 

# Thermal Dye Transfer Printing with Chelate Compounds

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## Abstract

Since thermal dye transfer printing has excellent characteristics in color and tone reproduction, this printing method can produce a color continuous-tone image like a silver halide photograph. However, there has been a very serious problem that the printed image of thermal dye transfer is faded easily when subjected to heat and exposed to ultraviolet and visible light.

We have studied the chelate complex system to solve this problem and have found that some sets of azo dyes and metal-ion-providing compounds result in very high stability of printed images.

## Introduction

For many years, the only practical method to produce a color continuous-tone image was silver halide photography. These days, we have also some other methods to produce images so beautiful that the printed images are sometimes mistaken for color photographs. Thermal dye transfer printing has excellent color and tone reproduction and is a typical method in this case. Unfortunately, thermal dye transfer prints suffer from poor image stability when subjected to heat and exposed to light.

The followings are candidates for the approach to improve the image stability, that is, (1) adding a protective layer on the receiver sheet with a UV-light-absorbing agent, (2) adding UV-light-absorbing agents and antioxidizing agents to the dye receiving layer, (3) hardening the dye receiving layer after thermal printing, (4) adding an adsorbent such as $SiO_2$ to the dye receiving layer, (5) employing a chemical reaction between a reactive dye and chemical agents in the dye receiving layer. Regarding (5), it is expected to be effective to utilize chelate compounds, mordant, newly developed dyes, or special compounds with chemical reactivity to dyes.

The interaction between dyes and some compounds on receiver sheets would certainly increase the image stability. It was reported that the interaction between cationic dyes and alkylammonium-modified montmorillonite clays could result in good image stability, where the protection from organic solvent and from hot water was observed[1]. In this study, the clays were added into a receiving layer of the receiver sheet. The enhanced stability is mainly ascribed to the ion binding. The covalent binding can also bring the increase in the image stability. The immobilization of transferred dyes was found with the following systems: dyes containing pendant primary aliphatic amine groups transferred to receiver polymers containing β-ketoester/amide groups, or dyes containing activated carbonyls (β-ketoester or aryl carbonate) transferred to receiver polymers containing primary or secondary aliphatic amino groups[2]. In this experiment, the amount of dyes on a plasticized PVC coversheet when the coversheet had been placed over a printed image and kept it in a 50•C/50%RH oven under one-kg weight.

In the present study, we have utilized the chelate reaction of azo dyes with metal ions to form stable dye-metal complexes and have observed drastically enhanced image-stability against heat and light exposure.

## Experimental

Dyes and metal-ion-providing compounds were newly synthesized in the present study. Absorption spectra of dyes and dye-metal complexes were measured with Hitachi U-3300 spectrophotometer.

The dyes were dissolved in organic solvent with polymers and coated on a PET film. Other layers could be added as needed. The PET film as a substrate was approximately 5μm thick, and the dye donor layer 0.5 to 1.0 μm thick. Various kinds of polymer compounds, such as poly acrylate, butyral resin, and cellulose were tested for a binder component in the dye donor layer. A thin layer was coated on the back side of the dye donor sheet to prevent a thermal head from sticking to the PET substrate film. In addition to containing slipping agents such as silicone compounds, the backing layer could be composed of resin hardened by the chemical reaction of such compounds as isocyanate in order to make the backing layer heat resistant. A typical dye donor sheet is shown in Fig.1(A).

The dye receiver sheet basically consisted of a dye receiving layer of 3 to 4μm thick and a substrate. Resin-coated paper or synthetic paper can be used as the substrate because their whitness and touch are similar to photographic paper. We used synthetic paper in the present study. A typical dye receiver sheet is shown in Fig.1(B).

Thermal dye transfer printing was carried out with the printer, CHC-S845-5C (Shinko Electric Co.) that was on the market. 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.

We examined the effect of heat and humidity upon the stability of printed images. 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 lightfastness of printed images was also evaluated by measuring the optical density after irradiated with a xenon lamp for prescribed time.

