

Thermal Dye Transfer Printing with Chelate Compounds

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With its excellent color and tone reproduction, thermal dye transfer printing produces continuous-tone color images that rival silver halide photography. However, conventional thermal dye transfer images fade easily when subjected to light or heat. To solve this problem, we have studied a chelate compound system and have found that certain sets of azo dyes and transition metal cation-providing compounds produce dye-metal complexes, or "chelate compounds", that provide exceptionally high image stability.

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Introduction

For many years, the only practical method of producing high-quality continuous-tone color images was silver halide photography. But today, several new technologies offer images so beautiful that they are often mistaken for color photographs. Thermal dye transfer printing, with its excellent color and tone reproduction, is one such technology.

Unfortunately, thermal dye transfer prints typically suffer from poor image stability when exposed to visible or ultraviolet light or if subjected to heat. Many approaches have been taken to solve this serious problem, including the addition of a protective layer over the dye receiver sheet,¹ addition of UV-light-absorbing agents and antioxidizing agents to the dye receiving layer,^{2–4} addition of dye adsorbents to the dye receiving layer,^{5,6} hardening of the dye receiving layer after thermal printing,⁷ and employment of chemical reactions between reactive dyes and chemical agents in the dye receiving layer.^{8–12}

Each of these approaches has had some success, but the latter approach has been most promising. In exploring the utility of chemical reactions between reactive dyes and chemical agents in the dye receiving layer, four likely avenues suggest themselves: the control of mordants by ionic bonding force, the production of relatively high molecular weight dyes within the dye receiving layer, the reaction of special agents such as UV-absorbing and/or antioxidant agents with dyes, and the chelate reaction of dyes.

Examples of mordants controlled by an ionic bond include a dye with a phenolic OH group and a mordant with a base, as reported by Fuji Photo Film researchers,¹² and a mixture of cationic dyes and alkylammonium-

modified montmorillonite clays that provide protection from organic solvents and from hot water, as reported by Sony researchers.¹³

An example of a high molecular weight dye produced in the dye receiving layer is an arylidene dye produced by the reaction between a coupling agent and an electrophilic compound, as seen in an Eastman Kodak patent.⁸

While the reaction with dyes of such special agents as UV-absorbing and/or antioxidant agents holds promise, no published reports of research in this area are currently available.

However, perhaps the most successful avenue has been to exploit the chelate reaction of dyes.^{14,15} In this study, we investigated newly synthesized dyes and transition metal cation-providing compounds. We utilized the chelate reaction of azo dyes with transition metal cations to form stable dye-metal complexes, that we refer to as chelate compounds, and observed dramatically enhanced image stability under exposure to light and heat.

Experimental

The basic structure of the samples studied are shown in Fig. 1. For the dye donor sheet, a PET film substrate was used, with a thin backing layer to prevent sticking against the thermal heads. In addition to lubricants such as silicone compounds, the backing layer was occasionally composed of a resin hardened by chemical reaction with such compounds as isocyanate in order to make the backing layer heat resistant. On the obverse side of the dye donor sheet, a subbing layer was coated. Following that, dyes dissolved in an organic solvent with polymers were coated to create a dye donating layer. The relative dye concentration was about 40% in weight. These four layers constituted the basic structure of the dye donor sheet.

For the dye receiver sheet, either resin-coated or synthetic paper could have been used as the substrate because the whiteness and touch of each are similar to photographic paper. We chose to use synthetic paper be-

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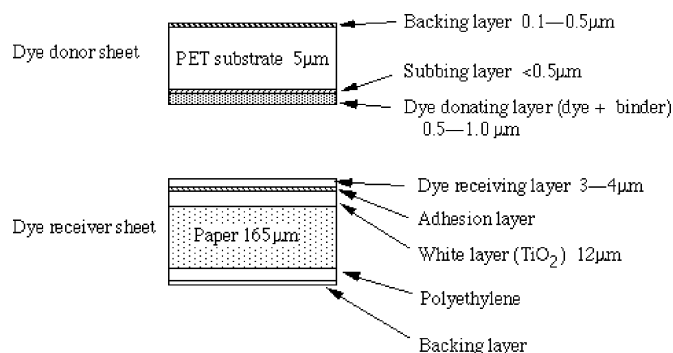


Figure 1. Structure of samples studied.

cause of its higher thermal transfer sensitivity allowed easier observation of the systems under study. The reverse side consisted of a polyethylene layer and then a backing layer. The obverse side consisted of a TiO₂ white layer, then an adhesion layer, and, finally, a dye receiving layer. The receiving layer contained vinyl chloride–vinyl acetate copolymer as a binder and a metal cation-providing compound to produce dye-metal complexes. The relative concentration of the metal cation-providing compound was about 40% in weight. The whiteness of the receiver sheet was similar to conventional silver halide photographic paper and the values of (L, a*, b*) were (93–95, 0.5, –2.0).

