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The effect of hydroxyarylbenzotriazoles containing a singlet oxygen quenching moiety on the photofading of dyes on a polymer substrate

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Abstract

Numerous potential UV absorbers were synthesized to prolong the life of colorants for printing and imaging systems. The effect of these compounds in reducing photofading was examined on a polymer substrate. The use of a simple UV absorber was not necessarily useful in improving the light fastness of the colorants. Nickel hydroxyphenylbenzotriazolesulfonates, however, markedly suppressed the photofading rate of a triphenylmethane dye. The fading of an xanthene dye was completely depressed in the presence of nickel 2-(5-methyl-2H-benzotriazol-2-yl) naphthol-4-sulfonate. It is proposed that nickel complexes of hydroxyphenylbenzotriazolesulfonic acid and its derivatives may be used as effective stabilizers in the fading of indicator dyes for printing and imaging systems.

Keywords: Stabilizer; UV absorber; Colorant; Singlet oxygen; Polymer substrate

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1. Introduction

The chemistry of ink jet dyes has recently become particularly important in connection with the rapid development of information recording systems. Xanthene and triphenylmethane dyes are of commercial importance for use in ink jet printing. Very bright magenta ink jet prints are obtained using xanthene dyes, as exemplified by CI Acid Red 52. Dyes of this type give brilliant, usually bluish magenta shades but exhibit very poor light fastness, typically rated as 1. Cyan dyes based on the triphenylmethane structure are very bright. However, as with xanthene magenta dyes, they also exhibit poor light fastness (approximately a rating of 1–2). Thus, improvement in the light fastness of these dyes is currently being sought [1].

The ability of dyed polymers to withstand prolonged sunlight exposure without fading or undergoing physical deterioration is largely determined 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-

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oxidation reactions may involve oxygen free radicals, singlet oxygen or superoxide ions [2]. The auto-oxidation reaction of dyes is generally considered to occur on exposure to UV radiation and is prevented by the addition of UV absorbers or antioxidants such as hindered phenols or naphthylamines. The contribution of singlet oxygen to the photofading of dyes has been examined by several workers. For example, it has been reported that arylazonaphthols, triphenylmethanes and acylamidostilbenes undergo self-sensitized or dye-sensitized photo-oxidation in solution [3–5]. While the rates of photofading of these dyes are suppressed by using an efficient singlet oxygen quencher, the majority of commercial quenchers pose several problems with regards to their use [6,7].

In previous papers, quenching groups have been studied as a means of improving the light fastness of certain dyes in solution and in the solid state. It was found that some dyes containing nickel sulfonate as intramolecular singlet oxygen quenching group displayed enhanced photochemical stability towards visible light [8,9]. Further, the effect of nickel complexes of phenyl ester UV absorbers on the photofading of acid dyes has been studied on polymer substrates. It was found that such absorbers containing a nickel sulfonate quenching group affected more marked improvement in the light fastness properties of dyes [10].

In this paper, the influence of benzotriazole type UV absorbers with and without an attached singlet oxygen quenching moiety, such as nickel sulfonate, on the photofading of dyes has been examined on cellulose acetate film. A novel approach for improving the light fastness of colorants for printing and imaging systems is now reported.

