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Photostabilisation of Colorants for Imaging and Data Recording Systems: Effect of Metal Carboxylates on the Lightfastness of Colour Formers

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ABSTRACT

Metal complexes of hydroxycarboxylic acids or dicarboxylic 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 is proposed that nickel or zinc salts of 1-hydroxy-2-naphthoic acid and its derivatives can be applied as effective stabilisers against the photofading of indicator dyes in pressure- (or heat-)sensitive recording systems. These metal carboxylates were also found to improve the image stability of the indicator dyes.

1 INTRODUCTION

The chemistry of colour formers has recently become of importance, particularly in connection with the rapid development of information recording systems. Crystal Violet Lactone (**1**) and 3-(*N*-ethylisopentyl-amino)-6-methyl-7-anilinofluoran (**3**) are extensively used as a functional

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dye in carbonless copy and heat-sensitive recording paper. The colour materials derived from these colour formers show a bluish violet (λ_{max} 605 nm) and black colour (λ_{max} 450 and 590 nm), but are not fast to light.[1] Dye **1** is a chromogenic compound in its colourless form. Acidic catalysts, e.g. acidic clay, open the lactone ring, thereby allowing the violet triarylmethane dye (**2**) to form. The parent structure of **2** resembles that of Crystal Violet.

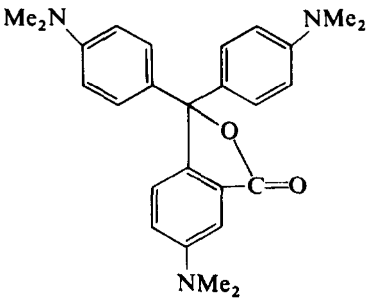
The photostability of cationic triphenylmethane dyes is particularly sensitive to environmental factors, such as the nature of the substrate and the presence of oxygen and water. For example, the lightfastness of CI Basic Blue 18 varies from less than 1 on cotton in the presence of moist oxygen up to 7 on Orlon in the presence of nitrogen.[2] Many reasons have been advanced to account for the roles water and oxygen play in the photofading reaction of triarylmethane dyes, but a definitive proof is still awaited. The reason for the higher lightfastness shown by triarylmethane dyes on polyacrylic fibres dyeable with basic dyes (e.g. Orlon) compared with that exhibited on other substrates has been investigated in detail by several workers.[3-8] Zollinger proposed that the nature of the dye counter-ion caused this behaviour, i.e. acrylic fibres contain sulphonic acid and sulphate groups, whereas cotton contains some carboxylic acid and carboxylate groups.[6] Porter & Spears observed a significant increase in the photostability of Malachite Green on sulphoethylated cotton compared with its stability on carboxymethylated or untreated cotton.[3]

Therefore, it can be expected that the contribution of dye counter-ions may be involved also in the photofading reactions of **2**. We have investigated the counter-ions of dyes **2** and **4** derived from **1** and **3**, and now report a novel approach for improving the lightfastness of colorants for imaging and data recording systems.

2 EXPERIMENTAL

2.1 Materials

Crystal Violet Lactone (**1**), 3-(*N*-ethylisopentylamino)-6-methyl-7-anilinofluoran (**3**), 3-(4-diethylaminophenyl)-3-(1-ethyl-2-methyl-3-indoyl)-phthalide (Blue-502) (**5**), 3-diethylamino-7,8-benzofluoran (Red-3) (**6**) and tetrachlorophthalic acid mono(ethylene glycol ester) zinc salt were obtained from a commercial source. The chloride of Crystal Violet (CI Basic Violet 3, λ_{max} 586 nm) (**7**), Methylene Blue (CI Basic Blue 9, λ_{max} 668 nm) (**8**), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and nickel dimethyldithiocarbamate (NMC) were commercial reagents (Tokyo Kasei Co. Ltd). Metal carboxy-



