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# New Developments in the Stabilization of Photochromic Dyes: Counter-ion Effects on the Light Fatigue Resistance of Spiropyrans

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## ABSTRACT

*Photochromic spiropyrans have attracted much current attention because of their potential applications including optical memories and light-controlling media. The colored form of the compound, however, is thermally unstable and bleached. Numerous potential metal complexes were synthesized to prolong the life of colored species. The protecting effect of these compounds against the decoloration reaction in the dark or photofading of photocolored species was examined on cellulose. It was found that the spiropyran in the presence of zinc 1-hydroxy-2-naphthoate or its derivatives shows excellent light fatigue resistance. © 1998 Published by Elsevier Science Ltd. All rights reserved*

*Keywords*: spiropyran, photochromism, durability, light fatigue resistance, counter-ion effect.

## INTRODUCTION

The chemistry of spiropyrans recently became particularly important in connection with the rapid development of information recording systems [1,2]. The ordinary photochromism of spiropyrans is known to involve the conversion of a stable colorless state I into a colored metastable state II with ultraviolet light. Reversion to the colorless state occurs either spontaneosly when the solution is stored in the dark, or by irradiation with visible light. The metastable state II is called photomerocyanine, as it resembles the structure of merocyanine dyes. The process which takes place in the photochromic system is shown in Scheme 1.

Application of the photochemical system in data storage requires that states I and II should be reasonably stable at ordinary temperatures in the absence of provoking illumination, and that the photochemical interconversion of states I and II should also be possible at ordinary temperatures. A great variety of spiropyrans which are photochemically active at room temperature have been synthesized, but not developed commercially until now [1,2]. A chief reason is the poor durability of spiropyrans. Almost all of them lose their photochromic ability easily upon exposure to sunlight. This lack of durability to sunlight irradiation is called light fatigue.

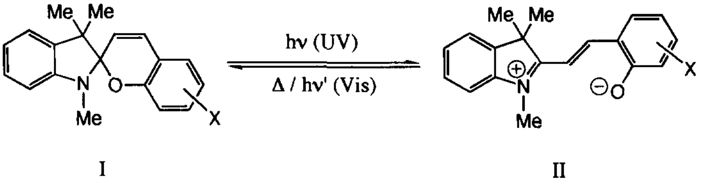
In a preliminary study [3], the influence of amphoteric counter-ions on the photochromic behavior of spiro-oxazines and related compounds was investigated on cellulose. It was found that zinc salt of 1-hydroxy-2-naphthoic acid is very effective for stabilizing the colored form of spironaphthoxazine. In recent years, it has been presented that the spiropyran derivatives which possess a co-ordinating group near the pyranyl oxygen atom can act as chelating agents in the colored merocyanine form. They formed chelates with divalent metal ions on irradiation with ultraviolet light [4–9]. The chelation induced significant retardation of the thermal decoloration rate in the dark [10]. Hence, it can be anticipated that metal complexes capable of acting as amphoteric counter-ion can contribute to stabilization of the photocolored species of spiropyrans and related compounds.

In the present study, the influence of various kinds of counter-ions on the photochromic phenomena of spiropyrans has been examined on cellulose and a novel approach for improving the light fatigue resistance of photochromic materials is now reported.

# EXPERIMENTAL

## Materials

6-Nitro-1′,3′,3′-trimethylspiro(lH-1-benzopyran-2,2′-indoline) (**1**) was a commercial reagent (Tokyo Kaseikogyo Co. Ltd.). Metal carboxylates were



**Scheme 1**

synthesized and recrystallized according to the procedures described in the literature [11].

