An Application of Functional UV Absorbers to Improve the Light Fastness of Gardenia Blue

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Abstract: Numerous potential UV absorbers were prepared to prolong the life of natural dye gardenia blue. The effect of these compounds in reducing photofading was examined on a polymer substrate. The use of commercial UV absorbers was not necessarily effective in improving the light fastness of the color. However, benzophenone type UV absorbers containing a built-in UV absorber moiety remarkably retarded the photofading rate. The combined use of these UV absorbers and singlet oxygen quencher played a very useful role in the photofading protection of natural dye. These stabilizers were deemed safe following evaluation of antimicrobial activity. It is proposed that 2,2’,4,4’-tetrahydroxy-5-benzotriazolylbenzophenone and its derivatives may be used as effective stabilizers in the fading of natural dyes.

(Received 11 September, 2012; Accepted 16 January, 2013)

1. Introduction

The application of natural dyes has recently become of importance particularly in connection with the use of naturally occurring pigments. However, one of the most difficult problems is that these pigments are unstable and easily converted to undesired substances on exposure to sun light. Their inferior fastness compared with synthetic dyes is a deterrent to their use. With the exception of indigo and logwood, most natural dyes have poor light stability. A number of studies have been reported on the application of natural dyes [1-3], but little effort has been made to improve the light fastness of such dyes [4-6].

Museum conservators have explored various methods for minimizing the degrading effects of light on textiles dyed with natural dyes. Despite such efforts, dyed textiles still undergo undesirable color change whilst on display. Conservation experts have speculated on the usefulness of UV absorbers as an alternative method of reducing fading [7].

Gardenia blue pigment is produced from an aqueous extract of gardenia fruits (Gardenia augusta Merr.) and its decomposed protein, as shown in Fig. 1 [8]. The chemistry of gardenia blue has been widely studied by many workers [9-11] but, although the mean molecular weight has been determined to be 15600 ± 400, based on the measurements of the osmotic pressure [12], the chemical structure has not yet been established. Historically, gardenia blue was used as a blue dyestuff for food colorants and cosmetics and also for the dyeing of cotton, silk and wool cloth. Nevertheless, the inherent poor light stability of this natural dye is a property that may limit its use in modern-day applications.

The ability of dyed or pigmented polymers to withstand prolonged sun light exposure without fading or undergoing physical deterioration is determined largely by the photochemical characteristics of the absorbing dyestuff itself. There are many different reaction pathways open to the light-excited dye molecule, such as ionization, dissociation into free radicals, oxidation, reduction, isomerization, etc. The light-induced fading of dyes in the presence of air usually entails oxidation, and such photo-oxidation reactions may involve oxygen free radicals, singlet oxygen or superoxide ions. Auto-oxidation reactions of dyes are generally considered to occur on exposure to ultraviolet (UV) radiation and are depressed by the addition of UV absorbers or antioxidants, such as hindered phenols [13]. The role of singlet oxygen in the photofading of dyes has also been studied by several workers. It has been shown that acylamidostilbenes, arylazophthols and indigo etc. undergo self- or dye-sensitized photo-oxidation in...
solution [14]. In a previous paper, the effect of various kinds of additives on the photofading of gardenia blue was investigated on cellulose [15]. The involvement of free radicals and singlet oxygen has been postulated in the photochemical oxidation of this color. The photofading rates of these dyes are slowed down with the addition of efficient singlet oxygen quenchers, but the majority of commercial quenchers possess some problems with regards to their use, e.g., instability of light (carotenes), intrinsic color (nickel complexes), etc. [16,17].

Many different types of UV absorbers have been proposed, but 2-hydroxybenzophenones, phenyl esters, cinnamic acids and hydroxybenzotriazoles have achieved commercial significance. The 2-hydroxybenzophenone I and benzotriazole II, which are relevant to this study, preferentially absorb the harmful UV radiation and convert it into heat energy by means of rapid tautomerism (see Fig. 2) [18].

In this paper, benzophenone type UV absorbers bearing benzotriazolyl groups (see Fig. 3), which may be capable of combined action of UV absorber I and II, were prepared, and the effects of the UV absorbers on the photofading behavior of gardenia blue were investigated on a polymer substrate. The effectiveness of these UV absorbers was also examined in the presence of singlet oxygen quencher. A novel approach for improving the light stability of gardenia blue is now reported.