2. Experimental

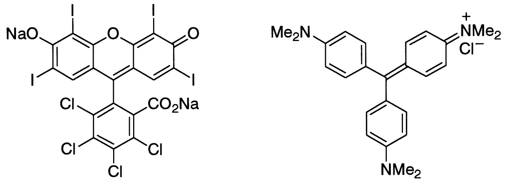
2.1. Materials

Rose Bengal (CI Acid Red 94) (dye **1**; λ_{max} 562, 521 nm) and Crystal Violet (CI Basic Violet 3) (dye **2**; λ_{max} 595, 560 nm) were purchased from Wako Pure Chemical Ind. Co., Ltd. The formulas of these dyes are shown in Fig. 1. 2-(2′-Hydroxy-5′-methylphenyl)benzotriazole (HMBT) were purchased from Tokyo Chemical Ind. Co., Ltd. Nickel 4-benzoyloxybenzenesulfonate (NBBS) was synthesized according to the procedures described previously [10]. All 2-[(2-nitrophenyl)azo]phenols and naphthol derivatives employed in this research were prepared by diazotization of 4-methyl-2-nitroaniline or 2-nitroaniline-4-sulfonic acid sodium salt and the subsequent coupling reaction with phenol or naphthol derivatives. The desired hydroxyarylbenzotriazoles were synthesized by reaction of the corresponding azo compounds with thiourea-S,S-dioxide and sodium hydroxide in a mixture of 2-propanol and water (1:1 vol./vol.) according to procedures described [11]. These compounds were purified by appropriate methods until chromatographically pure. Nickel sulfonates were prepared and purified as described previously [8].

2.2. Photofading procedure

Cellulose acetate (1 g) was dissolved in a solution of dyes **1** and **2** (5×10^{-4} mol dm^{-3}) in 10 cm^3 of a mixture of pyridine and water (4:1 vol./vol.) with or without (1×10^{-2} mol dm^{-3}) the nickel salts of sulfonic acids or HMBT. The solution was spread on a glass plate and dried at 150°C for 1 h. The film obtained was dried at room temperature under vacuum for 1 week.

The obtained films (30 μm thickness) were irradiated at 38°C and 30% RH with a 6 kW carbon arc Fade Ometer using a Pyrex filter (Suga Test Instruments Co., Ltd., FAL-5). The absorption spectra of the films were measured before and after irradiation using a Shimadzu recording spectrophotometer (UV-2200) and conversions



dye **1** dye **2**

Fig. 1. Dyes used in the present study.

were determined at the absorption maximum of each dye.

3. Results and discussion

3.1. Effect of various additives on the photofading of dyes

Recently, the role of singlet oxygen in the photofading of dyes was studied both in solution and in the adsorbed state. It was found that some dyes containing nickel sulfonate group showed enhanced photochemical stability towards visible light [8,9]. Nickel *p*-toluenesulfonate (NTS) was also found to be very effective in suppressing the catalytic fading of dye mixtures on nylon fabric [12]. If the protection against fading of dyes was imparted by the nickel sulfonate group, it would be of interest to study compounds containing this group as a means of improving the light fastness of dyes. In this work, various types of nickel arylsulfonates were prepared, and their effectiveness was examined by comparison with NTS or 2-(2′-hydroxy-5′-methylphenyl)benzotriazole (HMBT), a well known UV absorber, on cellulose acetate film. The results are shown in Table 1. When Rose Bengal (dye **1**) on the film was exposed for 1 and 4 h to carbon arc light, the dye faded by 70 and 100%, respectively. However, the dye showed 12 and 36% fading in the presence of nickel benzenesulfonate, the extent at protection being was similar to that of NTS. A similar stabilizing effect was also observed in the presence of naphthalene derivatives, and the protecting effects of these compounds was appreciably better than that of HMBT. Moreover, the fading rate of dye **1** was retarded to a great extent by the addition of a mixture of nickel benzenesulfonate and HMBT.

Similar behavior was observed in the case of Crystal Violet (dye **2**); the results are shown in Table 2. When dye **2** on the film was exposed for 1

Table 1
Effect of various nickel salts on the photofading of dye **1**

Run	Nickel salt	Photofading (%) after						
		1 h	2 h	3 h	4 h	5 h	10 h	15 h
1	None	70	90	95	100			
2	Benzenesulfonate	12	30	33	36	38	51	68
3	*p*-Toluenesulfonate	12	30	33	37	40	50	59
4	1-Naphthalenesulfonate	17	20	36	41	46	52	60
5	2-Naphthalenesulfonate	28	33	38	40	42	55	60
6	HMBT	37	46	56	59	63	70	83
7	HMBT + benzenesulfonate	11	15	17	20	21	35	37