### Photochromism of spiropyran on cellulose

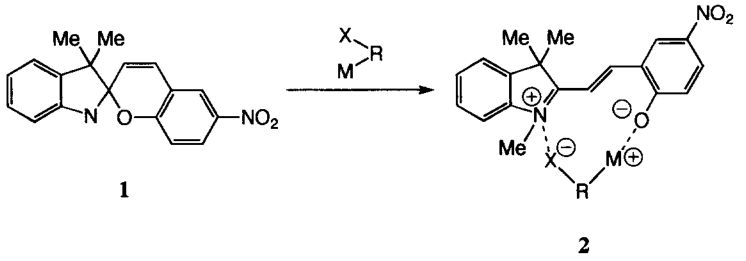
A solution of **1** ($8 \times 10^{-3}$ mol dm$^{-3}$) in ethanol or dimethylsulfoxide (10 cm$^3$) with or without an additive ($4 \times 10^{-2}$ mol dm$^{-3}$) such as metal carboxylates was prepared. Portions of the solutions ($1 \times 10^{-2}$ cm$^3$) were spotted on cellulose TLC plates using a microsyringe, and dried. The plates were irradiated at 25°C with an external 500 W high-pressure mercury lamp (Ushio Electric Inc., UI-501). Undesiable wavelengths were excluded using filters (Toshiba, Number UV-D36C, Y-52). The changes of color developed on irradiation with ultraviolet light were monitered with a thin-layer chromatoscanner. The percentage conversion was calculated by comparison with irradiated color for 1 min. The colored spots faded back to their original state in the dark. The dark decay reaction was also monitered in the same manner as above.

## RESULTS AND DISCUSSION

### Effect of various additives on the stability of the photocolored state of spiropyrans

Organic photochromic compounds have attracted much attention, because they change not only their colors but also their molecular properties and functions. Spiropyrans are among the most popular photochromic compounds. Many studies have been reported on the photochromism of spiropyrans reversibly forming photomerocyanines because of their potential usefulness as photoresponsive materials, e.g. reversible optical recording media, ornaments and reversible light filters [1, 2]. In such a case, it is essential to control the stability of the photocolored state. Up to the present time, main effort has been concentrated on the synthesis of new derivatives and on the practical applications [2]. Basic research into the understanding of the fatigue mechanism as well as photochemical and photopysical processes has been neglected. Recently, it was found that the amphoteric counter-ion effect plays a very important role in the stability of the photocolored state of spiro-oxazines and related compounds [3]. In contrast, it has been previously established that spiropyrans of the indoline series are able to complex with transition metal ions ($Zn^{2+}$, $Co^{2+}$, $Cu^{2+}$ etc.). Since the yeild of the complex increases on UV irradiation of spiropyran, it has been presumed that only the merocyanine form of the spiropyran is involved in the complexation reaction [4–9]. It was also revealed that the chelation induces significant retardation of the thermal decoloration rate in the dark [10]. Accordingly, it is of interest to prepare a series of metal salts capable of acting as the amphoteric counter-ion (X-R-M) in complex **2** with the spiropyran in its photomerocyanine form (see Scheme 2).

The quantitative determination of spectro-kinetic or photochemical parameters is generally achieved in solution but many applications require solid supports, such as plastic films, paper, semiconductors or other polymers [1, 2]. In this study, the effect of various kinds of additives on the photostability of the photomerocyanine derived from spiropyran (**1**) was examined on cellulose TLC plates. A preliminary study showed that zinc 1-hydroxy-2-naphthoate was highly effective for stabilizing the colored form of spirooxazines and related compounds [3]. The influence of some additives on the photofading of **1** on cellulose was investigated in air on exposure to filtered radiation ($\lambda = 365$ nm) from a 500 W high-pressure mercury lamp, and the results are shown in Fig. 1. Spiropyran (**1**) on cellulose develops color upon irradiation with ultraviolet light, but the color gradually fades upon continued irradiation. The photofading behavior was determined by comparison with the concentration of ultraviolet irradiation on **1** for 1 min. The spot of **1** faded rapidly in air on exposure to filtered radiation ($\lambda = 365$ nm) from a high-pressure mercury lamp source. The addtion of zinc benzoate in the photofading system afforded little protection against fading. However, the rate of photofading was considerably suppressed by adding zinc glycolate. The use of zinc 2-hydroxybenzoate or 1-hydroxy-2-naphthoate completely suppressed that fading. Such an enhanced photochemical stability may be a result of the contribution of amphoteric counter-ions as in the case of spironaphthoxazine [3]. A similar suppressing effect by these metal salts was also observed in the case of the dark decay reaction of **1**. The results are shown in Fig. 2. The colored form generated by illumination with ultraviolet light decayed to the colorless form readily on storage in the dark. The decoloration rate in the dark was clearly retarded by the addition of zinc glycolate to this system but scarcely retarded by zinc benzoate, monofunctional stabilizer. The addition of zinc 2-hydroxybenzoate or 1-hydroxy-2-naphthoate



