

## The Effect of a UV-Absorber on the Photostability of Acid Dyes on Silk

Ping Yueh Wang,\* Yu Ping Chen & Pei Zhen Yang

Department of Textile Engineering, National Taiwan Institute of Technology, Taipei,  
Taiwan 10772

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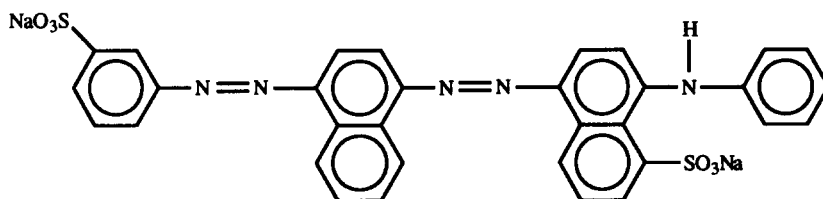
### ABSTRACT

*The effect of the ultraviolet absorber salicylic acid benzyl ester on the photostabilisation of CI Acid Blue 113 (azo type) and CI Acid Blue 40 (anthraquinone type) on silk fabrics has been investigated. The degree of photodegradation depends on the nature of dye and the amount of absorber applied to the silk. The addition of the UV-absorber resulted in a slight decrease in dye uptake and the addition of 2% owf salicylic acid benzyl ester afforded a good deal of protection against photodegradation. In addition, the photostability improvement was generally higher for CI Acid Blue 40.*

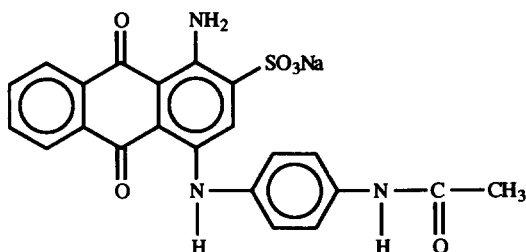
### 1 INTRODUCTION

One of the most important properties of a dye is its fastness to light and many efforts have been made to correlate this with the structure of the dye.<sup>1-4</sup> Additionally, UV-absorbers (UV-abs) have been utilized to protect polymeric materials from photodegradation caused by sunlight or ultra-violet rich artificial light.<sup>5-7</sup> Interest has now developed in the application of UV-abs during the dyeing of textile materials in attempts to obtain improved light fastness of the resulting dyed materials. Various UV-abs, including benzophenone, benzotriazole, benzoic acid esters and hindered amines, when used directly in the dyebath up to 2% owf, for polyester, wool, polyamide and polypropylene fibers caused a light fastness improvement ranging from 0 to 2 units.<sup>8</sup> Very little work has been reported on the influence of UV-abs on silk.

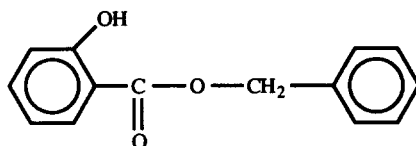
\*Corresponding author.



CI Acid Blue 113 (I)



CI Acid Blue 40 (II)



Salicylic acid benzyl ester

Fig. 1. Dyes and UV-abs used in the present study.

Sunlight has a marked effect on protein fabric, prolonged exposure causing phototendering, with deterioration in fiber strength, abrasion resistance and dye fastness. Much research has been carried out with the aim of finding ways to reduce the effects of sunlight on wool,<sup>8,9</sup> and some success has been achieved by applying various photostabilizers, particularly ultraviolet absorbers. For example, both photoyellowing and phototendering have been retarded by treatment of wool with sulfonated 2-hydroxybenzophenones or with sulfonated 2-(2'-hydroxyaryl)-2H-benzotriazoles. The extent of photostabilization achieved with such compounds depends on the nature of the substituents attached to the 2-aryl ring. The essential substituent is the *ortho*-hydroxyl group, which is capable of forming an intramolecular hydrogen bond.<sup>10-13</sup> Silk is more susceptible to the tendering action of light

than any other natural fiber. Yellowing generally accompanies photochemical degradation. The reaction mechanisms involved are complex and little understood. UV radiation is the most active component of light in the decomposition of fibroin. In this paper, a study of the dyeing of silk fabrics with CI Acid Blue 113 (I) and CI Acid Blue 40 (II), both of which give bright dyeings of medium light fastness, was carried out in the presence and absence of the UV-abs salicylic acid benzyl ester (Fig. 1). The photostabilization of fabrics dyed under differing conditions was investigated, and the results compared with reference samples dyed in the absence of the UV-abs.

## 2 EXPERIMENT

### 2.1 Materials

The plain weave fabric (density  $1.33 \text{ g cm}^{-3}$ ) used was woven from 100% silk (Taiwan Silk Co. Ltd). The following acid dyes (donated by Everlight Chemical Industrial Co. Ltd) were used: Everacid Milling Cyanine 5R Conc. (CI Acid Blue 113) and Everacid Levelling Blue A 2GH/C (CI Acid Blue 40). The ultraviolet absorber salicylic acid benzyl ester was used without further purification.

