New Thermal Dye Transfer Media for Digital Photo Usage

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Abstract

Recently, the mega-pixel Digital Still Camera (DSC) has become very popular in Japan. This has led to a demand for a digital hard-copy method with the quality of a silver halide photo.

One possible printing method that could be used for this application is thermal dye transfer technology. Desirable features that speak to this technology's suitability include its high image quality and its quick drying process. Though the image quality of thermal dye transfer printing is as high as the silver halide photo, one of the disadvantages is its durability. Once the image has been laid down on the surface of the dye-receiving layer, it is necessary to over-print a protective layer to give durability to the image.

A newly developed protective layer improves light stability to a level equal to that of the silver halide photo; in particular, it reduces "catalytic fading" of the cyan dye. Additionally, improved stiffness, surface gloss and surface color meet the demand that the new receptor paper be cosmetically more similar to conventional photo paper (RC paper).

Introduction

The popularity of the Digital Still Camera has increased tremendously since last year. In 1998, over 3.2 million DSC's were shipped worldwide, and this number is expected to reach more than 4 million in 1999. Its image quality has steadily been improved by increasing the number of pixels of the CCD. This is especially true in Japan, where it is estimated that nearly half of the DSC's shipped in 1998 had CCD's of over 1 million pixels. This year, the movement towards higher image quality has quickened: many manufactures have launched DSC's which feature CCD's containing over 2 million pixels, with a price tag of around $8000.[1]

In addition to the above trends, serious attention is being paid to thermal dye transfer technology as a highly suitable digital hard-copy method for DSC. It has been maintained that the image quality, originating from the generally-used 1.3 million pixel DSC and printed by a thermal dye transfer printer with a resolution of 300 dpi, is as high as a silver halide photo (image size: 3in. × 5in.).[2]

In this report, we would like to introduce a newly developed thermal dye transfer media which has better durability than ever before, and which will give resolution compatible with the main output of DSC. With its existing advantages, we believe that thermal dye transfer printing will be able to take over from silver halide photography in this field.

Ink Ribbon

Dye Layer

In the thermal dye transfer printing method, panels coated with the process colors are printed in the following order: Y, M and C. The dyes then mix together in the receiving layer. In general, disperse dyes, which are used in thermal dye transfer printing, have poor light-stability. Furthermore, the mixing of the different dyes accelerates light fading. This phenomenon is called "catalytic fading", and is well known in the field of textile dyeing, where the topic has generated many reports.[3] Among the dyes which are used in thermal dye transfer printing, cyan dye (e.g. indophenol dye) is generally the weakest. Therefore, in thermal dye transfer printing, catalytic fading is often seen when neutral gray images change to reddish images when exposed to light.

After reviewing available options to reduce the catalytic fading seen in the cyan dye, it was decided that the dye should be augmented with a new cyan pyrazolo-azomethine dye. The dye-formulation of the other colors was also reviewed.

Over Protect Layer

The Over Protect Layer (OP layer) is thermal transferred over the receiver layer by the thermal print head after the image is formed by the Y,M,C printing. Besides protecting the image, transference of the OP layer improves the gloss appearance of the image by flattening the surface of the receiver layer and thus reducing diffused reflection. Therefore, the optical density of the dark potions of the image is increased and the dynamic range is expanded.

The newly developed OP layer is constructed of an anti-plasticizer layer and a heat seal layer. The anti-plasticizer layer protects the image from fingerprints, plasticizers, humidity, oxygen and others. It is made from a clear acrylic resin. The heat seal layer is fused to the receiver layer with heat, and makes light stability even better. It consists, mainly, of UV light absorber and a newly developed condensation resin.

In the thermal dye transfer printing method, dyes transferred and diffused into the receiving layer are not chemically bound to the thermoplastic resin, which forms the receiver layer, but are physically bound only by van der Waals forces. Therefore, when the OP layer is transferred, the already-printed dyes are thermally re-diffused into the receiver layer and also diffused into the heat seal layer of the OP layer. Taking advantage of this phenomenon, light stability was improved by the use of a modified heat seal resin with an affinity for the cyan dye.

