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New developments in the stabilization of leuco dyes: effect of UV absorbers containing an amphoteric counter-ion moiety on the light fastness of color formers

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Abstract

Color formers are extensively used in information recording systems or thermochromic systems for textiles, but their light fastness properties are poor. The improvement of light fastness is therefore being sought at the present time. Various kinds of stabilizers have been synthesized to prolong the life of colored species derived from color formers. The suppressing effect of these compounds towards photofading was investigated on cellulose. It was found that the UV absorbers bearing the groups capable of acting as an amphoteric counter-ion play very important role in improving the light fastness of colorants for imaging and data recording systems. Zinc and nickel 2,4-dihydroxybenzophenone-3-carboxylates have been proposed as effective stabilizers against the fading of color formers.

Keywords: Color former; Counter-ion effect; UV absorber; Photofading; Improvement

1. Introduction

The chemistry of color formers has recently become of importance, particularly in connection with the rapid development of information recording systems and thermochromic systems for a diverse range of applications [1–3]. Thermal recording systems using heat-sensitive paper have been widely used in facsimiles, word-processors, printers and point of sale labels, etc. because of its workable properties. Moreover, a heat-sensitive recording method has been used in prepaid cards. These information recording systems have recently become more and more common in our daily life [1]. In the systems, the image is recorded by the color-forming reactions upon heating. This process is an intermolecular acid-base equilibrium reaction. Thus, the coloration occurs when basic color formers react with acidic developments, e.g. bisphenol-A [2].

In addition, the color formers are also employed in the making use of thermochromism. Examples of the use of these materials include temperature indicator for children's food by color change plastic mugs, indicator stripes on beer to indicate correct chilling, and on milk cartons to indicate that they have been refrigerated. In the novelty area, logos on mugs and printed textiles such as ski wear or promotional T-shirts are common uses. Such pigments are actually composites formulated from three components, the color former, an acidic catalyst and a non-polar co-solvent medium. The thermochromism centers around the interaction of color former and developer which occurs in a low-melting hydrophobic medium: the color of pigment changes when heated above its melting point and returns instantaneously on cooling and solidification [3]. However, functional dyes

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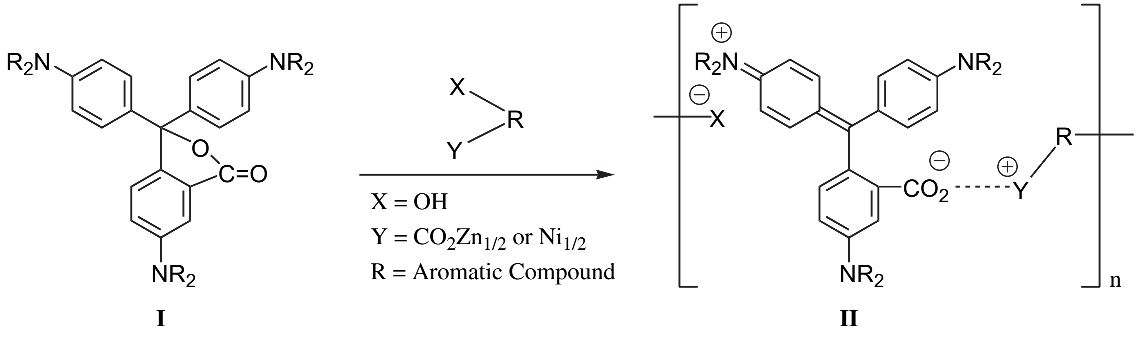


Scheme 1

of this type gradually fade and so improved light fastness is currently being sought [1].

In previous papers [4–8], the photofading behaviors of Crystal Violet lactone and related compounds were investigated in solution and in the adsorbed state. Zinc or nickel salts of 1-hydroxy-2-naphthoic acid and its derivatives provided more marked improvements in the light fastness of color formers than did conventional stabilizers. It was found that the amphoteric counter-ion effect plays a very important role in the photostability of color formers. Therefore, it is of interest to prepare a series of compounds capable of acting as the amphoteric counter-ion (X-R-Y) in complex **II** with color former (see Scheme 1). An UV absorber with attached amphoteric counter-ion residues is particularly noteworthy.

