# Photo-Quality Single Pixel Full-Color Rewritable Sheets with Leuco Dyes

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**ABSTRACT**

*We have developed a laser-addressed photographic-quality rewritable sheet by using a 426-ppi single pixel full-color structure of a thin stacked C/M/Y thermochromic leuco-dye system with an unrecognized parallax. This development will facilitate new applications of on-demand rewritable image design on various surfaces.*

## 1 INTRODUCTION

Non-volatile reflective displays consume less power and reduce the use of paper, aiding a sustainable society. Reflective displays rarely achieve a wide color gamut because their brightness is limited by environmental light. The color-filter approach using RGB sub-pixels commonly achieves a full-color reflective display; however, it limits light efficiency to less than 1/3. To improve light efficiency, single pixel full-color displays such as electrochromic displays and electrowetting displays have been developed [1, 2]. The displays have vertically stacked cyan (C)/magenta (M)/yellow (Y) layers. Glass substrates with thin film transistors (TFTs) are inserted into each set of colored layers to change each C/M/Y color, causing a parallax and restricting the viewing angles. In other words, it limits the resolution to avoid color mixing due to the parallax effect; therefore, photographic image quality has not yet been achieved in these reflective displays. A single pixel full-color electrophoretic display with a single-layer TFT backplane has been reported on [3] that has achieved a 200-ppi resolution. Another approach to non-volatile displays that does not require frequent image updating is a laser-addressed full-color rewritable sheet with photographic image quality we proposed [4, 5]. Its effects are achieved with a stack of C/M/Y-thermochromic layers that have a mixture of leuco dyes, developers, photothermal conversion agents (PCAs), and a polymer matrix.

In this paper, we will review our previous report [4, 5] and discuss image characteristics, including the parallax characteristics of a single pixel full-color rewritable sheet that uses a stack of C/M/Y-thermochromic layers to achieve photographic quality images.

## 2 PRINCIPLES OF OPERATION

Figure 1 is a schematic cross-section of a full-color rewritable sheet we have developed. The sheet is a stack of three C/M/Y-thermochromic layers that heat insulation layers thermally and physically separated. The thermochromic layer is composed of a mixture of leuco dyes, developers, and PCAs that are dispersed in a polymer matrix. Leuco dyes and developers play an important role in thermochromic systems. In this system, a redox reaction between leuco dyes and developers induces color change [6]. Heat insulation layers between thermochromic layers prevent heat diffusion to neighboring layers and suppress the crosstalk between C/M/Y layers. However, the total thickness of C/M/Y layers is limited to 150 $\mu$m in order to suppress a parallax effect.

The multi-thermochromic layer was sandwiched between oxygen barrier layers. A hard-coat protective layer and a UV-light screening layer formed on top of the sheet. This sheet was laminated on a reflective substrate using an adhesive layer.

Figure 2 (a) is the configuration of PCAs absorbing NIR light with different wavelengths ($\lambda_1<\lambda_2<\lambda_3$) in C/M/Y-thermochromic layers. Each PCA shows an absorption peak between 700 and 1000 nm. When the thermochromic layers are irradiated by NIR laser light

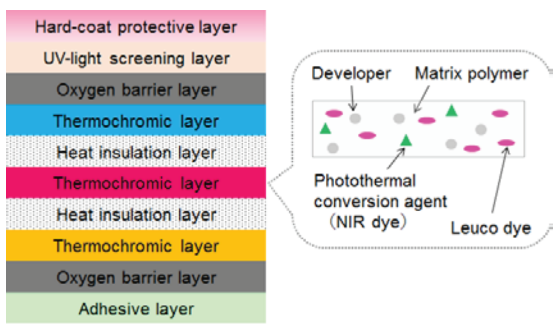


**Fig. 1 Schematic cross-section of full-color rewritable sheet.**

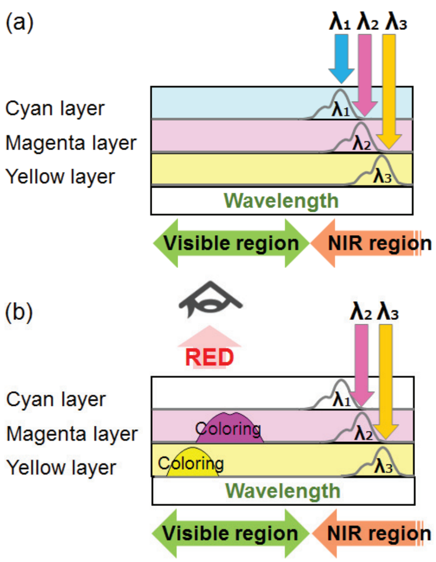


**Fig. 2 (a) Configuration of PCAs with different absorption wavelengths in C/M/Y-thermochromic layers and (b) principle for drawing red color.**

