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Thermal Recording Media Using Clay–Fluoran Dye Intercalation as a Stable Colour Former

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ABSTRACT

*Clay–fluoran dye intercalation was studied to evaluate their performance as thermal recording media. Clay previously incorporated with a bulky alkylammonium ion promoted the intercalation of the fluoran cationic dye. The insoluble coloured clay pigment was readily formed both in non-aqueous suspension and on polymer film, including the modified clay with tetra-*n*-decylammonium ion and the cationic fluoran dye. The procedure could be applied to stabilize the thermally developed coloured image. © 1997 Elsevier Science Ltd*

Keywords: clay–dye intercalation, alkylammonium modified clay, cation exchange reaction, stable colour former, fluoran dye, thermal recording media.

INTRODUCTION

Fluoran dyes are well known as colour formers for monochromatic thermal printing paper or other recording media [1] and are widely used for commercial applications such as barcode, facsimile and video printing. The leuco dye is a type of colourless dye precursor, and blue or black is colour produced on contact with an acidic substance in the thermal recording

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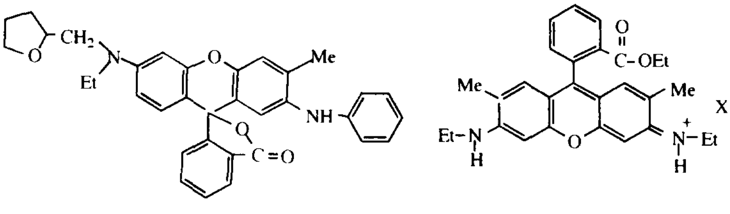
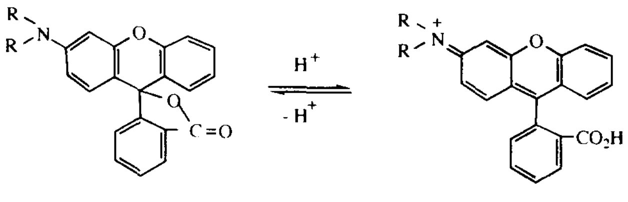
system. The lactone ring of the leuco dye is sensitive to acid and it produces the cationic fluoran dye when it is fused with an acidic developer as shown in Fig. 1. The leuco fluoran dye has excellent sensitivity to develop colour, but the reaction is reversible and the coloured image then easily disappears when it is stored in conditions of high humidity or when it is in contact with certain types of plasticizers. Several approaches to solve these problems have been made, e.g. stable dimeric fluoran dye [2], the use of a developer with less solubility [3], and the formation of irreversible coloured derivative with epoxy resin [4].

We have recently studied the adsorption of the cationic dye onto clay dispersed in a hydrophobic solvent or on a polymer film, and we have proposed the potential applications of clay for dye fixation [5]. The mechanism of dye fixation is clay–dye intercalation based on the ion exchange reaction between the cationic dye and the previously incorporated hydrophobic alkylammonium ion in the clay. The adsorption of cationic dyes into negatively charged clay has been observed from spectroscopic studies of Rhodamine 6G [6] and Methylene Blue [7] and by the determination of the cationic exchange capacity (CEC) of clay by using Methylene Blue or Crystal Violet [8]. The binding ability for the complex formation of cationic dye and montmorillonite is much greater in an aqueous suspension ($K = 10^9 M^{-1}$) than that of an inherent inorganic monovalent cation ($K = 1$ for Na^+-clay) [9]. The strong stability of cationic dyes intercalated into the clay makes it possible to provide a good



Color Former, CF-51

Rhodamine 6G (R6G)



Colorless

Colored

Fig. 1. Chemical structures of cationic dyes used and the acid–base equlibrium of the fluoran dye.

reproduction of a hard copy that is almost comparable to a photograph in quality. Thus, we studied the clay–dye intercalation to stabilize the coloured form in polymer matrices and evaluated the exchange reaction of several alkylammonium ions with the cationic dye in the clay.

EXPERIMENTAL

General

Rhodamine 6G (R6G, Ramdaphysic, Laser grade, USA) and Fluoran (colour former CF51, Hodogaya Chemical, Tokyo) were used without further purification. The clay used was commercially available Na-montmorillonite (Kunimine Mining, Tokyo, Japan) and the CEC of the clay was reported to be 115 meq/100 g clay. The alkylammonium perchlorates were prepared by anion exchange of the corresponding halides (Cl^- or Br^-) (Tokyo Kasei) with sodium perchlorate in ethanol. Alkylammonium ions used were: alkyl-trimethyl (decyl- and tetradecyl trimethylammonium ion), dialkyl-dimethyl (didodecyl and dioctadecyl dimethylammonium ion) and tetraalkylammonium ions (tetraethyl, tetrabutyl, tetrahexyl and tetradecylammonium ion). Clays modified with alkylammonium ions were prepared as described previoulsy [5,9].

