Alteration of reflection spectra of images from color-formers in a single-sheet thermal imaging system

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Abstract

In a single-sheet multi-layer thermal imaging system images are formed due to the transformation of colorless crystalline materials to colored amorphous forms, achieved by melting or dissolution in suitable solvents. The reflection spectra of the colored forms in printed images may vary due to the presence of other components, such as thermal solvents, polymeric binders required for imaging, and can cause undesirable color combinations in printed images. Such variations may be the results of aggregation of the colored amorphous forms, or formation of different colored forms from the same colorless crystals due to a change in the mechanism of reaction. Addition of appropriate components to the imaging systems can alter the spectra of the printed images to make them suitable for improved image quality.

Introduction

A direct thermal system, described in Figure 1, consists of three dye layers coated on a single sheet [1]. The color-forming layers are separated by thermal insulating layers. Full-color images are generated by optimizing the duration and intensity of energy applied to each layer. Amorphochromic materials, which are colorless in crystalline form, but are colored in amorphous form, are used in these systems [2]. The change occurs during thermal imaging process, as shown in Figure 2.

Thermally resistant topcoat
High melting color-forming layer
Thermally insulating layer
Intermediate melting color-forming layer
Thermally insulating layer
Low melting color-forming layer
Substrate

Figure 1*.Structure of a direct thermal printing medium*

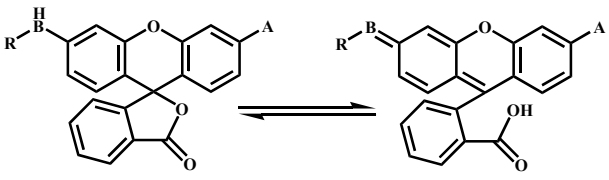
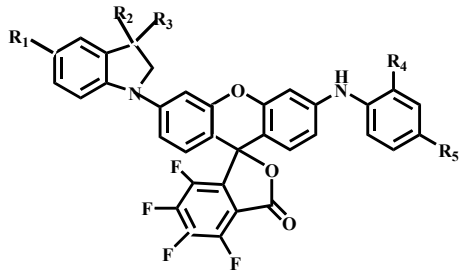


Figure 2. *Colorless and colored forms of an amorphochromic color-former*

The temperature of color formation is the temperature at which the crystalline color former is converted to an amorphous form, which may be through melting or dissolving in suitable thermal solvents (TS). These thermal solvents are required to melt in the temperature ranges optimum for the imaging of each of the layers in which the color formers are placed. In some cases low levels of developers (D) are included with the color formers and thermal solvents for facilitating the color formation under the required imaging conditions. Several amorphochromic color formers of varying melting temperatures have been tested in different layers of the imaging system. However, the additives required for modulating melting temperature of an amorphochromic material can change the spectrum of the printed images due to aggregation of the transformed color formers, or reaction with other components present in the imaging or adjacent layers. Addition of various types of materials to the combinations of color formers can decrease or eliminate such undesirable color formation, by changing the aggregations or decreasing the reactions leading to undesirable colors. A few examples of such combinations are described in this paper.

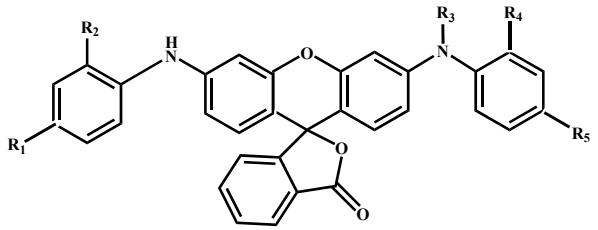
Experiments

The general structures of cyan, magenta and yellow color formers used in these experiments are shown in Figures 3A, 3B and 3C, respectively. The types and positions of the substituents were selected for achieving the required chromophores and melting temperatures of the color formers. The thermal solvents used for modulating melting temperatures of the color formers were substituted aromatic ethers, as shown in Figure 4. The developers used were substituted phenols or non-phenolic substituted sulfonylureas.



