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Influence of Metal Quinolinecarboxylates on the Image-stability of Colorants for Information Recording Systems

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ABSTRACT

Metal complexes of carboxylic acids were prepared, and the protecting effect of these compounds towards the photofading of colour materials derived from colour formers was examined on cellulose. It was proposed that nickel or zinc salts of 8-hydroxyquinoline-2-carboxylic acid and its derivatives can be applied as effective stabilisers against the photofading of indicator dyes in heat- (or pressure-) sensitive recording systems. These metal carboxylates were also found to be very useful for stabilising the coloured form of spironaphthoxazine. © 1998 Elsevier Science Ltd

Keywords: metal quinolinecarboxylates, photofading, information recording systems.

INTRODUCTION

The chemistry of colour formers has recently become the focus of great interest, particularly in connection with the rapid development of information recording systems. The dye crystal violet lactone is of commercial importance for use in copying paper, but it gradually fades and so improved light fastness is currently being sought [1, 2]. Fluoran dyes, e.g. 3-(*N*-ethyl-*N*-isobutylamino)-6-methyl-7-anilinofluoran, are well known and have been used widely as typical thermally sensitive black colour formers, mainly for high-performance facsimiles because of high whiteness on thermally sensitive paper and excellent behaviour on colour-forming. Extensive studies on fluoran-type thermally sensitive colour formers have been carried out as a means of improving the stability of their colouring images towards light, heat, moisture, etc. [3]. Until now, however, the major effort has been concentrated on the synthesis of new derivatives and on the practical applications. Fundamental research into the understanding of the fatigue mechanism as well as the photophysical and photochemical processes has been scarce.

The work of spiropyrans has also become especially important in connection with the rapid development of information recording systems [4–8]. The ordinary photochromism of spiropyrans has been used for the conversion of a stable colourless state into a coloured metastable state with ultraviolet light. Reversion to the colourless state occurs either spontaneously when the solution is stored in the dark, or by irradiation with visible light. Many kinds of spiropyrans have been synthesised, but not developed commercially until recently [9, 10], one main reason being the poor durability of spiropyrans. Almost all of them lose their photochromic ability easily on exposure to sunlight. This sensitivity to sunlight irradiation is called light fatigue. Photochromic spironaphthoxazines have recently received attention as functional dyes for reversible image recording medium on account of their high fatigue resistance in the reversible reaction of colouring and decolouring [10]. In such a case, it is important to control the stability of the photocoloured state.

In previous papers [11, 12], the influence of amphoteric counter-ions on the photochemical stability of colorants for imaging and data recording systems was examined on cellulose. It was found that zinc salts of 1-hydroxy-2-naphthoic acid and its derivatives markedly improve not only the photostability of colour formers but also the stability of photocoloured species of photochromic materials.

In this paper, the influence of a variety of quinoline derivatives on the photostability of colour formers and photochromic materials has been investigated on cellulose and a new approach for improving the image-stability of colorants for information recording systems is now reported.