Table 2
Effect of various nickel salts on the photofading of dye **2**

Run	Nickel salt	Photofading (%) after					
		1 h	3 h	5 h	7 h	10 h	15 h
1	None	12	30	46	55	65	75
2	Benzenesulfonate	1	2	4	5	7	12
3	*p*-Toluenesulfonate	2	4	5	6	8	12
4	1-Naphthalenesulfonate	1	3	4	5	7	9
5	2-Naphthalenesulfonate	1	3	4	6	8	10
6	HMBT	3	8	13	17	23	32
7	HMBT + benzenesulfonate	1	1	2	3	4	6

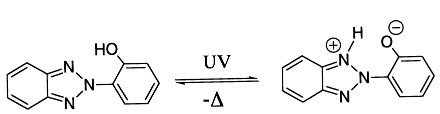
and 15 h to carbon arc light, the dye faded by 12 and 75%, respectively. However, dye **2** showed 1 and 12% fading in the presence of a 20-fold molar excess of nickel benzenesulfonate in relation to the concentration of this dye. Similar protection towards fading of dye **2** was also observed in the presence of NTS. This finding implies that the introduction of a methyl group into the stabilizer is not beneficial in improving light fastness, whereas a nickel sulfonate group plays a very important role in the photostabilization of dyes. Furthermore, such a high degree of protection against fading of dye **2** was also achieved in the presence of naphthalene derivatives.

In contrast, the addition of HMBT imparted less protection against fading than the nickel complexes. Nevertheless, the addition of a mixture of nickel benzenesulfonate and HMBT to the photofading system afforded a high degree of protection as was found in the case of dye **1**. These results suggest that the combined use of a benzotriazole type UV absorber and a nickel complex is very effective in reducing the fading of xanthene and triphenylmethane dyes.

3.2. Stabilizers derived from benzotriazole UV absorbers and photostabilization of xanthene dye

A number of different types of UV absorbers, containing absorbing groups, are available for protecting dyes on fabrics, but only four fundamentally different classes have achieved commercial significance. These are the derivatives of 2-hydroxybenzophenone, phenyl esters, cinnamic acids and hydroxyphenylbenzotriazoles. The latter type of compound, which are used in this work, protect the dye by preferentially absorbing the harmful UV radiation and converting it into heat energy by means of rapid tautomerism (Scheme 1).

In a preliminary study, the influence of various additives on the photofading of dyes was examined on a polymer substrate. It was found that the phenyl ester type UV absorbers containing the nickel (II) sulfonate quenching group imparted excellent fading suppression [10]. In the above section, it was reported that a mixture of HMBT and nickel benzenesulfonate markedly retarded the rate of dye photofading. It was therefore considered of interest to investigate benzotriazole type UV absorbers bearing the nickel sulfonate group as a means of improving the light fastness of dyes. Various types of related stabilizers were prepared, and the effectiveness of these compounds was examined on cellulose acetate film. The formulas of the stabilizers used in this study are shown in Fig. 2. The influence of various nickel complexes of hydroxyarylbenzotriazolesulfonic acids on the photostability was examined using dye **1** as a model xanthene dye, the results are summarized in Table 3.



Scheme 1.

When dye **1** on the film was exposed for 1 and 4 h to carbon arc light, the dye faded by 70 and

