ELSEVIER

Dyes and Pigments 48 (2001) 151–157

DYES and PIGMENTS

An approach to the photostabilization of dyes: the effect of UV absorbers containing a built-in photostabilizer moiety on the light fastness of acid dyes

Hironori Oda *

Department of Education, Nagoya Women's University, 1302, Takamiya, Tenpaku, Nagoya 468-8507, Japan

Received 7 September 2000; accepted 24 October 2000

Abstract

The photofading behaviors of some acid dyes were investigated in polymer substrate. The contribution of singlet oxygen to those fadings was suggested. Various phenyl ester type UV absorbers were prepared, and the protecting effect of these compounds towards the photofading of acid dyes was examined in cellulose acetate film. It was proposed that nickel complexes of 4-benzoyloxybenzenesulfonic acid and its derivatives can be applied as effective stabilizers against the fading of indicator dyes for printing and imaging systems. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Photofading; UV absorber; Singlet oxygen; Acid dye

1. Introduction

The chemistry of acid dyes has recently become the focus of great interest, particularly in connection with the rapid development of information recording systems. The azo and xanthene dyes are of commercial importance for use in ink jet printing, but they gradually fade and so improved light fastness 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-oxidation reactions may involve oxygen free radicals, singlet oxygen or superoxide ions [2]. Auto-oxidation reaction of dyes is generally considered to occur on exposure to UV radiation and prevented by the addition of UV absorbers or antioxidants such as hindered phenols or naphthylamines.

In recent years, the contribution of singlet oxygen to the photofading of some dyes such as arylazonaphthols, acylamidostilbenes, etc. has been also investigated in solution [3,4]. The fading rates of these dyes are retarded by using an efficient singlet oxygen quencher. However, the majority of the commercial quenchers pose several problems with regards to their use, e.g. instability to light

---

* Tel.: +81-52-801-1133; fax: +81-52-805-3875.
E-mail address: oda@nagoya-wu.ac.jp (H. Oda).

PII: S0143-7208(00)00096-6

(carotenes), intrinsic color (extensive conjugated systems and nickel dimethyldithiocarbamate), tendency to induce radicals (DABCO) and poor quenching efficiency in the adsorbed state [5,6].

In a previous paper quenching groups have been investigated as a means of improving the light fastness of certain dyes in solution and in the adsorbed state. It was found that some dyes containing nickel sulfonate groups as intramolecular singlet oxygen quenching groups show an enhanced photochemical stability towards visible light [7,8].

In the present work, the effects of various phenyl esters with and without attached singlet oxygen quenching moiety, such as nickel sulfonate, on the photofading of acid dyes has been examined in cellulose acetate film. And 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 (C.I. Acid Red 94) (dye 1; λ_{max} 521, 562 nm) and Orange I (C.I. Acid Orange 20) (dye 2; λ_{max} 474 nm) were purchased from Wako Pure Chemical Ind. Co., Ltd. 2-Hydroxybenzophenone (HBP) was purchased from Tokyo Chemical Ind. Co., Ltd. Various kinds of benzoyloxy derivatives were synthesized by reaction of benzoylchloride with the corresponding phenols or naphthols in a mixture of anhydrous *N,N*-dimethylformamide (DMF) and pyridine or in anhydrous pyridine solution according to the procedures described in the literature [9]. The resulting arylesters were then purified by repeated recrystallization from 50% acetic acid. Nickel sulfonates were prepared and purified as described previously [7].

2.2. Photofading of dyes in cellulose acetate film

Cellulose acetate (4 g) was dissolved into solution of dye 1 (5×10^{-4} mol dm^{-3}) in 40 cm^3 of mixture of acetone and DMF (1:1 v/v) with or without the additive (1×10^{-2} mol dm^{-3}) such as metal salts of sulfonic acids or HBP. 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.

Similarly cellulose acetate (4 g) was dissolved into 40 cm^3 of the solution of dye 2 (2×10^{-3} mol dm^{-3}) in acetone:DMF mixture (1:1 v/v) with or without the additive (1×10^{-2} mol dm^{-3}) and the solution was spread on a glass plate and dried.

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

3. Results and discussion

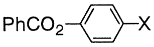
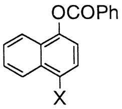
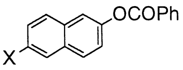
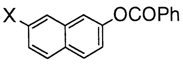
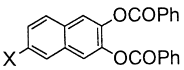
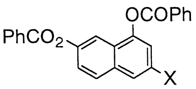
3.1. Effect of UV absorbers on the photofading of dyes

A lot of work has been done to determine chemicals that would stabilize organic dyes against UV light [10–13]. The effectiveness of a given UV stabilizer, however, varies considerably with the dyes to be stabilized and other characteristics of the dyeing area. A number of different types of UV absorbers, containing absorbing functions, 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 ester, cinnamic acids and 2-(2H-benzotriazol-2-yl)phenols. The two classes that are relevant to this study are the benzophenones and phenyl esters. The most important members of latter type are resorcinol monobenzoate and phenyl salicylate, but substituted arylsalicylates and diarylterephthalates or isophthalates are also sold as UV absorbers.