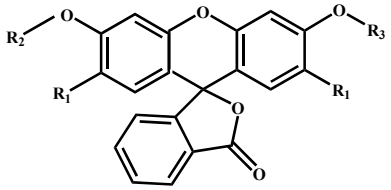
R_1, R_2, R_3, R_4, R_5= H, alkyl or alkoxy

Figure 3A. *General structure of cyan amorphochromic color-formers*



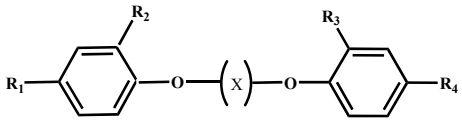
R_1, R_2, R_3, R_4, R_5 = H, alkyl or F

Figure 3B. *General structure of magenta amorphochromic color-formers*



R_1, R_2, R_3= H, alkyl or aryl

Figure 3C*. General structure of yellow amorphochromic color-formers*



R_1, R_2, R_3, R_4 = H, alkyl or CN; X = H, alkyl or aryl

Figure 4*. General structure of thermal solvents*

Each of the color formers and their combinations with additives was tested individually as monochromes. The color formers, thermal solvents and developers were dispersed in water using non-ionic surfactants. Coating fluids were prepared by mixing required amounts of the dispersions with a polymeric binder. Fluid for thermally-resistant topcoats contained a meltable lubricant and colloidal silica with polyvinyl alcohol as the binder. The fluids were coated on an opaque substrate, such as a voided, biaxially-oriented polypropylene, using Meyer rods. The coatings were imaged by using a standard type thermal printhead for monochrome prints such as one manufactured by Toshiba, model no. F3788A, 1890 ohms. The reflection spectra of the prints were recorded using a Gretag SPM50 densitometer. The conditions for the measurements were: illumination = D50, observer angle = 2^o, density standard = ANSI A, reflection standard = white base, and no filter. The reflection spectra of the printed images were recorded where the reflection density of the corresponding color was close to 1. For proper comparison each spectra was normalized at lambda max.

Results and Discussion

Figure 5 shows reflection spectra, normalized at lambda max, of a cyan color former C, without any additive, suitable for the top layer of the imaging system, and in presence of additives for the middle and bottom layers. The results indicate significant spectral shift in presence of the additives TS-2 and D-2 for bottom layer, compared to the effects of the additives TS-1 and D-1, present in the combination suitable for middle layer. The spectra of the middle-layer combination and the color former without any additive are similar to each other, but the bottom-layer additives appear to cause a large spectral shift. This difference may be due to formation greater extent of aggregates during printing of the system for bottom layer.

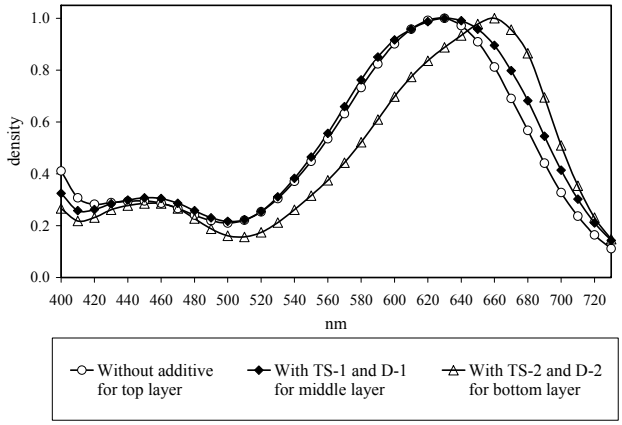


Figure 5*. Effects of additives on normalized reflection spectrum of image from a cyan color former.*

The observed spectral shift of the printed bottom layer combination can have an undesirable effect on the image quality. If the spectral shift is due to aggregation of dye molecules generated from the conversion of the color former, additives that are not involved in direct transformation may disrupt aggregation and reduce spectral shift. In order to test this hypothesis, various quaternary ammonium compounds were added to the combination of color former and additives for bottom layer. An example of the effect of a quaternary compound on the reflection spectrum of the color former C with additives for bottom layer is shown in Figure 6. In the presence of the quaternary compound the reflection spectrum of the print containing additives for the bottom layer is much closer to that of the color former without any additive.

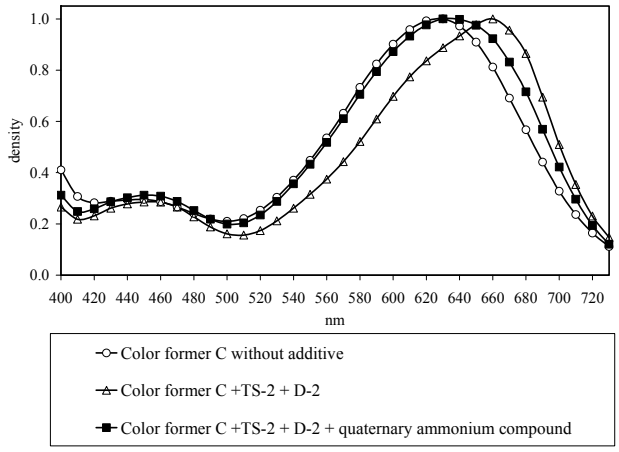


Figure 6*. Effects of a quaternary ammonium compound on normalized reflection spectrum of image from a cyan color former and additives.*