2. Experimental

2.1 Materials

Crystal Violet (CI Basic Violet 3: $\lambda_{\text{max}} = 586$ nm), Fuchsine (CI Basic Violet 14: $\lambda_{\text{max}} = 547$ and 489 nm), Methylene Blue (CI Basic Blue 9: $\lambda_{\text{max}} = 668$ nm), 2,6-di-t-buthylphenol (HP) and 1,4-diazabicyclo[2,2,2] octane (DABCO) were purchased from Wako Pure Chemical Ind. Ltd. 2,2',4,4'-Tetrahydroxy-benzophenone (HBP) and 2-(2-benzotriazolyl)-p-cresol (BTC) were purchased from Tokyo Chemical Ind. Co. Ltd. Nickel p-toluenesulfonate (NTS; $\lambda_{\text{max}} = 233$ nm) was prepared and purified as described previously [19]. Gardenia blue ($\lambda_{\text{max}} = 599$ and 284 nm) was supplied from Kiriya Chemical Co. Ltd. A series of monobenzotriazolyl (UV1-4) and dibenzotriazolyl-benzophenones (UV 5 - 12) was synthesized and purified according to the procedures described in the literature [20]. The formulas of these materials are shown in Fig. 3 together with HBP and BTC.

2.2 Photofading procedure

Cellulose acetate (1 g) was dissolved into a solution of gardenia blue (0.07 g) in a 10 cm$^3$ mixture of pyridine and water (8 : 2 v/v), with or without an additive (1×10$^{-2}$ mol dm$^{-3}$) such as HP, DABCO, NTS or UV absorbers. The solution was spread on a glass plate using a bar coater and dried at 50°C for 90 min. The film obtained was dried at room temperature under vacuum for 1 week. The thickness of the films prepared was measured using a Dial thickness gauge and all measurements fell within the range 80 ± 1 μm.

The obtained films were irradiated at 65 ± 2°C with a xenon arc solar box (1500 e, CO. FO. ME GRA . SRL., Italy). The absorption spectra of the films were measured before and after exposure to xenon arc light (550 W m$^{-2}$) using a JASCO V-550 spectrophotometer and conversions were determined at the absorption maximum of gardenia blue ($\lambda_{\text{max}} = 599$ nm).

2.3 Assessment of antibacterial activity

Evaluation of the antibacterial activity of new UV absorbers on cotton was carried out according to JIS L 1902; 1998 standard method [21]. Cotton fabric samples (3 × 3 cm) were placed in pyridine aqueous solution of each UV absorber (3 % owf), and kept at 90°C for 30 min, at a liquor to goods ratio of 30 : 1. The fabric samples were removed from the solution and dried. In order to evaluate the antibacterial activity of the UV absorbers on the cotton fabrics, Eschechia coli K 12 W 3110 (E. coli)
Table 1 UV-visible absorption spectra data of UV absorbers in DMF

<table>
<thead>
<tr>
<th>UV absorber</th>
<th>λ_{max} / nm (ε / 10^4 dm^3 mol^-1 cm^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTC</td>
<td>338 (1.11), 296 (1.25)</td>
</tr>
<tr>
<td>HBP</td>
<td>337 (1.08), 285 (1.09)</td>
</tr>
<tr>
<td>UV 1</td>
<td>355 (1.72), 281 (2.14)</td>
</tr>
<tr>
<td>UV 2</td>
<td>351 (1.90), 287 (2.04)</td>
</tr>
<tr>
<td>UV 3</td>
<td>353 (1.63), 287 (1.97)</td>
</tr>
<tr>
<td>UV 4</td>
<td>351 (1.46), 284 (2.04)</td>
</tr>
<tr>
<td>UV 5</td>
<td>353 (3.12), 285 (3.74)</td>
</tr>
<tr>
<td>UV 6</td>
<td>352 (3.13), 289 (3.28)</td>
</tr>
<tr>
<td>UV 7</td>
<td>351 (1.80), 286 (2.59)</td>
</tr>
<tr>
<td>UV 8</td>
<td>353 (2.10), 283 (2.73)</td>
</tr>
<tr>
<td>UV 9</td>
<td>353 (2.75), 284 (3.86)</td>
</tr>
<tr>
<td>UV 10</td>
<td>349 (3.41), 284 (4.76)</td>
</tr>
<tr>
<td>UV 11</td>
<td>357 (2.49), 285 (3.75)</td>
</tr>
<tr>
<td>UV 12</td>
<td>350 (2.32), 284 (3.41)</td>
</tr>
</tbody>
</table>

1) for key see Fig. 3.