All of the metallizable dyes and metal cation-providing compounds were synthesized in our laboratory. The matters concerning the synthesis are described in another paper.¹⁶

Thermal dye transfer printing was performed by an off-the-shelf CHC-S845-5C (Shinko Electric Co.) printer. No modification of hardware was made to accommodate the thermal dye transfer material samples fabricated for study, and color management was performed using computer software, not computer hardware.

The absorption spectra of dyes and chelate compounds were measured with an Hitachi U-3300 spectrophotometer, and we examined the effects of light and heat upon the stability of printed images. The lightfastness of printed images was evaluated by measuring optical density after irradiation with a xenon lamp. To determine color fading, printed image samples were placed in an incubator at controlled temperatures for prescribed periods, and the optical density of the printed images were then measured. In addition, the degradation of image-edge sharpness was evaluated by measuring the optical density around image-edges with a microdensitometer.

Results and Discussion

The system utilizing chelate compounds consisted of metallizable dyes and transition metal cation-providing compounds and Fig. 2 shows the fundamental structure of the metallizable dyes. From the report on metal complexes of *o*-hydroxyazobenzenes,¹⁷ the chelate sites are expected to be located as shown in Fig. 2.

These metallizable dyes had to meet a long list of requirements. They had to have sufficient reactivity with transition metal cation-providing compounds to produce the dye-metal complexes that we refer to as chelate compounds. The dyes had to be highly soluble in organic solvents in order to provide high manufacturing productivity of the dye donor sheets. They had to transfer efficiently from the dye donor sheet to the dye receiver sheet under the heating conditions of a conventional

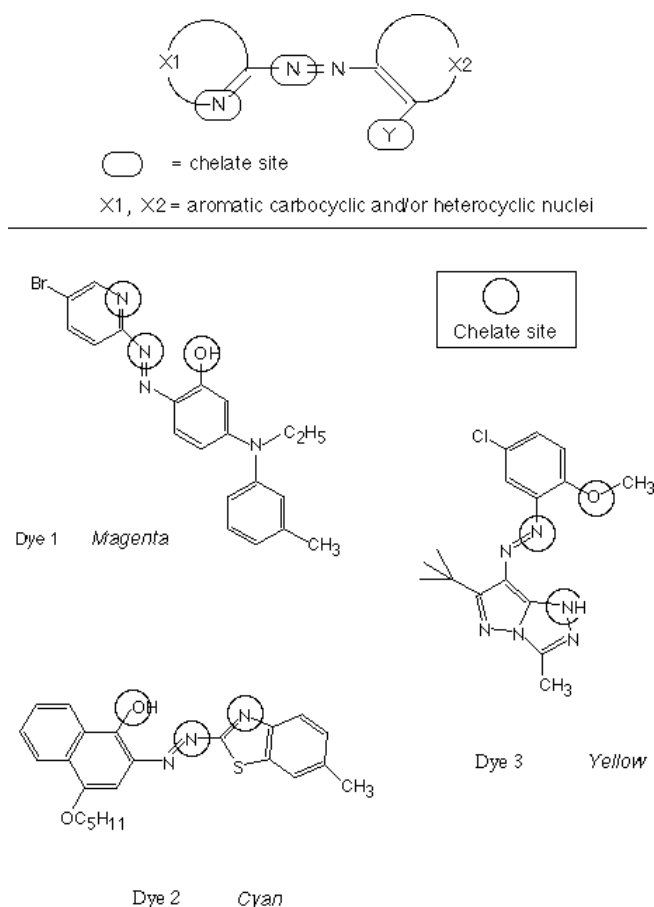


Figure 2. Metallizable dyes. Azo dyes with three metal chelate sites performed best.

thermal dye transfer printing system. Also, they had to serve product development demands for long shelf life, faithful color reproduction, product safety, and environmental protection. To all of these demands, the best performance was found in azo dyes with three metal chelating sites for a transition metal cation.