with the wavelengths of $\lambda_1/\lambda_2/\lambda_3$, the C/M/Y-thermochromic layer heats up independently and turns into its colored state. Figure 2 (b) helps us explain drawing a red color on the sheet. When the laser lights with $\lambda_2$ and $\lambda_3$ are irradiated on the sheet, the M and Y thermochromic layers respectively absorb the laser light $\lambda_2$ and $\lambda_3$ and heat up, turning into the M and Y colored states, resulting in a red image. Thus, we can get a single pixel full-color image with a wide color gamut by irradiating laser lights with the wavelength of $\lambda_1/\lambda_2/\lambda_3$.

## 3 EXPERIMENT

The full-color sheet was manufactured by gravure-coating on a plastic film with the mixture of leuco dyes, developers, PCAs, the polymer matrix, and heat insulation materials. The oxygen barrier layers, the UV-light screening layer, and the hard-coat protective layer were laminated onto the film. Every process was a roll-to-roll (R2R) process. The total thickness of the C/M/Y layers was 150 μm. Then, a roll of the sheet was cut into appropriate sizes and laminated onto a white-color polyethylene terephthalate (PET) film whose brightness was L* = 95. For integration into a product, an additional protection film or glass can be assembled on top of the sheet if necessary. Finally, laser writing is applied on the top.

Figure 3 is a schematic diagram of the optical system for laser irradiation. Writing and erasing were performed by three different NIR lasers with a maximum power of 5 W. They were precisely aligned such that a single beam was formed with dichroic mirrors and focused on the thermochromic layers. Thus, a high-resolution single pixel full-color pixel was achieved. The beam was steered by an x-galvano mirror through an Fθ lens and synchronized to

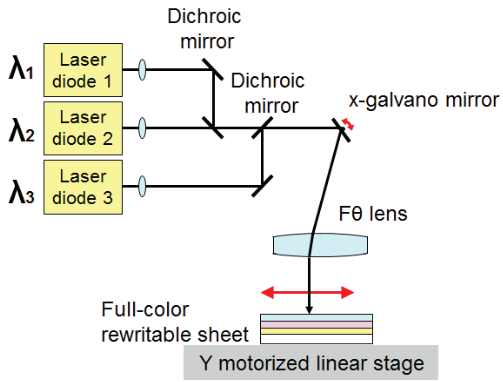


**Fig. 3 Schematic illustration of wavelength-multiplex laser irradiation equipment for writing and erasing operation.**

a Y motorized linear stage. This achieved fast drawing and precise control of the position corresponding to 426 ppi. To write an image, the laser power and the focus were set so that each laser beam heated a thermochromic layer above its melting point. The color point and optical density (OD) were controlled by the power of each NIR laser. To erase an image, the defocused laser beam was irradiated to keep the temperature of the thermochromic layer just above the decomposition temperature. Thus, writing and erasing could be done with the same equipment.

OD and CIELAB color space parameters (L*, a*, b*) were measured by a spectrophotometer to evaluate images.

## 4 RESULTS

### 4.1 Image Characteristics

Figure 4 shows the absorption spectra of a colored sheet with C/M/Y maximum color depth and a decolored sheet. Clear absorption peaks by the corresponding C/M/Y-colored leuco dyes were observed in the colored state, and no absorption peak was observed in the decolored state. The OD of each color was estimated to be approximately 1.5.

