Materials for Providing High Print Quality and High Image Stability

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Abstract

In order to rival the quality of silver halide photographs, digital printing systems need to satisfy issues of high print quality as well as image stability. Our research and development efforts have focused on thermal dye transfer and ink jet printing systems, with extraordinarily good results in each system.

Discussion will focus on the chelate reaction between dye molecules and metal ions in the thermal dye transfer printing system, which has greatly improved the image stability issues, well in excess of original targets.

As for ink jet printing, attention was paid to improving the print quality. These efforts led to the world's first production of micro porous printing media with an RC-paper base. The combination of the printing media and dye inks brings the expected print quality together with other features such as quick drying cased by high ink-absorption speed, resistance to water.

Work on improving image stability in ink jet systems will also be discussed.

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. The other technology is ink jet printing with glossy printing media and dye inks.

Thermal dye transfer prints typically suffer from poor image stability when exposed to visible or ultraviolet light or subjected to heat. This fact is based on the inherent chemical properties of dye molecules. Many approaches have been taken to solve this serious problem including the employment of chemical reactions between reactive dyes and chemical agents in the dye receiving layer. We have taken notice of the chelate reaction between newly synthesized azo dyes and transition metal cation-providing compounds, and observed dramatically enhanced image stability under exposure to light and heat.[1-3]

In ink jet printing systems, the improvement of print quality has recently been one of the most interesting subjects. When plain paper is used for an ink receiver, ink penetrates into the space among fine cellulose fibers. Since the cellulose fibers usually wind around each other at random, the direction of the ink penetration is not controlled and consequently an ink droplet can not create real circle on the paper. This phenomenon is known as “feathering” and leads the degradation of print quality.

On the other hand, some glossy media coated with special ink absorptive layers can provide very high print quality. Mixture of silica particles and poly(vinyl alcohol), abbreviated to PVA, is a typical composition of the ink absorptive layers. Alumina is also used instead of silica. Swellable materials such as gelatin are also used for the ink absorptive layers to get high print quality.

We have developed micro porous ink jet printing media with an RC-paper base. The ink absorptive layers contain silica particles and PVA. We will explain about this media in more detail in this paper.

Improving the image stability of ink jet prints is the most urgent matter to be solved. We have dealt with this subject in terms of the use of pigmented inks. Metallic shining appearance or bronzing phenomenon at an area of high optical density and lack of gloss uniformity are typical faults of pigmented-ink images. We have developed the micro porous printing media targeted specially to pigmented inks and been able to find the clues to overcoming these image faults.

Thermal Dye Transfer Printing

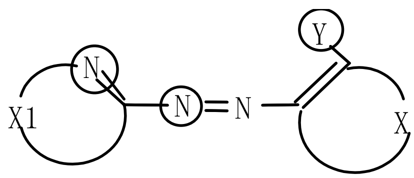
The following efforts have been made to improve the image stability by many R&D people: (1) the addition of a protective layer over the dye receiver sheet,[4] (2) the addition of UV-light-absorbing agents and anti-oxidizing agents to the dye receiving layer,[5] (3) the addition of dye adsorbents to the dye receiving layer,[6] (4) the hardening of the dye receiving layer after thermal printing,[7] and (5) the employment of chemical reactions between reactive dyes and chemical agents in the dye receiving layer.[8] We have examined (5) and focused on the chelate reaction.

For the dye donor sheet, a PET film substrate was used, with a thin backing layer to prevent sticking against the thermal heads. 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 since the whiteness and touch of each are similar to photographic paper. We chose to use synthetic paper because 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 TiO_2 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.

All of the metallizable dyes and metal cation-providing compounds were synthesized in our laboratory. The matters concerning the synthesis was described in a previous paper.[9]

Figure 1 shows the fundamental structure of the metallizable dyes. On the analogy of metal complexes of ortho-hydroxyazobenzenes, the chelate sites are expected to be located as shown in Fig. 1.



○ = chelate site
X1,X2 = aromatic carbocyclic and/or heterocyclic nuclei

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

Figure 1. Fundamental structure of metallizable dyes and metal cation-providing compounds.

Next, we examined the effect of heat and humidity upon the stability of printed image. 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. Image blur resulted from dye migration has not been observed in the chelate system as shown in Fig. 2.

The lightfastness of printed images was also evaluated by measuring the optical density after being irradiated with a xenon lamp for prescribed time. The results are shown in Fig. 3.

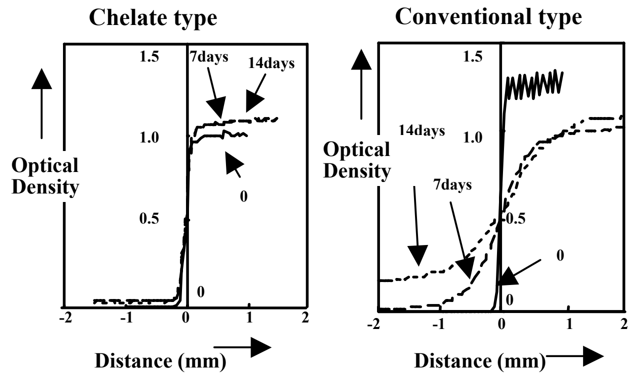


Figure 2. Image blur. Printed samples were kept at 85C.

