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Structure/Activity Relationship of Post-Chelating Azo Dyes in Thermal Dye Transfer Printing System

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Abstract

In dye diffusion thermal transfer printing, there has been two major issues on image preservation. One has been the deterioration of image quality resulting from the bleeding and migration of transferred dyes, and the other has been the poor light stability of the dyes.

To counteract these issues, we have developed a new concept with new azo dyes having certain moieties and transition metal ion providing compounds. The moieties make dyes possible to react with metal ions to form metal-dye complexes. The complexes have high molecular weight to lower the transferability greatly. It makes the images stronger against bleeding, heat-migration, smearing by finger printing, and so on. The transition metal makes dyes stronger against light-induced decomposition. As a resut, the images are resistive to post-printing thermal diffusion and, in addition, possess good light stability.

Introduction

For many years, the only practical method to produce a color continuous-tone image was silver halide based photography. We have now some other new methods to produce photography-like images. Thermal dye transfer printing has excellent color and tone reproduction and is the most promising candidate for such use. Unfortunately, thermal dye transferred image suffers from light induced decomposition of dyes as well as heat induced smearing.

In the dye diffusion thermal transfer printing process, thermal energy forces dyes into receiving layer in extremely short time and dyes must have good transferability accordingly. Unfortunately, the transferability leads to the issues of the unwanted post-printing diffusion. The transferability also restricts the molecular weight of dyes; the restriction makes the dyes difficult to attach light-stabilizing moieties on.

To counteract these issues, many approaches have been proposed. Typical examples are

1) Adding a protective layer on the dye receiving sheet with UV-light absorbing compounds.
2) Adding UV-light absorbing compounds and anti-oxidizing compounds to the dye receiving layer.
3) Adding an adsorbent such as SiO_2 and clay to the dye receiving layer.[1]
4) Hardening the dye receiving layer after thermal printing.
5) Employing reactive dyes with reactive compounds, which can make covalent bonds between them in the dye receiving layer.[2]
6) Employing ionic dyes with ionic compounds, which can make electrostatic bonds between them in the dye receiving layer.

In the present study, we have developed a new concept to counteract the issues; we have utilized a chelating reaction of certain azo dyes with metal ion providing compounds to form stable dye-metal complexes. As a result, we have gotten a drastically enhanced image stability against heat and light exposure.

Experimental

Compounds in the Present Study

Dyes were synthesized from their corresponding phenols, naphthols, or heterocyclic compounds and anilines or hydrazines through conventional coupling reactions. Metal ion providing materials were synthesized from their ligand compounds and transition metal salts. The ligand compounds were synthesized from commercially available reagents. All compounds were identified with NMR and mass spectra. Absorption spectra of dyes and dye-metal complexes were measured with Hitachi U-3300 Spectrophotometer. Rate constants of the chelating reaction were measured with UNION GIKEN Stopped-Flow Spectrophotometer RA-401.

Thermal Printing Materials

The dyes were dissolved in organic solvent with polyvinyl butyral and coated on a PET film base. A thin layer was coated on the back side of the dye donor sheet to prevent a thermal head from sticking to the PET base. A typical structure of dye donor and receiver sheet is illustrated in Figure 1.

Thermal dye transfer printing was carried out with the CHC-S845-5C printer (Shinko Electric Co.). No change of hardware was added to fit to the printing system of the present study. The data of images for color management was controlled through a computer software.

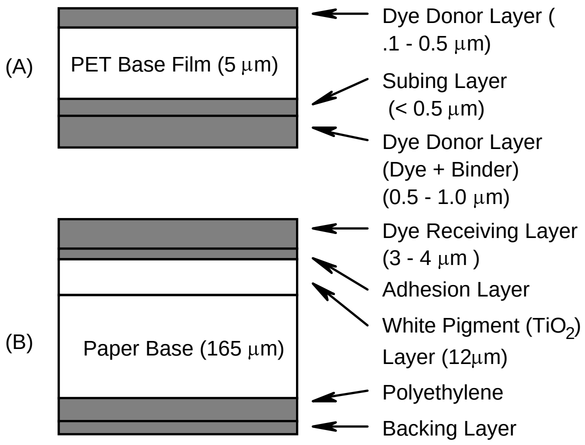


Figure 1. Structures of dye donor sheet (A) and dye receiving sheet (B)

Evaluations of Dye Fastness Under Heat and Light Exposure

Printed image samples were placed in an incubator of which temperature and humidity were controlled at a certain level. After prescribed period, optical density of the printed images was measured to determine the color fading. The degradation of image-edge sharpness was evaluated by measuring the optical density around an image-edge with a microdensitometer.