Receiver Paper

Base Sheet

The base sheet of the receiver paper is constructed by laminating micro-voided film, which possesses superior heat insulating and cushioning properties, to coated paper. The receiver paper was constructed to give it the appearance and quality of the resin-coated paper that is ordinarily used as the base sheet for silver halide photo imaging. This was achieved by developing a high-gloss micro-voided film and adjusting the thickness of the coated paper. Furthermore, to adjust the whiteness of the paper's surface, an intermediate layer between the receiver layer and the micro-voided film was added. The intermediate layer consists mainly of binder resin, titanium dioxide and fluorescent whitening dye. In general, the fluorescent whitening dye has poor light stability and can cause catalytic fading. To prevent migration of the fluorescent whitening dye to the receiver layer, which mainly consists of hydrophobic thermoplastic resin, the binder resin and fluorescent whitening dye chosen for the intermediate layer are both hydrophilic.[4]

Receiver Layer

The receiver layer consists mainly of a dyeable thermoplastic resin and a releasing agent. For the dyeable thermoplastic resin, vinyl chloride-vinyl acetate copolymer was chosen because of its dyeing properties with dispersion dyes. Modified dimethylsiloxane was chosen as the releasing agent. The proportion of phenyl groups added and the molecular weight were optimized to give the best releasabilities of the dye layer and the adhesion properties of the OP layer.

Durability

Various evaluations of the durability of the thermal dye transfer media have been carried out using comparison with silver halide photo and other digital color printed samples.

The following printed samples are used for this evaluation.
1) Samples printed by thermal dye transfer
2) Silver halide photo (Konica QA paper P7 type)
3) Samples printed by Ink Jet
4) Samples printed by Thermo Autochrome
5) Pictography
6) Samples printed by Cycolor

Durability to Water, Fingerprint and Plasticizer

The half-gray section of the printed sample (initial optical density: 0.3 to 0.5) was checked by sight for degradation in image quality for each of the following cases:

1. Water Resistance

Scratching 50 times back and forth across the image with an applicator soaked in water or ethanol.

2. Fingerprint Resistance

Putting a fingerprint on the image and leave it one week at room temperature.

3. Plasticizer Resistance

Scratching 50 times back and forth with a plastic eraser.

The results are shown in Table 1.

Table1. Durability to water, fingerprint and plasticizer

Printing method	Water	Ethanol	Finger-print	Plasticizer
Thermal Dye Transfer	Good	Good	Good	Good
Silver Halide Photo	Good	Good	Good	Good
Ink Jet	Poor	Fair	Fair	Good
Thermo Autochrome	Fair	Good	Good	Good
Pictography	Fair	Good	Good	Good
Cycolor	Good	Good	Good	Good

By using the OP layer, the durability of printed samples using the thermal dye transfer method has been much improved. Furthermore, the table shows that, when printing using this method, there is good resistance shown towards fingerprints and plasticizers, both of which caused problems in the past.

Stability to Heat and Humidity

The heat resistance and humidity resistance tests were carried out using a printed sample, which had a gradation pattern of yellow, magenta, cyan and gray.

Heat resistance and humidity resistance tests were conducted by measuring the change of color from an initial optical density of around 1.0. Samples were then:

a) left for two weeks under conditions of 60ºC, 30%RH in the case of the heat resistance test; and
b) left for one month under conditions of 40ºC, 90%RH in the case of the humidity resistance test.

The result is shown in Fig. 1 and Fig. 2.

On inspection after the tests, the thermal dye transfer and silver halide photo samples showed no apparent change from their starting appearance. On the other hand, serious discoloration is seen on the TA and Cycolor printed samples in both test conditions. In addition, the TA and Pictography samples, which both use hydrophilic coloring material, show blotted images and serious damage.