EXPERIMENTAL

Materials

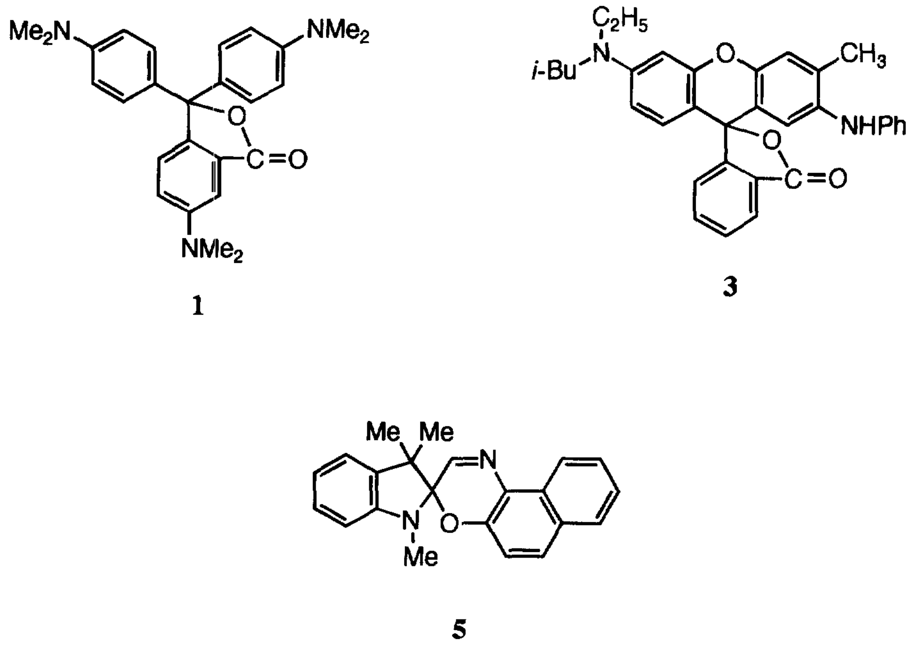
Crystal Violet Lactone (**1**), 3-(*N*-ethyl-*N*-isobutylamino)-6-methyl-7-anilinofluoran (**3**) and 1,3,3-trimethylspiro(indoline-2,3′-(3H)naphtho(2, 1-b)(1,4)oxazine) (**5**) were obtained from a commercial source. The chloride of Crystal Violet (CI Basic Violet 3, λ_{max} 586 nm) (**6**), 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A) and nickel dimethyldithiocarbamate (NMC) were commercial reagents (Tokyo Kaseikogyo Co. Ltd). 8-Methoxyquinoline-2-carboxylic acid, mp 160–161°C ([13], 158–159°C), and 8-hydroxyquinoline-2-carboxylic acid, mp 215–216°C ([13], 211°C), were prepared by the methods of Irving and Pinnington [13]. 3-Hydroxyquinoline-2-carboxylic acid, mp 200–201°C ([14] 196–198°C), was synthesised by the method of McBreiding and Zeeck [14]. Metal carboxylates were synthesised and recrystallised according to the procedures described in the literature [15].

The formulae of the colour formers and photochromic material are shown in Fig. 1.

General procedure for photofading of colour formers and related colorant

A solution of **1** (8×10^{-3} mol dm^{-3}) in pyridine-water (4:1 v/v) or dimethylsulphoxide (10 cm^3) with or without an additive (4×10^{-2} mol dm^{-3}) such as metal carboxylates or NMC, was prepared in the presence of bisphenol-A (54.8 mg), and then stirred at 90°C for 1 h.

Portions of the solutions (1×10^{-2} cm^3) were spotted on cellulose TLC plates using a microsyringe, and dried. 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 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 colour was scanned using a Shimadzu thin-layer chromatoscanner (CS-920 type). The



1

3

5

Fig. 1. Colour formers and photochromic material used in this study.

percentage conversion was calculated by comparison with unirradiated colour. A similar procedure was also used for dyes **3** and **6**. The irradiation times were 5 h for **3**, and 23 h for **6**.

Photochromism of spironaphthoxazine

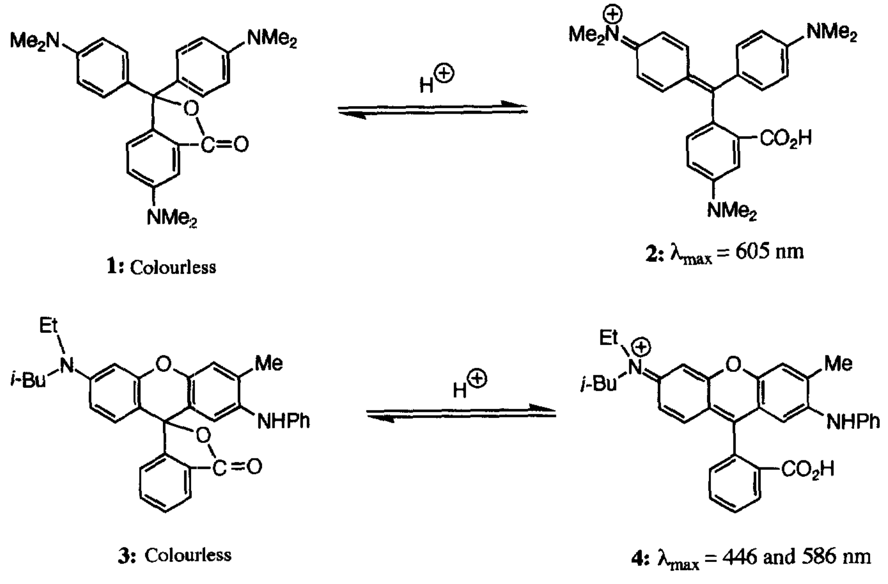
A solution of **5** (8×10^{-3} mol dm^{-3}) in pyridine-water (4:1 v/v, 10 cm^3) with or without an additive (8×10^{-2} mol dm^{-3}) such as metal carboxylates was prepared. Portions of the solutions (1×10^{-2} cm^3) were spotted on cellulose TLC plates using a microsyringe, and dried. The plates were irradiated at 25°C with an external 500 W mercury lamp (Ushio Electric Inc., UM-501). Undesirable wavelengths were excluded using filters (Toshiba, Number UV-D36C). The changes of colour developed on irradiation with ultraviolet light were monitored with a thin-layer chromatoscanner. The percentage conversion was calculated by comparison with irradiated colour for 30 s. The coloured spots faded back to their original state in the dark. The dark decay reaction was also monitored in the same manner as stated earlier.