In this paper, the influence of a functional UV absorber containing an amphoteric counter-ion moiety on the photofading behavior of color formers was investigated on cellulose, and a novel approach for improving the light fastness of colorants for imaging and data recording systems is now reported.

2. Experimental

2.1. Materials

Crystal Violet lactone (**1**), 3-diethylamino-7,8-benzofluoran (**3**),3-(N-ethylisobutylamino)-6-methyl-7-anilinofluoran (**5**) and tetrachlorophthalic acid mono (ethylene glycol ester) zinc salt (PEG-Zn) were obtained from a commercial source. The chloride of Crystal Violet (CI Basic Violet 3, $\lambda_{\max}^{H_2O}$ 586 nm) (**7**), 2,2-bis (4-hydroxyphenyl)propane (bisphenol-A), nickel dimethyldithiocarbamate (NMC), 2-(2′-hydroxy-5′-methylphenyl)benzotriazole (HMBT) and 2-hydroxybenzophenone (HBP) were purchased from Tokyo Chemical Ind. Co., Ltd. Cellulose TLC plates (0.1 cm thickness) were purchased from Merk Co., Ltd. 2,6-dimethoxybenzoic acid ethyl ester was obtained by treating 2,6-dimethoxybenzoic acid with anhydrous ethanol in the usual way. 2,4-dihydroxybenzophenone-3-carboxylic acid (mp 203-4 °C) was synthesized by Friedel-Crafts reaction of benzoylchloride with 2,6-dimethoxybenzoic acid ethyl ester in anhydrous dichloromethane solution containing aluminum chloride according to the procedure described in the literature [9]. The compound was recrystallized from methanol-2-propanol after the column chromatography and identified by ^{1}H NMR, Mass, IR and elemental analyses. Metal carboxylates were prepared and purified as described previously [5,10].

The formulas of dye **7** and these materials are shown in Figs. 1 and 2.

2.2. General procedure for photofading of color formers and related colorant

According to the procedure described in the previous papers [5–8], a solution of **1** (8×10^{-3} mol dm^{-3}) in 10 cm^3 of a mixture of pyridine and water (4:1 v/v) with or without additive (4×10^{-2} mol dm^{-3}) such as carboxylic acids, metal salts, HMBT, HBP or NMC, was prepared in the presence of bisphenol-A (54.8 mg), and then stirred at 80 °C for 1 h.

Portions of the solutions (1×10^{-2} cm^3) were spotted on cellulose TLC plates using a micro-syringe and dried at 150 °C. The plates were held at a distance of approximately 5 cm from the light source (100 W high-pressure mercury lamp; Ushio Electric Inc., UM-102

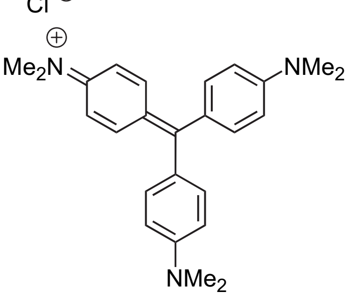
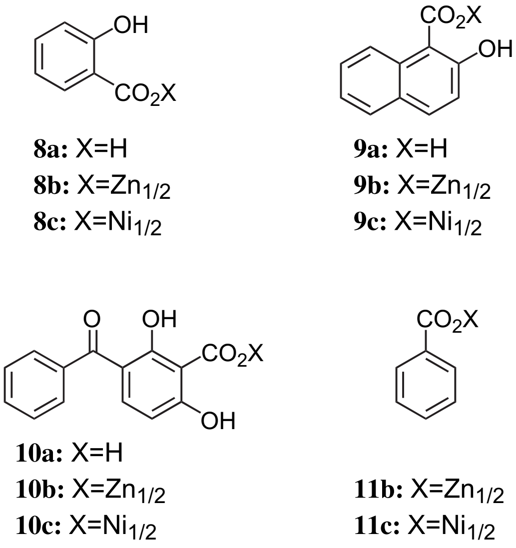


Fig. 1. Chemical structure of dye **7**.