The light fastness of the printed images was also evaluated by measuring the optical density after irradiated with a xenon lamp for prescribed time.

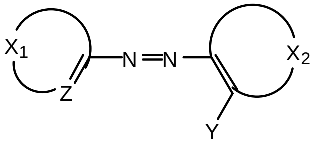
Results and Discussion

General Structures of Materials

The most important materials in the present study are metallizable dyes and metal ion providing compounds. Figure 2 illustrated the general structure of the metallizable dyes. The dyes have azo moiety as well as two heteroatomic chelating sites. The dyes must have:

1) High reactivity with metal ion providing materials, which makes dyes to form dye-metal complexes rapidly in the dye receiving sheet.
2) High transferablity to the dye receiving sheet, which makes high dye density with comparable heat energy as conventional thermal dye transfer printing system.
3) High solubility in organic solvents, which is required to manufacture dye donor sheets with high productivity.
4) Good color hue, which is necessary to make photographic-like full-color images.
5) Safety and non-polluting.

The metal ion providing compounds are the metal ion source in the system. They are consisted of transition metal cation, ligand compounds, and counter anions as illustrated in Figure 2. The transition metal ion controls color hue, heat stability, and light stability of printed images. Cobalt, nickel, copper, zinc, and aluminum are preferably used for this purpose. The ligand compounds influence the reactivity with the metallizable dyes, heat and light stability, shelf life, whiteness, and the solubility of the metal ion providing compounds in organic solvents. The counter anions also have an influence on that solubility.



(A)

Z, Y : chelating site
X_1, X_2 : aromatic carbocyclic or heterocyclic nuclei

$$M^{2+}\,(Lig)_n\,(X)_m$$

(B)

M:	Transition metal
Lig:	Metal chelating ligand
X:	Counter anion
n:	2 or 3
m:	0 or 2

Figure 2. General structures of the metallizble dye (A) and the metal ion providing compounds (B).

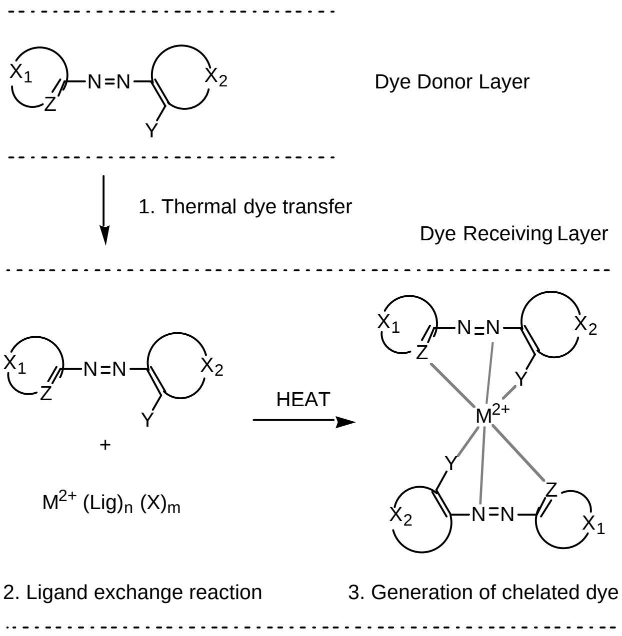


Figure 3. Principle of the "post-chelating" process

Principle of the Chelating System

Figure 3 illustrates a fundamental principle in our technology utilizing chelating reactions. The process, which we refer as "post-chelating process," is consisted from the following three-step:

1) Dye transfer step with heat energy
2) Ligand exchange reaction step between the azo dyes and the metal ion providing compounds
3) Generation step of the chelated dyes

As completion of the post-chelating process, we can get the following merits:

-- color hue control
1) bathochromic shift
2) enhancement of the light absorption efficiency (ε)
3) sharp and steep absorption curve

-- enhancement of image permanence
1) enhancement of the stability against light (Figure 4)
2) enhancement of the stability against heat and humidity (Figure 5)
3) suppression of the post-printing dye diffusion (“smearing”)

