Application of Clay-Cationic Dye Intercalation to Image Fixation in Thermal Dye Transfer Printing

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A novel method for fixation of thermal cationic dye transfer images using clay–dye intercalation is presented. Instead of conventional disperse dyes, modified cationic dyes are transferred to a dye receiving layer that includes a clay that has exchangeable organophilic ammonium cations. The color image formed in the interior of the clay by superposition of cyan, magenta, and yellow dyes is stored as an insoluble and infusible pigment. The mechanism of fixing cationic dyes for practical thermal dye transfer printing is discussed.

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Introduction

Recently, demand has risen in the field of thermal dye transfer printing to provide excellent fixing properties comparable to those of photographic prints.[1] To obtain a fixed image, we have examined intercalation, which has been successfully applied to stabilization of dye molecules on carbonless copying paper[2] and to adsorption of organic molecules and catalysis.[3] We have recently studied the adsorption isotherm of Rhodamine 6G on organophilic montmorillonite and reported the potential use of intercalation for fixation of thermally transferable dye.[4] This new proposal for fixing dye molecules is illustrated schematically in Fig. 1. In this system, thermally transferable dye cations are intercalated into the clay layer and fixed through ion exchange reactions in the polymer matrix.

We have attempted to build a full-color system on the basis of such a mechanism and to take advantage of intercalation in practical use.[5] In trying to fix the superposed images in conventional printing systems, however, we experienced some difficulties. In thermal dye transfer printing, it is necessary to obtain sufficient sensitivity and well-balanced hues and to fix completely the transferred dyes within a practical printing time. These problems were successfully solved by using hydrophobic cationic dyes and ion exchangeable organophilic ammonium cations bound in the clay. We attempted to make the practical system intercalate the cationic dyes into the clay dispersed in the conventional resin. This study concerns a newly devised

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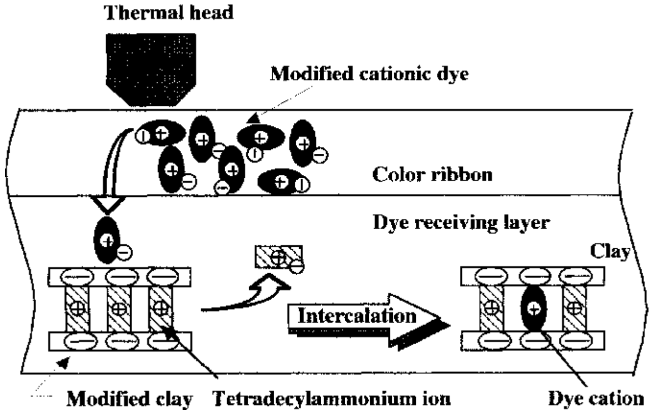


Figure 1. Schematic representation of fixation mechanism (intercalation).

intercalation technique and the fixing effect in practical thermal dye transfer printing.

Experimental

General. The clay used, Na-montmorillonite, was commercially obtained (Nakarai Tesque, Kyoto, Japan), and the cation exchange capacity (CEC) of this clay was 64 meq/100 g clay. Rhodamine 6G (Basic Red 1, C.I. 45160) and an oxazine dye (Basic Blue 3, C.I. 51004) were selected as model compounds. Commercial cationic dyes (Basic Yellow 2, C.I. 41000; Basic Red 46; and Basic Blue 75) as respective yellow, magenta, and cyan dyes, were applied in color printing. The counter anion of each of these cationic dyes was replaced by dodecylbenzenesulfate (DBS) or by dodecylsulfate (DS) anion to render the dye soluble in polymer matrices, and we describe the dyes as *modified cationic dyes*. A disperse dye, (Disperse Blue 7, C.I. 62500) was used as a reference dye.

Montmorillonite modified with tetra-*n*-decyl ammonium cation [$(C_{10}H_{21})_4N^+$, abbreviated 4C10N$^+$] was prepared by a conventional ion exchange method, using an aqueous ethanol solution of tetra-*n*-decylammonium bromide.[4] A similar method was followed for preparation of each dye cation–montmorillonite complex, except that a toluene suspension was used. An exchange reaction of Rhodamine 6G (R6G–DBS) or the oxazine dye (Ox–DBS) with 4C10N$^+$/montmorillonite was also carried out and equilibrated at 25°C for 48 h (adsorption isotherm).