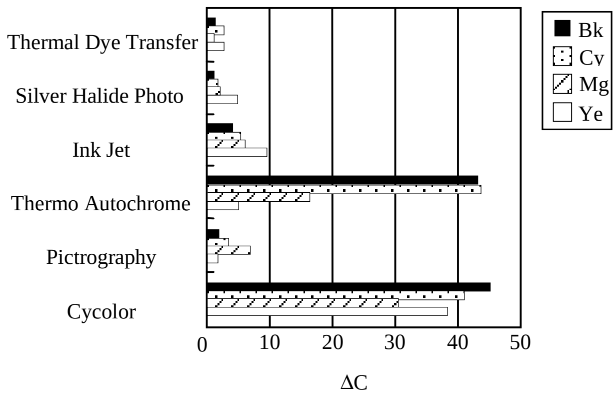

Figure 1. Heat Resistance (60ºC, 30%RH, 14days)

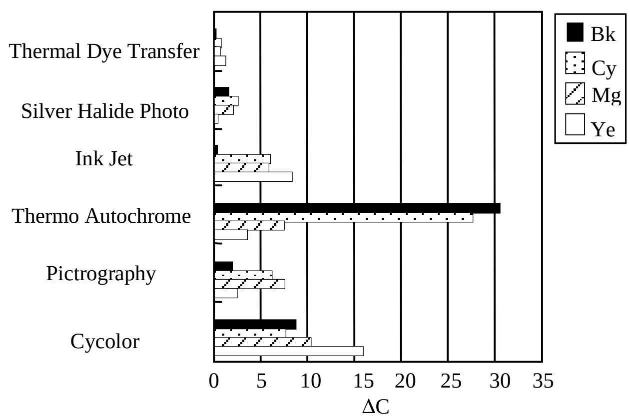

Figure 2. Humidity Resistance (40ºC, 90%RH, 30days)

Light Stability

An Atlas Ci 35 Fade-o-meter and a Fluorescent tube Fade-o-meter (Toyo Seiki Seisaku-sho, Ltd.) are used for light stability tests with each printed sample, which has a gradation pattern of yellow, magenta, cyan and gray.

The set-up of each piece of equipment is as follows:

[Xenon lamp exposure test]

Equipment: Atlas Ci 35 Fade-o-meter
Light Source: Xenon lamp (2,400-4,400W)
Light Intensity: 1.2 W/m^2 (at 420nm)
Illuminance: ca.1.1×10^5 Lux
*Black-Panel Temp. : 45º*C
*Chamber Temp. ; 25º*C
Chamber Humidity; 50%RH
Filters; Inner --- IR absorbing filter
Outer --- Soda lime glass
Operation; continuous (no dark cycle)
Exposure; 400 kJ/m^2

[Fluorescent tube exposure test]

Equipment: Fluorescent tube Fade-o-meter
(Toyo Seiki Seisaku-sho, Ltd.)
Light Source: Toshiba mellow white FL20SS-N/18
(Color Temp.: 5000K, 18W), 16 tubes
Illuminance: 1.5×10^4 Lux
Black-Panel Temp. : 50ºC
Chamber Temp. : 36~38ºC
Chamber Humidity: 20~25%RH
Operation: continuous (no dark cycle)
Exposure Time: 350 hrs.

The test conditions simulated by the Xenon Fade-o-meter are equivalent to 3 months' continuous sunlight exposure through a south-facing window. Assuming an average ambient illuminance of 500 Lux, 10 hours per day, the above test condition is equal to 5.6 years. Making the same assumptions with the Fluorescent Tube Fade-o-meter, the test condition is equal to approximately 3 years.[5] Fig. 3 and Fig. 4 (both shown below) show the discoloration of each printed sample from an initial optical density of around 1.0.

