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Single-Sheet High-Definition Trichrome Laser Thermal Imaging

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Abstract

Polaroid's SUNSPOT is a novel imaging system comprising a thermal imaging medium designed to produce a full-color, high-resolution transparent image in a single sheet, addressed by a set of three diode lasers, each emitting at a different wavelength between 750 and 950 nm.

The medium contains three active layers, each of which can provide an image in one of the three subtractive primary colors. A digitized image is written onto the Sunspot medium by the lasers, one for each color. Absorption of the radiation leads to local heating of an imaging layer to an extremely high temperature, causing an irreversible thermal reaction in which a colored material is formed.

Innovations in two types of dyes make the system practical: infrared-absorbing squaraine dyes exhibiting high specific absorbance in a narrow waveband as well as very low visible absorption, and thermal color-forming materials which are extremely stable at room temperature for many years, but undergo a rapid unimolecular thermal conversion to stable dyes under imaging conditions.

The medium is conveniently imaged using diode lasers rated at 100 to 500 milliwatts and provides full-color images with very high color saturation (density >3.0) and resolution (as small as three microns). Imaging requires no pre- or post-processing, the medium can be handled in ambient light before and after imaging, and no by-products or waste are produced.

In a typical application, the medium may be coated onto a plastic "blank" which comprises the image area and the mount of a conventional 35 mm slide. This "blank" may be inserted into a printer, imaged, and then used immediately in a slide projector with no further steps involved.

Introduction

Most conventional laser-addressed thermal media involve transfer of material from one substrate to another, typically by ablation, diffusion, or differential adhesion. There are a number of disadvantages with such media, not least of which is the need for registration of multiple images if a full-color picture is required. In SUNSPOT, by contrast, color is generated *within* the heated layer, enabling a full-color image to be formed *in situ* in a single sheet.

Powerful diode lasers emitting in the near infrared (NIR) region are now readily available. It is possible to selectively heat a spot in a medium containing a NIR absorbing dye[1] with a laser whose emission is tuned to the absorption maximum of the dye. If the medium also contains a leuco dye which is irreversibly converted from an invisible to a colored form by heating, a monochrome image can be written by scanning the laser.[2]

Polaroid's SUNSPOT imaging system represents an extension of this concept to trichrome imaging. In principle, a trichrome medium could consist of three monochrome layers, each sensitive to a different wavelength in the NIR, and each containing a different leuco thermal image dye. In practice, a number of problems have to be addressed: development of new classes of dyes with strong, narrow NIR absorption peaks but with minimal absorption in the visible, invention of new types of thermally activated leuco image dyes, thermal insulation of layers one from another, minimization of other types of crosstalk, design of efficient optomechanical exposure devices, and selection of software solutions to produce a high-quality image.

Chemistry

1. Infrared Dyes

At the time we initiated these investigations, it was known that certain squaraine (or squarylium) cyanine dyes were characterized by appropriate NIR and visible absorbance for our needs. Only a few simple examples of this class of dye were known,[1] however, permitting limited optimization of properties. We have developed a family of squaraines based upon benzpyrylium, benzthiopyrylium, and mixed dyes which allow us to tailor such properties as NIR absorption maximum and extinction coefficient, peak width, solubility, aggregation, and visible absorption.[3] We have also developed methods for preparing the previously unknown class of aminosquaraine dyes whose members and derivatives provide additional opportunity to tune absorption wavelength, solubility, aggregation, and binding, as well as to attach the dyes covalently to a wide variety of substrates.[4] We have prepared dyes with solution absorbance maxima at virtually every wavelength between 750 and 900 nm. (Longer wavelengths are available from analogous dyes based upon benzselenopyrylium salts or upon croconic acid. We have not used these classes because of potential toxicity issues for the former and because of the wide absorbance peaks and higher visible absorbance of the latter.) Many of these dyes exhibit specific molar absorptivities between 200,000 and 450,000 $LM^{-1}cm^{-1}$, peak width at half height between 30 and 40 nm, and visible absorbance peaks less than 3% as high as the NIR absorbances. For application to SUNSPOT, the dyes were engineered to give fast relaxation from the photo-excited state to maximize generation of heat from a brief intense laser pulse.