8a: X=H
8b: X=$Zn_{1/2}$
8c: X=$Ni_{1/2}$

9a: X=H
9b: X=$Zn_{1/2}$
9c: X=$Ni_{1/2}$

10a: X=H
10b: X=$Zn_{1/2}$
10c: X=$Ni_{1/2}$

11b: X=$Zn_{1/2}$
11c: X=$Ni_{1/2}$

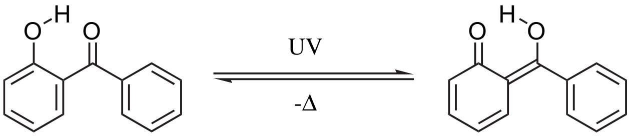
Fig. 2. Carboxylate additives used in the present study.

type) and exposed to light ($\lambda > 300$ nm) in air. The apparatus was kept at 30±2 °C. After irradiation for 3 h, the plates were developed with 60% acetic acid. The spot of separated color was scanned using a Shimadzu thin-layer chromatoscanner (CS-920 type). The percentage conversion was calculated by comparison with unirradiated color. A similar procedure was also used for dyes **3**, **5** and **7**. The irradiation times were 5h in the case of **3** or **5**, and 23 h in the case of **7**.

3. Results and discussion

3.1. Improvement of the light fastness of Crystal Violet lactone

Dye **1** is a chromogenic compound in its colorless form. Acidic catalysts, e.g. acidic clay, open the lactone ring, thereby allowing a violet triarylmethane dye (**2**, $\lambda_{max}^{95\%AcOH}$ 605 nm) to form, as illustrated in Scheme 2 [2]. Generally, the dye derived from the color former has a poor fastness to light, and an improvement of the property is requested.

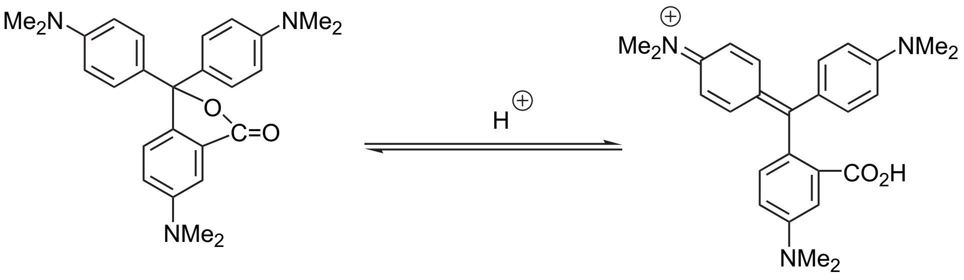


Scheme 3

A number of different types of UV absorbers, containing absorbing groups, are available for protecting dyes on fabrics, but only 4 fundamentally different classes have achieved commercial significance. These are the derivatives of cinnamic acids, phenyl esters, hydroxyphenylbenzotriazoles and 2-hydroxybenzophenone. The latter type of compound, which is 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 (see Scheme 3) [11].

In preliminary studies [5–8], the effect of various counter-ions on the photofading of color materials derived from color formers was investigated on cellulose plate or heat-sensitive recording paper. It was found that the amphoteric counter-ion effect plays a very important role not only in the photostability but also in the image stability of color formers. It is therefore of interest to investigate benzophenone type UV absorber bearing a built-in amphoteric counter-ion moiety as a means of improving the light fastness of phthalide-type color former. Various types of related stabilizers were prepared, and the effectiveness of these compounds was examined on cellulose plate. The formulas of dye **7** and the stabilizers used in this study are shown in Figs. 1 and 2. The influence of various additives on the photofading of dye **2** on cellulose was investigated in air on exposure to filtered radiation ($\lambda > 300$ nm) from a 100 W high-pressure mercury lamp, and the results are shown in Table 1.