The transition metal cation-providing compounds that function as metal cation sources consist of a transition metal cation, ligands, and counter anions (if the ligand has no charge), as shown in Fig. 3. The transition metal cation strongly affects the hue, light stability, and heat stability of the printed images, as well as reactivity with the metallizable dyes; we examined cobalt, copper, zinc, and nickel. The metal chelating ligands influence reactivity with metallizable dyes, as well as shelf life, whiteness, and the solubility of the transition metal-cation-providing compound in organic solvents; we examined ethylene diamine, α -amino acid amide, and β -diketone ligands. The counter anions, when present, also influence solubility in organic solvents.

As reported previously,¹⁸ high performance, in terms of the requirements listed above, was best obtained with chelate compounds that resulted from azo dyes in reaction with a nickel metal cation and β -diketone ligands. The image stability described below is the image stability of this chelate compound.

Generally, chelate reactions result in a marked shift of the light absorption spectra of a chemical compound, and observation of this spectrum shift can often be used to determine if a chelate reaction has occurred. We observed

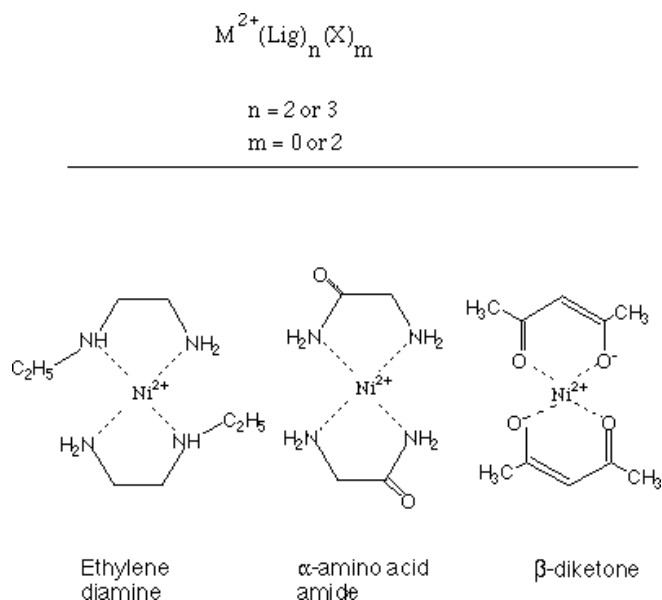


Figure 3. Transition metal cation-providing compounds. M = transition metal cation, Lig = ligand, X = counter anions.

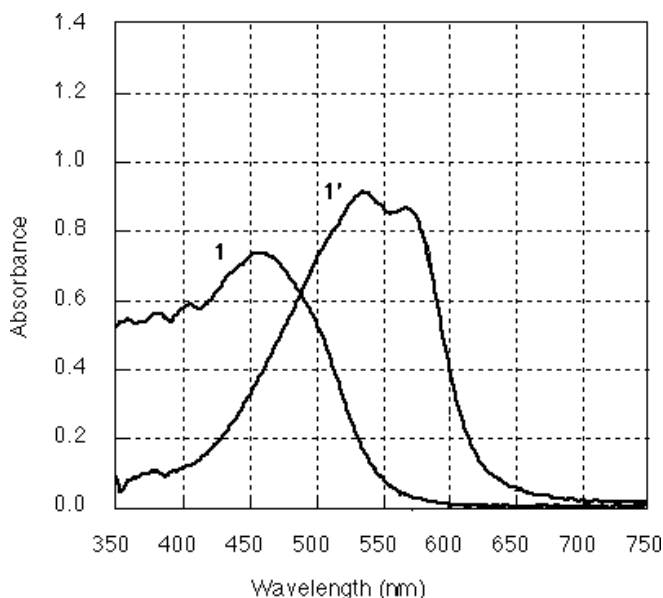


Figure 4. Absorption spectra of Dye 1, Fig. 2. 1 = Dye 1 before chelate reaction, 1' = Dye 1 after chelate reaction.

just such shifts of absorption spectra in this study, as seen in Fig. 4, strongly suggesting that chelate reactions were occurring in the dye receiving layers.

Figure 5 shows the chelate reaction as we applied it. 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 transition metal cation-providing compounds waiting in the dye receiving layer, resulting in chelate compounds. We will refer to a thermal dye transfer printing system that employs this process as a chelating system.