Maerov and Kobsa [23] observed improvements in light fastness of basic dyes on polyester in the range of 200-300 % when 2,2’-dihydroxy-4,4’-dimethoxybenzophenone was applied in the dyebath. Grantz and Summer [24] contended that substituted benzophenone absorbers remarkably improve the light fastness of dyes faded by UV radiation.

Since new UV absorbers exhibit very high absorption in solar UV region, it is of interest to examine the use of these compounds as means of improving the light fastness of natural dyes. The effects of various additives on the photofading of gardenia blue were examined on cellulose acetate film, and the results are shown in Fig. 4. The fading rate of gardenia blue was suppressed by the addition of DABCO, singlet oxygen quencher [14]. Further, the rate was also retarded in the addition of HP, free-radical scavenger [13]. These observations suggest the involvement of free radicals and singlet oxygen in the photochemical oxidation of gardenia blue. The addition of BTC afforded a moderate protection against fading. On the other hand, the addition of HBP appreciably suppressed the fading rate. The retarding effect provided by HBP was somewhat superior to that of HP. It was therefore considered of interest to investigate the use of 2,2’,4,4’-tetrahydroxy-5-benzotriazolylbenzophenone (UV 1) and its derivatives (UV 2–4) as means of improving the light fastness of natural dyes. The effectiveness of these compounds was examined on the film, and the results are shown in Fig. 5.

When the gardenia blue on the film was exposed for 10 and 20 h to xenon arc light (550 W m^-2), the color faded in 55 % and 79 % conversion, respectively. However, in the presence of UV 1 gardenia blue showed an improvement to 15 and 23 % fading. Similar stabilizing effect was also observed using the other new UV absorbers (UV 2–4), while the use of UV 3 gave

Fig. 4 Effect of various additives (1 × 10^{-2} mol dm^-3) on the photofading of gardenia blue

Fig. 5 Effect of various UV absorbers (1 × 10^{-2} mol dm^-3) on the photofading of gardenia blue
slightly less efficient protection against the fading than UV 1. Such an enhanced photochemical protection may be attributed to the contribution of higher absorption in the UV region than conventional UV absorbers, HBP and BTC (see Table 1).

Consequently, these observations may suggest that the introduction of the benzotriazolyl group in the 5-position of 2,2',4,4'-tetrahydroxybenzophenone, i.e., benzophenone type UV absorbers containing a built-in benzotriazole UV absorber moiety, plays a very important role in photofading protection of gardenia blue, but the use of a chlorine group is not very beneficial for improving the light fastness of this color.

According to the results mentioned above, the influence of benzophenone type UV absorbers containing two benzotriazolyl groups on the photofading protection of this color was examined in the same manner as above. These results are shown in Table 2. The majority of dibenzotriazolyl derivatives examined markedly suppressed the rate of photofading of gardenia blue. In particular, the retardation effect given by UV 5 was excellent and fully prevented the fading of this color. The suppressing effect provided by UV 5 was superior to that of UV 1. On the contrary, the retarding effects provided by UV 6-11 were inferior to that of UV 1. This fact may indicate that the further introduction of a bulky substituent, for example a substituted benzotriazolyl group, into stabilizers is not necessarily a useful modification for the photofading protection of gardenia blue, because such a substituent may inhibit access of the UV absorber to this color. This inferior reason is now being investigated and will be reported later.

### 3.2 Effect of simultaneous use of NTS and UV absorbers on the photostability of color

McLaren [25] and Crews [26] proposed that the light fastness of synthetic dyes is fading primarily by UV radiation, whereas fugitive synthetic and natural dyes are susceptible to fade by both visible and UV light. The role of singlet oxygen in the photofading of dyes has been reported in solution and in an adsorbed state, and it found that some dyes bearing a nickel sulfonate group show an enhanced photochemical stability towards visible light [27]. NTS was also found to be very effective in suppressing the fading of dyes in visible light [19]. In the above section and previous paper [15], the contribution of singlet oxygen to the photofading of gardenia blue was suggested. Accordingly, the influence of various UV absorbers in the presence of NTS was further investigated on the photofading of this color by irradiation with xenon arc light.