Static Color Printing. Thermal transfer experiments with modified cationic dyes were carried out, transferring dye from a color ribbon to a printing sheet in a thermal press. This static printing procedure is useful for determining the transfer properties of the dye. Two different types of binder polymer were used for the color ribbon and the printing sheet, polyvinylbutyral (PVB, Sekisui, Tokyo) and vinylidene chloride–acrylonitrile copolymer (PVC–AN, Aldrich, Milwaukee), respectively. The color ribbon was made by coating a methyl ethyl ketone (MEK) solution of PVB and the dye salt (50 wt%) on polyethylene terephthalate (PET) film (6-μm-thick dye layer). A dye-receiving layer was made by coating a 5-μm layer of PVC–AN on the modified PET resin paper. The press time was 1 min at a pressure of 20 g/cm^2, with controlled temperature of the printing surface. The optical density of the transferred dye on the sheet was measured versus temperature. This result is shown in Fig. 2.

Practical Color Printing (Video Printing). Color ribbon was prepared according to the above procedure. A dye-receiving layer was prepared by coating PET resin paper with an MEK dispersion that included PVC–AN copolymer and modified clay powder, then drying. Thermal dye transfer was performed in a video thermal printer (CVP G-500, Sony, Tokyo). The energy supplied by the thermal head was 10 mJ/mm^2 per step in the thermal dye transfer experiments (Figs. 3, 8, and 10). The energy profile of the thermal head is as follows: 120 mJ/mm^2 for maximum applied energy; 0.169 W/dot for input power; 6 dots/mm for dot density.

TABLE I. Migration Test of Oxazine Dye Transferred in the Presence and Absence of the Clay

Presence of clay			Absence of clay		
Optical density		Residual % of dye*	Optical density		Residual % of dye*
Before	After		Before	After	
0.26	0.27	100	0.34	0.10	0
0.45	0.45	100	0.48	0.10	0
1.07	1.07	100	0.87	0.13	4
1.20	1.17	98	1.18	0.20	9
1.32	1.25	95	1.52	0.26	11

* Corrected for the background density.

X-Ray Diffraction. Clay powder adsorbed in the equilibrium experiment with the organic cation (hydrophobic alkylammonium cations and cationic dyes) was prepared for x-ray diffraction (XRD) by drying at room temperature under reduced pressure (2 mm, Hg for 24 h). Samples of color-receiving layers on the printing sheet were measured directly before and after printing. XRD patterns were obtained on a RAD III diffractometer (Rigaku, Tokyo, Japan), using monochromatic CuKα radiation.

Evaluation of Dye-Fixing Ability. Two kinds of tests were performed to evaluate the dye-fixing ability. One test is the back diffusion of oxazine dye to a white sheet; the other is solubilization by an organic solvent. The back diffusion test was performed by adhering the color sheet to a polyvinyl chloride film including 50 wt% dibutyl phthalate as plasticizer at room temperature for 24 h (migration test). After that the color density on the film was measured (shown in Table I). The solubilization tests comprised immersing the printing sheets in MEK solvent (30 s for the solubilization test of the black sheet) at room temperature. After that the dye concentration in the solution (oxazine dye) and/or on the sheet (black sheet colored by three primary dyes) was measured spectrophotometrically. The residual percentages of the dyes on the sheet were obtained from K/S values, using the Kubelka–Munk equation.[6]

Results and Discussion

Commercial cationic dyes are generally designed for dyeing and printing textiles and for use as biological stains. Thus, they are not very soluble in nonaqueous solvents. Such dyes were modified so that they could be dissolved in hydrophobic polymers used in color ribbons and in dye-receiving layers for thermal dye transfer printing. The counter anions (Cl$^-$) of cationic dyes were exchanged with appropriate hydrophobic anions (DBS and DS) to increase compatibility with such polymers. The modified cationic dyes used in this study are Rhodamine 6G (R6G–DBS) and an oxazine (Ox–DBS) dye as model dyes, and Basic Yellow–DS, Basic Red 46–DS, and Basic Blue 75–DS as practical yellow, red, and cyan dyes, respectively. The chemical structures for R6G–DBS and Ox–DBS are shown in Scheme 1.