The presence of additives and quaternary compounds can also alter the color generated from a color former to a more acceptable form, when needed. Figure 7 shows the reflection spectrum of a magenta color former M without any additives. The spectrum extends to the red region, rendering the printed color to be less acceptable for achieving optimum image quality. The same color former when combined with an organic ether as a thermal solvent, a substituted sulfonylurea as a developer and a quaternary ammonium compound the absorption in both red and blue regions decrease, a narrower spectrum is obtained in the green region and consequently a better image quality.

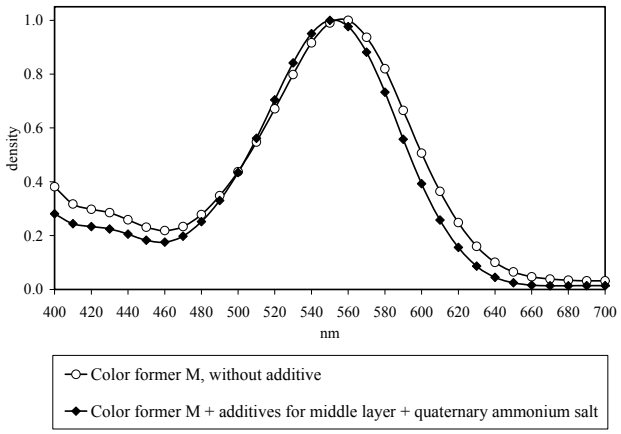


***Figure 7**. Effects of additives on normalized reflection spectrum of image from a magenta color former.*

The yellow color former Y, suitable for the top layer can be imaged without the presence of any thermal solvent. Because of the molecular structure of the color former, the presence of acidic or basic components can change its spectrum. Figure 8 shows the spectrum of a printed image in neutral environment. The spectrum shows a secondary peak and significantly high absorption in green region, which is not desirable for optimum image quality. Addition of organic acids, such as phenols or substituted anthranilic acids to the imaging system has been effective in decreasing the absorption in the green region and improving image quality.

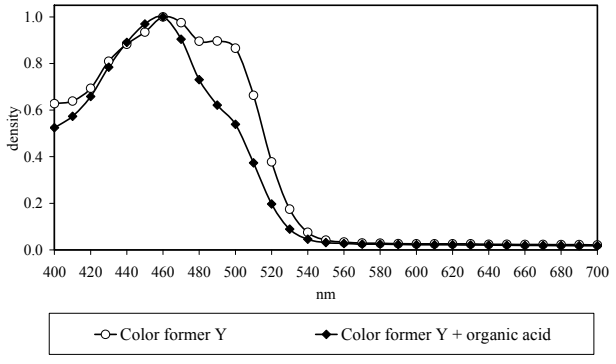


***Figure 8**. Effects of additive on normalized reflection spectrum of image from a yellow color former.*

Conclusions

Thermal imaging of amorphochromic crystals is achieved by melting or dissolution of colorless crystals to colored amorphous form. Aggregation of the colored form or other reactions associated with such transformation can alter reflection spectra of the printed images and consequent less than optimum image quality. Such spectral shifts can be altered by the addition of materials suitable for the imaging layer.

References

[1] F. B. Hasan, S. J. Telfer, "Modifications of Color Formers for Placement in Different Layers in a Single-Sheet Thermal Imaging System," Proc. NIP24, pg. 823 (2008).

[2] Stephen J. Telfer and William T. Vetterling, "A New, Full-Color, Direct Thermal Imaging System," Proc. NIP21, pg. 181. (2005); Michael P. Filosa, John L. Marshall and Kap-Soo Cheon, "Colorless Crystals of Tautomeric Fluoran Indicator Dyes," Proc. NIP21, pg. 193. (2005).

Acknowledgements

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Author Biography

Fariza Hasan, Senior Principal Scientist at Zink Imaging, Inc. received her PhD in chemistry from University of British Columbia, Canada. Her graduate and post-doctoral research studies included kinetics and mechanisms of inorganic, organic and biochemical reactions. The technical responsibilities in her current and previous positions consist of optimization and design of silver halide and digital imaging systems. She has a total of more than forty scientific publications and patents, and is a member of the IS&T and American Chemical Society.