An important point to note when comparing the chelating system under study with a conventional thermal dye transfer system is that achieving higher optical density does not necessarily depend on higher

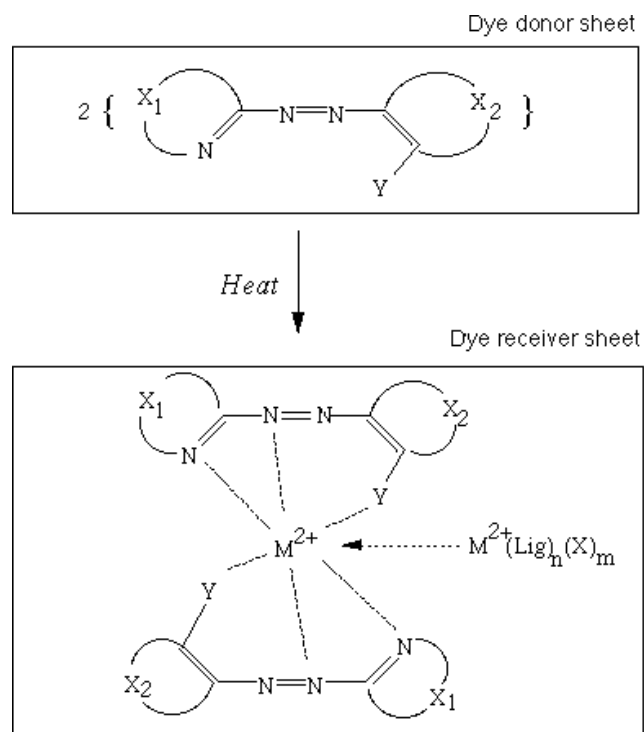


Figure 5. Chelating system.

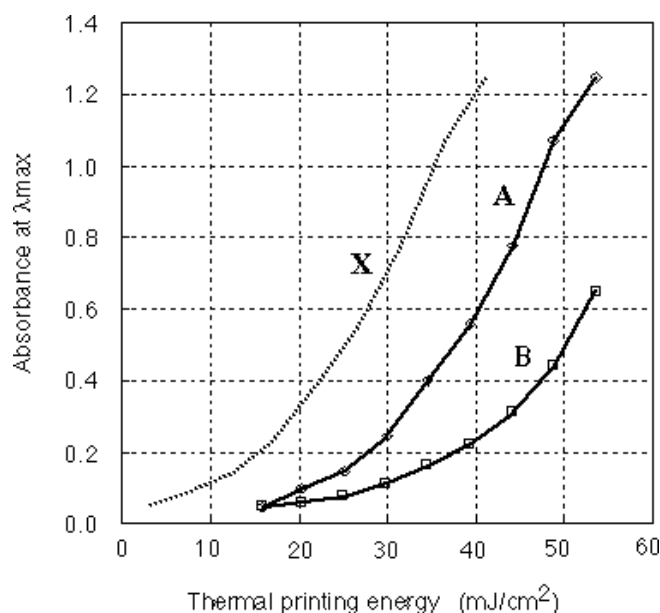


Figure 6. Higher optical density versus higher thermal transfer sensitivity. X = hypothetical substance acting as dye molecule sink, A = chelating system, B = conventional system.

thermal transfer sensitivity. As seen in Fig. 6, if a hypothetical substance in the dye receiving layer acts as a sink for the dye molecules, the diffusion of the dyes through the dye receiving layer can be expected to accelerate, and this higher thermal transfer sensitivity would, of course, result in higher optical density. However, note that dye transfer from the dye donating layer into the dye receiving layer with an actual chelating system begins at the same thermal energy level as a