RESULTS AND DISCUSSION

Effect of a variety of metal complexes on the photofading of colour formers

Dyes such as crystal violet lactone (**1**) and 3-(*N*-ethyl-*N*-isobuthylamino)-6-methyl-7-anilinofluoran (**3**) are extensively used as functional dye in carbonless copy and heat- (or pressure-) sensitive recording paper [2,3,16,17]. These are chromogenic compounds in their colourless form. Acidic catalysts, e.g. acidic clay, open the lactone ring, thereby allowing a violet triarylmethine dye (**2**, λ_{max} 605 nm) and black oxygen-bridged triarylmethine dye (**4**, λ_{max} 446 and 586 nm) to form, as illustrated in Scheme 1 [1]. Generally, the dyes derived from the colour formers have a poor fastness to light, and an improvement of the properties is required.

In a preliminary study [11], the effect of various counter-ions on the photofading of colour materials derived from colour formers was investigated on 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 colour formers. It is therefore of interest to progressively further investigate this amphoteric counter-ion effect as a means of improving the light fastness of colour formers (see Scheme 2). Various types of quinoline derivatives and related compounds were prepared, and their effectiveness examined on cellulose plates. The influence of various metal complexes of carboxylic acids was investigated in air on exposure to filtered



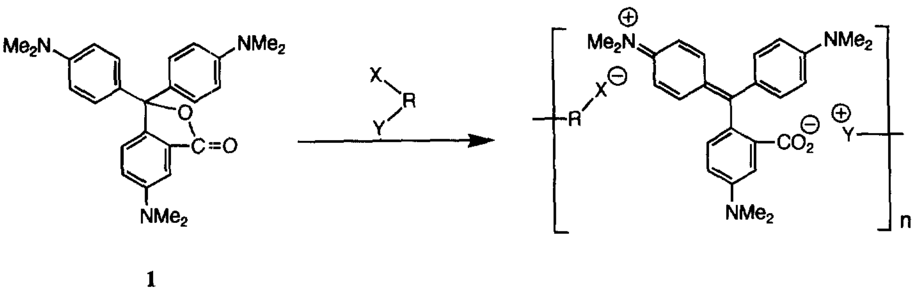
1: Colourless

2: $\lambda_{max} = 605$ nm

3: Colourless

4: $\lambda_{max} = 446$ and 586 nm

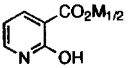
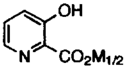
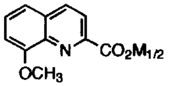
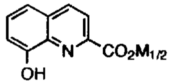
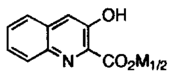
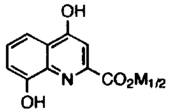
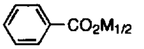
Scheme 1.



Scheme 2.

