Modifications of Color Formers for Placement in Different Layers in a Single-Sheet Thermal Imaging System

Fariza B. Hasan, Stephen J. Telfer; Zink Imaging, Inc.; Bedford, Massachusetts/USA

Abstract

A single-sheet multi-layer thermal imaging system consists of three layers of color-forming components, which are transformed from a colorless crystalline to a colored amorphous form during the imaging process. The temperature required for the conversion to the colored form is different for each of the color formers. These color-forming layers are separated by thermally-insulating layers that are required for addressing each color-forming layer independently, without any undesired color formation in other layers. The conversion temperatures of the crystalline materials can be altered by incorporation of additional components into the color-forming layers. Such additional components allow the placement of the same color-forming, crystalline material in different layers of the imaging system, eliminating the constraint of its intrinsic melting temperature.

Introduction

A direct thermal system consisting of three dye layers coated on a single sheet [1, 2] is illustrated in Figure 1.

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

Figure 1.*Structure of a direct thermal printing medium capable of rendering full-color images.*

Amorphochromic materials, which are colorless in crystalline form but colored in amorphous form, are used in these systems, as shown in Figure 2 [3]. The change from colorless to colored form can be induced by melting of the crystalline form during the imaging process of the system.

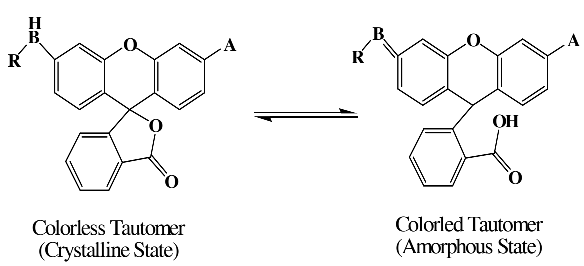

Figure 2. *Colored and colorless forms of an amorphochromic color former*

The color-forming layers are separated by thermally-insulating layers. Full-color images are generated by controlling the duration and intensity of heating of the surface of the direct thermal medium by a thermal print head. The uppermost color-forming layer is exposed to a high temperature for a short duration of time. In this case, the thermally-insulating layers prevent color formation in lower color-forming layers. The lower layers are imaged by heating the surface of the medium at lower temperatures, but for longer durations of time.

For proper separation of colors in a printed image it is essential to select color formers that produce color only at the particular temperatures required for each of the color-forming layers. The melting temperature range of color formers suitable for the top layer is 195 to 222°C. For the middle and bottom layers the ideal imaging temperature ranges are 150 to 160°C and 90 to 110°C, respectively.

The temperature of color formation is the temperature at which the crystalline color formers is converted to an amorphous form, which may be through melting or dissolving in another material. Selected additives can be combined with the color formers to modulate the color forming temperatures when the dissolving mechanism is used. The addition of such additives provides the flexibility of using color formers whose intrinsic melting temperatures may be unsuitable for a particular layer. This can allow the flexibility to circumvent some of the undesirable properties that may be associated with molecules whose intrinsic melting points are correct. For example, low-melting color formers may have low glass transition temperatures, which can lead to fading of printed images by allowing the reversal of the colored amorphous form to a colorless, crystalline form [4]. Additionally, color formers that have poor photostability, are prone to oxidation under ambient conditions or do not contain the proper chromophore can be replaced by more appropriate molecules whose intrinsic melting temperatures may not be ideal. Although combinations of additives and color-formers may not have exactly the same melting temperatures and sensitivities as single-component systems that melt to form color (without any diffusion being required), slight adjustments of the thermally-insulating layers and imaging conditions may allow such replacements to be practical, particularly for layers other than the topmost, highest-temperature color-forming layer (in which the time required for diffusion may be problematic).

Examples of several systems in which the same color former is placed in different color-forming layers of the imaging system are described in the following section.

Experiments and Results

The conversion of the amorphochromic color formers from the colorless crystalline form to an amorphous form may be effected by melting of the crystals or by dissolving the crystals in a suitable solvent. Crystalline materials that can act as thermal solvents (TS) can be incorporated in the coated layers containing the amorphochromic crystals. 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. The combinations of color formers, thermal solvents and developers can form eutectic mixtures that melt at the temperature range required for the imaging of a particular layer. The selection of the thermal solvents also depends on the rate of dissolution of the color formers in the time that is necessary for the imaging of the layer.