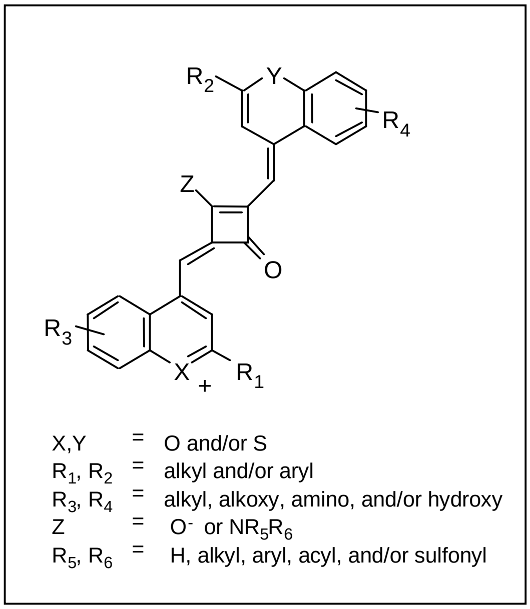

Figure 1. General structure of squaraine NIR absorbers

2. Thermal Image Dyes

The ideal thermal image dye is perfectly colorless in the leuco form, stable indefinitely at temperatures encountered by the medium before and after exposure and during viewing (including in slide projectors), and gives a clean, high-absorptivity cyan, magenta, or yellow color efficiently upon thermolysis. Given a very brief heating cycle (on the order of a microsecond at ca. 1000°C), monomolecular kinetics with an activation energy in excess of 30 kcal/mole are necessary. We have developed a set of three such image dyes, based upon our experience with photographic filter dyes. Formally, two of these leuco dyes can be considered to undergo thermal elimination of a phenolic residue, generating an isocyanate function which traps a triarylmethane system in the open (colored) form (see Figures 4-5). The leuco yellow dye relies upon an intramolecular transacylation reaction.[5] These color formers, in their open state, provide good color gamut and are relatively resistant to photofading.

3. Thermal Acid Generation

An alternative imaging mechanism which gives similar results entails replacing the leuco thermal image dyes with protonatable indicator dyes initially in the basic (leuco) form. In this case the image is formed by laser-induced generation of acid via thermolytic elimination of a sulfonic acid from a polymeric secondary sulfonate ester or of squaric acid from a squarate ester, followed by protonation of the image dye.[6] Sensitivity, resolution, and image stability are similar with either the thermal image dye or the thermal acid systems.

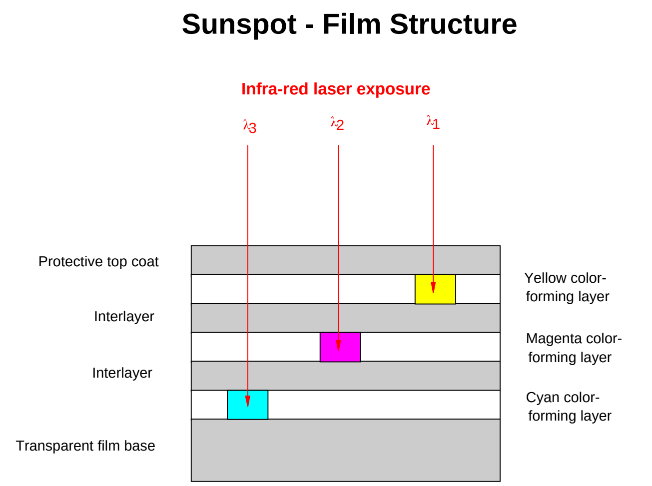

Figure 2. Overview of the structure of the medium

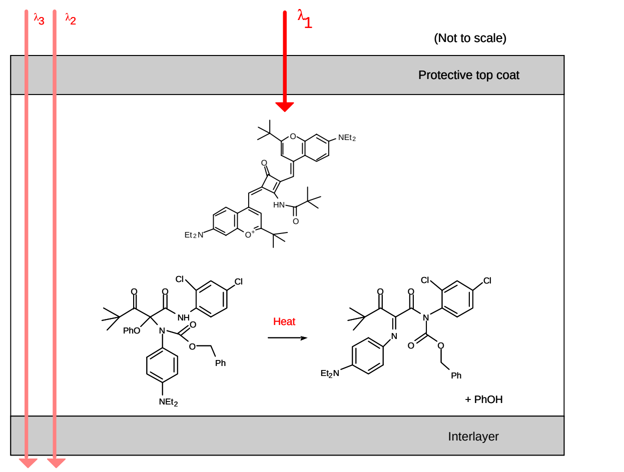

Figure 3. Exposure of yellow color-forming layer. Radiation of wavelength λ_1 is absorbed by short-wavelength NIR absorber, causing local heating. Longer wavelengths pass through layer unabsorbed. Thermal image dye is converted from colorless to colored form