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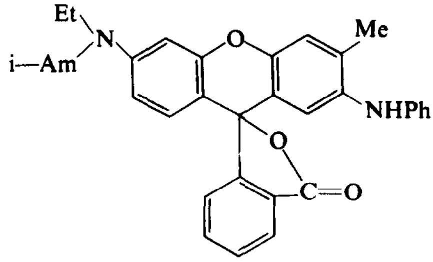

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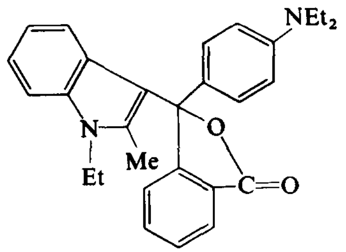

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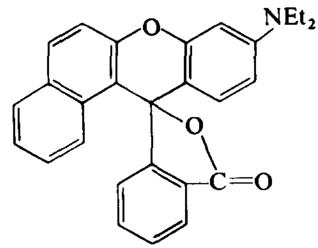

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Fig. 1. Colour formers used in this study.

lates were synthesised and recrystallised according to the procedures described in the literature.[9]

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

2.2 General procedure for photofading of colour formers and related colorants

A solution of **1** (8×10^{-3} mol dm^{-3}) in ethanol or dimethyl sulphoxide (DMSO) (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 80°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 percentage conversion was calculated by comparison with unirradiated colour. A similar procedure was also used for dyes **3**, **7** and **8**. The irradiation times were 24 h in the case of **7**, and 10 h in the case of **8**.

2.3 Photofading of colour formers on heat-sensitive recording paper

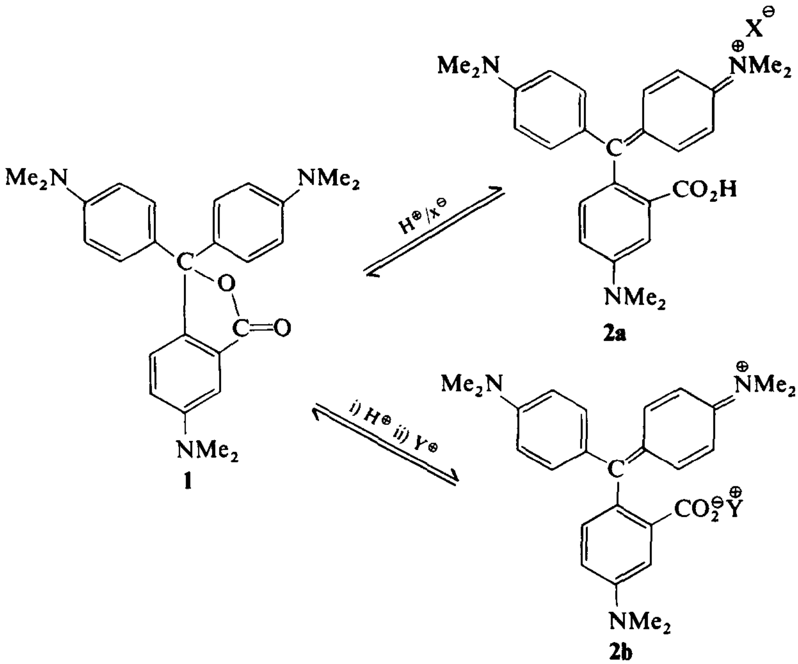
A liquid coating composition was prepared by mixing colour former (10 parts by weight), additive (10 parts by weight), bisphenol A (20 parts by weight), silicon dioxide pigment (oil absorption: $180\,cm^3/100\,g$) (30 parts by weight), 10% aqueous solution of poly(vinyl alcohol) (90 parts by weight) and water (350 parts by weight). The liquid coating composition was applied to an uncoated paper sheet (weighting $50\,g\,m^{-2}$) by a roll coater and dried (to a weight of $5{\cdot}3\,g\,m^{-2}$). The recording papers were each colour-developed by treating for 1 s at 150°C under a pressure of $2\,kg\,cm^{-2}$. The coloured portions were exposed to air and light through a Pyrex glass filter with a 300 W high-pressure mercury lamp. After a prescribed time of irradiation, the density of the colour was determined using a Macbeth densitometer (RD-918 type). The percentage conversion was calculated by comparison with unirradiated colour.