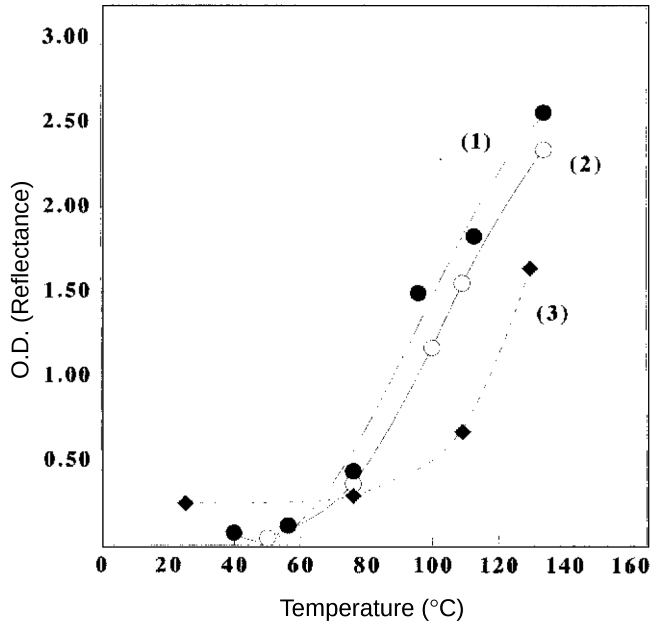
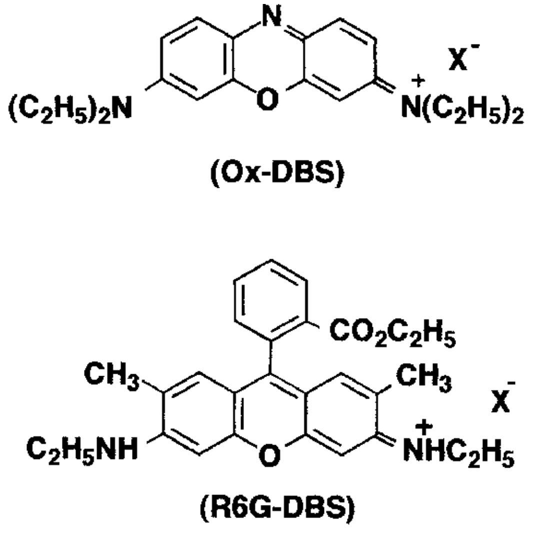


Figure 2. Optical densities, indicating amounts of the transferred dyes versus temperature (1) modified cationic dye (Ox-DBS); (2) disperse dye (Disperse Blue 7); (3) oxazine dye (Ox-Cl).



$X=C_{12}H_{25}\text{-}C_6H_4\text{-}SO_3^-$

Scheme 1. Chemical structures of modified dyes (oxazine dye and Rhodamine 6G).