When dye **2** adsorbed on cellulose was exposed for 3 h to filtered radiation, it showed 84% conversion, while in the presence of 2-hydroxybenzoic acid (**8a**) or 2-hydroxy-1-naphthoic acid (**9a**) showed 70 and 72%



1: Colorless

2: $\lambda_{max}^{95\%AcOH}$ = 605 nm

Scheme 2

Table 1
Effect of various additives on the photostability of colorants on cellulose

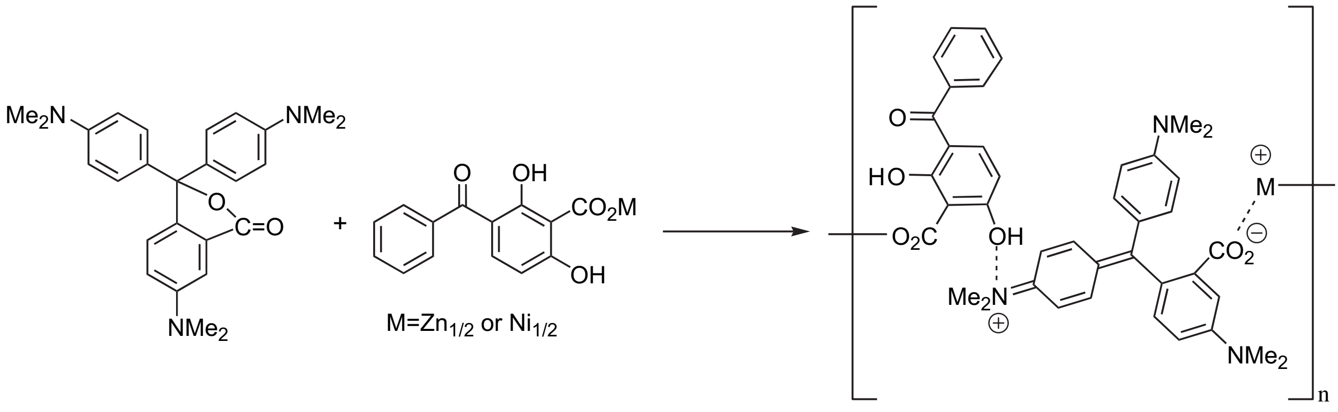
Additive[a]	Conversion (%)	
	2	**7**
None	84	61 (68)[b]
8a	70	–
8b	20	65[b]
8c	17	53[b]
9a	72	–
9b	40	68[b]
9c	19	58[b]
10a	63	–
10b	12	54
10c	0	47
11b	82	57
11c	62	37
HBP[c]	66	35
HMBT[d]	43	33
PEG-Zn[e]	82	–
NMC[f]	64	–

[a] For key see Fig. 2.
[b] Exposed for 24 h.
[c] 2-Hydroxybenzophenone.
[d] 2-(2′-Hydroxy-5′-methylphenyl)benzotriazole.
[e] Tetrachlorophthalic acid mono(ethylene glycol ester) zinc salt.
[f] Nickel dimethyldithiocarbamate.

conversion respectively. These carboxylic acids are incapable of acting as amphoteric counter-ions, and so had little influence on the rate of photofading. However, the addition of zinc salts of these acids (**8b**, **9b**) in the photofading system remarkably retarded the fading. A similar stabilization effect was also observed in the presence of nickel salts (**8c**, **9c**). The retardation effect provided by these compounds (**8b**, **c**, **9b**, **c**) were significantly better than those of the monofunctional zinc and nickel benzoates (**11b**, **c**), and the conventional stabilizers PEG-Zn and NMC. Such an enhanced photochemical stability may be due to the contribution of an intermolecular amphoteric counter-ion effect, since these zinc salts had little influence on the rate of fading of dye **7** which contains no lactone ring [5].

Furthermore, the influence of UV absorbers on the photofading of dye **2** was also examined on cellulose. When 2-hydroxybenzophenone (HBP), benzophenone type UV absorber, or 2-(2′-hydroxy-5′-methylphenyl)-benzotriazole (HMBT), benzotriazole type UV absorber, was added to the photofading system, dye **2** showed 66 and 43% conversion respectively. Benzophenone type UV absorber behaved in a very slightly inferior way to benzotriazole type UV absorber. A similar stabilizing effect was also observed in the presence of 2,4-dihydroxybenzophenone-3-carboxylic acid (**10a**). However, when zinc 2,4-dihyroxybenzophenone-3-carboxylate (**10b**) was added to the photofading system, dye **2** showed only 12% conversion. The nickel salt (**10c**) completely retarded the rate of photofading of dye **2** under the condition employed. Such an excellent degree of protection against the fading of dye **2** may be caused by combined function of amphoteric counter-ion effect such as **12** and UV absorbing ability by UV absorber, since these salts had little influence on the fading of dye **7** which contains no lactone ring [4] (see Scheme 4).