Ultraviolet spectra were measured with a Shimadzu UV-240 spectrophotometer. The absorber, dyes, and absorber-dye combinations were applied to silk fabrics using a rapid laboratory dyeing apparatus.

### 2.2 Methods

#### 2.2.1 Degumming

The raw silk fabrics were degummed by treating twice in 0.5% Marseilles soap solution, with liquor ratio of 1:50 for 40 min at 95–99°C, in 0.05%  $\text{Na}_2\text{CO}_3$  solution for 10 min at 45–50°C, and in water for 60 min at 90–93°C. The degummed silk was rinsed with hot and cold water, dried at room temperature. The degumming loss of the silk fabric was 27%.

#### 2.2.2 Dyeing

The degummed silk fabrics ( $5 \times 10 \text{ cm}$ ) were dyed in a rapid laboratory dyeing apparatus at a liquor ratio of 1:40 with 2% owf dye and 0.5–2% UV-abs. The pH was set to 4 with acetic acid, dyeing commenced at room temperature and the liquor then heated slowly to the boil and maintained at this level for 1 h. The dyed fabrics were rinsed with distilled water and squeezed. The Helmholtz coordinate  $P\%$  and  $K/S$  of the dyed fabrics were determined on an applied computer system (model CS-5).

### 2.2.3 Determination of dye and UV-abs uptake

A Shimadzu UV-240 spectrophotometer was used to obtain the calibration curves of acetone solutions of dye and UV-abs. The dye and UV-abs uptakes were determined by measuring the absorbances at 326 nm for the UV-abs, and 566 and 605 nm for dyes I and II, respectively. Calculations of the UV-abs content in the presence of dye were made after subtraction of the corresponding absorbance of the latter at 326 nm, which was determined by correlating the absorbance of the dyebath at its  $\lambda_{\max}$  and at 326 nm.

### 2.2.4 Photochemical degradation

The dyed fabrics were photolyzed at  $35 \pm 1^\circ\text{C}$  using a Rayonet photoreactor (RPR-100) equipped with a series of 16 lamps with maximum emission at 300 nm. Measurements of the absorbance were made at regular intervals, and the per cent conversion, and fading rate curves, were determined by the Helmholtz coordinate ( $P\%$ ) of each dyed specimen.<sup>14</sup>

## 3 RESULTS AND DISCUSSION

### 3.1 Molar extinction coefficients

The dyes and UV-abs used obeyed the Beer-Lambert law at the concentrations applied. The molar extinction coefficients ( $\epsilon$ ) for dyes I, II and UV-abs are given in Table 1. These values were used for their quantitative determinations.

TABLE 1  
UV Data for CI Acid Dyes and UV-abs

Sample	$\lambda_{\max}(\text{nm})$	$\epsilon (\text{mol}^{-1} \text{cm}^{-1})$	$\log \epsilon$	Solvent
Dye I	566	$8.20 \times 10^3$	3.91	water
Dye II	605	$1.11 \times 10^4$	4.00	water
UV-abs	326	$3.08 \times 10^2$	3.48	acetone

### 3.2 Dyeing results

Dye and UV-abs uptake,  $P\%$  and  $K/S$  on the dyed fabrics for various concentrations of UV-abs (0, 0.5, 1.0, 2.0% owf) are given in Table 2. Fabric dyed in the absence of the UV-abs was further used as reference sample for the photostabilisation test. Table 2 shows that the application of the UV-abs resulted in a slight decrease in dye uptake,  $P\%$  and  $K/S$  of dyed fabric, and higher dye uptake for dye II than dye I.

TABLE 2

Dye and UV-abs Uptake;  $P\%$  and  $K/S$  on the Dyed Fabrics for Various Concentrations of UV-abs

Dye	UV-abs (% owf)	Uptake			$P\%$	$K/S$
		UV-abs (%)	g UV-abs/100 g dyed fabric	Dye(%)		
I	0	0	0	90.0	39.93	8.86
	0.5	88.2	0.44	89.6	39.81	8.66
	1.0	90.4	0.91	87.1	38.83	8.58
	2.0	92.6	1.84	86.8	37.42	8.43
II	0	0	0	93.4	60.18	15.70
	0.5	90.4	0.45	93.0	60.16	15.65
	1.0	92.1	0.93	92.2	60.02	15.44
	2.0	93.5	1.86	91.7	59.94	15.36

Depth of dying: 2.0% owf.