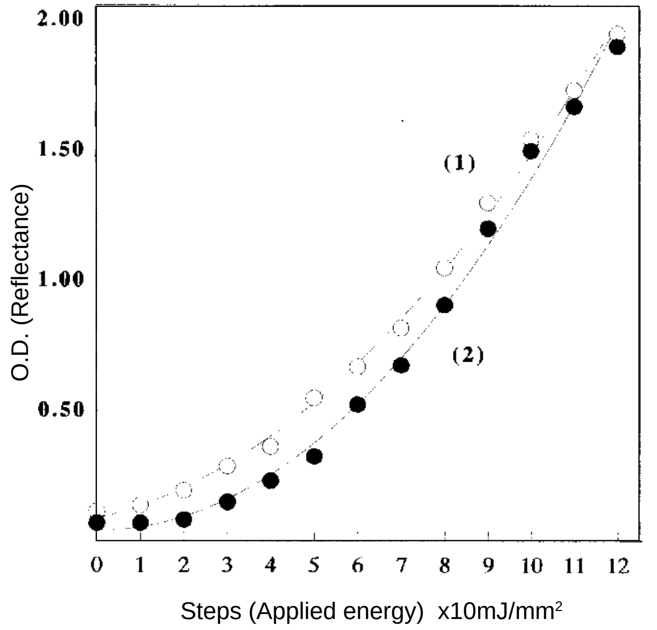


Figure 3. Optical densities, indicating amount of dye transferred versus input energy (1) modified cationic dye (Ox-DBS) and (2) disperse dye (Disperse Blue 7).

Figure 2 shows that the modified cationic dye Ox–DBS transfers (in static mode) from the color ribbon to the receiving layer with excellent sensitivity to increasing temperature, as does a conventional disperse dye. However, the corresponding commercial dye Ox-Cl^-, which has Cl^- as the counter anion, was not adequate from the viewpoint of energy used, color density gained, and fogging. These properties are required for practical dye transfer printing. Similarly, practical color printing was performed, and the result is shown in Fig. 3. Both the cationic dye and the disperse dye dissolved in polymer films (color ribbon) were effectively transferred to a receiver sheet by a thermal head. The transferred dye is acceptable as a continuous color image modulated by the controlled input energy of the printhead.

Storage of two different receiver sheets printed with the modified cationic dye and the disperse dye shows a distinct difference in thermal stability. The sheet dyed with Disperse Blue 7 changed to a faint color at 100°C because of the dye's sublimation, whereas with the modified cationic dye the colored sheet was scarcely changed. These results suggest that the modified dye is well accommodated in both polymer layers. The cationic dye Ox–DBS modified by exchanging Cl^- and the hydrophobic anion DBS showed a melting point decrease of 40°C and solubility in nonpolar solvents. Similar effects were observed for all other modified cationic dyes used. The commercial dyes, Basic Yellow 2, Basic Red 46, and Basic Blue 75, were substantially insoluble in toluene, whereas these dyes after exchange with DS showed considerable solubility in toluene (0.11, 17.4, and 19.3 g/100 mL, respectively). The thermal transfer of the modified dye between two layers has been proposed to follow the liquid diffusion mechanism, as suggested in previous work.[4,7]

Exchange reactions of montmorillonite–alkylammonium cation complex with R6G–AOT [AOT is bis(2-ethylhexyl) sulfosuccinate anion] were studied in detail in our previous work.[4] $4C10N^+$ bears a positive charge centered in the interlayer space. The binding ability between the clay layer and the bulky $4C10N^+$ cation is relatively low because of the reduced ionic interaction, which is attributed to the remote distance between oppositely charged ions and to the lower van der Waals forces. Clay mineral intercalated with the bulky ammonium cation was easily swollen in hydrophobic solvents and was highly effective for the ionic exchange reaction with the modified cationic dye. This modified clay was used in the organic solvent for adsorption experiments and/or in the dye-receiving layer for the video color printing.

Adsorption isotherms of R6G–DBS and Ox–DBS on the organophilic clay $4C10N^+$/montmorillonite depicted in Fig. 4 typify the reaction of the modified dyes with dispersed clay. Rhodamine 6G and the oxazine dye were saturated at 40 to 60 mmol/100 g clay. Adsorption of the cationic dye on organophilic clay modified with long double alkyl chains

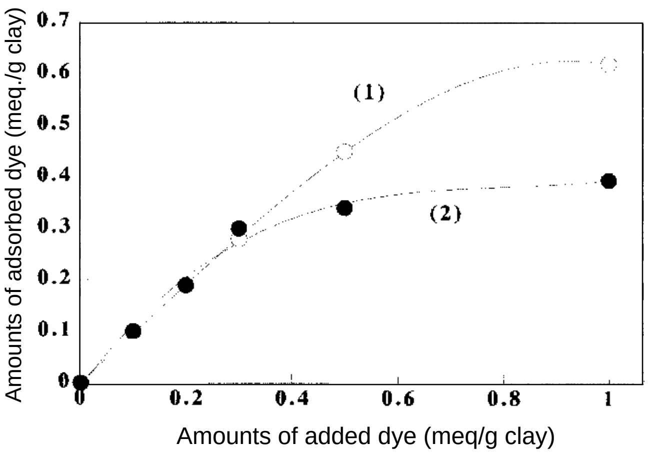


Figure 4. Adsorption of R6G-DBS and Ox-DBS on the modified clay ($4C10N^+$/clay) (1) Ox-DBS; (2) R6G-DBS.