The process of formation of complex **12** is now being studied and will be reported later. Moreover, the retarding effects provided by the nickel salts were generally superior to those of the zinc salts. Since the contribution of singlet oxygen to the photofading of Crystal Violet lactone has been proposed in recent years [12], this may result from the singlet oxygen quenching effects caused by nickel salts [5]. This hypothesis is supported by the fact that the retardation effect afforded by NMC, well-known singlet oxygen quencher [14], is somewhat superior to that of PEG-Zn, a conventional stabilizer for color former. Consequently, these observations suggest that the introduction of the groups capable of acting as an amphoteric counter-ion into UV absorber plays a very important role in the photostabilization of phthalide type color formers.



1 **12**

Scheme 4

3.2. Effect of UV absorbers on the photofading of fluoran dyes

Fluoran dyes **3** and **5** together with dye **1** are extensively used for technical reproduction, e.g. business forms for resisters or computers, or thermochromic systems for textiles. The colored materials **4** and **6** derived from color formers **3** and **5** shows a red color ($\lambda_{max}^{95\%AcOH}$ 490, 522 and 555 nm) and a black color ($\lambda_{max}^{95\%AcOH}$ 446 and 586 nm) respectively, as illustrated in Scheme 5, but their light fastness properties are as poor as dye **1** [1].

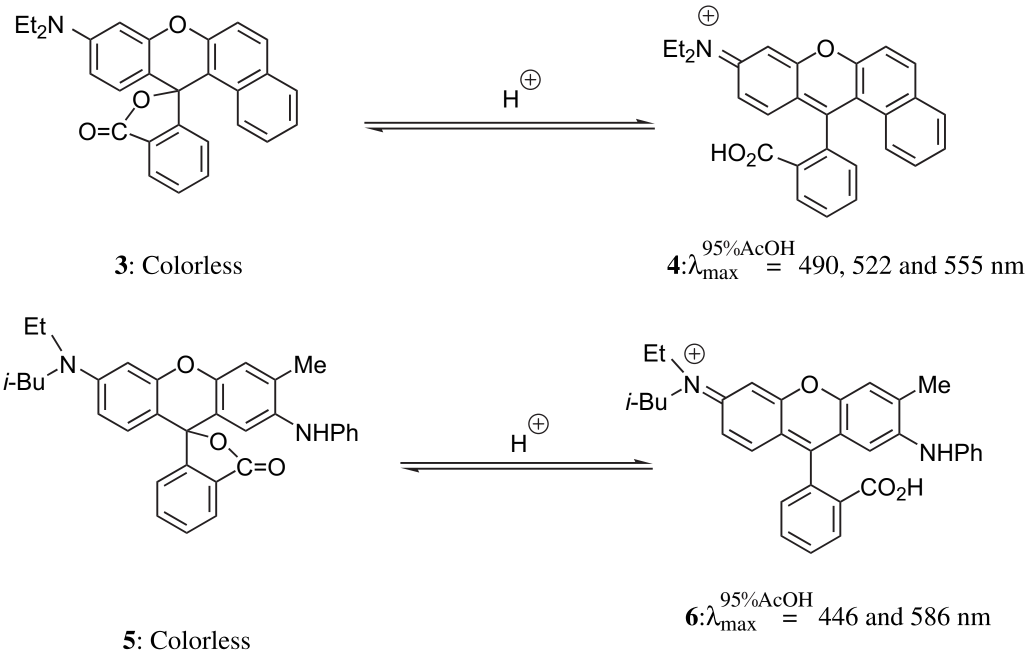
In the above section, it was found that metal hydroxyarylcarboxylates were highly effective for photostabilizing the colored material derived from Crystal Violet lactone. Particularly, functional UV absorbers (**10b**, **c**) were effective in preventing fading. Following this, it was considered of interest to further investigate the protecting effects of these stabilizers in connection with improving the light fastness of fluoran dyes. The influence of various stabilizers on the photostability of fluoran dyes was examined using dyes **4** and **6** in the same manner as above; the results are shown in Table 2. When dye **4** on cellulose was exposed for 5 h to filtered radiation, it showed 87% conversion, while in the presence of 2-hydroxybenzoic acid (**8a**) or 2-hydroxy-1-naphthoic acid (**9a**) showed 66% conversion respectively. These behaviors may be supported by the fact that the carboxylic acids, such as 2-hydroxybenzoic acid, capable of forming intramolecular hydrogen bonds gave little protection against the fading of color formers in solution and on silica gel [13]. However, the addition of 2-hydroxybenzoic acid zinc salt (**8b**) or 2-hydroxy-1-naphthoic acid zinc salt (**9b**) in the photofading system remarkably retarded the fading. A similar stabilizing effect was also observed in the presence of these nickel salts (**8c**, **9c**). Such an enhanced photochemical stability may be due to the contribution of amphoteric counter-ions as well as in the case of dye **1**.