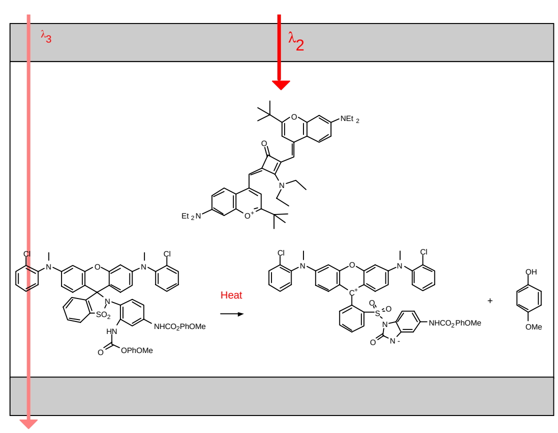

Figure 4. Exposure of magenta color-forming layer. Radiation of wavelength λ_2 is absorbed by mid-wavelength NIR absorber. Long wavelength radiation passes through unabsorbed; short wavelength radiation absorbed in yellow color-forming layer

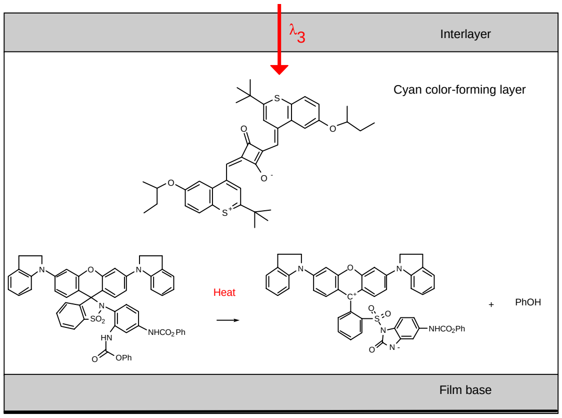

Figure 5. Exposure of cyan color-forming layer. Radiation of wavelength λ_3 is absorbed by long-wavelength NIR absorber

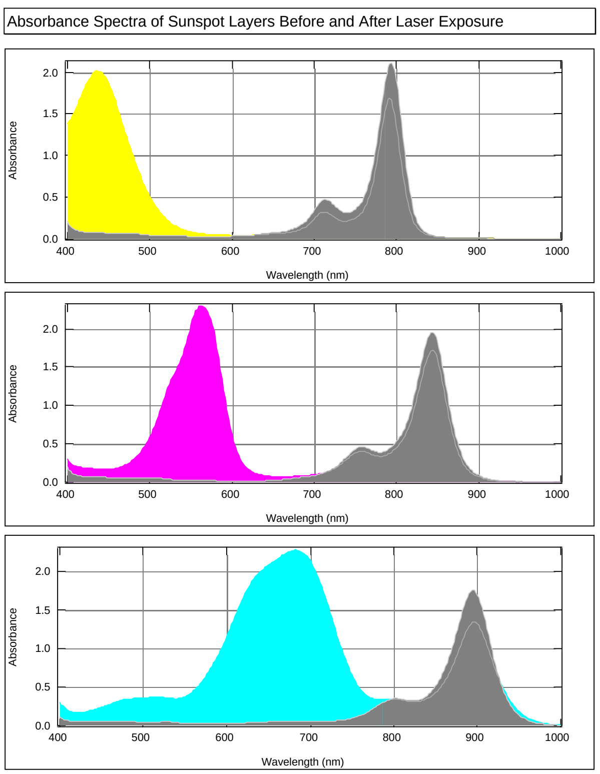

Figure 6. Film absorbance spectra before and after imaging. NIR absorbance decreases slightly, while visible absorbance increases from a low baseline to high color saturation.

Structure of the Medium

For the purpose of assembling a trichrome transparency medium a transparent film base (typically polycarbonate or polyethylene terephthalate) is coated with a 5-micron thick cyan-forming layer consisting of a cyan leuco image dye and a NIR-absorbing dye with an absorbance maximum around 920 nm, and a polymeric binder. The optical density in the NIR is approximately 2.0. On top of this is coated an inert interlayer of about 4 to 5 micron thickness to provide thermal insulation. Next, another image-forming layer is coated containing a magenta leuco image dye and a squaraine dye tuned to about 850 nm. Another interlayer is coated, then the upper image-forming layer, containing a yellow leuco image dye and a NIR absorber tuned to about 780 nm. Finally a top coat is applied, protecting the medium from imaging artifacts (laser-induced ablation and bubble formation[7]) and environmental insults (scratching, UV, etc.) For a 35-mm slide application the entirety of the 2 inch by 2 inch slide blank can consist of the medium, or the imaging area alone (36 by 24 mm) can be the medium, inserted into a 2 inch by 2 inch support.