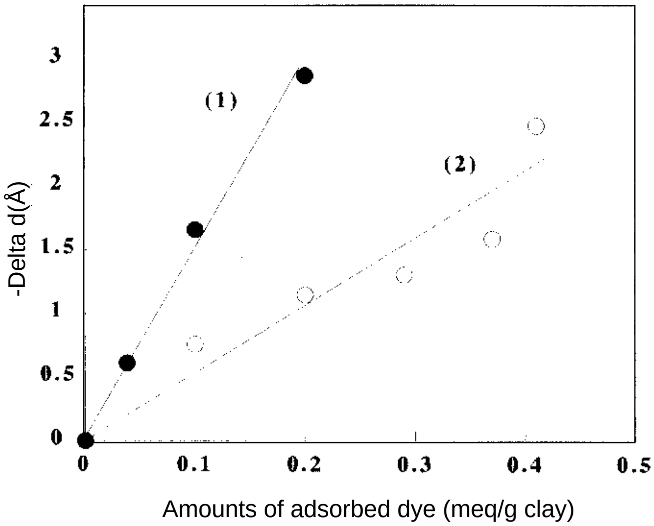


Figure 5. Contraction of the spacing (d_{001}) with adsorption of the dyes (1) Ox-DBS and (2) R6G-DBS.

(dimethyl dioctadecyl ammonium ion, $2C18N^+$) extended considerably beyond the CEC, a result ascribed to physical adsorption.[8,9] Weak adsorption owing to the physical interaction in addition to ionic binding was eliminated by using the clay modified with removable tetra-*n*-decylammonium ion.[4] Such physical adsorption brings about dye migration and results in a foggy image.

Furthermore, the change of the basal spacing (d_{001}) of the clay during the insertion reaction of the dye was observed by XRD analysis. The spacing (d) of the $4C10N^+$ modified clay before the adsorption of the dye was 23.6 Å.[4] With increasing adsorption of the dye, contraction of the spacing was observed. Figure 5 shows that the degree (Δd) of contraction is different for the two dyes (R6G and Ox), with greater contraction occuring in the latter dye. The spacings (d) of the clay saturated with R6G and Ox were 20.5 and 13.7 Å, respectively. The spacing of the clay may be influenced by the molecular structure, the molecular size, and the orientation of molecules intercalated. Such an intercalation as observed in the suspension is also expected to occur on the polymer film, where the dye transfer and the ion exchange reaction may occur effectively on heating, as is desirable in practical thermal transfer printing.