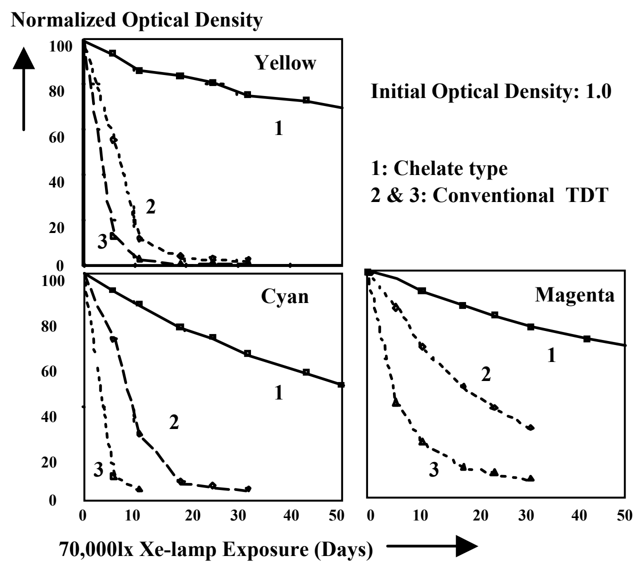


Figure 3. Color fading of printed images when exposed to 70000lx-Xe lamp.

Ink Jet Printing

Print quality of ink jet printing has improved markedly due to high-glossy printing media and high-performance printers. However, the image stability of printed images has not been improved so far. The relation between print quality and image stability is shown in Fig. 4.

Both print quality and image stability have to be upgraded from the present state especially when we apply ink jet printing systems to a photofinishing market. There are two routes to make the both to go together. The first one uses dye-based inks and needs reinforcement such as covering with a lamination film after printing. Over-coat of a resin layer on the printed surface is also useful to increase the image permanence. However, these actions may bring a new issue of raising costs. Pigmented inks are used in the second route that is our interest in this paper.

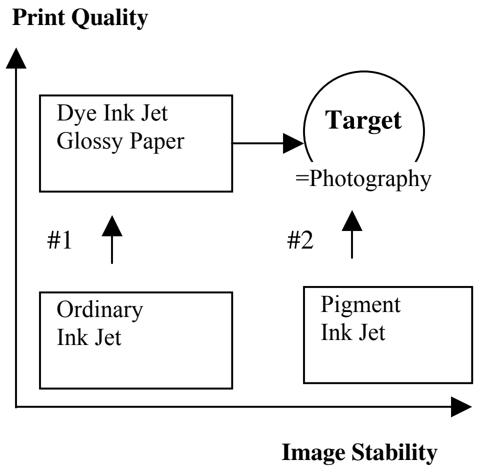


Figure 4. Situation of ink jet printing in terms of print quality and image stability.

We will describe below our developed micro porous ink jet media (#1 in Fig. 4) and an effort to improve the print quality of pigmented-ink prints (#2 in Fig. 4).

Micro Porous Ink Jet Printing Media

Micro porous ink absorptive layers consist of silica particles and PVA as a binder. Original silica particles, around 10 nm in diameter, gather and form secondary particles of several tens nm. These particles are mixed with PVA and bonded together with each other through the PVA that can react with silanol groups being on the surface of silica particles. Inks can penetrate easily and quickly into the space among the silica particles (Fig.5). As shown in Fig.6, micro porous printing media absorb inks rapidly. The difference in ink-absorption speed between micro porous media and swellable media is significant.

An image dot based on an ink droplet is affected by the characteristics of printing media. As seen in Fig. 7, a real circle is formed on the micro porous media even if the dot is put on the portion that has been printed by other color inks in advance. These characteristics leads excellent print quality.

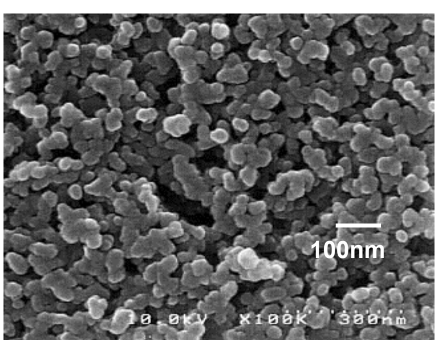


Figure 5. Microscopic photograph of the surface of the micro porous ink absorptive layer.

Our developed micro porous media with an RC-paper base have the following features:
- Quick drying cased by high ink-absorption speed.
- Good dot shape results in excellent print quality.
- Resistance to water and oil.
- Printability with pigmented ink.
- Good whiteness.
- No cockling.