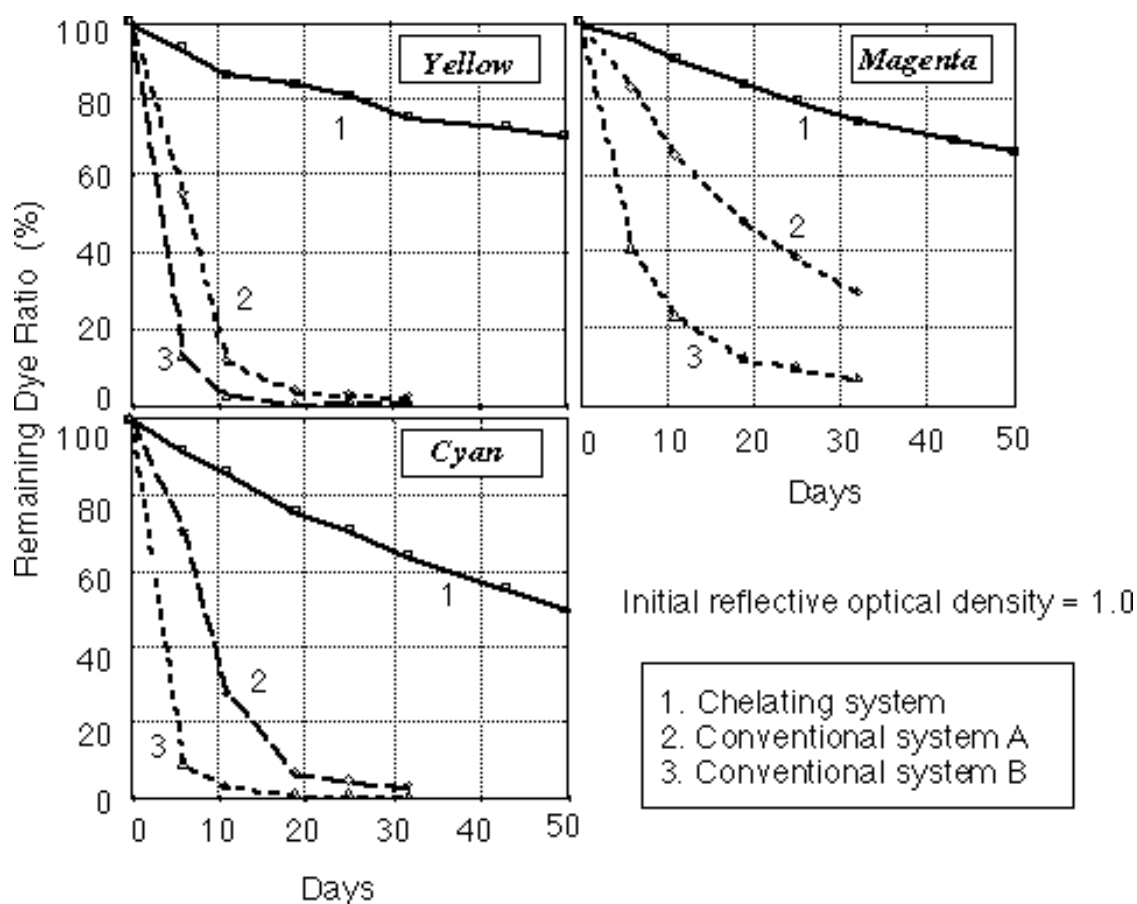


Figure 7. Color fading of printed images exposed to a 70000 lx Xenon lamp.

conventional thermal dye transfer system, with the threshold of the characteristic curves almost the same for both. This suggests that the transition metal cations do not act as a sink for the dye molecules. Yet the characteristic curve of the chelating system rises more steeply because the chelate compounds here have larger coefficients of light absorption than the conventional dyes, indicating higher optical density. At any point along the two characteristic curves, the chelating system exhibits approximately twice the absorbance at λ_{max} , which may be explained by the chelate compound having a light absorption coefficient of 32300 at 456 nm in acetone as compared to the conventional dye's 13500 at 392 nm in acetone.

The chelating system dramatically improves the light stability of printed images, bringing light stability almost to the level of silver halide photographic paper. Figure 7 shows the degree of color fading when the printed images have been exposed to a 70000 lx xenon lamp. For comparison here, if the illuminance of a typical room is assumed to be 500 lx, ten hours per day, our experimental condition of 70000 lx, 24 hours per day, for 20 days would be equivalent to about 18.4 years of typical room illuminance. Because the same kind of polymer binders were used in both the chelating and conventional systems here, the increased light stability that is evident can be attributed to the greater stability of the chelate compound over conventional dyes.

As seen in Fig. 8, the chelating system also strongly inhibits color fading when printed images are subjected to high temperatures, even to temperatures above the

glass transition temperature of the dye receiving layer, and it is important to note here that two color fading mechanisms appear to be active. At temperatures below the dye receiving layer's glass transition temperature of approximately 70°C, fading depends chiefly on the stabilities of the colorants. In the case of the chelating system, note carefully that the colorant consists not of the dyes, but of the chelate compounds of which the dyes are a part. In the conventional systems, however, the colorant is constituted by the dyes themselves. The lower intrinsic stability of the dyes in the conventional system explains the compensation provided by adding a protective layer, which acts as a barrier against air.