**Scheme 2**

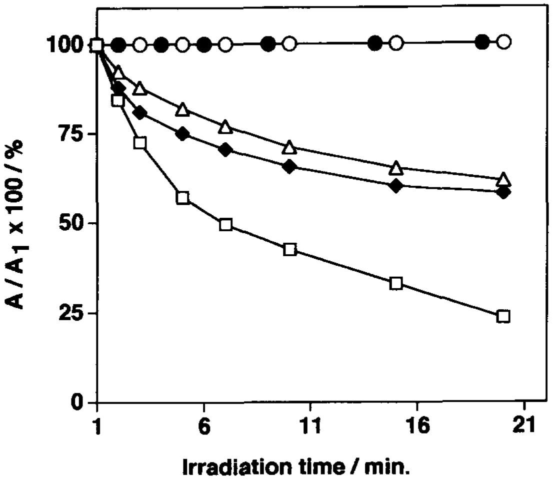


**Fig. 1.** Effect of additives on the photofading of **1** on cellulose: □ no additive; ◆, zinc benzoate; △, zinc glycolate; ○, zinc 2-hydroxybenzoate; ●, zinc 1-hydroxy-2-naphthoate.

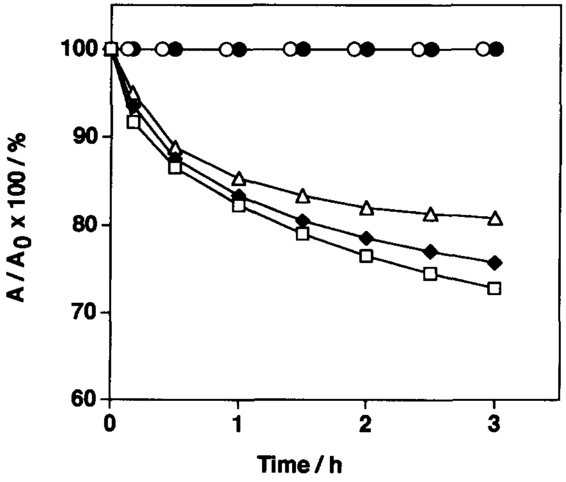


**Fig. 2.** Effect of additives on the decoloration reaction of **1** in the dark. (For key see Fig. 1).

perfectly stopped the rate of decoloration in the dark. These findings imply that a single amphoteric counter-ion effect is not very beneficial for stabilizing the colored form of spiropyrans, but that the combined use of amphoteric counter-ion effect and the $\pi$-conjugated ring system plays a very important role in the stabilization of photomerocyanine.

According to the above approach, some naphthalene derivatives were synthesized, and the protecting effect of these compounds towards decoloration in the dark or photofading of the photocolored species of **1** was examined on cellulose. These results are shown in Figs 3 and 4. Each additive used in this experiment afforded a similar protecting effect against the decoloration reaction in the dark or photofading of **1**. The use of zinc 1-hydroxy- or 3-hydroxy-2-naphthoate or 2-hydroxy-1-naphthoate completely stabilized the photocolored state of **1**. This fact indicates that a series of naphthalene derivatives capable of acting as the amphoteric counter-ion have an excellent effect on the stabilization of the photomerocyanine.

On the other hand, the use of metal dicarboxylates is also of interest in connection with the amphoteric counter-ion effect. The protecting effect of various metal dicarboxylates towards the decoloration of the merocyanine form of **1** in the dark was examined on cellulose. As shown in Fig. 5, the colored form generated upon ultraviolet irradiation decay thermally to the colorless form readily at ambient temperature. Zinc salt of oxalic acid was capable of moderate stabilization of the colored form. However, zinc salt of phthalic or 2,3-naphthalenedicarboxylic acid completely prevented decoloration in the dark. Such an enhanced photochemical stability may be due to the contribution of zwitterionic structure of the photomerocyanine, since these salts had no influence on the decoloration reaction of photocolored species of spironaphthoxazine assumed to be nonionic, keto type structure [2, 3, 12]. Additionally, this hypothesis may be supported by the fact that the zinc aryldicarboxylates are very effective in prolonging the life of color materials derived from color formers [13]. Similar effectiveness was examined also using the nickel salts. The nickel salts examined scarcely decreased the rate of decoloration in the dark. These phenomena may demonstrate that the nickel salts of arylcarboxylic acids are not appreciably useful in controlling