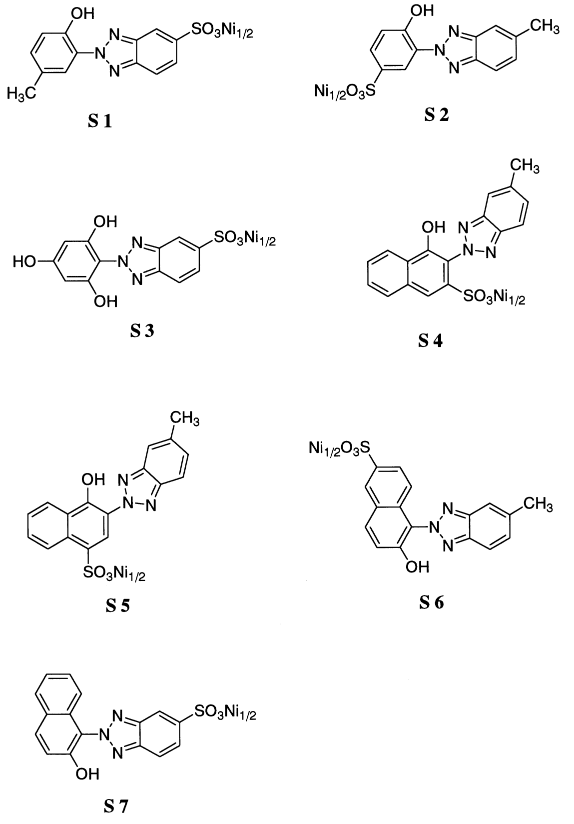


Fig. 2. Stabilizers used in the present study.

Table 3
Effect of various benzotriazole derivatives on the photofading of dye **1**

Run	Additive[a]	Photofading (%) after						
		1 h	2 h	3 h	4 h	5 h	10 h	15 h
1	None	70	90	95	100			
2	**S1**	11	12	13	13	14	18	20
3	**S2**	9	9	10	10	10	11	12
4	**S3**	0	0	0	1	1	5	8
5	**S4**	2	2	5	6	6	12	15
6	**S5**	0	0	0	0	0	0	0
7	**S6**	0	0	0	0	1	2	4
8	**S7**	1	2	2	3	5	11	13
9	HMBT	37	46	56	59	63	70	83
10	NBBS	7	15	22	28	31	42	50

[a] For key, see Fig. 2.

100%, respectively. However, dye **1** showed only 11 and 13% fading by addition of **S1**. Such a higher degree of protection against the fading of dye **1** was also observed in the presence of other hydroxyphenylbenzotriazole derivatives (**S2**, **S3**). Furthermore, the protecting effect of these compounds was significantly better than that of the conventional UV absorber, HMBT, and the phenyl ester type stabilizer, nickel 4-benzoyloxybenzenesulfonate (NBBS), proposed in a preliminary study (9, 10). The use of **S3** almost completely inhibited the photofading of dye **1**. Thus, these observations predict that the introduction of a nickel sulfonate group into the benzotriazole UV absorber plays a very important role in improving the light fastness of xanthene dyes. In particular, the introduction of this group in the phenol portion of the molecule may be effective in reducing fading, as the retarding effect conferred by **S2** was superior to that of **S1**. Moreover, **S3** showed higher reduction in fading of dye **1** than **S1** or **S2**. This finding implies that the introduction of a further hydroxyl group in the *o*-position of the phenol portion is very useful for retarding fading of dye **1**.

A similar stabilizing effect was also recognized in the presence of the naphthol derivatives **S4**–**S7**. The majority of naphthol derivatives examined greatly suppressed the rate of photofading of dye **1** and the protecting effect of these was significantly better than that of the phenol derivatives **S1**–**S3**. Particularly, it is noteworthy that the addition of **S5** or **S6** completely or almost completely suppressed photofading of dye **1**. Such an enhanced photochemical stability may be the result of the extension of the π-conjugated ring system. Furthermore, **S5** or **S6** gave far more protection in the case of dye **1** than did **S7**. This finding suggests that the introduction of a nickel sulfonate group in the phenol or naphthol portion of the molecule contributes to the photostabilization of xanthene dyes, since a similar phenomenon was recognized in the case of the phenol derivatives mentioned above. Nevertheless, the suppressing effect imparted by **S4** was inferior to that of other naphthol derivatives. This suggests that the introduction of this group in the 3-position of the naphthalene ring is not necessarily a useful modification for photostabilization of xanthene dyes.