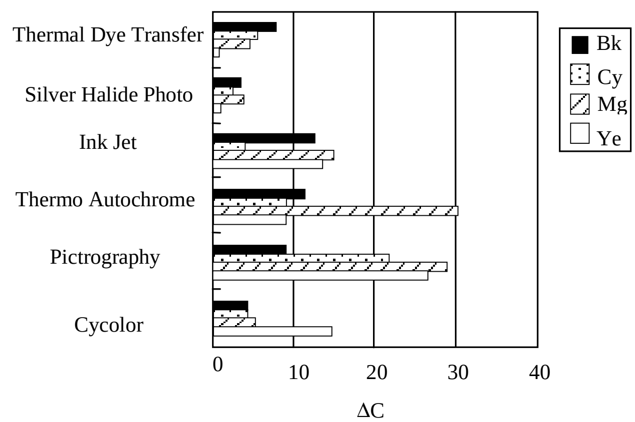

Figure 3. Light Stability (Xenon Lamp)

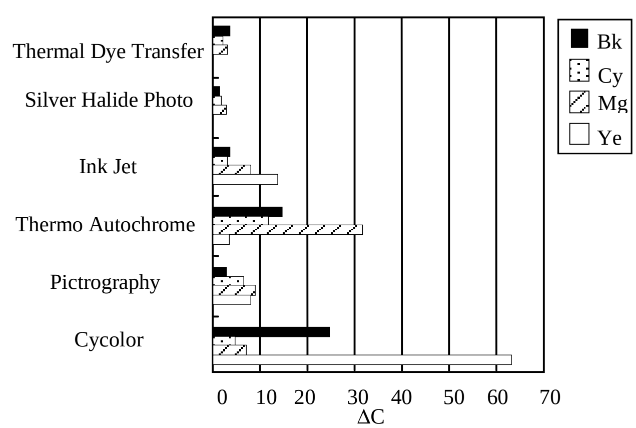

Figure 4. Light Stability (Fluorescent Lamp)

The thermal dye transfer printed sample method shows a good result when compared to the silver halide photo. If the light stability of a sample portrait is tested in the same conditions, the degree of discoloration is, on sight, almost the same as the silver halide photo.

The newly developed thermal dye transfer media has good light stability, as mentioned above. In comparison with previous thermal dye transfer media which utilized an OP layer, the degree of color change of gray-printed areas that tended to drift towards red is reduced by almost half. This improvement is mainly down to the new OP layer, which absorbs ultraviolet light and stabilizes all the dyes, especially the cyan. Figure 5 shows the result of an evaluation of the effect of OP layer printing on light stability.

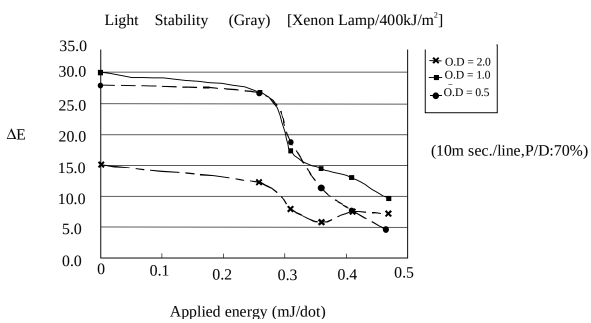

Figure 5. Effect of OP layer Printing Condition

It is obvious that light stability is largely dependent on the transferring energy with which the OP layer is printed, and that in order to actualize the superior propriety of this media, it will first be necessary to optimize the printing condition.

Conclusion

The development described in this report, to improve the durability and quality of thermal dye transfer media, was driven by the need to make available a digital photo media that would be able to provide a viable direct replacement for silver halide photo imaging. This media would also need to be able to be printed out easily from a digital input device such as DSC, while meeting the challenge of DSC's rapidly improving image quality. The paper's quality and appearance was improved with the addition of a newly developed glossy micro-void film. Furthermore, by optimizing the overall stiffness, a receiver paper was produced similar to the resin coated paper used as the base sheet of a silver halide photo. However, the paper's imaging properties were kept the same as before. With regard to the durability, much improvement has been made, especially in the area of light stability. This has been accomplished by applying a new cyan dye and using a newly developed OP layer. As a result of the various durability tests comparing thermal dye transfer printed samples with several other kinds of digital hard copy media, we have confirmed that thermal dye transfer media has the best durability, and it is almost equal to the silver halide photo.

References

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