At temperatures above the dye receiving layer's glass transition temperature, a second mechanism of fading takes additional effect. Above the glass transition temperature, the colorants suddenly have much greater freedom of movement, resulting in lateral diffusion of the colorants, which not only physically disperses the colorants but also results in greater exposure to such reactive agents as oxidizing and reducing agents. The result is a decrease in optical density. As seen here, both the chelating and the conventional systems are subject to this mechanism, but the chelating system is less strongly affected because the chelate compounds, composed of two dye molecules and a transition metal cation, are relatively large and heavy and are thus more inhibited in their movement. A complex composed of dye/metal/ligand = 1/1/1 may exist together with the [dye/metal = 2/1] complex. However, the results of spectroscopic and elementary-analytical study have indicated

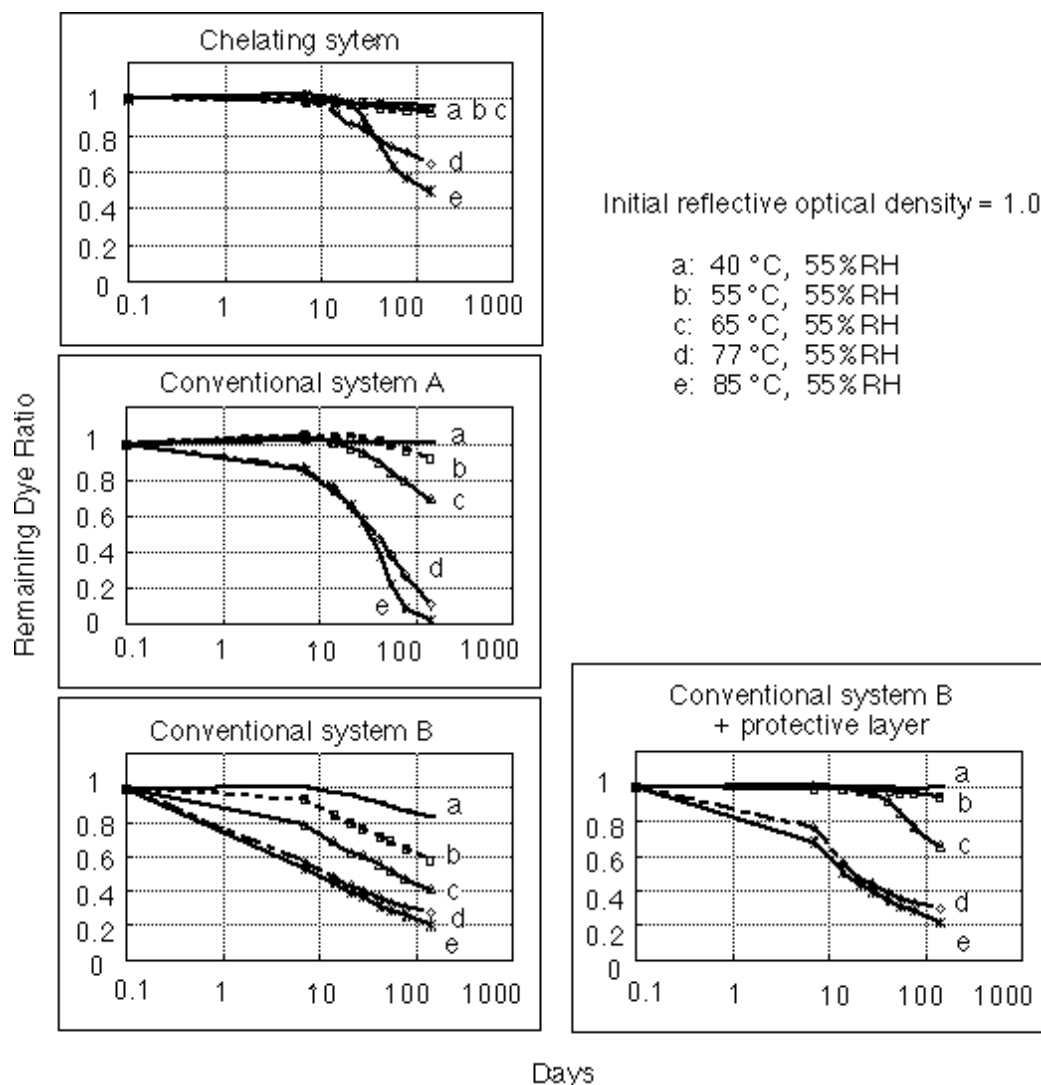


Figure 8. Color fading of printed images at high temperatures.

that the main part of the complexes is composed of dye/metal = 2/1. We report the results concerning the composition in Ref. 16.

