The Development of High Quality TA (Thermo-Autochrome) System

Hirokazu Shimada, Toshiyuki Watanabe and Akira Igarashi Fuji Photo Film Co., Ltd. Fujinomiya, Shizuoka, Japan

Abstract

A direct thermal full color recording system named "TA" (Thermo Autochrome) was first developed in 1994.

The TA system creates high quality, continuous full color tone prints without any accompanying wastes such as an ink ribbon or an ink cartridge. This permits a simplified printer design and a highly reliable, maintenance free system.

We recently developed a new TA system which realized clearer, more expressive highlights, smoother gradation, glossier and higher speed image printing. Then the print quality is very close to look of usual photographic color prints.

As a result, TA system is now used in various printers for businesses, amusement centers and homes. It is also used to produce photographic color prints for highresolution megapixel digital cameras.

In this paper we will describe the technologies which brought on these improvements.

Introduction

A direct thermal full color recording procedure has advantages over conventional recording procedures, such as using a simple apparatus which requires almost no maintenance is more effective. These advantages result from the feature of a direct thermal paper which can generate color itself by synthesizing dye in response to heat. Therefore there is no need for ink toner or developing solution. In addition, the color image remains stable when it comes in contact with oil and plasticizer.

This is because TA paper synthesizes color itself and the color image of TA paper is formed within the microcapsule directly on the base paper with no transfer of coloring agents.

TA system has a lot of advantages and we have developed a new TA system (new TA paper and new TA printer) recently, so that the new TA system is used in a wider variety of fields.

Mechanism of Image Formation

A simplified cross-sectional view of TA paper is shown in Figure 1. The outermost layer is a heat-resistant protective layer. The heat-resistant protective layer is exists to protect the color forming layers from the thermal-head which changes to a high-temperature.



Figure 1. Simplified cross-sectional view of TA paper



Figure 2. Full color recording process of the TA system

Under that layer is a UV absorbent precursor layer. This layer exists to provide superior light stability.

The yellow color-forming layer is comprised of a microencapsulated diazonium salt compound, an organic base, and a coupler which react to form a yellow azo dye. The magenta color-forming layer is also comprised of a microencapsulated diazonium salt compound, an organic base, and a coupler which react to form a magenta azo dye. The cyan color-forming layer is comprised of a basic leuco dye and a phenolic compound developer which react to form a cyan dye.

Under the cyan color-forming layer is a low oxygen permeability layer. This layer exists to provide superior light stability, as well.

A full color print is obtained through a five-step process with the TA system as shown in Figure 2.

- (1) The yellow color forming layer reacts to low levels of thermal energy to generate the yellow portion of the image.
- (2) The entire print is exposed to a 420nm ultraviolet lamp, which decomposes the diazonium salt compound remaining in the yellow color forming layer.
- (3) The magenta color forming layer reacts to mid-range levels of thermal energy to generate the magenta portion of the image.
- (4) The entire print is exposed to a 365nm ultraviolet lamp, which decomposes the diazonium salt compound remaining in the magenta color forming layer.
- (5) The cyan color forming layer reacts to high levels of thermal energy to generate the cyan portion of the image.

The Heat-Responsive Micro Capsule

A diazonium salt compound is an indispensable color forming material for TA paper. It gives both thermosensitivity and light-fixable properties to the yellow and magenta color forming layers. However, a diazonium salt compound has a high reactivity so it tends to react with a coupler even at room temperature.

To avoid this undesired reaction, the diazonium salt compound is dissolved in oil and microencapsulated. The diazonium salt compound is isolated from the coupler and the organic base completely by the capsule wall which provides good stability over a long period of time. The wall material of the microcapsule in TA paper is poly(urea/urethane). It is known that a poly(urea/ urethane) wall becomes permeable above its glass transition temperature (Tg). When the color forming layer is heated above the Tg of the capsule wall, the coupler and the organic base instantly permeate the wall and react with the diazonium salt compound (see Figure 3).

The Technologies for High Quality Prints

The new TA system produces improved whiteness and gloss-finish characteristics in addition to clearer, more expressive highlights, smoother gradations and sharper contrasts.

The high whiteness of the new TA paper was developed in order to prevent stains from diazonium salt

compounds and to use the particular fluorescent whitening agent in the substrate. The concrete technologies will be described in the following sections.