3 RESULTS AND DISCUSSION

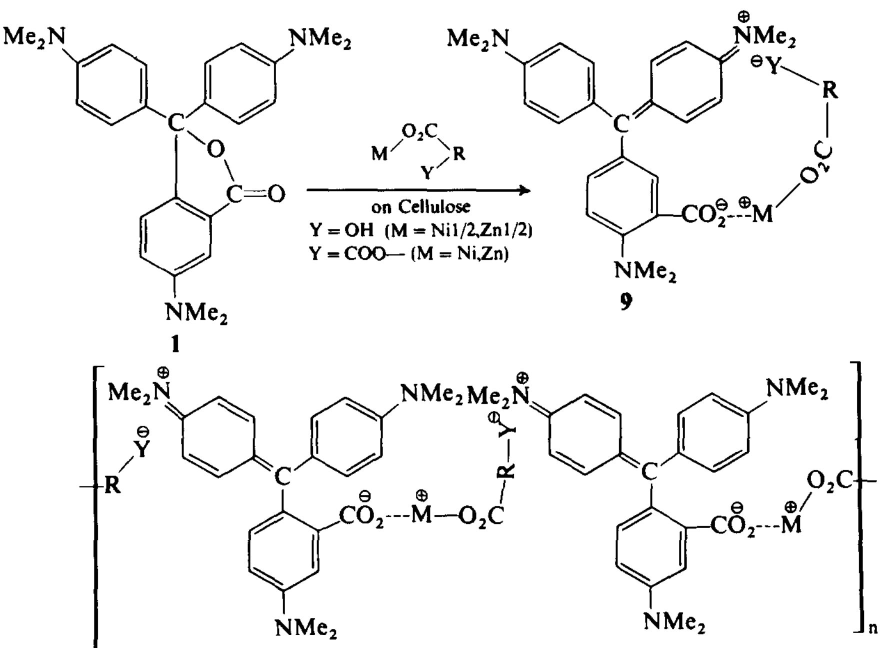
3.1 Effect of various metal complexes on the photofading of colorants

Dye **2** formed in the acid reaction of the lactone contains both carboxylate and ammonium residues, and hence there are two types of counter-ion, i.e. X^- or Y^+, as shown in Scheme 1. In preliminary studies,[10,11] the effect of various counter-ions on the photofading of **2a** and **2b** has been investigated in the presence of a UV absorber. It was found that dye counter-ions providing a considerable suppressing effect against the fading of **2a** and **2b** were 1,2-benzenedicarboxylic acid, 2-hydroxybenzoic acid or the perchlorate anion in the case of X^-, and tetrachlorophthalic acid mono(ethylene glycol ester) zinc salt or hexadecyltrimethylammonium cation in the case of Y^+. However, these counter-ions had no influence on the rate of photofading in the absence of UV absorber. It was thus of interest to prepare the stabiliser, i.e. a metal carboxylate, capable of the contribution of amphoteric counter-ion such as **9** and/or **10** on the photostability of the colour former, since it could provide more marked improvements in the lightfastness properties of colour formers than do conventional stabilisers in solar radiation (see Scheme 2).

The influence of various metal complexes of hydroxycarboxylic acids on the photofading of 2 on cellulose was investigated in air on exposure to filtered radiation ($\lambda > 300\,nm$) from a 100 W high-pressure mercury lamp, and it was found that the zinc or nickel complex affords an excellent suppressing effect on that fading. These results are summarised in Table 1.