Preparation of clay–dye complex

The clay–R6G complex was obtained from a dispersed mixture of R6G (7.18 mmol) and Na^+ ± montmorillonite (3 g) in distilled water (1000 ml), which was kept at room temperature for 1 week. After equilibrium was reached, the mixture was filtered, washed with water and dried at 60°C under vacuum. The basal spacing (d_{001}) of the complex was determined to be 20.92 Å by XRD analyses. The clay modified with alkylammonium ion ($(C_{10}H_{21})_4N^+$/clay) was used for the preparation of the clay–dye complex in organic suspension. A similar procedure was applied for the preparation of the clay–fluoran dye complex except an acidic acetone suspension was used (50 ml of acetone and 2 ml of 60% perchloric acid). Insoluble cationic fluoran dye incorporated into the clay was characterized by XRD (d_{001}; 21.64 Å) and FTIR ($\nu_{C=0}$;1770 cm^{-1}).

Adsorption isotherms

0.2 g of the clay–R6G complex (2 mmol dye/g clay) was dispersed in 20 ml of acetone by ultrasonic wave treatment. An acetone solution of the alkyl ammonium perchlorate was added to the clay–dye complex suspension and equilibrated at 25°C for 24 h. The dye desorption was spectroscopically determined from the absorbance at 527 nm for R6G and 594 nm for coloured CF51 after filtering the clay cloud.

The adsorbed amount ($[D]_{\mathrm{adsorbed}}$) of the dye on the clay is given by subtracting the released dye ($[D]_{\mathrm{released}}$) in solution from the initial dye concentration $[D]_0$ in adsorption isotherms, as shown in the relationship:

$$[D]_{\mathrm{adsorbed}} = [D]_0 - [D]_{\mathrm{released}}$$

Preparation of thermal paper

A thermosensitive layer (thickness = 10 microns) was prepared by casting an aqueous suspension of the leuco dye (CF51), a developer (*p*-hydroxybenzoic acid), the modified clay ($(C_{10}H_{21})_4N^+$/clay), a trace amount of non-ionic emulsifier, and polyvinylalcohol (Tokyo Kasei) as a binder resin on synthetic paper. Before casting, the mixture was sonificated to the size of submicron particles. The composition of dye, developer, binder, clay and water in the suspension was in the weight ratio of 1:3:0.2:2:80 (weight ratio), respectively. As a blank test calcium carbonate was employed instead of the clay.

Thermal recording

Thermal paper was exposed to the thermal press at 20 g/cm^2 for 1 min instead of a thermal head. The optical density (OD) of the printed area was varied according to the controlled temperature of the thermal press.

Humidity resistance test

Thermal paper with the heat exposed area was stored at 25°C and 95% relative humidity for 1 week. Before and after the test, the optical density (OD) of the printed and non-printed area was measured and the residual rate (R) was calculated from the following relationship:

$$R(\%) = ({}^{\mathrm{after}}\mathrm{OD}_{\mathrm{printed}} - {}^{\mathrm{after}}\mathrm{OD}_{\mathrm{non-printed}})/({}^{\mathrm{before}}\mathrm{OD}_{\mathrm{printed}} - {}^{\mathrm{before}}\mathrm{OD}_{\mathrm{non-printed}})$$

RESULTS AND DISCUSSION

The leuco fluoran dye (CF51) exhibits a blue or black colour in contact with acidic material on heating (Fig. 1). The coloured cationic fluoran dye is restored to the original colourless leuco dye during a long period. As illustrated in Fig. 2, the cationic dye may be rapidly transferred into clay by the exchange reaction with the alkylammonium ion. The intercalation is mainly induced by ionic binding and π–π interaction [5]. The alkylammonium ion is used to make the clay swell in an organic solvent or in the hydrophobic polymer and also to effectively exchange with the cationic dye. In order to accomplish the strict adsorption of the cationic dye onto the clay, the effect of alkylammonium ions on the binding ability of the clay–dye complex must be evaluated quantitatively.