Figure 3. Heat-responsive microcapsule

All components for color forming are included in the TA paper. And all components exist after the image formation process. The photodecomposition reaction of diazonium salt compound is very complicated and it forms a lot of compounds. As some photo-decompositions absorb visible rays, they don't become white perfectly after the photodecomposition reaction. We are calling these colored compounds "stains". It was very difficult to prevent all photocomposition reactions which formed stains, so we achieved the high whiteness by developing a new technology which is able to photocompose the stains again. Figure 4 shows the structure of model free radical initiators. That free radical and photodecompositions from diazonium salt react with each other to form colorless compounds. So, the coloring compounds in TA paper's background were prevented drastically because the diazonium salts and free radical initiators exist in the microcapsule together.

In addition, we realized higher whiteness without deteriorating the fixable sensitivity of diazonium salt by using a fluorescent whitening agent in the substrate (see Figures 5 and 6).



Figure 4. Structure of model free radical initiators



Figure 5. Structure of a model fluorescent whitening agent



Figure 6. Effect of the fluorescent whitening agent for reflectance spectrum of TA paper



Figure 7.Relationship between viscosity and temperature of PVA solution



Figure 8. Relationship between pigment particle size and gloss

The high gloss of the new TA paper was realized through the development of the new protective layer.

Gloss is under the influence of smoothness of surface. So we had to develop a new protective layer which stays smooth before and after printing without losing the printability of TA systems.

Before printing, smoothness of surface is decided by coating process conditions and drying process conditions. At the drying process, the higher the viscosity of coating solution for the surface layer, the smoother the surface of TA paper becomes. We realized the smoothness of surface by developing the new binder which has high temperature dependency on the viscosity (see Figure 7).

In addition, some pigments were used in the protective layer to provide mechanical strength for better printability. The usual pigments decreased the smoothness of surface. We discovered that by using smaller pigments, we were able to prevent the gloss decrease (see Figure 8).

Finally, the new protective layer is composed of new binder and small particle pigments for a smoother surface without losing good printability.

In addition, a new high-resolution thermal print system adds extra precision and accuracy, and prevents bleeding and over-saturation. These technologies and the over 300 dpi resolution enable an output quality that is very close to the look of 35mm color prints.

New Applications for TA System

As the new TA system has these merits it is now used in a wider variety of fields. One is a home use digital photo printer. The FinePix NX-500 is the printer which produces photographic color prints for high-resolution megapixel digital cameras (see Figure 9).



Figure 9.NX-500

In addition, the TA system is used for business opportunities. The Aladdin DigiCam Picture Center is a new digital camera output machine (see Figure 10). This system's controller reads most major digital camera memory media. Operating the system couldn't be easier. Simply insert the memory card in the slot, choose the images you want on the controller's screen, and press "Print". The system gives you a variety of printing options from single to multiple-frame (2, 4, 9, or 16) prints as well as index prints, and stickers. This printer takes only 35 seconds to print a 3R-size full color print.

Moreover the new TA system is used in amusement centers and convenience stores. They are good fields which make the most of TA system's characteristics.



Figure 10. Aladdin DigiCam Picture Center

Conclusion

The new TA system is able to create higher quality image printing. This was achieved by developing new TA paper and new TA printers. The new TA paper realized high whiteness and high gloss. The high whiteness of the new TA paper was realized to prevent stains from diazonium salt compounds and uses a particular fluorescent whitening agent in the substrate. The high gloss was achieved by introducing a new protective layer. And the new TA printers have the high-resolution thermal print system.

Because the print quality is very close to the look of usual photographic color prints, the new TA system is used in a wider variety of fields.

Now we are researching the next TA system which will achieve better preservation and better stability.

References

- T. Usami and A. Igarashi, The Development of Direct Thermal Full Color Recording Material, Journal of Inf. Recording, 22, 347-357(1996)
- (2) S. Sano, K. Minami, A. Igarashi and M. Takashima, New Light Stability Technology in TA Paper Proc. IS&T's PICS Conference, pp. 106(1998)

Biography

Hirokazu Shimada joined the Fujinomiya research laboratories of FUJI PHOTO FILM in 1984 after completing his BS degree in chemical science at Hiroshima University.

From 1984-1998 he did research on conventional thermal recording materials. Since then he has been working on full color direct thermal recording materials.