Several amorphochromic color formers of varying melting temperatures have been tested in different layers of the imaging system. For example, one of the two cyan color formers, C-1 melting at 210°C or C-2 melting at 198°C can be placed in the top layer of the system. In the same system a yellow color former, Y-1, melting at 95°C can be placed in the bottom layer. A magenta color former, M-1 melting at 152°C and a phenolic developer that melts at 162°C can be placed in the middle layer; the melting temperature of the mixture has been recorded to be 151°C. In another variation of the system a yellow color former Y-2, melting at 202°C has been placed in the top layer and high melting cyan and magenta color formers are placed in the middle and bottom layers, in combination with suitable crystalline thermal solvents that melt at the imaging temperature ranges required for those layers.

The melting temperatures of the components and the eutectic mixtures are determined by differential scanning calorimetry (DSC). Examples of some of the combinations are described below.

High melting color formers in middle layer

Combination 1.
M-2, melting temperature 222°C
TS-3, melting temperature 172°C
D-2, melting temperature 211°C
Eutectic melting temperature 159°C

Combination 2.
M-2, melting temperature 222°C
TS-5, melting temperature 167°C
D-2, melting temperature 211°C
Eutectic melting temperature 154°C

Combination 3.
C-2, melting temperature 198°C
TS-5, melting temperature 167°C
D-2, melting temperature 211°C
Eutectic melting temperature 150°C

High melting color formers in bottom layer

Combination 4.
C-1, melting temperature 210°C
TS-1, melting temperature 125°C
D-1, melting temperature 162°C
Eutectic melting temperature 95°C

Combination 5.
C-2, melting temperature 198°C
TS-1, melting temperature 125°C
D-1, melting temperature 162°C
Eutectic melting temperature 92°C

Combination 6.
C-2, melting temperature 198°C
TS-2, melting temperature 109°C
D-1, melting temperature 162°C
Eutectic melting temperature 105°C

Combination 7.
C-2, melting temperature 198°C
TS-4, melting temperature 129°C
D-1, melting temperature 162°C
Eutectic melting temperature 119°C

Combination 8.
M-2, melting temperature 222°C
TS-4, melting temperature 129°C
D-2, melting temperature 211°C
Eutectic melting temperature 119°C

Combination 9.
Y-2, melting temperature 202°C
TS-4, melting temperature 129°C
D-3, melting temperature 129°C
Eutectic melting temperature 121°C

Figure 3 illustrates the effects of two thermal solvents, TS-3 and TS-4 on the melting temperatures of mixtures containing color former M-2 and developer D-2 (combinations 1 and 8).

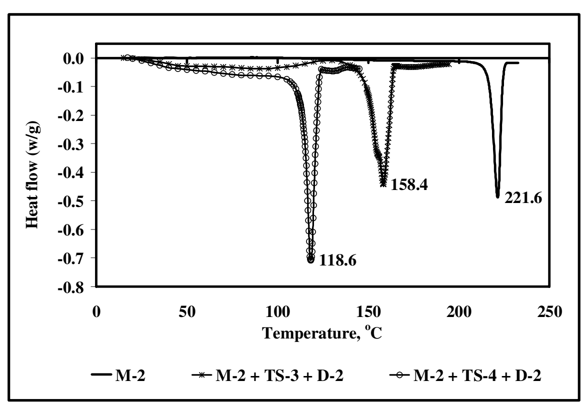

Figure 3. *Comparison of the effects of two thermal solvents on the melting temperatures of eutectic mixtures containing the same color former.*

The sensitometric curves of some of these systems are shown in Figures 4, 5 and 6. Figure 4 shows a comparison of printed densities of three combinations of magenta color formers, using the printing conditions for the middle layer. The color former M-1 in combination with developer D-1 melts at 151°C, which is slightly lower than the melting temperatures of the eutectic mixtures of a higher melting color former M-2, developer D-2 and two different thermal solvents, TS-3 and TS-5 (combinations 1 and 2). The sensitivities and slopes of these systems follow the trend of the melting temperatures of the mixtures.