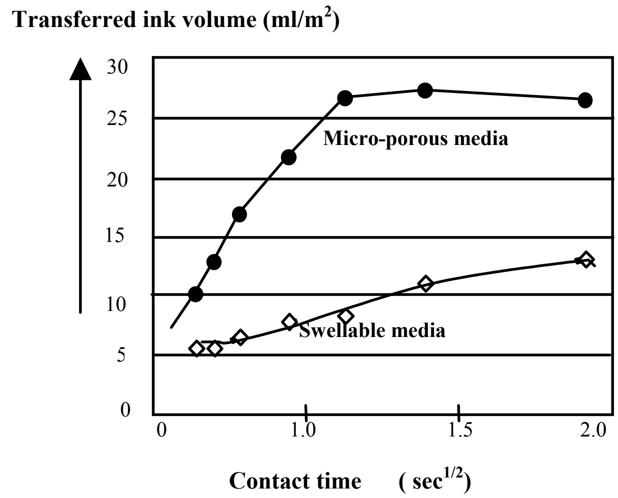
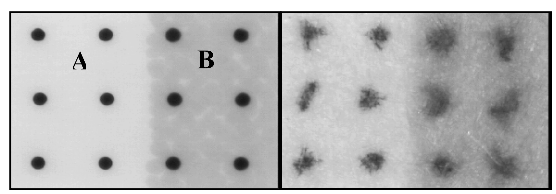


Figure 6. Speed of ink absorption. By Bristow method.



Micro porous media Plain paper
A: Fresh media surface.
B: Dots were printed on yellow solid image.

Figure 7. Dot shape.

Improvement of Print Quality of Pigmented Ink Prints

Printing with pigmented inks brings some strong points and also some weak points. Typical strong points are excellent image stability and no image blur even if printed images are kept under the circumstance of high humidity and high temperature. On the other hand, weak points are metallic shining appearance or bronzing, lack of gloss uniformity, weakness in scratching, and coarse grain impressions of images.

Since pigment particles have the ability to aggregate, the diameter of an image dot printed with pigmented ink is generally smaller than dye-based ink as shown in Fig. 8.

This fact relates to the coarse grain impressions of images. Accordingly it will be required that print heads are changed from dye-based inks to pigmented inks to obtain high print quality.

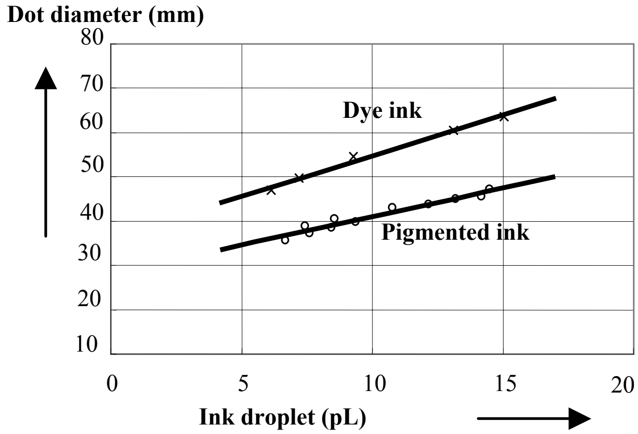


Figure 8. Dot size difference between dye inks and pigmented inks.

The physical and optical properties of printed surface are determined by the state of pigment particles aggregated there. Bronzing phenomenon, lack of gloss uniformity, and weakness in scratching are related to the state of pigment aggregation.

In order to change the state of the surface printed with pigmented inks, we have tried to set a special layer on a silica-micro-porous layer and processed the over-coat layer with heat and pressure after printing. The results have been affected by the composition of the over-coat layer as well as the conditions of processing.

Through the work described above, we have come to the conclusion that both print quality and image stability can be satisfied together with ink jet printing systems using pigmented inks.

Summary

1. Chelate reaction has been applied to a thermal dye transfer printing system. This innovative action has brought noticeable improvement to image stability.
2. Micro porous ink absorptive layers consisting of silica and PVA have been coated on an RC-paper base. These ink jet media can produce excellent print quality.
3. We have shown the possibility to manage both of image stability and print quality by using new micro porous printing media with a special layer for pigmented inks.
4. The products based on our results are now on the market: “Konica Photo Chelate” for thermal dye transfer and “Konica QP” for ink jet.

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Biography

Takao Abe received his doctoral degree in industrial chemistry after completing the graduate course at the University of Tokyo in 1976. He joined Konica Corporation that same year.

Dr. Abe's main activities at Konica over the past 27 years have been in the science and technology of imaging materials.

He has left Konica this year and now is a full professor of Shinshu University, a national university of Japan.

He is also a Board Member and Vice President of the Society of Photographic Science and Technology in Japan and is Chief of NIP Technology Committee, a subcommittee of Technical Committee of the Imaging Society of Japan. Among his many honors and accomplishments, he has been awarded "The Prize of Articles" and the "Technology Award" by the Society of Photographic Science and Technology of Japan in 1977 and 1998, respectively. He is also the recipient of the "Society Award" of the Society of Synthetic Organic Chemistry in Japan in 1998.