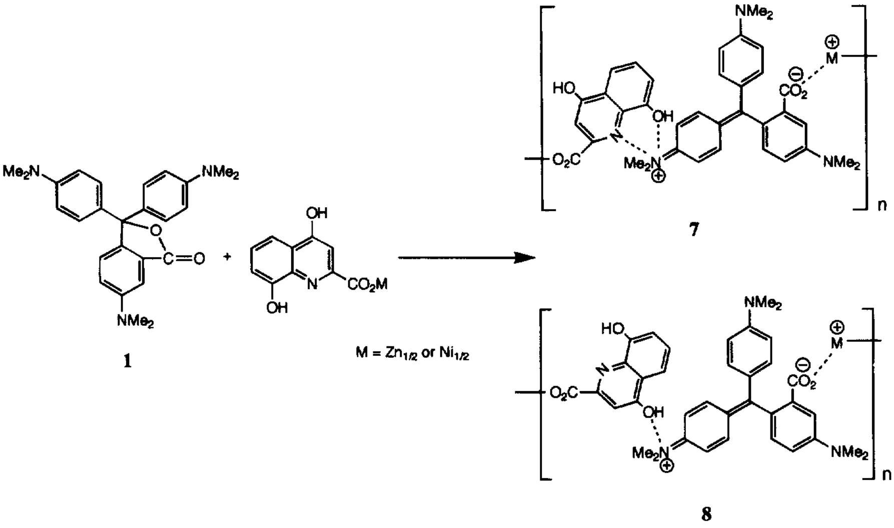
radiation ($\lambda > 300$ nm) from a 100 W high-pressure mercury lamp, and the results are shown in Table 1. The majority of zinc or nickel complexes examined greatly retarded the rate of photofading of **2**, and the protecting effects of these were significantly better than those of the monofunctional, zinc or nickel benzoate, and conventional stabiliser, NMC. Such an enhanced photochemical stability may be due to the contribution of amphoteric counter-ions, since these metal salts had little influence on the rate of **6** which contains no lactone ring [11]. Moreover, the retardation effects provided by metal (Zn or Ni) 8-hydroxyquinoline-2-carboxylates are appreciably superior to those of metal 3-hydroxy or 8- methoxyquinoline-2-carboxylates. Such a higher degree of protection against the fading of **2** may

TABLE 1
Effect of Metal (Zn, Ni) Carboxylates on the Photochemical Stability of Colorants on Cellulose

Run	*Additive*		*Conversion (%)*		
			2	***4***	***6***
1	None		84	86	61
2		M = Zn	37	38	61
		Ni	25	26	52
3		M = Zn	12	17	61
		Ni	3	3	37
4		M = Zn	38	45	59
		Ni	0	27	31
5		M = Zn	18	19	57
		Ni	0	9	40
6		M = Zn	35	—	61
		Ni	33	25	56
7		M = Zn	0	14	57
		Ni	0	0	32
8		M = Zn	82	77	57
		Ni	62	76	37
9	NMC		64	77	—

be caused by the action of an amphoteric counter ion like complex **7** in Scheme 3. Furthermore, metal 3-hydroxypyridine-2-carboxylates gave a far more efficient protecting effect against the fading of **2** than did metal 2-hydroxypyridine-3-carboxylates. In particular, it is noteworthy that the addition of zinc or nickel 4,8-dihydroxyquinoline-2-carboxylate completely suppressed the rate of photofading of **2**. Such an excellent stability may be a result of the contribution of bifunctional amphoteric counter-ions such as **7** or **8** (see Scheme 3). The process of formation of complex **7** or **8** is now being studied and will be reported later. A similar suppressing effect by the metal complex was observed also in the case of **4**.

On the contrary, 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 colour formers has been proposed in recent years [18], this may result from the singlet oxygen quenching effects caused by nickel salts.

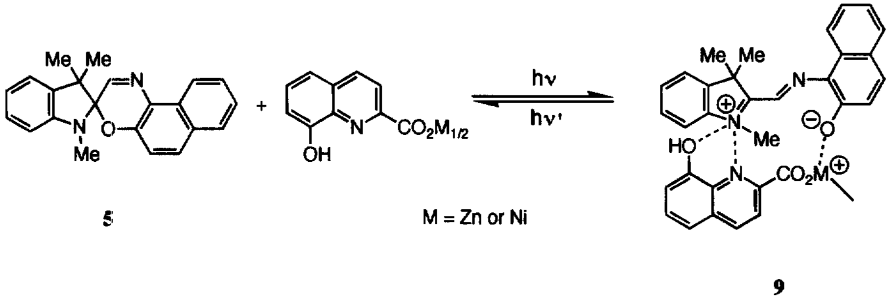


Scheme 3.