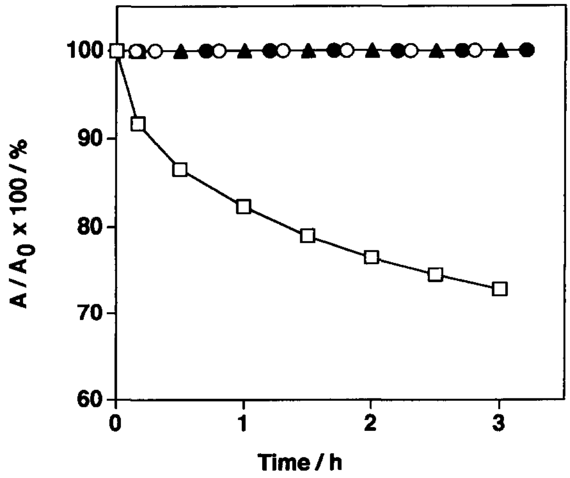


**Fig. 3.** Effect of additives on the decoloration reaction of **1** in the dark: □, no additive; ●, 1-hydroxy-2-naphthoate; ▲, 2-hydroxy-1-naphthoate; ○, 3-hydroxy-2-naphthoate.

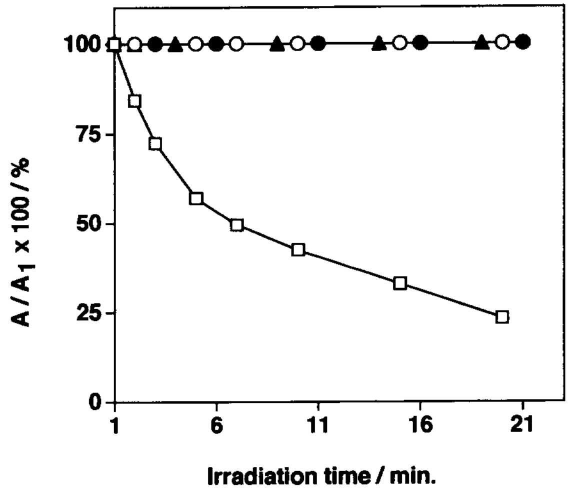


**Fig. 4.** Effect of additives on the photofading of 1 on cellulose. (For key see Fig. 3).

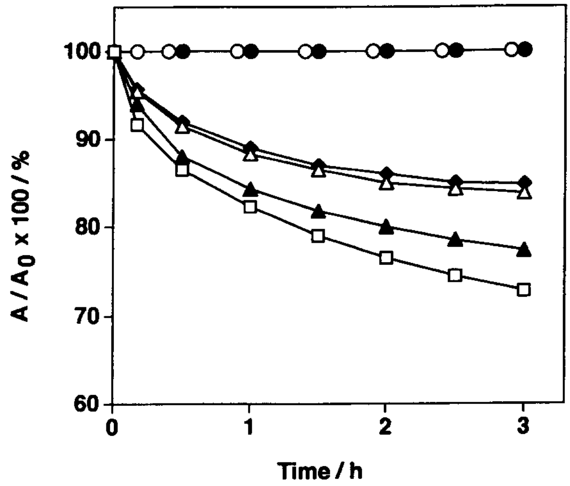


**Fig. 5.** Effect of additives on the decoloration reaction of **1** in the dark: □, no additive; ◆, oxalic acid zinc salt; ○, phthalic acid zinc salt; ▲, phthalic acid nickel salt; △, nickel 2-hydroxybenzoate; ●, zinc 2,3-naphthalenedicarboxylate.

the decoloration rate in the dark. A similar stabilizing effect by these metal (Zn, Ni) salts was also observed on the photofading behavior in ultraviolet light. As shown in Fig. 6, the spot of **1** faded drastically in air on exposure to filtered radiation ($\lambda = 365\,\mathrm{nm}$) from a high-pressure mercury lamp source. However, the addition of a series of zinc aryldicarboxylates in the photofading system afforded considerable protection against fading. A similar protecting effect was also recognized in the presence of oxalic acid zinc salt.