Exposure of the Medium

Typically, for an application such as preparation of 35-mm transparencies, the output of three lasers or gangs of lasers, representing 100 to 500 milliwatts total power per color, is scanned in a raster mode across the medium on a flat bed. (Alternatively, the medium can be wrapped around a cylindrical support and rotated with translation to effect a helical exposure path). Each of the laser beams is focussed to a rectangular spot. In the direction perpendicular to the writing the rectangle is 20 microns in width (see Figure 7), and the imaging can be considered binary on this axis. In the direction of writing the rectangle is five microns in width. Using run-length modulation, the laser can be turned on and off to effect digital generation of the image, or an analog media response can be obtained by modulating the laser at frequencies higher than can be resolved as individual dots. The degree of resolution attainable in the system is dependent upon the protocols used for image manipulation, but in one favored mode of operation the addressing of the medium corresponds to 18-micron square pixels, which in the direction of scanning are subdivided into pels, so as to give three bits (eight levels) of gray per color per pixel. Intermediate levels of gray, in this case, can be rendered by using error diffusion techniques. Scan speed is on the order of 0.5 meter per second at the 500 milliwatt power level. All three color signals can be written simultaneously.

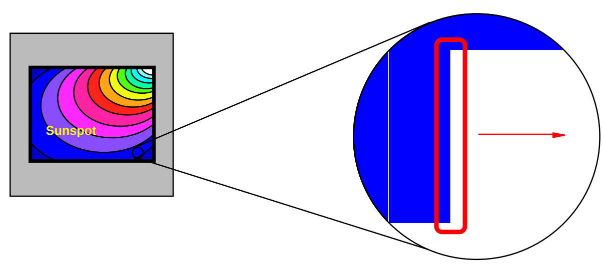

Figure 7. Detail of exposure by scanning laser

Performance of the System

All goals for the system were met or exceeded. Crosstalk, a major concern, proved to be minimal. The

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interlayers provided excellent thermal insulation, and the small amount of spectral overlap between the NIR dyes caused no problems.

The SUNSPOT system, as described, is best suited for small-format transparency products. The energy requirement is rather high, on the order of 1000 millijoules per cm^2 for each color, and the residual visible absorbance of the NIR dyes imparts a Dmin absorbance of about 0.10 (transmission). Within these restrictions, however, the performance is excellent. Color gamut and saturation are extremely good. In the transparency format the yellow Dmax is 2.5, while the magenta and cyan Dmax are each about 3.0. Resolution is on the order of three microns in the direction of scanning, giving an image at least equal to that of the best silver-based digitally-exposed 35-mm slide products.

Exposure time for a 35-mm transparency is approximately two minutes for 500 milliwatt lasers and five minutes using a single-mode 100-milliwatt diode laser. Slides can be produced one at a time, as needed, ready for projection. The medium is insensitive to ambient light before and after exposure, and survives thermal and photochemical assault by powerful projectors. The medium is stable, dry, and self-contained, requires no processing, and produces no waste.

Other Applications

With minor modifications, the medium can be used for other small-format color applications such as microfiche, ID cards,[8] color filters,[9] and lenticular displays.[10] Portions of this technology should also be useful for NIR-addressed curing of thermally initiated prepolymers and other applications requiring laser-addressed local heating, especially in materials requiring low visible absorption.

Acknowledgements

This account represents the culmination of a large body of work performed by a number of Polaroid employees, including the authors listed as inventors in the cited Polaroid patents. The author also thanks Dr. Stephen Telfer for assistance in preparation of this manuscript.

References

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Biography

The author is a Research Associate at Polaroid Corporation. He received his SB degree from Massachusetts Institute of Technology in 1967 and his PhD from Rensselaer Polytechnic Institute in 1975. After two years of postdoctoral work at University of New Hampshire he worked at SISA Inc. in Cambridge, Massachusetts. He has been employed by Polaroid Corporation since 1979, working first in the Chemical Development Laboratory, and presently in the Imaging Materials Laboratory. His present research interests include synthesis of dyes and other components for digital imaging products and design and development of advanced imaging systems.

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