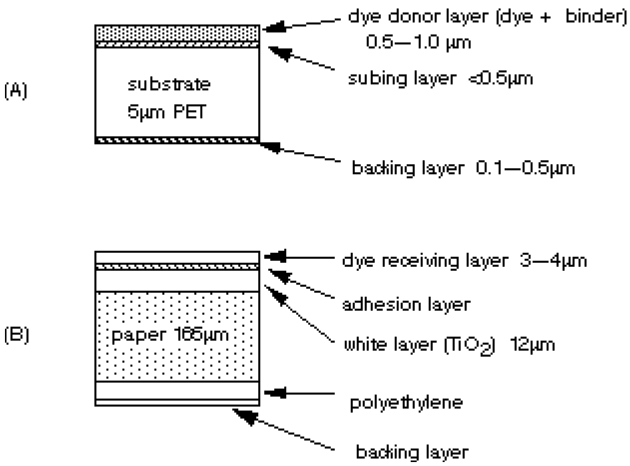


*Fig.1 Dye donor sheet (A) and dye receiver sheet (B)*

## Results and Discussion

The most important materials in the chelating system are metallizable dyes and metal ion sources. Figure 2 shows the fundamental structure of metallizable dyes[3]. The typical dyes are azo-type ones with three metal chelating sites for a metal ion. The dyes must have the reactivity with metal-ion-providing compounds to produce dye-metal complexes. High solubility in organic solvents is also required to manufacture dye donor sheets with high productivity. The dyes also have the ability to transfer from a dye donor sheet to a dye receiver sheet under the same heating condition as a conventional thermal dye transfer printing system. In addition to the above factors, the dyes have been developed from various viewpoints such as long shelf life, suitable color to make full-color images, safety, and non-polluting.

The metal-ion-providing compound as a metal ion source is consisted of a transition metal cation, ligands, and counter anions as shown in Fig.3. The transition metal ion affects strongly hue, heat stability, and light stability of printed images. We examined cobalt, nickel, copper, zinc, aluminum, and so on. The metal ions change the light absorption spectra as well as heat and light stability. The ligand components influence reactivity with metallizable dyes, light stability, shelf life, whiteness, and the solubility of the metal-ion-providing compound in an organic solvent. The counter anions also have an influence on that solubility.

As reported previous study[4], we observed a high-performance with post-chelate colorants using azo dyes with nickel complex incorporating β-diketone ligands. The same colorants have also been used to investigate image stability described below.

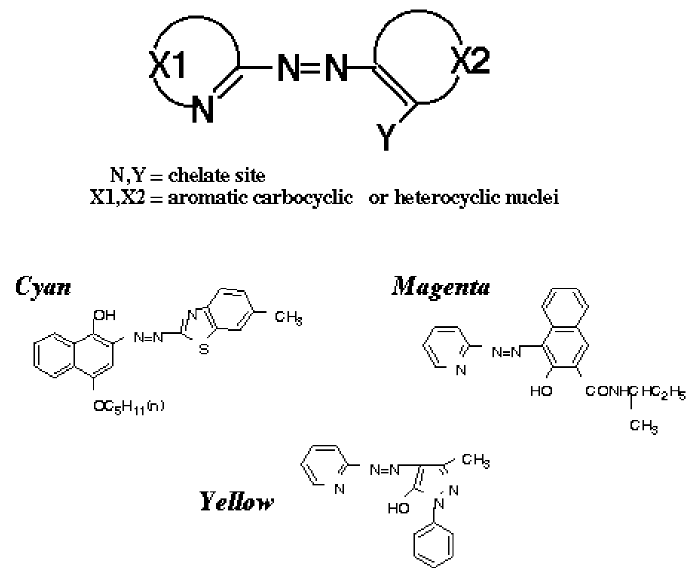


*Fig.2 Fundamental structure of metallizable dyes*

$$M^{2+}(Lig)_n\,(X)_m \qquad n = 2 \text{ or } 3 \qquad m = 0 \text{ or } 2$$

*Fig. 3 Metal-ion-providing compound*

Figure 4 shows a fundamental principle in our technology utilizing chelate reactions. When metallizable azo dyes move from the dye donor sheet to the dye receiver sheet, the dye molecules take the place of the ligands of the metal-ion-providing compounds waiting in the dye receiving layer. We refer to this as a post-chelate process.

The dye transfer from the donor sheet to the receiver sheet can occur under the same condition as the conventional thermal dye transfer printing. Figure 5 shows this fact. As seen in this figure, the threshold of rising of the characteristic curves is almost the same between post-chelating type and conventional dye transfer system. This fact suggests that metal ion does not necessarily play as a sink for dye molecules to accelerate the diffusion of them from the dye donor sheet to the dye receiver sheet. Dye-metal complexes have often larger coefficients of light absorption than the conventional dyes. Accordingly, the characteristic curve of the post-chelating system often takes the upper position than the conventional thermal dye transfer system as seen in Fig.5.

The post-chelate process improves drastically the light stability of printed images. Figure 6 shows the degree of color fading when the printed images have been exposed to Xe lamp. It is expected that the stability of dye-metal complex itself has brought this improvement.