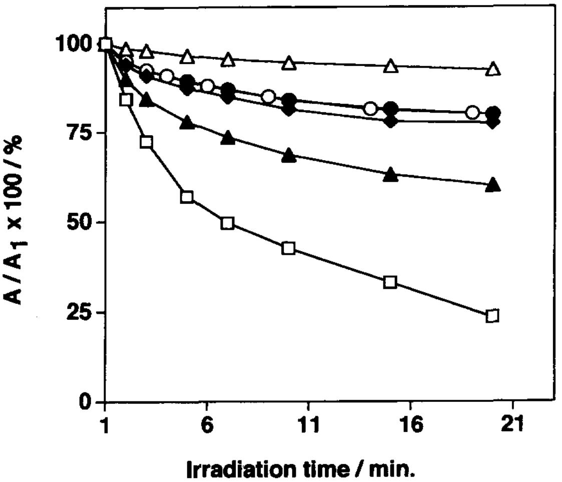


**Fig. 6.** Effect of additives on the photofading of **1** on cellulose. (For key see Fig. 5).

The suppressing effect provided by oxalic acid zinc salt was somewhat inferior to those of zinc aryldicarboxylates. Futhermore, the effect of the nickel salts on the photofading of **1** was examined in the same manner as above. As a general rule, the retarding effects provided by these nickel salts were inferior to those of the zinc salts (see Figs 1 and 6). These findings may imply that the nickelation of stabilizers is not necessarily useful for stabilizing the colored form of spiropyrans.

## Effect of various kinds of zinc arylcarboxylates on the photochromic durability of spiropyran

The technique used for investigation of photodegradation is the ultraviolet photolysis by repeated flashes and counting of the number of flashes necessary for reaching a decrease to the half of maximum optical density measured after the first flash. The photodegradation of spiropyrans in aerated solution occurs partially by oxidation and the identified products are carbon monoxide, carbon dioxide, substituted derivatives of salicylaldehide, oxindole and polycondensates.

For practical applications, however, a solid photochromic material is more useful than a liquid. Spiropyrans have been also grafted to anionic living polymers which have both flexible and rigid sequences. Initial studies were carried out on homopolymers, e.g. polystyrene, polymethylmethacrylate, polyhexylmethacrylate and polyisoprene, and subsequently on block copolymers. The photodegradation results showed that the polymer has no significant effect except in the case of polyisoprene for which degradation is linked to the unsuturation of the polymer chain [14].

In this work, the photochromic performance of spiropyran was investigated on solid supports. For the convenience of easy laboratory manipulations, cellulose was chosen as the solid support for evaluation. According to the results mentioned above, zinc salts of phthalic acid, 2-hydroxybenzoic acid and 1-hydroxy-2-naphthoic acid were chosen as the representative compounds, and the effect of these additives on the photocoloration and photobleaching process of **1** was examined on cellulose. The changes of **1** on cellulose are shown in Fig. 7. The spot of **1** was colorless, and upon irradiation with ultraviolet light ($\lambda = 365$ nm) a deep violet color was instantly formed. The colored spot was decolorized by visible light ($\lambda > 520$ nm). The spot decolorized by visible light was recolored upon ultraviolet irradiation. But its absorbance diminished to 88% of the maximum optical density measured after the first flash. The color gradually faded by prolonged exposure to ultraviolet light. The spot faded by ultraviolet light gave a rapid bleaching with a visible flash. Such photocoloration–photobleaching cycles could be repeated four times before to half the initial absorbance at ambient temperature. Figure 8 shows the photocoloration–photobleaching cycle of **1** in the presence of phthalic acid zinc salt. On irradiation at 365 nm, the optical density increased rapidly and reached a photostationary value for 1 min. The intense violet color disappeared rapidly upon irradiation by visible light. Furthermore, the color was regenerated upon ultraviolet irradiation, but the absorbance was reduced to 70% of its initial value. The color gradually faded upon continued ultraviolet irradiation. The colored spot was vigorously bleached by visible light. Such photocoloration–photobleaching cycles could be repeated four times as well as in the case of no additive. These behaviors suggest that the zinc salts of aryldicarboxylic acids have no

