and cotton-reactive dye systems. With nylon and cotton the wavelengths of significant influence were 372 nm and 259 nm, respectively. Photodegradation of the disperse dye in solution containing polyester also occurred maximally at *ca.* 316 nm. This implies that photodegradation of dyes on a fiber comes from the absorbed energy characteristic of the fiber and/or degradation products of the fiber formed at the characteristic wavelength.

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