# **Recent Developments in Thermal Dye Transfer Prints**

Masafumi Hayashi and Kazuya Yoshida, Information Media Supplies Laboratory, Dai Nippon Printing Co., Ltd. Okayama, Japan

#### **Abstract**

In recent years, thermal dye transfer technology has been recognized as a convenient method to print digital photographs. This technology produces high quality images that are comparable to silver halide.

In order for thermal dye transfer technology to be as widely used as silver halide to print digital photographs, further development of high quality print media is required. In particular, high image quality, long print durability and high speed print systems are needed in the world-wide market.

In this paper, we mainly introduce the development of key improvements to the donor material, with an emphasis on the thermal transfer dye as well introduce new print surface finishes. Furthermore, we also report the results of image durability tests that were conducted using various kinds of digital print material.

#### Introduction

We have developed thermal transfer media and systems for over two decades and provided various applications world wide as shown in Figure 1.

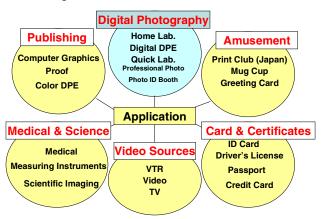


Figure 1. Applications in Thermal dye transfer system

In the past years, due to the rapid penetration of digital cameras and mobile phones with mega-pixel CCD cameras, the opportunity to take digital photographs has increased enormously. This means we have increased opportunities to print digital photographs to physically store the image, as compared to only storing the memory in the human brain. The ability to print photographs from digital data anytime, anywhere is being developed to be enjoyed by many people. Thermal dye transfer systems are dry, which means they do not use wet chemistry, and have the lower operating cost when compared to silver halide systems. Furthermore, thermal dye transfer systems are basically maintenance-free. They are most often used in photo kiosks, but are growing in use in mini-labs and at home in the world.

Along with increased usage, the technical requirements for thermal dye transfer media have increased as well. Typical examples of such demands are:

- High Print Quality
- High Speed Print (= High Sensitivity Media)
- Various Surface Finishes (Gloss, Semi-gloss, Matte)
- Long Print Durability

We have used these requirements for our media development and we introduce our key improvements below.

## Approach of donor development

In thermal dye transfer systems (Figure 2), due to the variable density method in the continuous tone, high print quality, similar to that of silver halide is generally obtained.

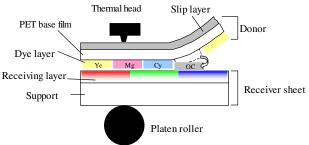


Figure 2. General Thermal dye transfer system

In addition to the essential recording principle, new thermal dyes have also been developed to accomplish high image quality, high sensitivity and high durability of digital prints. Various dyes, for example, pyridone-azo type dye and anthraquinoe type dye from the textile printing, dicyano-styryl type dye and benzene-azo type dye from plastic colorings, pyrazolo-triazole type dye and indophenol type dye from couplers of silver halide method, have been used as key components in the development. Furthermore, to improve the light stability in digital prints, we have studied the substituent group effect in various colorants. Figure 3 and 4 show representative results.

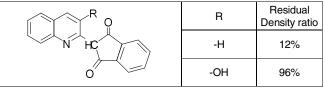


Figure3. Study of Quinophthalone type

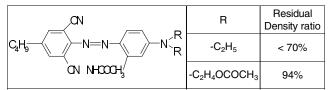


Figure 4. Study of Benzene-Azo type

In Figure 3, the effect of intra-molecular hydrogen bond is confirmed in the quinophthalone type dye of yellow. In Figure 4, the oxidation-reduction potential is optimally adjusted in the benzene-azo type dye of magenta. It is compared the residual optical density after transferring to the receiver under xenon light irradiation.

Next, thermal dye transfer donor has an overcoat layer in the final panel. After transferring dyes to the receiving layer on receiver sheet, the dyes are perfectly covered on the receiver sheet by the overcoat transfer. This is a great advantage for photographs produced using thermal dye transfer systems as compared to inkjet systems. It prevents image degradation from various external factors (i.e. active gas such as ozone, SoX and NoX, fluorescent, sunlight, water, finger mark, moisture, etc.). Since a UV absorption agent is added in the overcoat layer, resistance properties against the fluorescent and sunlight are also increased.