Directly related to this inhibited movement is the chelate system's resistance to the degradation of image edges, as seen in Fig. 9. In conventional systems, a degradation of image edges is often observed when printed images are subjected to high temperatures. Like the accelerated color fading that occurs at temperatures above the glass transition temperature of the dye receiving layer, this degradation of image edges results from the lateral diffusion of dyes. However, this degradation is not observed in the chelating system. If the dye-metal complexes are insoluble in the polymer matrix of the dye receiving layer, the complexes are not expected to move easily. However, we have observed the complexes show relatively high solubility there. Accordingly it is valid to consider again the size and weight of the chelate compounds inhibit their movement in the dye receiving layer.

Beyond the superior light stability, resistance to image fading at high temperatures, and minimized degradation of image edges reported above, the chelating

system also showed performance better than or equal to conventional systems by such measures as image transfer to PVC plastic sheets, color fading caused by finger prints, and image fading in the presence of ethanol.

Conclusion

A chelating system for thermal dye transfer printing that produces chelate compounds in the dye receiving layer consisting of a set of azo dyes, a nickel cation, and a β -diketone ligand dramatically increased light stability, reduced image fading, and minimized the degradation of image edges. $\blacktriangle$

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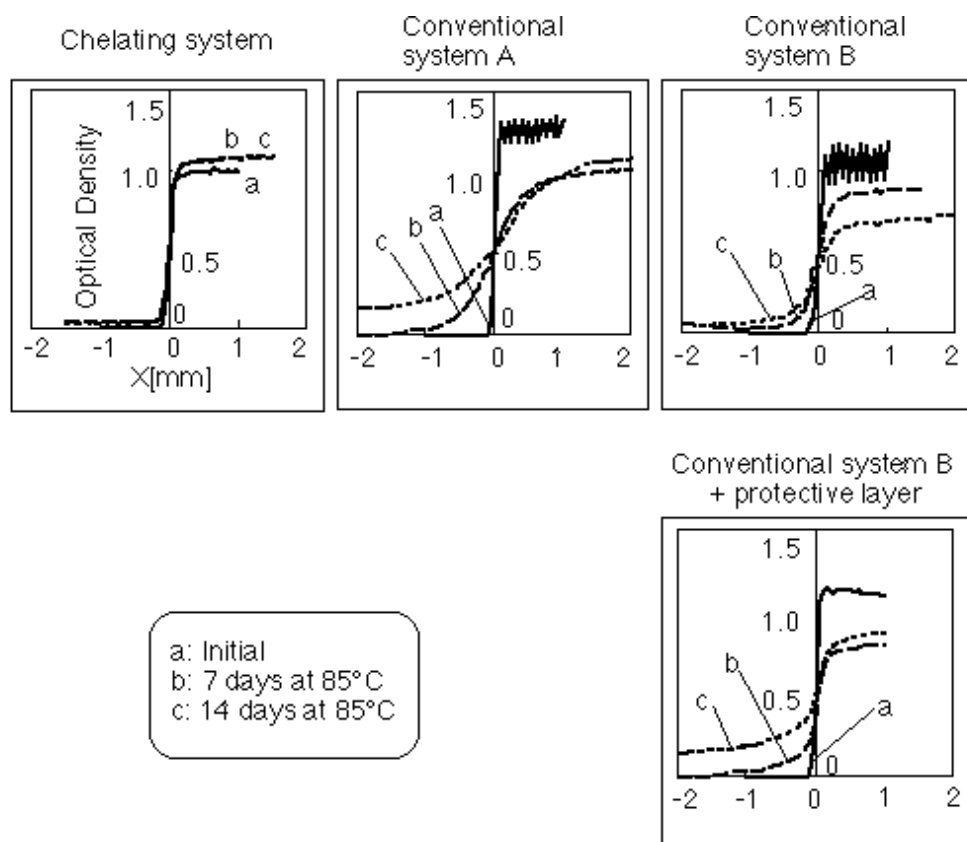


Figure 9. Degradation of image edges.

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