Two procedures may be considered in order to determine the equiliblium constant (K) of the cationic dye between the clay and the bulk solution. Firstly, the clay modified with the alkylammonium ion is prepared and then the cationic fluoran dye competes with the alkylammonium ion in interacting with the anionic hole of the clay. The exchange ratio is then determined. Alternatively, the clay–cationic fluoran dye complex is equilibrated by different types of alkylammonium salts and the amounts of cationic dye

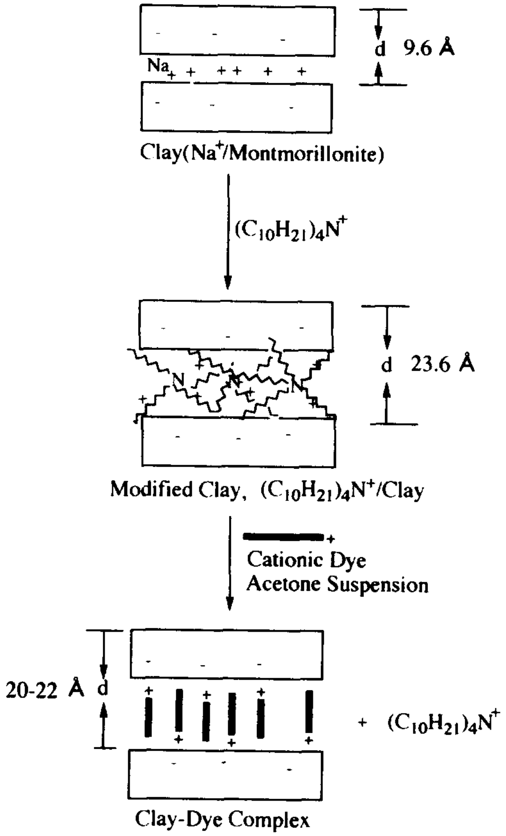


Fig. 2. Schematic representation of the proposed clay–dye intercalation.

released are then determined. In the former case, acid may often influence not only the ring-opening reaction of the leuco dye, but also the activity of the clay surface [10]. In this report, the latter procedure was applied to evaluate the equilibium of the clay–dye intercalation because of the easier determination of the dye concentration. However, the coloured cationic fluoran dye released from the clay cavity into the bulk solution may be changed to the colourless leuco form, which gives the uncertain equiliblium constant. Thus, Rhodamine 6G (R6G) was used as a model cationic dye since it is structurally similar to the fluoran dye but has more inherent stability. Ion exchange reactions between cationic dyes on the clay and the alkylammonium ions in the solution were evaluated spectrometrically.

Adsorption equilibrium can be represented by eqn (1); the dissociation constant, Kd, or binding constant, Kb, of the clay–dye complex is given by eqn (2)

$$\text{Clay} - \text{Dye}^+ + {}^1R\,{}^2R\,{}^3R\,{}^4RN^+ \underset{K_b}{\overset{K_d}{\rightleftharpoons}} \text{Dye}^+ + \text{Clay} - {}^1R\,{}^2R\,{}^3R\,{}^4RN^+ \tag{1}$$

$$K_d = \frac{[D]_0\alpha \times [\,{}^1R\,{}^2R\,{}^3R\,{}^4RN^+]_0\alpha}{[D]_0(1-\alpha) \times [\,{}^1R\,{}^2R\,{}^3R\,{}^4RN^+]_0(1-\alpha)} = \frac{\alpha^2}{(1-\alpha)^2} \tag{2}$$

where $[{}^1R^2R^3R^4RN^+]_0$ is the initial concentration of the alkylammonium ion, $[D]_0$ is the initial concentration of R6G or fluoran dye previously intercalated and α is a fraction, namely $\alpha = [D]/[D]_0 = [{}^1R^2R^3R^4RN^+]/[{}^1R^2R^3R^4RN^+]_0$.

$[D]$ is obtained experimentally from absorbance of the released cationic dye in equilibrium and, therefore, K_d or K_b was obtained from eqn (2). The results of the exchange reactions of the cationic dye with alkylammonium ions in acetone suspension of the clay are summarized in Table 1 for R6G and the fluoran cationic dye.

The calculated free energy ($-\Delta G = RT \ln K$) of the clay–dye complex formation was arbitrarily plotted against increasing (ionic) weight of the alkylammonium species (Fig. 3). As is seen in Fig. 3, it is evident that the structure of the alkylammonium ions markedly affects the ion exchange reaction of the cationic dye depending on the size and number of the alkyl chain. The clays substituted with bulky tetraalkylammonium ions (group A in Fig. 3) can exchange both cationic dyes most effectively (run 4 in Table 1), and are comparable with those of the clay complexes of alkyl trimethylammonium ions (group C) and dialkyl dimethylammonium ions (group B). Furthermore, larger size alkylammonium ions can exchange more easily with the cationic dye. Therefore, the most suitable alkylammonium ion for the dye intercalation is the more crowded one with four long alkyl chains. On this basis, the tetra-*n*-decylammonium ion is the most preferable. It seems likely that trimethyl alkylammonium ions with a long single chain can be