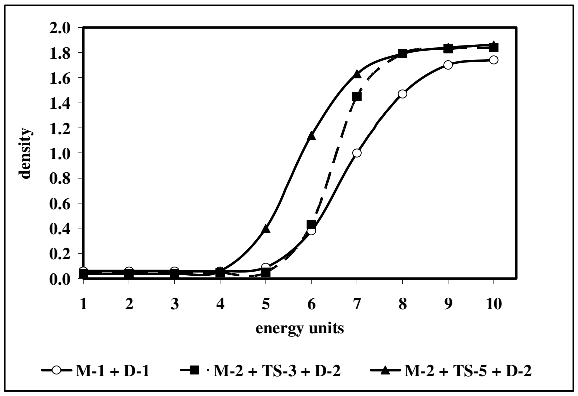

Figure 4. *Comparison of magenta color forming systems for middle layer.*

Figure 5 shows the effects of three thermal solvents on the sensitivity of a high melting color former C-2 when placed in the bottom layer (combinations 5, 6 and 7). The conditions for printing the bottom layer are used for printing these combinations. In this case also, the sensitivities and slopes of the curves show qualitative correlation with the melting temperatures of the eutectic mixtures.

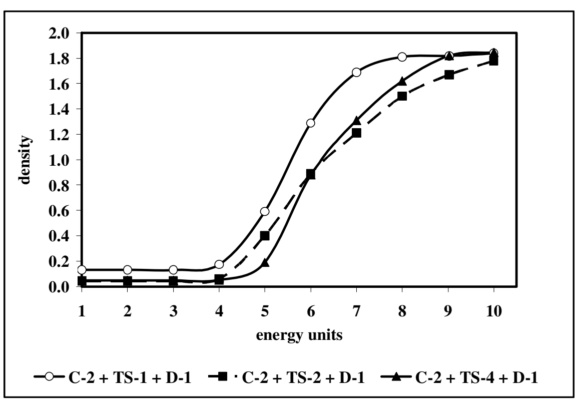

Figure 5. *Comparison of high melting cyan color former with different thermal solvents for bottom layer.*

In Figure 6 the printed densities of high melting color formers, C-2, M-2 and Y-2 in combination with a thermal solvent that melts in the temperature range required for imaging the bottom layer are compared (combinations 7, 8 and 9). These combinations were also printed by using the bottom layer printing conditions

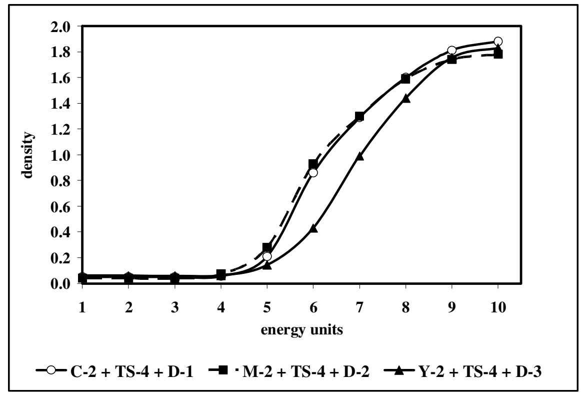

Figure 6. *Comparison of high melting cyan, magenta and yellow color formers with a low melting thermal solvents for bottom layer.*

Conclusions

In a single-sheet multi-layer thermal imaging system the color formation is achieved by the transformation of amorphochromic color formers from a colorless, crystalline state to an amorphous state by melting or dissolving the crystals. The selection of color former for a particular layer depends on the temperature required for such conversion, which can be altered by addition of thermal solvents that dissolve the amorphochromic crystals, causing the formation of color. Such a process allows the placement of the same color forming crystalline material in different layers of the imaging system.

References

[1] Stephen J. Telfer and William T. Vetterling, A New, Full-Color, Direct Thermal Imaging System, Proc. NIP21, pg. 181. (2005).
[2] Scott Wicker, Zink Imaging Overview, IMI 18th Annual Thermal Printing Conference. (2007).
[3] Michael P. Filosa, John L. Marshall and Kap-Soo Cheon, Colorless Crystals of Tautomeric Fluoran Indicator Dyes, Proc. NIP21, pg. 193. (2005).
[4] Fariza B. Hasan, Application of Thermal Printing Technology for Security Printing, Proc. NIP23, pg. 558 (2007).

Acknowledgements

Thanks to K. Cheon, M. Filosa, B. Fulton, X. Herault, Z. Hinz, Z. Huang, J. Marshall, T. Rodgers, D. Skyler, V. Solan, G. Widiger and A. Zhivich for synthesis of color formers and additives, and N. Weeks for thermal analysis, data interpretation and other technical support.

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.