Furthermore, an adhesive/barrier layer, which bonds the dye layer with PET base film, has also been developed to make a contribution to high speed print.<sup>2,3</sup> By using new adhesive/barrier layer as the primer, about 30% of the dye transcription efficiency is strengthened. Expressed in another way, it enables printing with lower energy.

## **Approach of Various Surface Finishing**

In the silver halide marketplace, it is well known that there are a variety of surface finishes (high-gloss, semi-gloss, matte and silk-like). Different print surfaces are especially important for portrait photography and when producing large-size prints, such as 8x10. The semi-gloss surface finish is much preferred in US and Europe. In order to offer thermal dye transfer as an alternative to semi-gloss prints produced on silver halide, we have developed new surface finishes technology. In this report, we introduce this new approach for semi-gloss finishing.

# Semi-gloss surface finishing

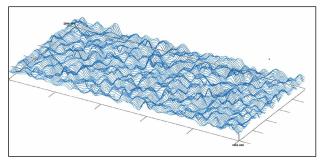


Figure.5 Target of Semi-Gloss Surface(Silver Halide Photograph)

Figure 5 shows our target roughness in 3-dimensions. This figure shows the roughness data from a semi-gloss photograph using silver halide.

In a thermal dye transfer system, it is not possible to use a rough receiver like this, because close contact between the thermal head and the receiver sheet surface is very important to achieve a high quality print. As a result, we thought of using an embossing process using a specialized device after printing to the smooth receiver sheet. In such a process, a special engraving embossing roller with high temperature and pressure is used to enhance the processing capability. Print sizes, ranging from 4x6 to 8x12, can be accommodated by this system. Figure 6 shows the results of using this new embossing process.

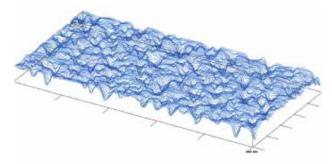


Figure 6. Semi-gloss surface finishing in Thermal dye transfer system

Next, we confirmed the durability of the prints after using the embossing roller (Figure 7). For our long-run test, we embossed many 4x6 size prints continuously. After every one thousand 4x6 sized prints, an 8x10 sized print is embossed and the appearance is checked by naked eye. In parallel, the surface glossiness of Gs60 degree is measured and compared with the initial data. In this report, we finished the surface glossiness evaluation after processing 20,000 prints and, at the present, we do not have a problem. We plan to conduct further long-run tests until we evaluate 100,000 prints.

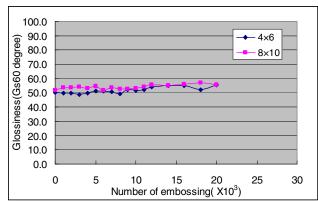


Figure 7. Durability test in embossing process

Regarding another durability tests of prints after embossing process, ie, plasticizer resistant test, finger mark test, water and alcohol resistant test, ozone resistant test and fluorescent test, same durability as the reference(Un-embossed print) is showed.

We can now offer three surface finishes (high-gloss, semigloss and matte) on thermal dye transfer system. Depending upon the customer's requirements, we can provide the optimum surface finish in the market.

## Approach To Improve Print Durability

The marketplace believes that silver halide prints are the most durable. It is imperative for thermal dye transfer and another technology to have comparable durability to silver halide for long term success. Our thermal dye transfer media has been continuously improved to increase durability. For example, we have improved dyes as described above, introduced the overcoat layer, made chemical improvements in the overcoat, etc. We will introduce our further efforts to improve image durability in this section.

#### **Experiments**

7 gradation color image(YMC, RGB, 3Bk) is printed in each method, as the evaluation sample.

A-D: Thermal dye transfer print E&F: Silver Halide print G&J: Inkjet print, pigment type H&I: Inkjet print, dye type

Figure 8 shows the current ability of thermal dye transfer media compared to other media in office environment.