TABLE 1

Relative Binding Ability (K_b) for the Complex Formation of Cationic Fluoran Dye and R6G to the Modified Clay[a]

Alkylammonium ion	*Rhodamine 6G*[b]			*Fluoran dye*[c]		
	[D]$_{released}$ *(mmol/l)*	K_b (= $1/K_d$)	$-\Delta G$ *(cal/mol)*	*[D]*$_{released}$ *(mmol/l)*	K_b (= $1/K_d$)	$-\Delta G$ *(cal/mol)*
1 Et_4N^+	1.62	1.08	47	2.63	0.894	−66
2 Bu_4N^+	0.75	11.5	1440	1.55	5.29	987
3 $(C_6H_{13})_4N^+$	0.26	136	2910	0.46	105	2750
4 $(C_{10}H_{21})_4N^+$	0.12	717	3890	0.13	1520	4340
5 $(C_{10}H_{21})Me_3N^+$	1.79	0.703	−209	3.18	0.360	−605
6 $(C_{14}H_{29})Me_3N^+$	1.63	1.04	24	2.84	0.633	−271
7 $(C_{12}H_{25})_2Me_2N^+$	1.33	2.18	460	1.37	7.54	1200
8 $(C_{18}H_{37})_2Me_2N^+$	1.12	58.1	2410	1.16	11.7	1460
9 Na^+	1.67	0.946	−33	3.58	0.179	−1020
Blank	0.03	—	—	0.03	—	—

[a] In acetone suspension (25°C).

[b] Initial dye concentration $[D]_0 = 3.29$ mmol/l.

[c] Initial dye concentration $[D]_0 = 5.11$ mmol/l.

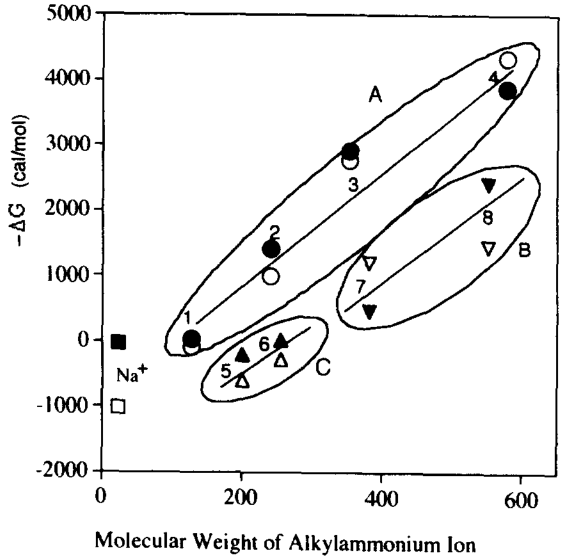


Fig. 3. Effect of clay–alkylammonium ion complex on intercalation of cationic dyes. ●, ▲ Rhodamine 6G; ○, △ fluoran dye. Numbers correspond to the numbers of the alkylammonium ions listed in Table 1.

more strongly intercalated into montmorillonite by favourable ionic binding of the terminal cation, due to the flat arrangement of the trimethyl alkylammonium ion where the interlayer distance is too narrow to insert the dye cation (d_{001} = 14.02 Å for ($C_{10}H_{21}$)Me_3/clay) [5]. This modified clay (($C_{10}H_{21}$)Me_3N^+/clay) is compared with the clay–complex of the bulky tetraalkylammonium ion, especially ($C_{10}H_{21}$)$_4N^+$/clay which bears a positive charge centered in the interlayer space (d_{001} = 23.60 Å). It can thus be considered that the binding ability between the clay layer and bulky cation is relatively low because of the reduced ionic interaction, attributed to the remote distance between opposite charged ions and the lower Van der Waal's forces. On adding the cationic dye into the acetone suspension of the clay, ($C_{10}H_{21}$)$_4N^+$/clay, the coloured pigment precipitated retaining the transparent solution. The interlayer distance (d_{001}) of both the clay–dye pigments shifted to 21.64 Å for fluoran (acetone suspension) and 21.48 Å for R6G cationic dye (ethanol suspension). In the case of the clay with a single long alkyl chain (($C_{10}H_{21}$)Me_3N^+/clay), the basal spacing of the complex was considerably smaller (d_{001} = 14.38Å). This implies an incomplete exchange reaction, which was shown by the coloured solution after filteration.