### 3.3 Photostabilization of the dyed fabrics

The degree of photodegradation is greatly affected by the nature of the dye and the amount of absorber applied to the silk. Significant differences in the fading conversion (%),  $P\%$ ,  $K/S$ , fading rate constant ( $k_0$ ) and efficiency of improved photostability ( $E\%$ ) of samples associated with various concentrations of UV-abs can be observed in Figs 2–4 and Table 3. As can be seen from Fig. 2, in the absence of the UV-abs in the dyeing process, there is a significant increase in the fading conversion % of dye I for 20 min after

TABLE 3

Rate Constants and Efficiency of Improved Photostability on the Dyed Fabrics for Various Concentrations of UV-abs

Dye	UV-abs	$k_0 (\times 10^{-2}, \text{mol}^{-1} \text{ l}^{-1} \text{ s})$	$\Delta k_0 (\times 10^{-2}, \text{mol}^{-1} \text{ l}^{-1} \text{ s}^{-1})$	Efficiency (%)
I	0	8.13	—	—
	0.5	8.03	0.1	1.23
	1.0	7.14	0.99	12.17
	2.0	5.55	2.58	31.73
II	0	2.17	—	—
	0.5	17.1	0.46	21.20
	1.0	1.46	0.71	32.72
	2.0	1.39	0.78	35.94

$$\Delta k_0 = k_0 \text{ without uv-abs} - k_0 \text{ with uv-abs}$$

$$\text{Efficiency of improved photostability \%} = \Delta k_0 / k_0 \text{ without uv-abs} \times 100.$$

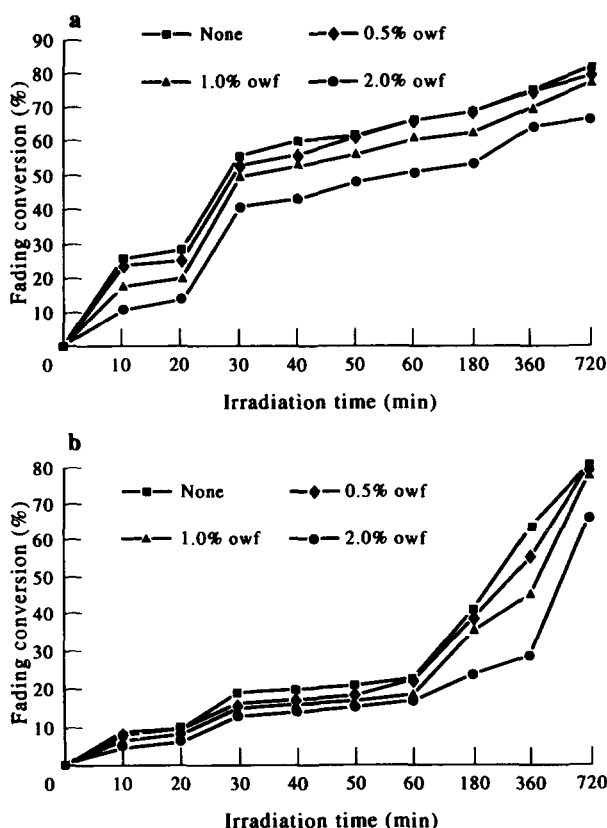


Fig. 2. Plot of relative per cent conversion versus irradiation time of dyed silk fabrics in various concentrations of UV-abs: (a) dye I, (b) dye II. Depth of dyeing: 2% owf.

irradiation, and 1 h after irradiation for dye II. Dyes based on the anthraquinone structure are generally characterized by a high fastness to light, anthraquinonoid dyes being generally recognized as superior in this regard to most other classes of dye. The results noted above appear to indicate that the photostability of dye II is greater than that of dye I and that an improvement in light fastness has been achieved by addition of the UV-abs in the dyeing process.

Figure 3 shows the fading rate curves associated with dyes in various concentrations of UV-abs. Many factors affect the light fastness of a colored substrate, including the chemical structure of the colorant, its physical state in the substrate and the chemical and physical nature of the substrate.<sup>15</sup> The physical condition and the environment of the colorant appear to be the principal factors determining the shape of the curve.<sup>16</sup> The light fading rate of dyed or pigmented materials can be divided into five main classes and some subgroups, according to the shape of the arithmetic plot of the rate of