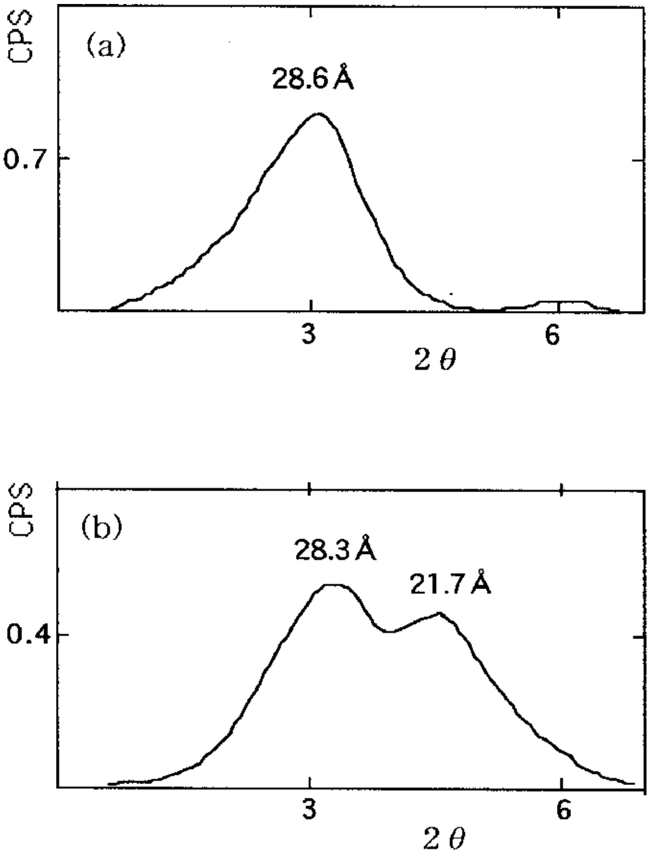


Figure 6. XRD spectra of a color-receiving layer (a) before printing and (b) after printing for the Ox-DBS dye transfer.

In thermal printing, a similar XRD study was carried out for the thermal transfer of the oxazine dye into the polymer film containing the $4C10N^+$ modified clay. XRD patterns of the clay show sharp contrast before printing [Fig. 6(a)] and after printing [Fig. 6(b)]. The basal spacings of the modified clay surrounded by polymer matrix produced a 28-Å peak in the nonprinted area and two peaks corresponding to 28 and 22 Å in the printed area. After printing, the appearance of a new signal (22 Å) may imply complex formation of the cationic dye with the clay, which results in the dye transfer from the color ribbon, followed by the ion exchange reaction. Such contraction of the spacing by exchanging bulky ammonium ion ($4C10N^+$) with the cationic dye may be considered to be a characteristic phenomenon that is dependent on the size and orientation of the molecule inserted into the clay. Use of the traditional Disperse Blue 7 instead of the cationic dye showed no change of the basal spacing. Compared with the spacing (d = 23.6 Å) of the modified clay in the powder form, the larger value (d = 28 Å) of the modified clay in the polymer matrix is particularly interesting. Clay complex modified with $4C10N^+$ cation may swell to this extent in the polymer and/or bind fragments of the polymer. Such a situation is supposed to be desirable for promotion of the ion exchange reaction in the polymer film for practical thermal printing. Figure 6 also shows that the original signal remains after printing; thus the remaining $4C10N^+$/clay is sufficient to react with subsequent cationic dyes. The cationic dye is considered to be distributed in the depth direction of the film, according to the concentration distribution, as described in a simulation study of the disperse dye distribution.[10]

Migration of the dye from a dye receiver sheet to a white sheet was tested by superimposing two polymer sheets,

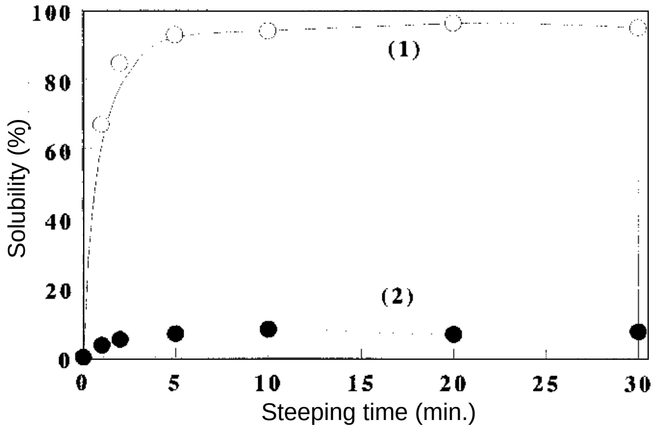


Figure 7. Solubilization test of Ox dye on the polymer sheet with MEK in the (1) absence and (2) presence of the modified clay.