As shown by the results in Fig. 6, the color-containing film faded excessively in air on exposure to xenon arc light (550 Wm⁻²), while the film with addition of NTS exhibited remarkably suppressed fading. Moreover, the fading rate of gardenia blue was suppressed to a much greater extent by the addition of a mixture of NTS and HBP. A similar stabilizing effect was also achieved with the combined use of NTS and BTC. In particular, it is noteworthy that the addition of a mixture

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**Table 2** Effect of various UV absorbers (1 × 10⁻² mol dm⁻³) on the photofading of gardenia blue

<table>
<thead>
<tr>
<th>Run</th>
<th>Additive</th>
<th>Photofading (%) after 1h</th>
<th>3h</th>
<th>5h</th>
<th>10h</th>
<th>15h</th>
<th>20h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>10</td>
<td>24</td>
<td>35</td>
<td>55</td>
<td>70</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>UV 5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>UV 6</td>
<td>3</td>
<td>9</td>
<td>13</td>
<td>21</td>
<td>26</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>UV 7</td>
<td>3</td>
<td>8</td>
<td>12</td>
<td>19</td>
<td>24</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>UV 8</td>
<td>1</td>
<td>6</td>
<td>8</td>
<td>16</td>
<td>21</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>UV 9</td>
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<td>11</td>
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<td>8</td>
<td>UV 11</td>
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<td>UV 12</td>
<td>0</td>
<td>4</td>
<td>5</td>
<td>11</td>
<td>14</td>
<td>18</td>
</tr>
</tbody>
</table>

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**Fig. 6** Effect of various additives (each 1 × 10⁻² mol dm⁻³) on the photofading of gardenia blue

**Fig. 7** Effect of various UV absorbers (1 × 10⁻² mol dm⁻³) on the photofading of gardenia blue in the presence of NTS (1 x 10⁻² mol dm⁻³)
of NTS and UV 1 showed higher inhibition against the fading of this color, even compared with a mixture of NTS and commercial UV absorber, HBP or BTC.

Accordingly, benzophenone type UV absorbers bearing various kinds of benzotriazolyl group were prepared and the substituent effects of these additives on the photofading of gardenia blue were examined in the presence of NTS on the film. These results are shown in Fig. 7. The majority of monobenzotriazolyl derivatives examined here greatly suppressed the fading rate of this color. Particularly, it is noteworthy that the addition of UV 4 achieved a higher degree of protection against the photofading of this color. Consequently, the results demonstrate that the benzophenone type UV absorbers containing a built-in benzotriazole UV absorber moiety can be applied as effective stabilizers against the photofading of natural dyes.

### 3.3 Antibacterial activity of new stabilizers

Preservation of the environment and human health is now perceived as more important than the profitability and efficiency of a business [30, 31]. Therefore, the antimicrobial activity of the new stabilizers (UV 1-12), together with three basic dyes on cotton fabrics, against two species of bacteria, was examined. The evolution of the antibacterial activity of these samples on cotton is shown in Table 4. The bactericidal activity against *S. aureus* was shown for the basic dyes, whereas, against *E. coli*, no activity was observed. None of the new stabilizers (UV 1-12) developed in this study showed activity against either bacterium. Accordingly, the results show that the successful technique for improving the light fastness of natural colors discovered here may be safe for environment and human health [32-34], but further clinical test may have to be carried out.

### 4. Conclusion

Because of the poor light fastness of natural dyes,
effective stabilizers have not been developed despite extensive previous research. In this study, an attempt to improve the light fastness of the natural dye gardenia blue has been carried out. Initial experiments showed that the addition of BTC or 2-hydroxybenzophenone afforded little suppression in the rate of fading. However, the rate of photofading of gardenia blue was remarkably suppressed by the addition of benzophenone type UV absorbers bearing benzotriazolyl groups. Also, the combined use of these absorbers and singlet oxygen quencher was especially effective in reducing the fading of this color. These stabilizers were deemed safe (with regard to the environment, human health) following evaluation of antimicrobial activity. Thus, the use of the UV absorbers discovered in this study may be a successful technique for improving the light fastness of natural dyed fabrics.

Acknowledgement

This work was partly supported by Grant-in-Aid for Scientific Research (No. 23500905) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References