A New, Full-Color, Direct Thermal Imaging System

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Abstract

A direct thermal printing medium is described that incorporates two color-forming layers separated by a thermally-insulating layer. Any combination of the two colors may be obtained by heating with a conventional thermal print head. Independent addressing of each color is achieved by controlling the time of heating and the power supplied to the heating elements of the print head. In combination with a third color-forming layer that is printed from the reverse side of the medium, full-color imaging with photographic quality is possible using two passes with a single thermal print head or a single pass with two print heads. A novel thermal color-forming process based upon phase change of colorless crystals provides images of excellent quality and stability.

Introduction

Continuing progress in thermal printing technology has resulted in the development of a wide variety of thermally-sensitive media. Such media are of two types: 1) those that rely on thermal transfer, in which heat is used to move a colorant from a donor to a receiver sheet, and 2) direct thermal systems, in which heat is used to convert a colorless composition coated onto a substrate into a colored form. The direct thermal method requires only a single sheet, and is the preferred approach from the standpoint of system cost and complexity. However, despite the great success of monochrome direct thermal media, it has not hitherto been possible to provide a full-color, direct thermal image without significant compromise. The closest approach has been Fuji's Thermo-Autochrome,[1] a light-sensitive medium requiring multiple printing passes.

Our goal has been to make a single-sheet, direct thermal printing medium on which any color may be printed simply by heating, preferably in a single printing pass with a single print head. The medium is to be stable before and after printing, and insensitive to normal room light. Such a printing medium, we believe, will finally realize the potential of the direct thermal printing method. In this paper we describe a first step towards this ultimate goal.

Principle of Operation

There are numerous examples of direct thermal printing systems providing partial color. For example, as shown in Figure 1, it is possible to coat each side of a transparent substrate with a different thermally-sensitive layer, such that one side provides a different color from the other when heated.[2]

An opaque, white layer is coated over one of the two thermally-sensitive layers so that a composite image of the two colors may be viewed from the opposite side of the transparent substrate against the white background. Independent addressing of two colors is achieved by heating each side of the medium in a separate pass with a thermal print head, the color-forming layer on the side bearing the opaque layer being heated through the opaque layer. A medium of this type suffers, of course, from the problem that independent addressing of *three* primary colors is required for a full-color image. At least two colors must therefore be independently addressable from one side of a transparent substrate if a full color gamut is to be rendered.

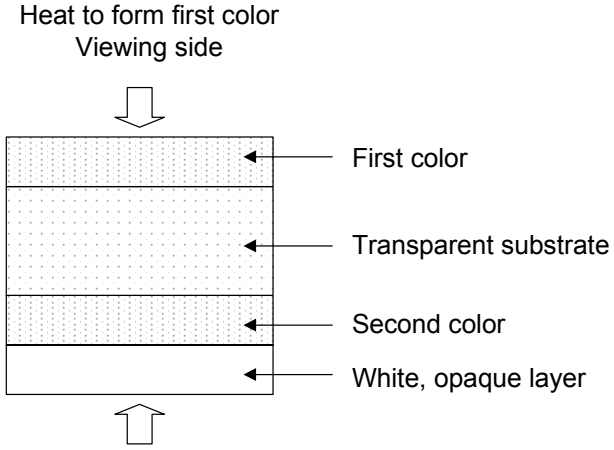

Figure 1. Independent addressing of two colors by heating either side of a direct thermal printing medium.

Two-color direct thermal systems have been devised in which only one side of the medium is addressed, and in which formation of a first color is achieved by heating to a relatively low temperature, while a second color is added to the first by printing at a higher temperature.[3] In more sophisticated versions the first color is bleached at the temperature required to produce the second color.[4] In all designs of this general kind, however, the addressing of the second color is not independent of the addressing of the first color, so that printing of arbitrarily chosen combinations of the two colors is not possible.

In truly independent addressing of colors, at least each of the following four outcomes must be attainable: no color, the first color, the second color, and the combination of first color and the second color. In the methods described above, either one color is added to another (making the printing of the second color alone impossible), or one color replaces another (so that the combination of the two together cannot be realized). This lack of independent addressing of colors arises fundamentally from the fact that one is trying to address a two-dimensional space of color combination with only a single parameter (the surface temperature of the medium).

Our solution to this problem was to recognize that there are actually two independent variables available in a thermal printer, namely, the power that is supplied to the heating elements of the thermal print head, and the length of time during which the power is supplied. The higher the power that is applied to a print head heating element, the higher will be the temperature of that element and therefore the higher will be the temperature of the surface of the medium with which it is in contact. Independent addressing of colors can consequently be achieved as shown schematically in Figure 2, in which the two axes represent the surface temperature of the medium and the time of heating of the surface at that temperature.