Table 2
Effect of various stabilizers on the photofading of fluoran dyes

Additive[a]	Conversion (%)	
	4	6
None	87	86
8a	66	63
8b	41	14
8c	38	14
9a	66	63
9b	41	20
9c	37	9
10a	57	26
10b	30	13
10c	11	0
HMBT	63	36
HBP	60	30

[a] For key see Fig. 2 and Table 1.

On the other hand, dye **4** showed 57% conversion by adding **10a**, which must be capable of acting as an UV absorber. The protecting effect was almost equal to that of HBP or HMBT, good UV absorbers. The use of **10b** or **10c**, however, showed higher inhibition against the fading of dye **4** compared with **10a**. Similar behavior was also observed in the case of dye **6**. When dye **6**,



3: Colorless

4: $\lambda_{max}^{95\%AcOH}$ = 490, 522 and 555 nm

5: Colorless

6: $\lambda_{max}^{95\%AcOH}$ = 446 and 586 nm

Scheme 5

adsorbed on cellulose, was exposed for 5 h to filtered radiation ($\lambda > 300$ nm) and air, it showed 86% conversion, and in the presence of **8a** and **9a** showed 63% conversion, respectively. When HBP or HMBT was added to the photofading system, dye **6** still showed 30 and 36% conversion respectively. Similar incomplete protection has also been observed in the presence of **10a**. This fact implies that the application of simple UV absorbers is not necessarily useful for improving the light fastness of color formers.

On the contrary, the addition of **8b**, **c** significantly suppressed the rate of photofading of dye **6**, the retardation effects given by these compounds being almost equal to those of **9b**, **c**. Such a higher degree of protection against the fading of dye **6** was also afforded by the use of **10b**, **c**. As a general rule, the retardation effect provided by **10b** was somewhat superior to that of **8b** or **9b**. The suppressing effect given by **10c** was also superior to that of **8c** or **9c**. In particular, it is noteworthy that the nickel salt (**10c)** was perfectly retarded the rate of photofading of dye **6** under the condition herein described. Consequently, these results demonstrate that the benzophenone type UV absorber containing an amphoteric counter-ion moiety can be applied as effective stabilizers against the photofading of color formers, and especially nickel complex is effective.

4. Conclusions

While the contribution of counter-ions to the photofading of cationic dyes has been previously investigated by several workers, there is no study pertaining to the use of counter-ions as a means of improving the light fastness of color formers.

In this study, the influence of various compounds capable of acting as an amphoteric counter-ion on the photostability of color materials derived from color formers has been examined on cellulose. While some of these have been shown to offer some degree of improvement, the most positive protection was given by the presence of UV absorber bearing a built-in amphoteric counter-ion moiety. The functional UV absorbers discovered in this study may be applied as effective stabilizers against photofading of color formers.

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