Scheme 1



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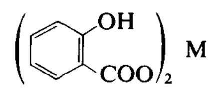
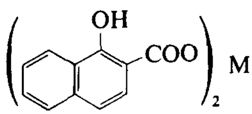
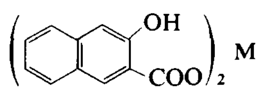
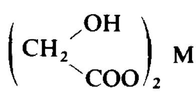
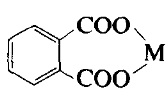
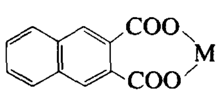
Scheme 2

When **2** absorbed on cellulose was exposed for 3 h to filtered radiation ($\lambda >$ 300 nm) and air, it showed 84% conversion, and in the presence of the zinc complex of 2-hydroxybenzoic acid or 1,2-benzenedicarboxylic acid showed 20% and 31% conversion, respectively. Such an enhanced photochemical stability was also achieved with the zinc complex of the naphthalene derivatives or hydroxyacetic acid. The protecting effects of these were significantly better than those of the monofunctional and conventional stabiliser (runs 8–10). A similar suppressing effect by the zinc complex was observed also in the case of **4**. However, these complexes had little influence on the rate of photofading of **7** which contains no lactone ring. These

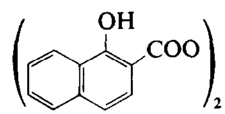
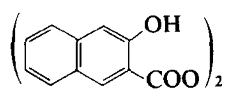
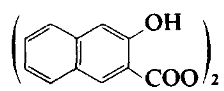
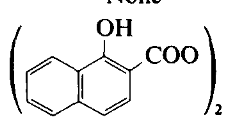
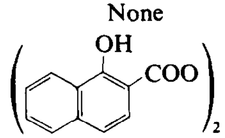
TABLE 1
Effect of Metal (Zn, Ni) Carboxylates on the Photochemical Stability of Colorants on Cellulose

Run	*Additive*		*Conversion (%)*		
			2	**4**	**7**
1	None		84	70	68
2		M = Zn	20	11	65
		M = Ni	17	—	53
3		M = Zn	15	5	68
		M = Ni	12	—	59
4		M = Zn	20	7	66
		M = Ni	0	—	37
5		M = Zn	15	—	63
		M = NI	0	—	51
6		M = Zn	31	—	65
		M = Ni	16	—	44
7		M = Zn	36	—	64
		M = Ni	0	—	27
8	$(PhCOO)_2M$	M = Zn	82	41	—
		M = Ni	62	—	—
9	(o-$HO(CH_2)_2OOCC_6Cl_4COO)_2Zn$		82	—	—
10	NMC		64	63	—

observations suggest that the influence of the amphoteric counter-ion on the photostability of the colour former could be as indicated in Scheme 2. The processes of formation of compound **9** and/or **10** are now being investigated and will be reported later.

In a previous paper,[12] we proposed the contribution of singlet oxygen to the photofading of **2** or **4**. Therefore, it was of interest to examine the influence of the nickel complex of these carboxylic acids on the photostability of **2**, because it may be much higher than that of the zinc complex. As shown in Table 1, a much higher degree of protection against the fading of **2** was achieved by the addition of the nickel complex. It is especially noteworthy that the nickel complexes of 3-hydroxy-2-naphthoic acid, hydroxyacetic acid or 2,3-naphthalenedicarboxylic acid completely suppressed the rate of fading of **2** under the conditions employed. Additionally, these metal complexes also retarded the rate of photofading of

TABLE 2
Effect of Additive on the Lightfastness of Colour Formers on Heat-Sensitive Recording Paper

Run	*Colour former*	*Additive*	*Photofading (%) after:*			
			28 h	*65 h*	*89 h*	*115 h*
1	**1**	None	18·2	45·2	58·2	66·4
2	**1**	 Zn	0	11·0	14·0	14·0
3	**1**	 Zn	9·7	16·2	20·7	24·1[a]
4	**1**	 Ni	0	2·4	5·1	7·2[a]
5	**5**	None	19·0	43·8	44·2	44·6
6	**5**	 Zn	0	0	0·5	1·8
7	**6**	None	17·3	35·6	46·2	53·8
8	**6**	 Zn	5·9	16·1	16·9	17·8

[a] Exposed for 119 h.