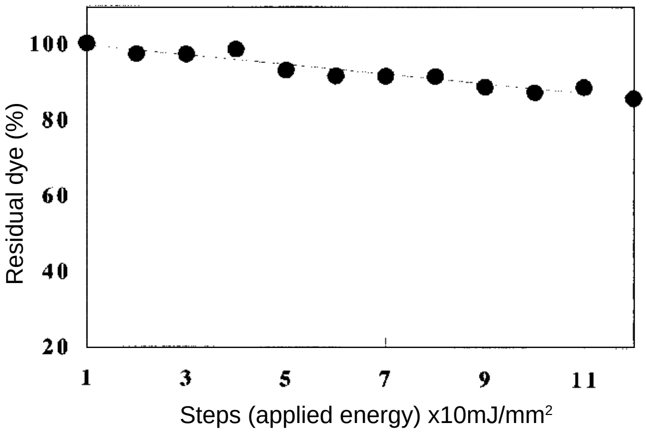


Figure 8. Solubilization test of black image (mixture of yellow, magenta, and cyan) on the polymer sheet containing the modified clay, using MEK as solvent.

and a further solubilization test was carried out by immersing the printed sheet in MEK solvent. Extensive color retention on the receiver sheet is clearly the case in the presence of the modified clay, as shown in Table I for the back diffusion (migration) of Ox and in Figs. 7 and 8 for solvent resistance of the printed sheets. Without the clay the dye is almost fully dissolved in MEK (Fig. 7). Figure 8 also shows that the black color formed by superposition of three dyes (yellow, magenta, and cyan) was almost unchanged by immersing the printed sheet in MEK, even with the high amount of dye transferred.

By making use of the liquid diffusion transfer of the dyes between two layers and further by fixing the modified dyes with the modified clay, the yellow, magenta, and cyan dyes were used for color video printing. The reflection spectra of the dyes are presented in Fig. 9. The amount of dye transferred as a continuous-tone color image is dependent on the controlled input energy of the printhead. The relationship between the color density and the applied energy for the dye transfer is given in Fig. 10. The color density on the receiver sheet increased linearly with increasing energy, giving similar curves for the three dyes selected. The solvent resistance of the color image was examined for the three dyes superposed on the receiver sheet. The K/S value of each step tested for solvent resistance gave an excellent result, as shown in Fig. 8. Colored pictures obtained by thermal cationic dye printing with or without the clay are demonstrated in Fig. 11. Without the modified clay, the color diffused markedly upon immersion in MEK, whereas in the presence of the modified clay the color density was not changed. The preservation of the picture for a long period (more than one year) in a photographic album had no influence on migration to a separate sheet, fading, and blurring.

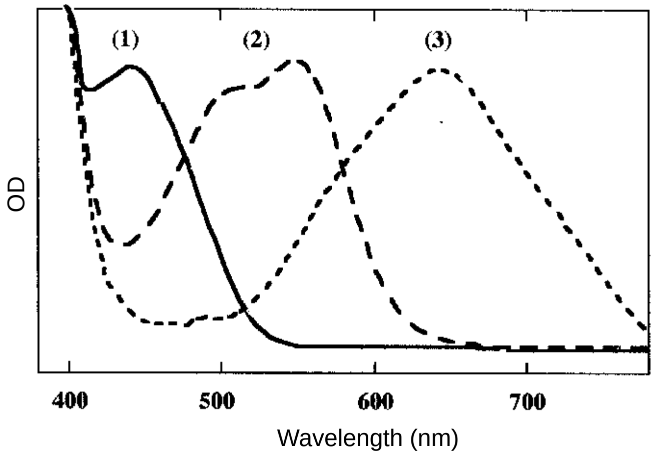


Figure 9. Reflection spectra of three dyes for color image: (1) Basic Yellow 2-DS (2) Basic Red 46-DS; and (3) Basic Blue 75-DS.