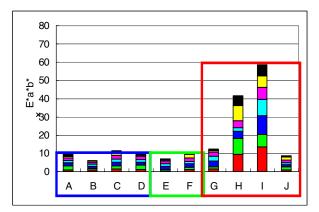


Figure 8. Delta E change in office environment

In Figure 8, each sample was displayed on the wall in the office environment without a glass or a plastic cover (ie, in the bare state) for one year. The exposed conditions are below.

Fluorescent illumination: 700 lx in the average of working time Ozone concentration: 10 ppb

Environment : 25 degree C, 50 %RH in the average

In Figure 8, the vertical scale is the accumulated value which added Delta E in each color. Delta E is measured the change from the initial value in Optical Density 1.0.

Next, we studied which environmental factor was dominant when the printed image became discolored. We focused the impact of Ozone gas, Fluorescent light and Humidity which exists in the office environment in general. From Figure 9 to 11, the Delta E change for each experiment is shown. When one factor is focused, another factors is possible omitted the impact.

Figure 9 is the accelerated fluorescent test result. The experiment conditions are below.

Illumination intensity and time: 9,000 lx and 400 hrs

Environment : 37 degree C Ozone concentration : < 2ppb

The total illumination intensity corresponds about one year of exposure.

(It is calculated at the rate of 6000 lx per day.)

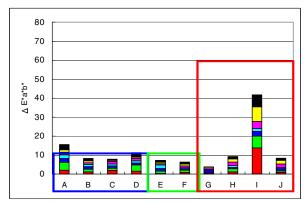


Figure 9. Delta E change under fluorescent irradiation

Figure 10 is the accelerated ozone resistant test. The experiment conditions are described below.

Exposure concentration: 40 ppm\*hrs

Environment: 25 degree C, 50 %RH in the dark condition The accumulated 40 ppm\*hrs is hypothecated one year exposure.

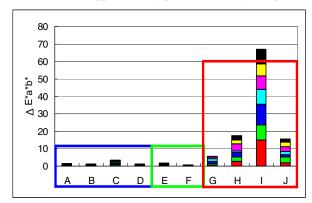


Figure 10. Delta E change under high concentration Ozone

Finally, In Figure 11, the humidity influence is examined. The experiment condition is described below.

Environment: 40 degree C, 90 %RH

Storage condition: 336 hrs in the dark condition

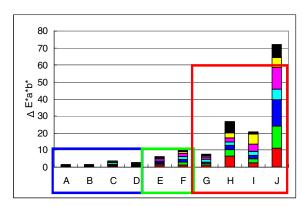


Figure 11. Delta E change under high humidity

#### Results

As shown in figure 8, the discoloration of thermal dye transfer prints is very small even after one year in the actual exposure test without a glass or a plastic cover. Furthermore, it also shows equivalent performance to silver halide.

When compared Figure 8 and Figure 9-11 regarding thermal dye transfer prints, we understand that its discoloration is affected by ozone gas. The moisture impact is also same. It shows the overcoat layer described above is very effective. Stated another way, thermal dye transfer prints is just affected by the fluorescent light. Depending on some differences in each discoloration, A-D of Figure 9 shows a correlation with that of Figure 8, similar to silver halide photographs.

We are now checking the impact of reciprocity failure in the accelerated fluorescent test.

In contrast, in inkjet prints, when compared Figure 8 and Figure 9-11, we understand its discoloration isn't affected by

either factor only. In the accelerated test assumed the real exposed environment, various factors should be considered.

#### Conclusion

We have discussed next generation digital media and systems to replace silver halide photographs. The development described in this report was designed to make thermal dye transfer a viable replacement for silver halide. With our thermal dye transfer technology, we can produce various kinds of print surfaces, similar to silver halide. This is very important to our customers. Regarding image durability, the test results for one year of typical office exposure was shown in this report. It shows that digital prints produced by thermal dye transfer media have no discoloration when displayed without a glass or a plastic cover. This is also important to our customers. Thermal dye transfer media and systems the best choice in digital prints from various aspects.

## References

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### **Author Biography**

Masafumi Hayashi received his master's degree in industrial chemical science from Tokyo Metropolitan University in 1991. After graduation, he has been working on the media development in Thermal transfer method and Electro photography at Dai Nippon Printing.