Improvement of the light fatigue resistance of spironaphthoxazine

Spiropyrans and spironaphthoxazines are of considerable interest for various applications, e.g. none-silver high resolution photography, optical devices and variable transmission materials, photovoltaic and holographic systems [9,10]. The spiropyrans are not widely used because of their poor durability to sunlight irradiation [9,10]. Photochromic spironaphthoxazines, however, have attracted attention as functional dyes for reversible image recording media on account of their high fatigue resistance in the reversible reaction of colouring and decolouration [10,19]. It is important to control the stability of the photocoloured state. Until now, the chief effort has been concentrated on the synthesis of new derivatives and on the practical applications [10]. Basic research into the understanding of the fatigue mechanism as well as photophysical and photochemical processes has been neglected. It was recently found that the amphoteric counter-ion effect plays a very important role in the stability of the photocoloured state of spiropyrans and related compounds [12]. Thus, it was of interest to examine the effect of a series of metal hydroxyquinolinecarboxylates on the photostability of spironaphthoxazine in connection with the amphoteric counter-ion effect by action of complex such as **9** (see Scheme 4).

The quantitative determination of spectro-kinetic or photochemical parameters is generally achieved in solution but many applications require solid supports, such as semi-conductors, paper, plastic films or other polymers



Scheme 4.

[9, 10]. In this study, the effect of various kinds of additives on the photostability of the photomerocyanine derived from spironaphthoxazine (5) was examined on cellulose TLC plates. The influence of some additives on the photofading of 5 on cellulose was investigated in air on exposure to filtered radiation ($\lambda = 365\,\text{nm}$) from a 500 W high-pressure mercury lamp, and the results are shown in Fig. 2.

Spironaphthoxazine (5) on cellulose develops colour on irradiation with ultraviolet light, but the colour gradually fades on continued irradiation. The photofading behaviour was determined by comparison with the concentration on ultraviolet irradiation of 5 for 30 s. The spot of 5 faded rapidly in air on exposure to filtered radiation ($\lambda = 365\,\text{nm}$) from a high-pressure mercury lamp source. However, the addition of a series of zinc hydroxypyridinecarboxylates in the photofading system afforded considerable protection against fading. A similar protecting effect was also observed in the presence of zinc

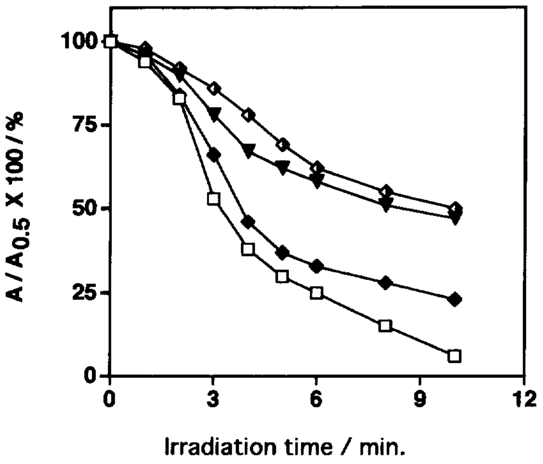


Fig. 2. Effect of additives on the photofading of 5 on cellulose. —□— No additive; —◆— zinc 3-hydroxypyridine-2-carboxylate; —▼— zinc 2-hydroxypyridine-3-carboxylate; —◈— zinc 8-hydroxyquinoline-2-carboxylate.

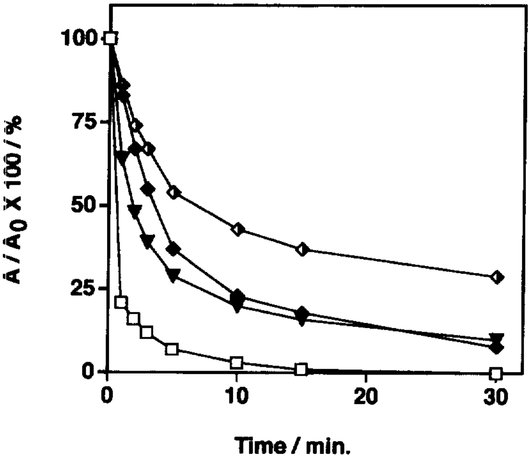


Fig. 3. Effect of additives on the decolouration reaction of **5** in the dark on cellulose (for key see Fig. 2).