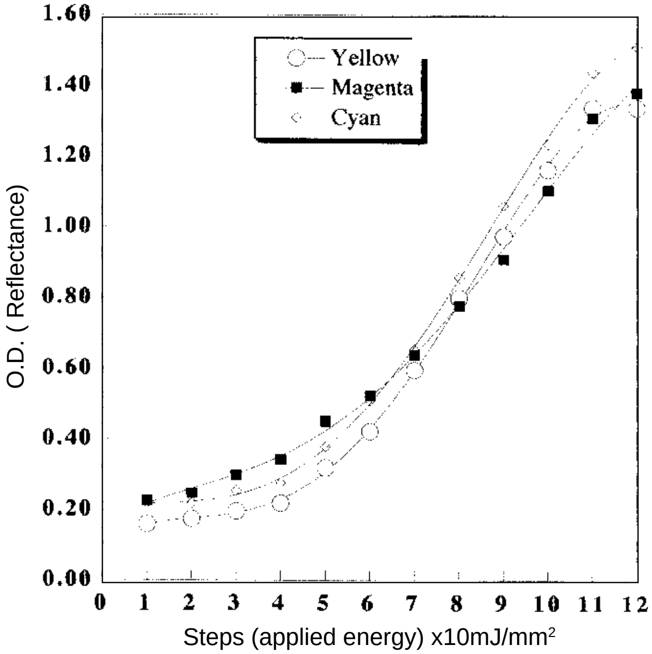


Figure 10. Characteristic curves for full-color images using three primary colors (Basic Yellow 2-DS, Basic Red 46-DS and Basic Blue 75-DS).

This information provides a new system for full-color printing.

Conclusion

This study was concerned with applying cationic dyes in thermal transfer diffusion printing and fixing the dyes inside a clay layer by intercalation. Modification of cationic dyes with hydrophobic organic anions improved the sensitivity of the thermal transfer and made it possible to form full-color images with printing speeds comparable to

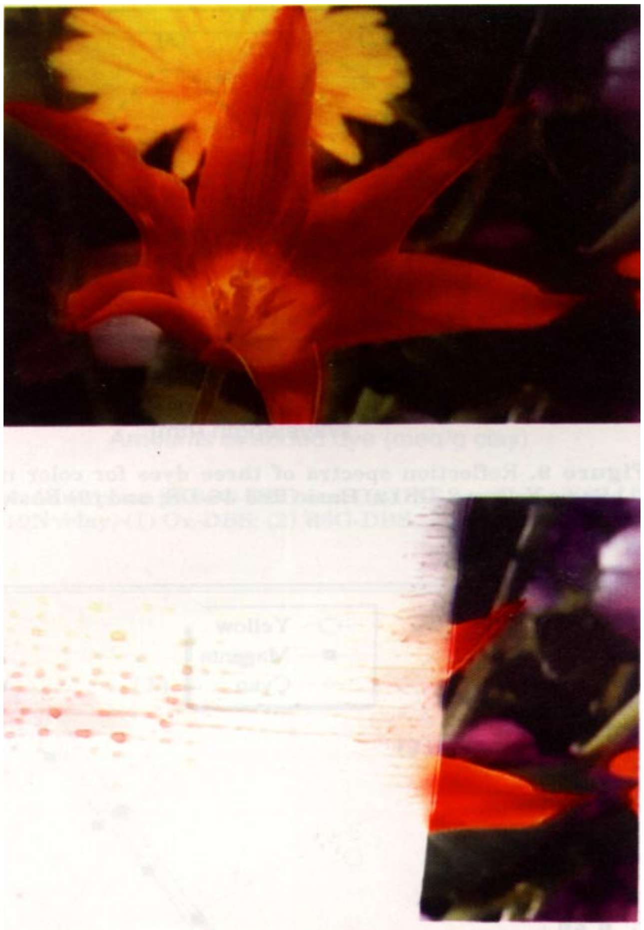


Figure 11. Solvent (MEK) resistance. Colored pictures copied by means of thermal cationic dye printing (Video printing): (*top*) in the presence of the modified clay and (*bottom*) in the absence of the clay.

those of conventional disperse dye printing. X-ray studies of the colored clay obtained by the ion exchange reaction between the modified cationic dye and the tetra-*n*-decylammonium cation–montmorillonite complex showed that the basal spacings of the intercalated clay decreased during the ion exchange reaction in the clay dispersion. Cationic dyes were transferred inside the clay, where the exchangeable bulky ammonium ion was easily substituted for by the dye cation. When dyes of the three primary colors were applied to the polymer film containing the modified clay, the full-color print formed by superposition of the dyes was retained as an insoluble and nondiffusible pigment image.

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