3.3. Effect of functional UV absorbers on the photofading of a triphenylmethane dye

In the above section, it was found that hydroxyarylbenzotriazolesulfonic acid nickel salts imparted more improvement in the light fastness properties of xanthene dyes than conventional stabilizers. Accordingly, it was considered of interest to further investigate the protecting effects of these stabilizers in connection with improving the light fastness of triphenylmethane dyes. The influence of hydroxyarylbenzotriazolesulfonic acid nickel salts on the photostability of triphenylmethane dyes was examined using dye **2** in the same manner as above; the results are shown in Table 4. The majority of nickel complexes examined greatly retarded the rate of photofading of dye **2**, and the protecting effect of these was significantly better than that of the monofunctional UV absorber, HMBT. In particular, the use of nickel hydroxyphenylbenzotriazolesulfonates (**S1**–**S3**) completely retarded the rate of photofading of dye **2** under the conditions herein described, and these compounds were appreciably superior to those of naphthol derivatives (**S4**–**S7**) in contrast to the case of dye **1**. This finding suggest that the introduction of a singlet oxygen quenching group, such as nickel sulfonate, into hydroxyphenylbenzotriazoles contributes to the improvement of

Table 4
Effect of various benzotriazole derivatives on the photofading of dye **2**

Run	Additive[a]	Photofading (%) after					
		1 h	3 h	5 h	7 h	10 h	15 h
1	None	12	30	46	55	65	75
2	**S1**	0	0	0	0	0	0
3	**S2**	0	0	0	0	0	0
4	**S3**	0	0	0	0	0	0
5	**S4**	0	0	0	1	4	7
6	**S5**	0	1	2	4	6	10
7	**S6**	0	0	0	0	1	6
8	**S7**	0	0	0	0	1	2
9	HMBT	3	8	13	17	23	32
10	NBBS	0	0	0	0	1	2

[a] For key, see Fig. 2.

light fastness of triphenylmethane dyes. However, a simple extension of the π-conjugated ring system might not necessarily be a useful modification for photostabilization of the dyes. Moreover, **S7** showed higher inhibition against fading of dye **2** compared with other naphthol derivatives and the suppressing effect was nearly equal to that of the phenyl ester type stabilizer, NBBS. This implies that the introduction of a nickel sulfonate group in the benzotriazole portion of the molecule is beneficial in stabilizing triphenylmethane dyes in contrast to xanthene dyes. On the other hand, the use of **S4**, which showed lower inhibition against fading of dye **1** compared with other naphthol derivatives, significantly suppressed the rate of photofading of dye **2**. In contrast, the addition of **S5** completely suppressed the rate of photofading of dye **1**, but did not show perfect inhibition against fading of dye **2**. Such a difference of protecting effect might be attributed to the chemical structure of the dyes, since the effectiveness of a given UV absorber is well known to vary considerably with the dyes to be stabilized.

Consequently these results demonstrate that the benzotriazole type UV absorbers containing nickel(II) sulfonate quenching group can be applied as effective stabilizers against the photofading of triphenylmethane dyes, and especially hydroxyphenylbenzotriazole derivatives are effective.

4. Conclusion

In recent years, there has been a growing demand for ink jet printers with color capabilities to be used in conjunction with business and home-based personal computers. Full-color printing is now becoming very important. In the case of wide-format ink jet prints that are used for graphic arts and display purposes, the print must be protected against solar radiation, which otherwise would cause the images to fade or discolor and the substrate to deteriorate. For this purpose, various kinds of UV stabilizer compounds have been recently synthesized to prevent or minimize polymer degradation and color loss. The contribution of singlet oxygen to the photofading of dyes has been also studied by several workers. However, there are few experiments related to the use of UV absorbers bearing $^1O_2$ quencher as a means of improving the light fastness of dyes. In this paper, the effect of functional benzotriazole UV absorbers on the fading of dyes has been examined on polymer substrate. The results provide a novel approach for improving the light fastness of colorants for printing and imaging systems. The compounds discovered in this study may be applied as effective stabilizers against photofading of the colorants.

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