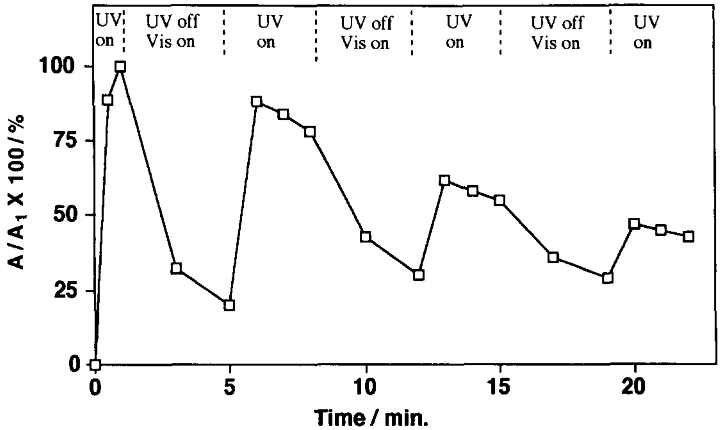


**Fig. 7.** Reversibility of photochromic changes of **1** on cellulose: □, initial concentration: (1) $8 \times 10^{-3}$ mol dm$^{-3}$.

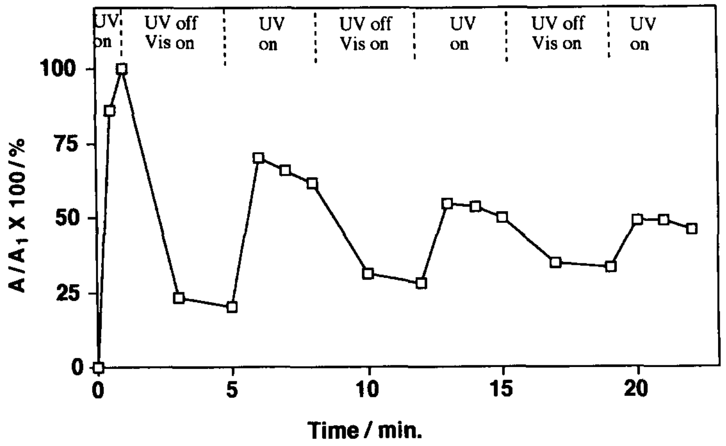


**Fig. 8.** Reversibility of the photochromic changes of **1** in the presence of phthalic acid zinc salt on cellulose: □, initial concentrations: (1) $8\times10^{-3}$ mol dm$^{-3}$, additive $4\times10^{-2}$ mol dm$^{-3}$.

influence on the photochromic cycles of spiropyrans. In contrast the changes of **1** in the presence of zinc 2-hydroxybenzoate are shown in Fig. 9. The spot of **1** was colorless, and upon irradiation with ultraviolet light a deep violet color was instantly formed. The color was rapidly photoerased with visible light. The violet color photoerased by visible light could be completely restored by irradiation of ultraviolet light for 3 min. Once again the colored spot could be decolorized by visible light. On irradiation at 365 nm the optical density rapidly increased again and reached a photostationary state for 3 min. Such photochromic cycles could be repeated many times without

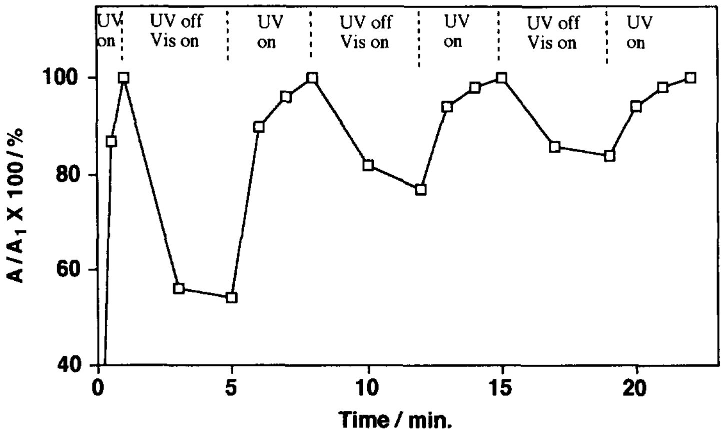


**Fig. 9.** Reversibility of the photochromic changes of **1** in the presence of zinc 2-hydroxybenzoate on cellulose: □, initial concentrations: (1) $8\times10^{-3}$ mol dm$^{-3}$, additive $4\times10^{-2}$ mol dm$^{-3}$.