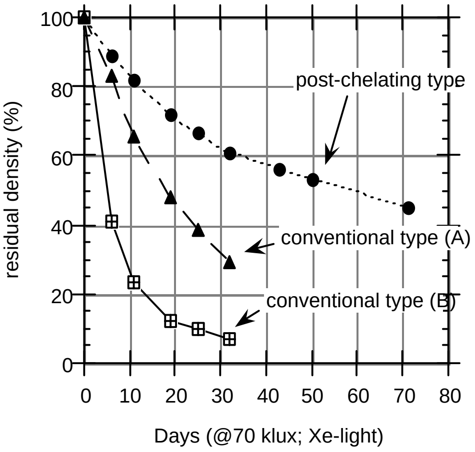


Figure 4. Image stability against light

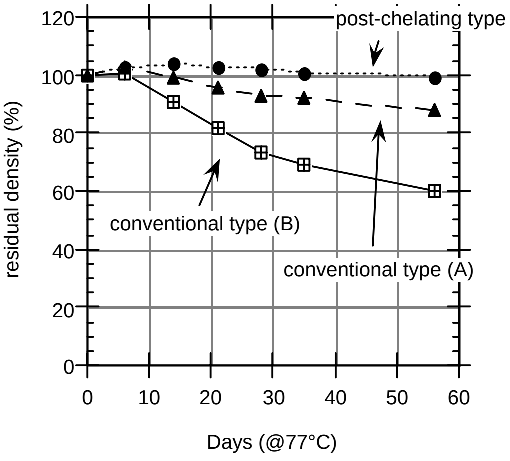


Figure 5. Image stability against heat

Mechanistic Study: Structure/Activity Relationship

In order to clarify the relationship between the dye-structure and its activity in the post-chelating process, we have synthesized four new dyes M-1 to M-4, and evaluated their absorption characteristics in acetone solution. Their structures are illustrated in Figure 6 and the results are summarized in Table 1.

As described above, the bathochromic shift and the enhancement of light absorption efficiency (molar absorption coefficient; ε) are the typical effects of the chelating. We chose changes in absorption characteristics with and without metal ion to evaluate the relationship.

In Table 1, M-1 and M-2 showed larger bathochromic shift and the enhancement in ε values. On the contrary, M-3 and M-4 showed no bathochromic shift and no enhancement in ε values; the value even decreased to one-half in M-3 with metal ion. The difference between the M-1/2 and M-3/4 structures is the number of chelating sites. M-1 and M-2 dyes have three sites but M-3 an M-4 dyes have only two sites. We think that at least three chelating sites are necessary to make a stable chelated dye, and affected to improve absorption characteristics accordingly.

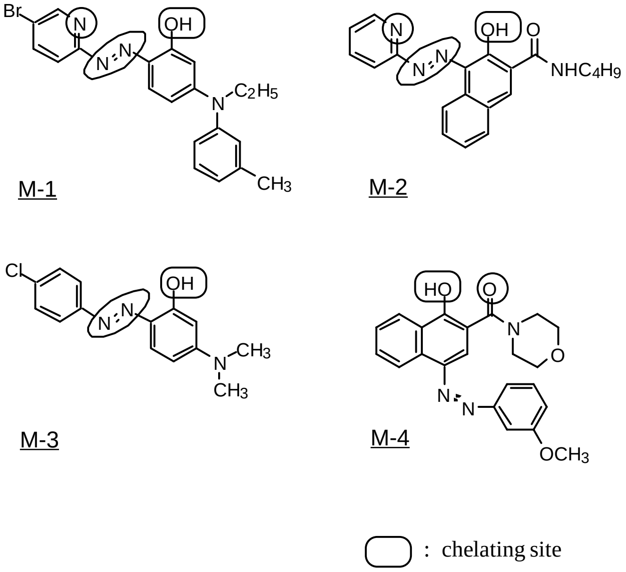


Figure 6. Structures of metallizable magenta dyes

Table 1. Absorption maxima and ε values of dyes M-1 to M-4.

dye	λmax (ε) (without metal)	λmax (ε) (with metal)
M-1	456 nm (41,700)	536 nm (43,200)
		564 (38,300)
M-2	477 nm (19,700)	527 nm (23,300)
		564 (28,200)
M-3	457 nm (42,100)	450 nm (26,800)
M-4	395 nm (14,200)	474 nm (16,400)
	474 (8,600)	

Conclusion

We have developed "post-chelating" thermal dye transfer printing system. Using metallizable dyes and metal ion providing compounds, we have observed good color hue and high image stability against heat and light exposure. We have found that the metallizable dyes must have at least three chelating sites in their structure to make a stable chelated dye.

References

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2. K. B. Lawrence, et al., *Proceeding of IS&T's NIP 13th*, 237 (1996).

Biography

Atsushi Tomotake graduated from University of Tsukuba and took his Ph.D. degree in synthetic organic chemistry at Department of Chemistry, University of Tsukuba in 1987. He joined Konica Corporation in the same year. He was working to develop new materials for color silver halide photographic paper for many years. Now his interest is focused on the materials for color hard copy, such as thermal dye transfer printing and ink jets.