With these two independent variables we gain considerable flexibility in controlling the temperature histories experienced by each of the color-forming layers in the medium. We can, in particular, follow trajectories in the temperature/time plane starting from the origin (i.e., ambient temperature, zero heating time) that lead to regions in which one color is formed without necessarily encroaching on regions in which another color is formed. For example, one color may be formed in a region of high temperature and short time (region A in Figure 2), while a second color may be formed in a region of low temperature and long time (Region C in Figure 2).

In the imaging medium described below, region A provides yellow and region C provides cyan coloration. Yellow is also formed in portions of region B, but in this region may be contaminated with cyan. Likewise, cyan is produced in portions of region B, but in this region may be contaminated with yellow. It can be seen, then, that for independent color addressing, the regions in which pure colors are formed should typically be arranged on a line of negative slope in a time/temperature diagram such as Figure 2. Provided the range of times and temperatures is sufficiently large, any number of colors can, in principle, be independently addressed according to such a scheme.

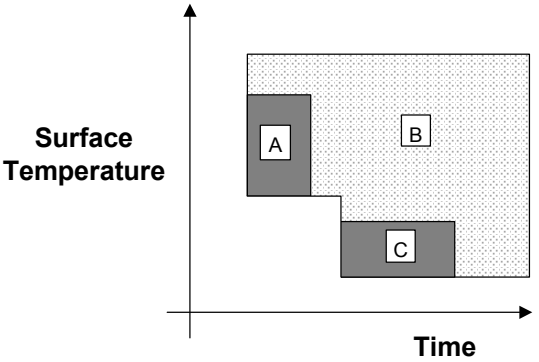

Figure 2. Times and temperatures of heating required for independent addressing of two colors from one surface of a direct thermal printing medium.

The precise shape of the printing regions in practice will not of course be rectangular as shown in Figure 2, but will depend upon the detailed physics of the particular imaging medium and printing apparatus. Figure 2 is intended merely to illustrate the basic principle underlying the design of our new medium.

Readers may recognize an analogy of this printing method with techniques used in cooking. Many culinary effects derive from independent control of time and temperature of heating: for example, browning the surface of a dessert without overcooking the interior requires a high temperature for a short time, while warming a dish with a heat-lamp without burning its surface requires a relatively low temperature for a long time.

Structure of the Imaging Medium

The structure of our thermal imaging medium is shown in Figure 3. In this paper, we describe a version in which two colors (yellow and cyan) are addressed from one side of the a transparent substrate (the bichrome side), while the third color (magenta) is addressed from the back (the monochrome side) as was described above with reference to Figure 1. It is obviously more straightforward to solve the problem of independently addressing two colors from one side than all three. In the discussion that follows, the independent addressing of two colors from the bichrome side of the medium will be described in more detail.

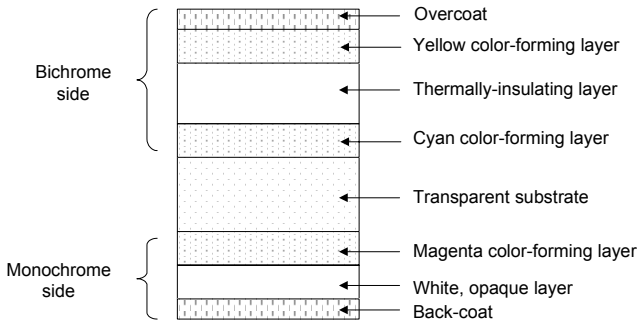

Figure 3. Structure of a direct thermal printing medium capable of rendering full-color images.

As indicated in Figure 2, each dye is taken to have a temperature threshold below which it will not colorize. In short times of heating, at high surface temperatures, a gradient of temperature will be set up within the medium in such a way that the surface is much hotter than the interior. Therefore, in our medium, the color-forming layer with the highest temperature threshold for coloration (the yellow color-forming layer) is the closest to the surface. This is the opposite order of layers from previous direct thermal media designed to produce more than one color. The thermally-insulating spacer layer is made sufficiently thick that during the printing of the yellow color-forming layer, the cyan color-forming layer does not reach its threshold temperature for coloration, even though this threshold is lower than that for the yellow color-forming layer. Moreover, when the heat transferred into the medium while printing yellow eventually diffuses throughout the structure, the temperature reached by the cyan color-forming layer still does not exceed the threshold temperature for its coloration. The "high power" situation illustrated in Figure 4 corresponds to the printing of yellow.