In addition to the data on the interlayer distance of the clay–dye pigments, ($C_{10}H_{21}$)$_4N^+$ cation was successfully exchanged by the cationic fluoran dye in the acetone suspension of the clay (($C_{10}H_{21}$)$_4N^+$/clay), as shown by IR analysis [5]. This showed that both the C-H absorption at 2920 and 2850 cm^{-1} due to the alkylammonium reduced and the carbonyl peak at 1770 cm^{-1} of the fluoran dye appeared after the exchange reaction.

Therefore, it is reasonable to conclude that bulky alkylammonium ion intercalated in advance will be effectively exchanged by the cationic fluoran dye on the clay layer, whereas natural Na^+-montmorillonite has a much lower ability to bind the cationic dye in acetone, although it has a greater binding ability for the cationic dye in water. Interestingly, the exchanging ability of the clay tetradecylammonium ion complex for the cationic fluoran dye (K_b = 1520) is 8500 times greater than that of Na^+ ion (K_b = 0.179) in acetone.

To confirm the fixing or insoluble property of the cationic dye, the ability of Na^+/montmorillonite (natural clay) to bind the dye was compared with the modified clay in acetone. When an appropriate quantity of hydrochloric acid was added to the white acetone suspension including the leuco fluoran dye and montmorillonite modified with tetradecylammonium ion (($C_{10}H_{21}$)$_4N^+$/clay), black precipitates were isolated immediately leaving a colourless and transparent acetone solution. The black particles obtained from this procedure scarcely faded when kept in hot water (90–100°C) for 10 h or in diethylphthalate as a representative plasticizer for 3 months. On the contrary, the black dispersion of the natural clay did not precipitate under the same conditions. After filtration, the white clay was recovered, which indicated no intercalation had occurred. This remarkable contrast is well consistent with the results reported earlier, and provides evidence that a stable clay–dye pigment is easily obtained from the cationic dye in an organic suspension by this procedure. As shown in the spectroscopic study of Methylene Blue [7], flat dye molecules often form the dimer and aggregates in the clay, due to intermolecular dipole–dipole and/or π–π interactions. The enhanced insolubility of the cationic dye intercalated in the clay is mainly ascribed to the ionic interactions between the anion charged clay and the cationic dye molecule, and the mutual interactions among the planar dye molecules.

Practical thermal printing methods combined with this intercalation procedure exhibited considerable resistance to colour disappearance of the image by humidity, which was in striking contrast to the traditional method (Table 2). As seen in Table 2, the remarkable improvement in the humidity resistance is attained over all concentrations tested. The thermal paper with the clay ($(C_{10}H_{21})_4N^+$/clay) in particular showed good humidity resistance, even at a relatively low optical density area. This result also strongly demonstrates that such an intercalation technique is very useful in stabilizing the colour image made of the cationic dyes dissolved in the hydrophobic polymer film in thermal printing.

CONCLUSION

The aim of this study was the stable fixation of cationic fluoran dye inside a clay layer by an ion exchange reaction in non-aqueous medium. To evaluate the ion exchange reaction between the cationic dye in bulk solution and the

TABLE 2
Humidity Test of the Thermally Printed Image[a]

Intercalation method (in the presence of modified clay)[b]			*Traditional method (without clay)*		
OD[c]		*Residual rate*[d]	*OD*[c]		*Residual rate*[d]
Before	*After*	*(%)*	*Before*	*After*	*(%)*
2.22	2.13	95.4	2.36	1.20	47.4
1.14	1.08	93.6	1.22	0.50	38.1
0.64	0.61	93.3	0.69	0.16	16.9
0.26	0.25	90.9	0.32	0.05	0

[a] See the Experimental section for a description of the test.
[b] Tetra-decylammonium ion ($(C_{10}H_{21})_4N^+$) was used for the modified clay.
[c] OD, optical density.
[d] $R(\%) = ({}^{\text{after}}\text{OD}_{\text{printed}} - {}^{\text{after}}\text{OD}_{\text{non-printed}})/({}^{\text{before}}\text{OD}_{\text{printed}} - {}^{\text{before}}\text{OD}_{\text{non-printed}})$.

alkylammonium ion intercalated previously into the clay layer, adsorption equilibrium of the cationic dye onto the clay was examined. As a result, it was confirmed that the modified clay, especially a bulky tetradecylammonium ion–clay complex had a great advantage in promoting the ion exchange reaction with cationic R6G or fluoran dye. This intercalaton method provides an effective technique to obtain an insoluble clay–cationic dye complex (clay–dye pigment) using the modified clay dispersed in an organic solvent or polymer film.

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