8-hydroxyquinoline-2-carboxylate. The suppressing effect provided by zinc 8-hydroxyquinoline-2-carboxylate is somewhat superior to those of zinc hydroxypyridinecarboxylates. The retardation by these compounds was observed also in the case of decolouration of **5** in the dark. The results are shown in Fig. 3. The coloured form generated by illumination with ultraviolet light decayed to the colourless form readily on storage in the dark. The decolouration rate in the dark was clearly retarded by the addition of zinc 8-hydroxyquinoline-2-carboxylate to this system, but slightly retarded by others. These facts suggest that a single amphoteric counter-ion effect is not very beneficial for stabilising the coloured form of spironaphthoxazine, but that the combined use of an amphoteric counter-ion effect and extension of the π-conjugated ring system play a very important role in the stabilisation of photomerocyanine.

In addition, the substituent effect of additives on the stability of the photocoloured species of **5** was examined on cellulose. As shown in Fig. 4, the coloured form generated on ultraviolet irradiation decayed thermally to the colourless form readily at ambient temperature. Zinc 4,8-dihydroxyquinoline-2-carboxylate remarkably decreased the rate of decolouration in the dark. However, the protecting effect of zinc 8-methoxyquinoline-2-carboxylate towards decolouration in the dark was inferior to that of zinc 8-hydroxyquinoline-2-carboxylate. A similar stabilising effect by these zinc salts was also observed on the photofading behaviour in ultraviolet light. As shown in Fig. 5, the spot of **5** faded drastically in air on exposure to filtered radiation ($\lambda = 365$ nm) from a high-pressure mercury lamp source. The addition of the zinc complex of 8-methoxyquinoline-2-carboxylic acid in the photofading system afforded a little protection against fading. However, the rate of

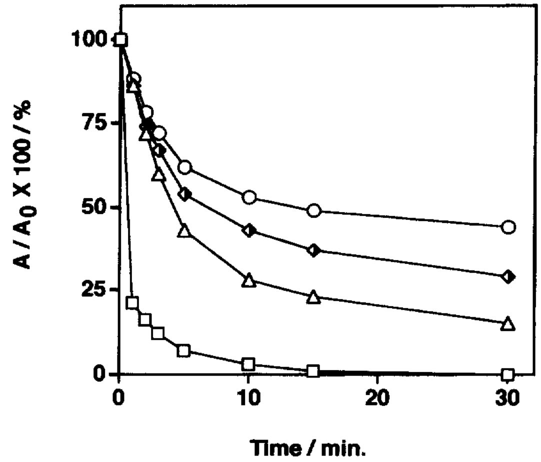


Fig. 4. Effect of additives on the decolouration reaction of 5 in the dark on cellulose. —□— No additive; —△— zinc 8-methoxyquinoline-2-carboxylate; —◆— zinc 8-hydroxyquinoline-2-carboxylate; —○— zinc 4,8-di-hydroxyquinoline-2-carboxylate.

photofading was appreciably retarded by the zinc complex of 8-hydroxyquinoline-2-carboxylic acid or 4,8-dihydroxyquinoline-2-carboxylic acid. In particular, the suppressing effect of the zinc salt of 4,8-dihydroxyquinoline-2-carboxylic acid was excellent. These results indicate that introduction of hydroxyl groups into the stabiliser is very effective for stabilising the photocoloured species of spironaphthoxazine. Furthermore, the effect of the nickel salts on the decolouration reaction in the dark and the photofading of 5 was examined in the same manner as above. These results are shown in Figs 6 and 7. As a general rule, the suppressing effects provided by these nickel salts