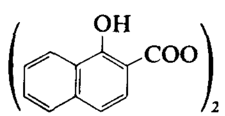
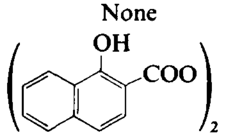
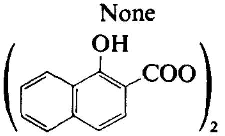
7, in contrast to the effect of the zinc complexes. Furthermore, when dye **8**, a good singlet-oxygen sensitizer, adsorbed on cellulose was exposed for 10 h to filtered light ($\lambda > 300$ nm), it showed 75% conversion; with the addition of the nickel complex of 2,3-naphthalenedicarboxylic acid or 3-hydroxy-2-naphthalic acid showed conversion values of 19% and 26%, respectively were obtained. Accordingly, these results imply that the nickel complexes have singlet-oxygen quenching effects, in addition to the amphoteric counter-ion effect shown by the zinc complexes.

3.2 Some properties of metal carboxylates as a stabiliser for heat-sensitive recording paper

On the basis of the above results, representative metal carboxylates, i.e. 1-hydroxy-2-naphthoic acid zinc salt, 3-hydroxy-2-naphthoic acid zinc salt and 3-hydroxy-2-naphthoic acid nickel salt, were chosen, and their protecting effect against the photofading of some colour formers was examined on heat-sensitive recording paper. The influence of additives on the photostability of **1**, **5** and **6** is summarised in Table 2.

The retardation effect of these representative additives of each series on the photofading of the colour former is also apparent, and the photostability

TABLE 3
Effect of 1-Hydroxy-2-naphthoic acid Zinc Salt on the Image Stability of Colour Formers on Heat-Sensitive Recording Paper

Colour former	*Additive*	*Discolouration (%) after*			
		2 h	*6 h*	*10 h*	*22 h*
1	None	40·0	60·0	67·2	69·6
1	 Zn	1·5	4·5	6·0	6·1
5	None	45·0	62·2	65·8	66·7
5	 Zn	0	2·9	5·9	11·0
6	None	50·0	62·7	70·4	73·2
6	 Zn	3·4	6·7	8·1	8·7

increases significantly on the addition of metal carboxylates. The results indicate that these metal carboxylates can be applied as effective stabilisers against the fading of colour formers.

Subsequently, the recording paper sheets were tested for resistance to plasticiser, because the colour materials derived from colour formers are likely to discolour on contact with a plasticiser. These sheets were each colour-developed as above and superposed on a film of poly(vinyl chloride) containing 50% of di-isobutyl adipate as a plasticiser. The relation between the lapse of time and the optical density of the images was evaluated using a Macbeth densitometer RD-918, and the percentage discoloration was determined. These results are shown in Table 3. The images of colour formers markedly discoloured on contact with a plasticiser, but only slight discoloration occurred in the additive system containing the 1-hydroxy-2-naphthoic acid zinc salt. The observations apparently indicate that these metal carboxylates can also improve the image stability of indicator dyes in heat- (or pressure-)sensitive recording systems.

4 CONCLUSION

Whilst the contribution of counter-ions to the photofading of cationic dyes has been previously investigated by several workers, there are few studies pertaining to the use of counter-ions as a means of improving the lightfastness of indicator dyes in pressure- (or heat-)sensitive recording systems. We have, in this present study, investigated the influence of amphoteric counter-ions on the photofading of colour material derived from colour formers and our results provide a novel approach for improving the lightfastness of colorants for imaging and data recording systems. The metal complexes examined in this study also can be anticipated to improve the image stability of the Cycolor process.

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