These compounds have very low absorption in the solar UV region. However, after exposure to sunlight for a time, they show an increase in absorption in the 290–400 nm region, and after sufficient exposure their spectra resemble those of 2-hydroxybenzophenones. The compounds owe their effectiveness to a light-catalyzed rearrangement that converts them to 2-hydroxybenzophenones. The products of this Fries rearrangement are the actual UV absorbers. The precursor ester, therefore, has less initial color (in the visible spectrum) than most other types of UV absorbers, and this makes whiter, brighter products possible. Additionally, the phenyl ester is more compatible with many polymeric substrates, and can be uniformly incorporated into the vehicle at higher concentrations to provide longer protection from UV light. The esters should be cost competitive with other conventional UV absorber [14].

According to the concept mentioned above, various kinds of phenyl ester derivatives were synthesized, and the protecting effect of these compounds towards the fading of Rose Bengal (dye 1) was examined in cellulose acetate film. As shown in Table 1, the majority of the phenyl ester compounds used in this experiment had a little influence on the photofading rate of dye 1. And the protecting effects were similar to that of 2-hydroxybenzophenone (HBP), a good UV absorber. The insufficient protection by these compounds was observed also in the case of Orange I (dye 2). These results are summarized in Table 2. When dye 2 in the film was exposed for 1 and 7 h to carbon arc light, the dye faded in 36 and 91% conversion, respectively. However, dye 2 showed 36 and 85% conversion in the presence of sodium 4-benzoyloxybenzenesulfonate, respectively. Such a lesser degree of protection against the fading of dye 2 was also observed in the presence of naphthalene derivatives. This fact implies that the application of simple UV absorbers is not necessarily useful for improving the light fastness of acid dyes. This incomplete protection may be due to the instability of dyes 1 and 2 towards visible light.

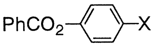
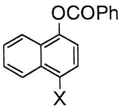
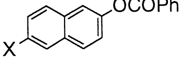
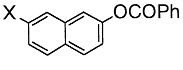
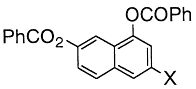
Table 1
Effect of various sodium salts ($X = SO_3Na$) on the photofading of dye 1

Sodium salt	Photofading (%) after						
$X = SO_3Na$	1 h	2 h	3 h	4 h	5 h	6 h	7 h
None	70	90	95	100			
HBP	44	61	69	73	78	81	84
	35	56	65	70	73	75	77
	40	61	70	74	77	79	80
	45	62	68	73	75	79	80
	50	62	70	74	78	81	83
	44	58	65	68	73	77	80
	47	63	70	74	78	81	84

3.2. *Effect of various nickel salts on the photofading of dyes*

In recent years, it was reported that some dyes containing nickel sulfonate groups as intramolecular singlet oxygen quenching group show an enhanced photochemical stability towards visible light [7,8]. It is, therefore, of interest to progressively further investigating this quenching group effect as a means of improving the light fastness of acid dyes.

Table 2
Effect of various sodium salts ($X = SO_3Na$) on the photofading of dye 2

Sodium salt	Photofading (%) after						
$X = SO_3Na$	1 h	2 h	3 h	4 h	5 h	6 h	7 h
None	36	53	67	78	84	88	91
HBP	24	45	59	66	71	75	79
	36	50	66	75	80	83	85
	36	50	67	75	79	81	84
	26	49	67	78	84	88	91
	25	47	63	71	75	79	81
	26	50	64	76	82	86	88

Various types of nickel arylsulfonates were prepared, and their effectiveness were examined in cellulose acetate film.

As shown in Table 3, the film containing dye 1 excessively faded in air on exposure to carbon arc light, while the addition of nickel *p*-phenolsulfonate in the photofading system considerably retarded the fading. Moreover, the fading rate of dye 1 was suppressed to a much greater extent by the addition of a mixture of nickel *p*-phenolsulfonate and HBP. A similar stabilizing effect was also observed in the presence of naphthalene derivatives, and the protecting effects of these were significantly better than those of UV absorbers tested above. In particular, it is noteworthy that nickel 2-naphthol-6-sulfonate showed higher inhibition against the fading of dye 1, even compared with a mixture of nickel *p*-phenolsulfonate and HBP. Such an enhanced photochemical stability may be due to the contribution of nickel sulfonate group. On the other hand, the addition of nickel 1-naphthol-4-sulfonate gave less efficient protection against the fading than other nickel complexes.