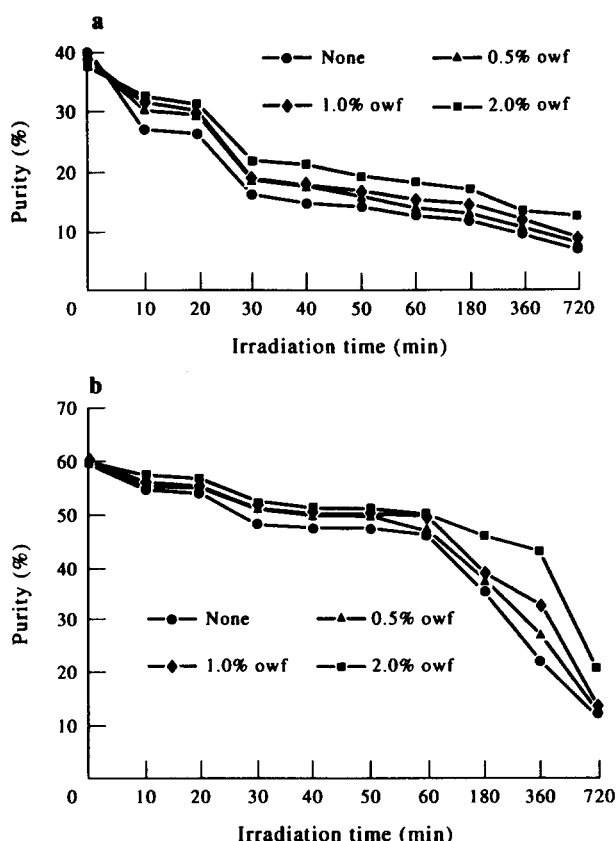


Fig. 3. Fading rate curves given by dyes on silk fabrics with different concentrations of UV-abs: (a) dye I, (b) dye II. Depth of dyeing: 2% owf.

dye loss. The physical state of the dye within its substrate is believed to be important in determining the photostability of the dye. There is evidence, from electron micrographs, that dye aggregates are formed in the polymer with some dyes of good light fastness.<sup>17</sup> As can be seen from Fig. 3(a), dye I shows a first-order fading, and dye I is present as a molecular dispersion; the light fastness of silk dyed with this dye is very low. Dye II (Fig. 3b) fades in zero-order, followed by a first-order curve, i.e. showing a slow fading initially and then a fading which accelerates with time, caused by continued breakdown of colorant particles; the light fastness of silk dyed with this dye is higher than that from dye I. Figure 4 shows the relation between the logarithm of rate curves,  $\log(P_0/P_t)$ , and the irradiation time of dyed fabric in various concentrations of UV-abs. With respect to the influence on the photofading of the amount of UV-abs, it is seen that 2% owf UV-abs was the most effective. The effect of the amount of UV-abs on the photofading

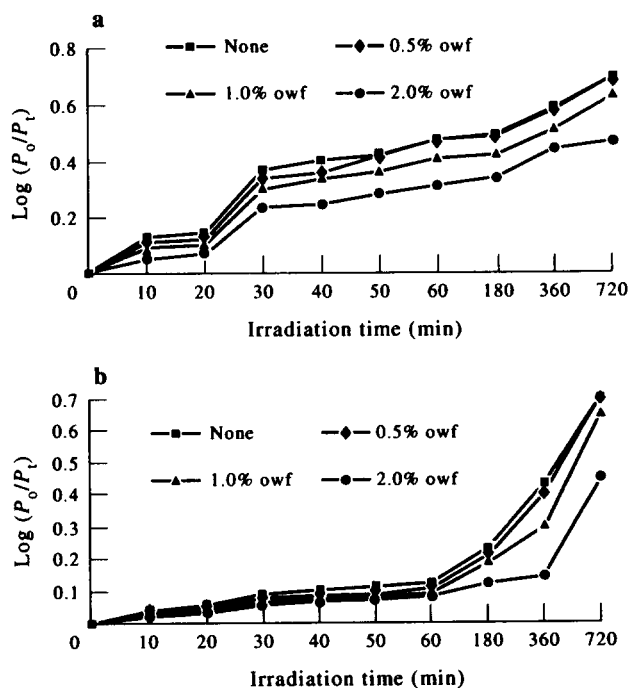


Fig. 4. Rate curves (logarithmic scale) for fading of acid dyes on silk fabric with different concentration of UV-abs: (a) dye I, (b) dye II. Depth of dyeing: 2% owf.

kinetics of the dyes is shown in Table 3. Smaller fading rate constant ( $K_0$ ) and greater efficiency of improved photostability ( $E\%$ ) were obtained at higher concentrations of UV-abs, and comparison of the photostability improvement between dyes I and II fabrics dyed under the same conditions showed that the application of the UV-abs was more effective for dye II dyeings than those of dye I at 2% depth of dyeing (see Table 3).

#### 4 CONCLUSIONS

This investigation involved irradiation of silk fabric dyed with each of two acid dyes either in the presence or absence of the UV-abs. We have found that the UV-abs was absorbed almost quantitatively onto fabric under the dyeing conditions used. The presence of the UV-abs in the dyeing process resulted in a slightly lower dye uptake. When the concentration of the UV-abs in the dyebath was increased, the rate constant for the photofading of the dye on silk decreased. The best improvement in photostability was achieved by addition of 2% owf of UV-abs; the photostability improvement was generally higher for CI Acid Blue 40 than for CI Acid Blue 113.



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