The post-chelating dye system also affects the color fading when printed images are placed under the environmental condition with high temperature and high humidity. Figure 7 shows the effect of temperature. In comparison with the conventional thermal dye transfer printing, as seen in Fig.7, the post-chelating dye system has an obvious advantage. Even if an additive layer such as an over-protecting layer is applied on a dye receiving layer of the conventional dye transfer system, the increase in image stability is smaller than the post-chelating system.

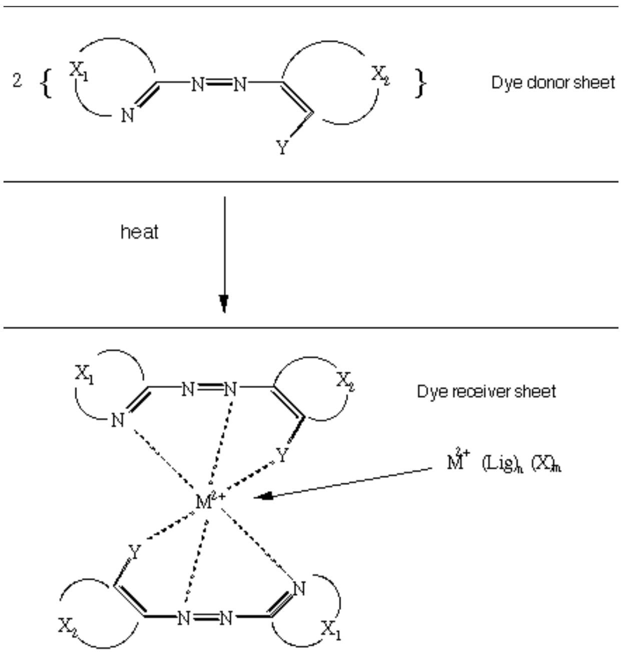


*Fig. 4 Principle of post-chelate process*

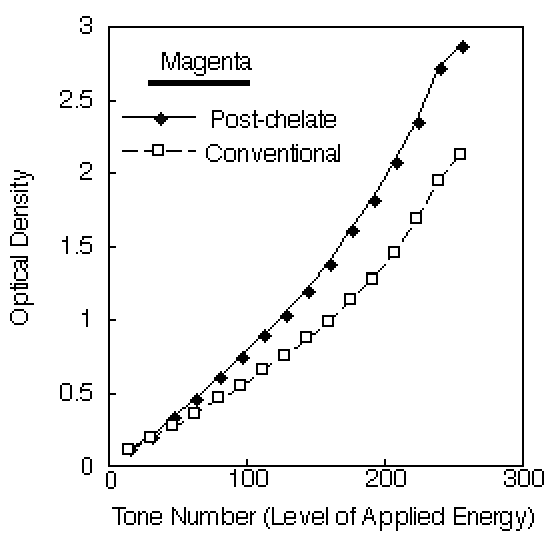


*Fig. 5 Characteristic curves of Thermal Dye Transfer*

The degradation of an image-edge is often observed on printed images of the conventional thermal dye transfer printing, after the printed images have been kept in high temperature circumstances. This phenomenon is based on the dye diffusion toward lateral direction in the dye receiving layer. In the post-chelating system, however, such the degradation of an image-edge has not been observed. Since the complex composed of two dye molecules and one metal cation with counter anions is larger and heavier than the original dye molecules, the dye-metal complex does not move so easily in the dye receiving layer.

We have also observed other effective matters brought by the post-chelate process as follows: reducing image transfer to plastic sheets like a PVC film, decreasing in color fading caused by finger prints, and increasing in the resistance against the image disappearance when immersed in oil.