Similar behaviors were observed also in the case of dye 2. These results are summarized in Table 4. When dye 2 in the film was exposed for 1 and 7 h to carbon arc light, the dye faded in 36 and 91% conversion, respectively. However, dye 2 showed 3 and 24% conversion by adding a five-fold molar excess of nickel *p*-phenolsulfonate over the concentration of this dye, respectively. Such a high degree of protection against the fading of dye 2 was also achieved in the presence of naphthalene derivatives. Further, a much higher degree of protection against the fading of dye 2 was achieved by the addition of nickel *p*-phenolsulfonate together

Table 3
Effect of various nickel salts on the photofading of dye 1

Nickel salt	Photofading (%) after						
	1 h	2 h	3 h	4 h	5 h	6 h	7 h
None	70	90	95	100			
p-Phenolsulfonate	21	35	42	51	57	60	63
1-Naphthol-3-sulfonate	15	25	32	38	44	48	53
1-Naphthol-4-sulfonate	56	75	81	84	86	88	90
2-Naphthol-6-sulfonate	9	20	28	35	42	46	50
2-Naphthol-7-sulfonate	16	29	40	46	50	54	56
2,3-Dihydroxynaphthalene-6-sulfonate	26	42	51	55	57	59	60
1,7-Dihydroxynaphthalene-3-sulfonate	30	44	50	53	54	55	56
HBP + *p*-phenolsulfonate	21	31	40	45	48	50	52

Table 4
Effect of various nickel salts on the photofading of dye 2

Nickel salt	Photofading (%) after						
	1 h	2 h	3 h	4 h	5 h	6 h	7 h
None	36	53	67	78	84	88	91
p-Phenolsulfonate	3	10	14	17	20	22	24
1-Naphthol-3-sulfonate	9	16	19	24	29	34	38
1-Naphthol-4-sulfonate	10	25	44	57	64	69	73
2-Naphthol-6-sulfonate	2	6	10	14	17	20	22
2-Naphthol-7-sulfonate	6	12	17	21	24	26	29
1,7-Dihydroxynaphthalene-3-sulfonate	4	7	11	13	15	17	19
HBP + *p*-phenolsulfonate	2	5	9	12	15	16	18

with HBP. These findings suggest that the combined use of UV absorber and nickel salt is very effective for protecting the fading of acid dyes such as azo or xanthene dyes. Nevertheless, the addition of nickel 1-naphthol-4-sulfonate to the photofading system afforded a little protection against fading in a similar manner as the case of dye 1. This fact may predict that the introduction of nickel sulfonate group in the 4-position of naphthalene influences to a lesser extent the protecting effect against the fading of acid dyes.

3.3. *Effect of UV absorbers bearing $^1O_2$ quencher on the photofading of dyes*

According to the above approach, various phenyl ester derivatives containing nickel sulfonate group were prepared, and the effectiveness of these additives on the photofading of dye 1 was examined in cellulose acetate film. The influence of these additives on the photostability of dye 1 is summarized in Table 5. When dye 1 in the film was exposed for 1 and 4 h to carbon arc light, the dye faded in 70 and 100% conversion, respectively. However, dye 1 showed 7 and 28% conversion by adding nickel 4-benzoyloxybenzenesulfonate, respectively. This protecting effect is much more superior to that by the addition of a mixture of nickel *p*-phenolsulfonate and HBP. Such higher degree of protection against the fading of dye 1 was also achieved in the presence of naphthalene derivatives. The suppressing effects of these compounds synthesized in this experiment were significantly better than that of combined use of a nickel salt and an UV absorber. In particular, the retarding effect of the nickel complex of 1-benzoyloxynaphthalene-3-sulfonic acid was excellent. Consequently, these observations may demonstrate that the introduction of a singlet oxygen quenching group into the UV absorbers plays a very important role in the improvement of light fastness of acid dyes.

In addition, the retarding effect conferred by nickel 2,3-dibenzoyloxynaphthalene-6-sulfonate was

Table 5
Effect of various nickel salts ($X = SO_3Ni_{1/2}$) on the photofading of dye 1