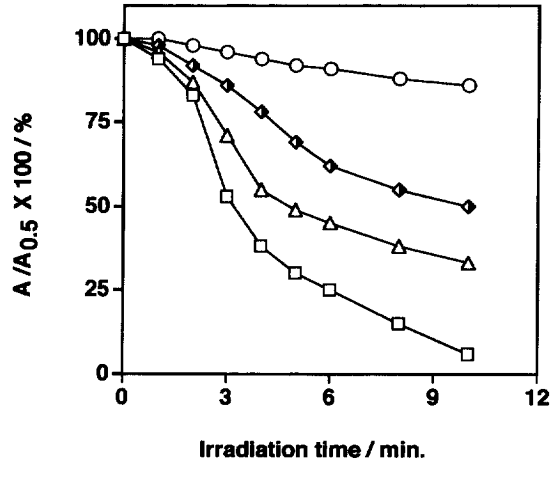


Fig. 5. Effect of additives on the photofading of 5 on cellulose (for key see Fig. 4).

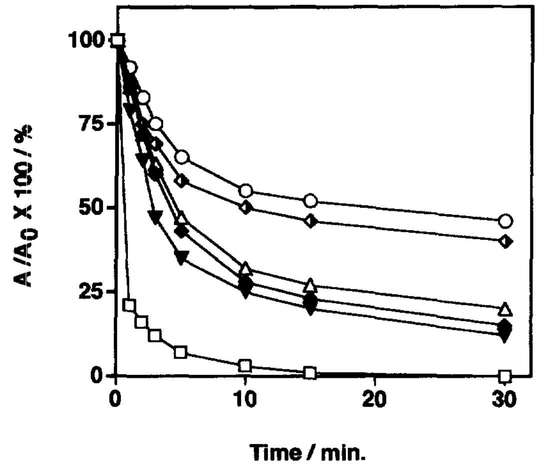


Fig. 6. Effect of nickel salts on the decolouration reaction of **5** in the dark on cellulose. —□— No additive; —◆— nickel 3-hydroxypyridine-2-carboxylate; —▼— nickel 2-hydroxypyridine-3-carboxylate; —△— nickel 8-methoxyquinoline-2-carboxylate; —◇— nickel 8-hydroxyquinoline-2-carboxylate; —○— nickel 4,8-dihydroxyquinoline-2-carboxylate.

were superior to those of the zinc salts. It is especially noteworthy that nickel 4,8-dihydroxyquinoline-2-carboxylate gave a far more efficient protecting effect not only against the decolouration reaction in the dark but also against photofading of **5** than did others. Such excellent stability of the photomerocyanine derived from spironaphthoxazine may be due to the contribution of bifunctional amphoteric counter-ions as in the case of colour formers mentioned above.

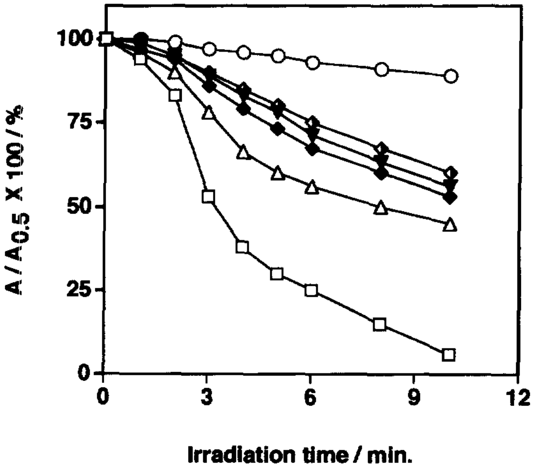


Fig. 7. Effect of nickel salts on the photofading of **5** on cellulose (for key see Fig. 6).

CONCLUSION

The chemistry of colour formers and spironaphthoxazines has recently become particularly important in connection with the rapid development of information recording systems. A colour former is used extensively as a functional dye in carbonless copy and heat- (or pressure-) sensitive recording paper, but its light fastness property is poor. Improvement of light fastness is therefore being sought at the present time. In this paper, the influence of amphoteric counter-ions on the photostability of colour materials derived from colour formers has been examined on cellulose. The results provide a novel approach for improving the light fastness of colorants for imaging and data recording systems. Moreover, the effect of counter-ions on the stability of photocoloured species of photochromic material has been also investigated on solid state. The results suggest a valuable method for improving the photostability of functional dyes for a reversible image recording medium.

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