being faded thermally. A similar higher degree of photoreversibility was achieved also by the addition of zinc 1-hydroxy-2-naphthoate in the photochromicsystem. As shown in Fig. 10, the spot was initially colorless, and by ultraviolet irradiation a violet color was immediately generated. The colored spot was not faded thermally, but was decolorized by visible light ($\lambda > 520\,\text{nm}$). The spot decolorized by visible light was recolored upon ultraviolet irradiation. Such photocoloration–photobleaching cycles could be repeated many times. Even if this recolored spot was stored in the dark for nine or more days at room temperature, it was completely stable and maintained a deep violet color. A similar enhanced photochemical stability was also accomplished with zinc 3-hydroxy-2-naphthoate. These results may indicate that zinc hydroxyarylcarboxylates are very useful in controlling the photochromic cycles of spiropyran. Such excellent stability of the photomerocyanine derived from spiropyran may be due to the contribution of amphoteric counter-ions such as **3** (see Scheme 3). The process of formation of compound **3** is now being investigated and will be reported later.

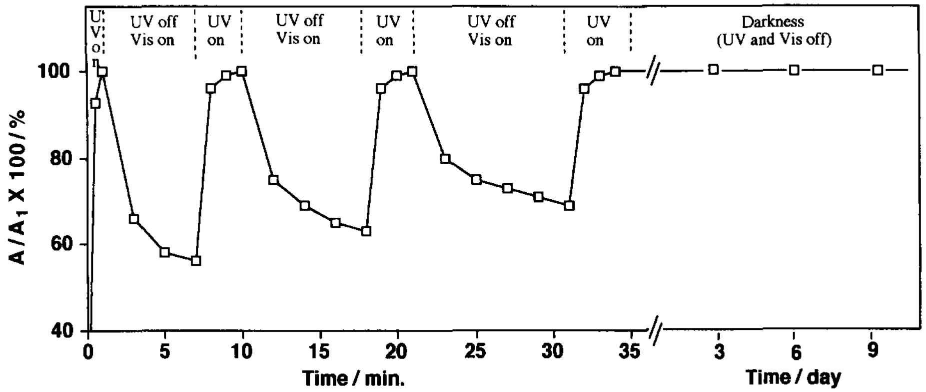
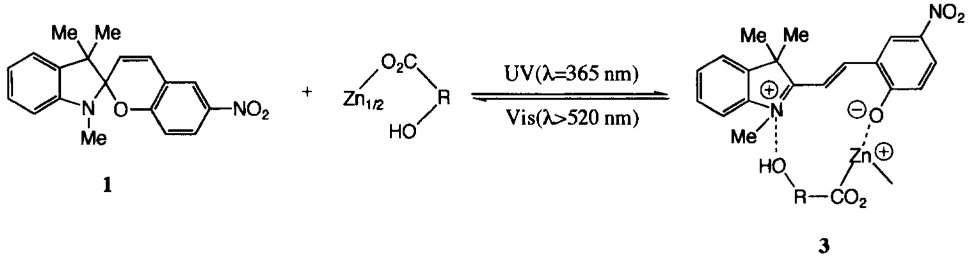


**Fig. 10.** Reversibility of the photochromic changes of **1** in the presence of zinc 1-hydroxy-2-naphthoate on cellulose: □, initial concentrations: (**1**) $8\times10^{-3}\,\text{mol dm}^{-3}$, additive $4\times10^{-2}\,\text{mol dm}^{-3}$.



**Scheme 3**

## CONCLUSION

The spiropyrans and related compounds continue to arouse a strong interest in connection with their applications in various fields such as non-silver high resolution photography, optical devices and variable transmission materials, photovoltaic and photographic systems. However, none have been found to have wide-scale industrial applications. One of the prime reasons for the lack of industrial applications for photochromic materials is their poor durability [2]. Almost all organic compounds lose their photochromic ability easily upon exposure to sunlight. Whilst the contribution of counter-ions to the photofading of cationic dyes has been previously investigated by several workers [15–17], there are few studies pertaining to the use of counter-ions as a means of improving the photodegradation of photochromic materials. In this paper, the effect of amphoteric counter-ions on the photochromic durability of spiropyrans has been examined on solid state. The results provide a novel approach for improving the photodegradation of functional dyes for reversible image-recording media. The metal complexes discovered in this study may permit the use of spiropyrans for practical photochromic materials.

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