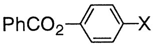
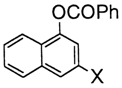
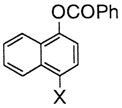
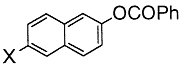
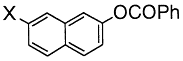
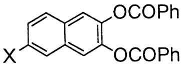
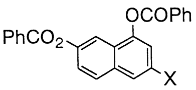
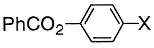
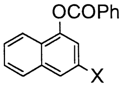
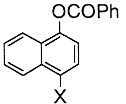
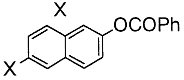
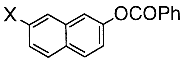
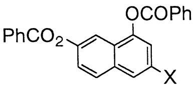
Nickel salt	Photofading (%) after						
$X = SO_3Ni_{1/2}$	1 h	2 h	3 h	4 h	5 h	6 h	7 h
None	70	90	95	100			
HBP + nickel *p*-phenolsulfonate	21	31	40	45	48	50	52
	7	15	22	28	31	34	37
	6	11	15	19	22	25	27
	10	21	28	36	41	45	47
	8	14	19	23	27	30	32
	12	19	24	27	30	32	34
	12	19	24	29	33	36	40
	14	20	23	27	30	32	34

Table 6
Effect of various nickel salts ($X = SO_3Ni_{1/2}$) on the photofading of dye 2

Nickel salt	Photofading (%) after						
$X = SO_3Ni_{1/2}$	1 h	2 h	3 h	4h	5h	6h	7h
None	36	53	67	78	84	88	91
HBP + nickel *p*-phenolsulfonate	2	5	9	12	15	16	18
	2	5	7	9	11	12	14
	7	14	18	20	23	24	26
	3	9	14	17	20	22	24
	1	4	7	10	12	14	15
	2	6	9	12	14	16	17
	1	4	8	10	12	13	15

slightly inferior to that of nickel 2-benzoyloxynaphthalene-6-sulfonate or 2-benzoyloxynaphthalene-7-sulfonate. This phenomenon may describe that the introduction of further bulky substituents, e.g. a benzoate group, into stabilizers is not very beneficial for improving the light fastness of xanthene dyes. This hypothesis is supported by the fact that the retardation effect provided by nickel 1,7-dibenzoyloxynaphthalene-3-sulfonate is somewhat inferior to that of nickel 1-benzoyloxynaphthalene-3-sulfonate or 2-benzoyloxynaphthalene-6-sulfonate.

The influence of these stabilizers on the photofading is further examined using dye 2 and the results are shown in Table 6. The addition of nickel 4-benzoyloxybenzenesulfonate afforded remarkable retarding effect also on the rate of photofading of dye 2 as well as in the case of dye 1. This suppressing effect was superior to that of a mixture of nickel *p*-phenolsulfonate and HBP. Such an enhanced protection against the fading of dye 2 was also achieved in the presence of naphthalene derivatives. Particularly the addition of nickel 2-benzoyloxynaphthalene-6-sulfonate or 1,7-dibenzoyloxynaphthalene-3-sulfonate afforded greater extent of photochemical stability on that fading. These results indicate that the phenyl ester type UV absorbers containing nickel(II) sulfonate quenching group can be applied as effective stabilizers against photofading of acid dyes.

4. Conclusions

A number of different types of UV stabilizer compounds have been previously reported to prevent or minimize polymer degradation and color loss. The contribution of singlet oxygen to the photofading of some dyes has been also examined by several workers. However, there are few experiments related to the use of UV absorbers bearing singlet oxygen quencher as a means of improving light fastness of dyes. In this paper, the effect of nickel complexes of phenyl ester UV absorbers on the photofading of acid dyes has been investigated in polymer substrate. The results provide a valuable method for improving the light fastness of colorants for printing and imaging systems. The metal complexes discovered in this study may be able to improve the image stability of the system.

References

[1] Kenyon RW. Ink jet printing. In: Gregory P, editor. Chemistry and technology of printing and imaging systems. London: Blackie Academic & Professional, 1996.

[2] Allen NS, McKellar JF. Photochemistry of dyed and pigmented polymers. London: Applied Science Publishers, 1980.

[3] Griffiths J, Hawkins CJ. J Chem Soc Chem Comm 1977; 463.

[4] Oda H, Kuramoto N, Kitao TJ. Soc Dyers Colour 1981;97:467.

[5] Wasserman HH, Murray RW. Singlet oxygen. New York: Academic Press, 1979.

[6] Griffiths J, Hawkins CJ. J Appl Chem Biotechnol 1977;27:558.

[7] Oda H, Kitao T. J Soc Dyers Colour 1985;101:177.

[8] Oda H, Kitao T. J Soc Dyers Colour 1986;102:305.

[9] Finnegan RA, Mattice JJ. Tetrahedron 1965;21:1015.

[10] Smith WE, Reynolds GA. US Patent 1977; 4050938.

[11] Smith WF, Eddy KL. US Patent 1977; 4042394.

[12] Weber WW, Heseltine DW. US Patent 1977; 4045229.

[13] Cieciuch RFW, Schlein NHM. US Patent 1977; 4025682.

[14] Kresta JF. Polymer additives. New York: Plenum Press, 1984.