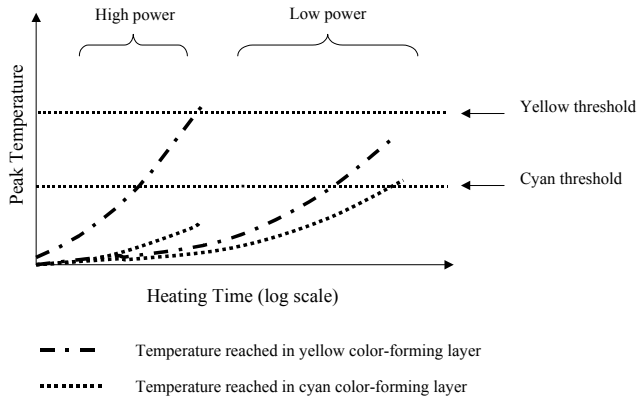

Figure 4. Temperatures reached in color-forming layers on bichrome side when addressing yellow (high power) and cyan (low power).

To print the buried, cyan color-forming layer, a longer time of heating is required at a relatively low surface temperature (i.e, low printing power). Heat diffuses through the first color-forming layer at a temperature below its coloration threshold. The amount of heat transferred into the medium is greater than was the case when printing the yellow color-forming layer, and the bulk of the medium is thus heated to a higher temperature than it was when printing yellow, with the result that the threshold for coloration of the buried layer is exceeded. These printing conditions are summarized in Figure 4, the "low power" case.

New Color-Forming Chemistry

An assumption was made in the above discussion that the temperature thresholds for coloration were independent of the heating time. In conventional color-forming chemistry for direct thermal imaging this is unfortunately not the case. Typically, two or more chemical compounds that react together to produce a color change are coated in a single layer in such a way that they are segregated from one another, for example, as dispersions of small crystals. Melting, either of these compounds themselves or of an additional fusible vehicle, brings them into contact and causes a visible image to be formed.[5] Compositions of this type suffer from the drawback that the temperature required to form an image in a very short time (i.e., on the order of a millisecond) may be substantially higher than the temperature required to form color during longer periods of heating. The difference is caused by the fact that the rate of the diffusion needed to mix the molten components together is rate-limiting for color formation, and the rate of diffusion depends exponentially on the temperature. The temperature may need to be raised well above the melting points of the individual components to allow fast enough diffusion for image formation in short times. During long periods of heating, however, the temperature at which coloration takes place may actually be lower than the melting point of either individual component, and occur at the eutectic temperature of the mixture of crystalline materials.

Time-dependent temperatures of coloration, in which longer periods of heating require lower temperatures for coloration, can defeat the mechanism for color addressing proposed above. We therefore needed to devise a new mechanism for formation of color in which the transition temperature was essentially time-independent. Such a mechanism is provided by a first-order phase transition, such as melting of a single crystalline material. Thus, we required color formation from a single colorless component, that when melted would form a color without the requirement of diffusional mixing with another component.

As described in an accompanying paper ("Colorless Crystals of Tautomeric Fluoran Indicator Dyes", by Michael P. Filosa et al.) we have discovered materials that can exist in at least two different forms (tautomers) that interconvert in the amorphous state. At least one of these forms is colored, and at least another is colorless. As shown in Figure 5, the colorless form is trapped by crystallization, and maintained in the colorless state by the lattice energy of the crystal. Upon melting, the amorphous state is attained, in which both the colorless and colored interconverting tautomers are present. Thus, a colorless crystal is melted to produce a colored glass, without the requirement for any other component. Because the colored form of the molecule is present only in the amorphous state, we have termed these new materials "amorphochromic color-formers".

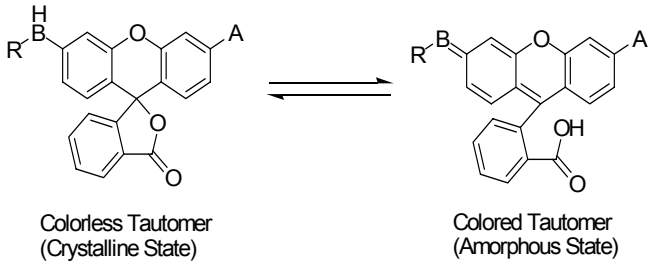

Figure 5. Colored and colorless forms of an amorphochromic color-former. Choice of groups A and B determine, among other properties, the color of the dye produced and the position of the equilibrium between colorless and colored states.