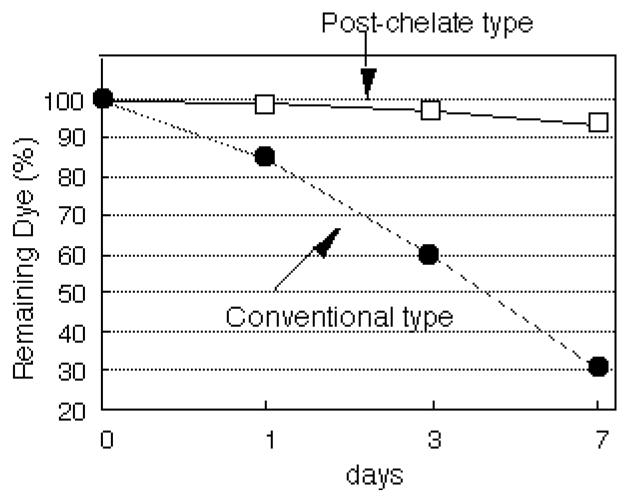


*Fig.6 Lightfastness (Cyan) Xe lamp 70,000lx*

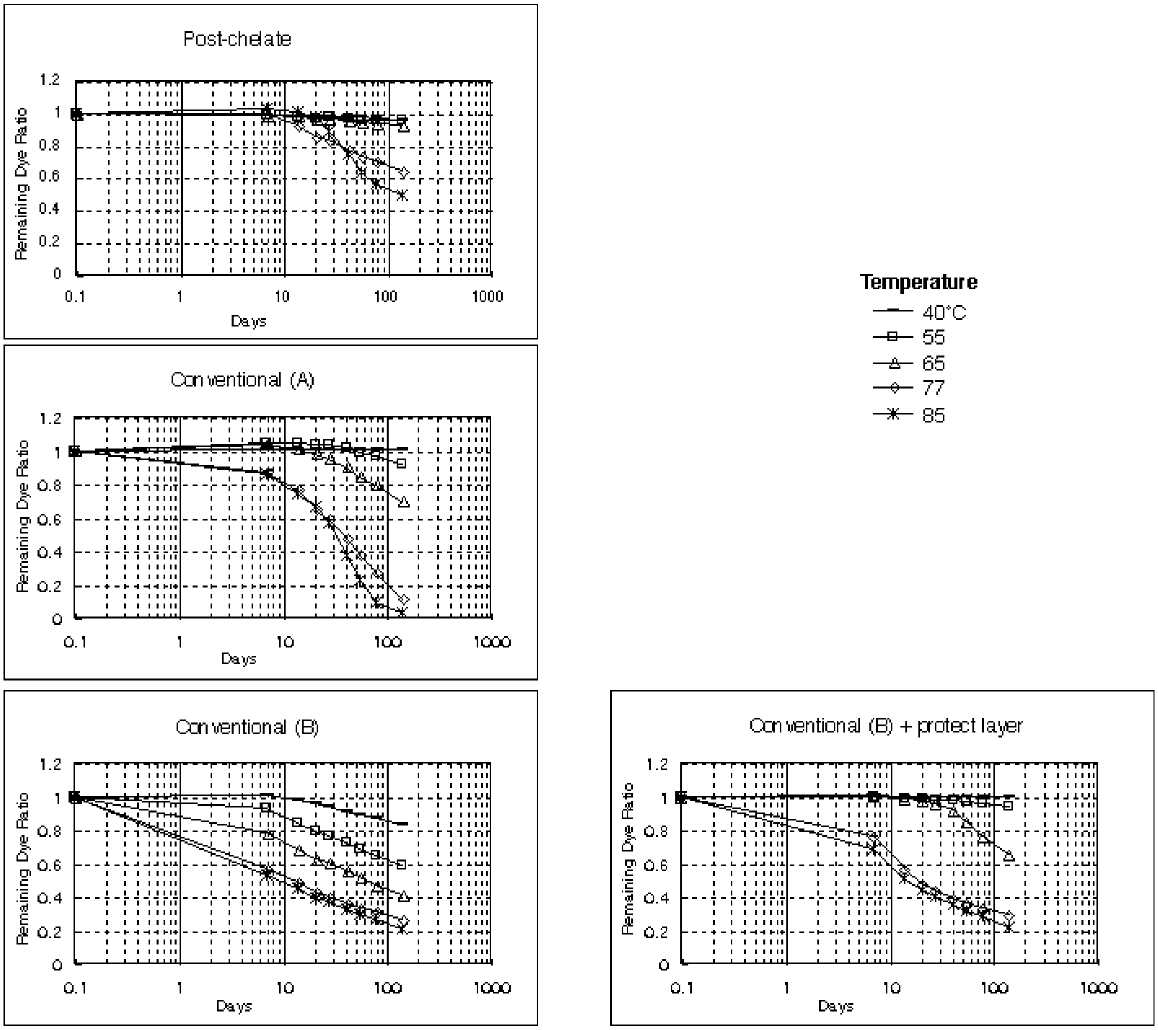


*Fig. 7 Color fading by temperature (Cyan images)*

## Conclusion

We have developed a post-chelating dye system in thermal dye transfer printing. A set of azo dyes and metal-ion-providing compound incorporating nickel ion and β-diketone ligand has shown a high performance about image stability. The following drastic effect of the post-chelating dye system on the printed images has been observed: (1) Lightfastness is increased. (2) Image fading is reduced in the circumstnances with high temperature and high humidity. (3) Degradation of image-edge is decreased.

## References

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