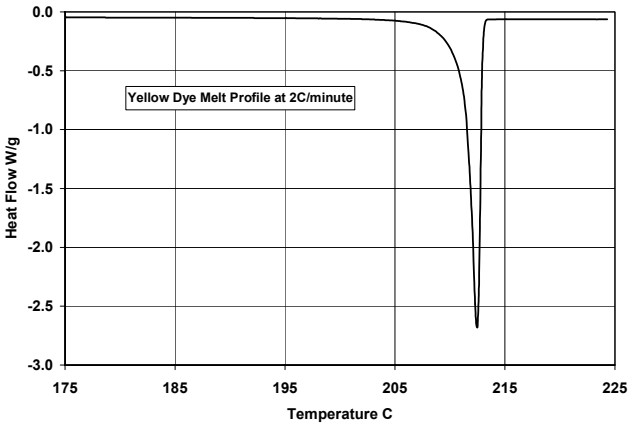

Figure 6. Melting of yellow amorphochromic color former.

The threshold temperature for coloration of a layer containing a dispersion of crystals of an amorphochromic material is simply the melting point of the crystalline form of the material. Melting can

occur over a very narrow range of temperatures, as is shown in Figure 6, in which the melting behavior of the yellow color-former used in our new medium is shown. In order to produce a stable image, the amorphous form must be stable against recrystallization, and this is possible if its glass transition temperature, Tg, is sufficiently high. Figure 7 shows the glass transition temperature for the yellow color-former.

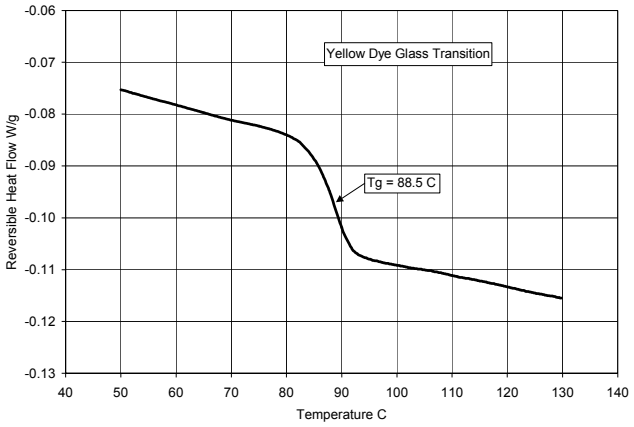

Figure 7. Glass transition temperature of yellow amorphochromic color-former.

Summary

This paper describes a new direct thermal imaging medium and a method for independently addressing at least two different colors from one side of the medium using a single thermal print head. In order to make the method practical, a new mechanism for thermal color formation has been devised in which the temperature at which color is produced is essentially independent of the time of heating.

References

1. T. Usami and A. Igarishi, "The Development of Direct Thermal Full Color Recording Material", *Journal of Information Recording*, **22**, 347-357 (1996).
2. Such a system is described in U.S. Pat. No. 4,956,251.
3. An example can be found in U.S. Pat. No. 3,895,173.
4. An example can be found in U.S. Pat. No. 4,020,232.
5. See, for example, "Imaging Processes and Materials", Neblette's Eighth Edition, J. Sturge, V. Walworth, A. Shepp, Eds., Van Nostrand Reinhold, 1989, pp. 274-275, or Yoshihiro Hatano, Chemistry and Applications of Leuco Dyes, R. Muthyala, ed.. (Plenum Press, New York, 1997) pg. 199.

Author Biographies

Stephen J. Telfer received his B.A. in Natural Sciences (1981) and a Ph.D. in Chemistry (1985) from the University of Cambridge (U.K.). He held post-doctoral positions at Stanford University and the University of California, Berkeley. He joined Polaroid Corporation in 1988, where he is currently Senior Science and Technology Fellow. He has worked on a variety of digital imaging projects, including laser-exposed thermal media, acid amplified imaging, new methods for three-dimensional display, the Opal thermal transfer system and the new direct thermal printing technology. He is the inventor of 50 issued United States Patents, and is a Patent Agent.

William T. Vetterling received his A.B. in Physics from Amherst College (1970) and his Ph.D. in Physics from Harvard University (1976). He served on the physics faculty of Harvard until 1984. Currently he is a Science & Technology Fellow of Polaroid Corporation and manager of the Polaroid Image Science Laboratory in Waltham, MA. He is a co-inventor of the OPAL thermal transfer and the new direct thermal photo-printing systems, and has previously engaged in research on novel print media, on CCD, CID and CMOS electronic imagers, and on color liquid-crystal displays.