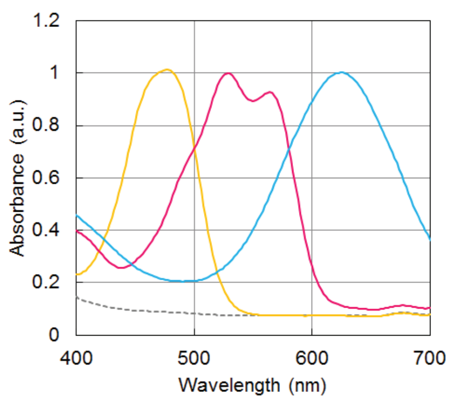


**Fig. 4 Absorption spectra of colored sheet (solid line) and decolored sheet (broken line).**

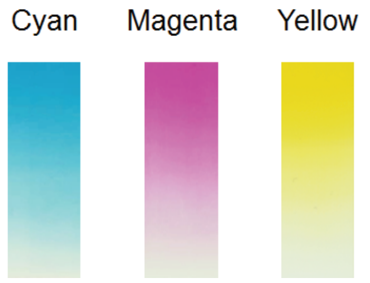


**Fig. 5 Image of C/M/Y-gradation patterns of sheet (3.5 cm x 10 cm, each pattern).**

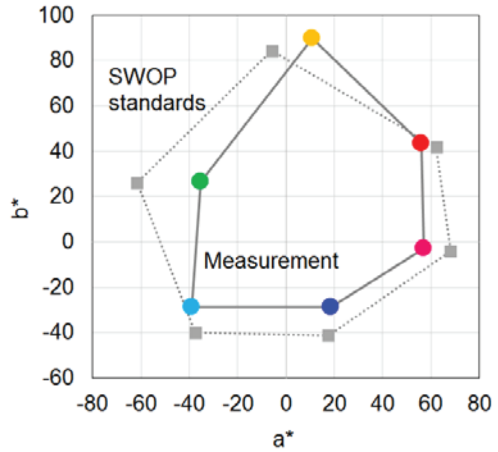


**Fig. 6 Color gamut of colored sheet (solid line) and Specifications for Web Offset Publications (SWOP) standards (broken line).**

Figure 5 shows the gradation patterns of the sheet irradiated by each laser light with modulations of power. We confirmed smooth gradations with 256 levels. The measurement of the a*, b* value proved that the optimized sheet had a wide color gamut with 70% coverage of the Specifications for Web Offset Publications (SWOP) standards, as shown in Fig. 6.

### 4.2 Viewing Angle Characteristics

Figure 7 shows photographs of Red (R), Green (G), Blue (B), and Black (BK) colored 60 μm-width line-and-space (L&S) patterns taken from 0° (perpendicular), 30°, 45°, and 60° angles to the normal of the surface plane. R/G/B/BK colors were achieved by combining corresponding C, M, and Y colored layers. We confirmed that no parallax effect was observed due to our optimum design of materials, optical structure, and thermal management to achieve thin C/M/Y layers.

Figure 8 is a high-resolution full-color image corresponding to 426 ppi taken from four directions with horizontal and vertical angles 60° to the normal of the surface. Our sheet showed perfect Lambertian reflectance. No color shifts and no image quality degradation were observed, which is consistent with the results of the no parallax effect shown Fig.7.

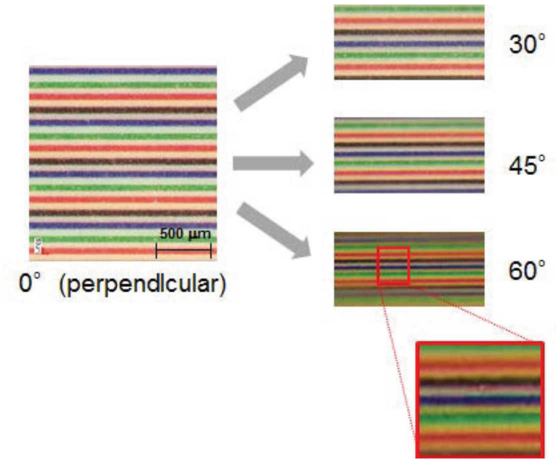


**Fig. 7 Photographic Images of R/G/B/BK colored 60 μm-width L&S pattern taken from 0° (perpendicular) 30°, 45°, and 60° to normal of surface.**

**Fig. 8 Horizontal and vertical viewing angle dependence of full-color image taken from 60° to normal of surface (12 cm x 8 cm).**

### 4.3 Rewritability

Figure 9 (a) is gradation pattern images obtained from a cyclic writing/erasing test. The full range of gradations were drawn at each writing step. After the laser erasing operation, the gradation pattern disappeared clearly with no image sticking. The OD of each color gradation after rewriting exhibited the same level as the initial OD values.

Figure 9 (b) shows the results of the rewrite endurance test. The OD did not show significant change in the colored state or the decolored state during repeated writing and erasing operations because of our careful design of the reversible thermochromic system concerning the materials and composition and the condition of laser irradiation.

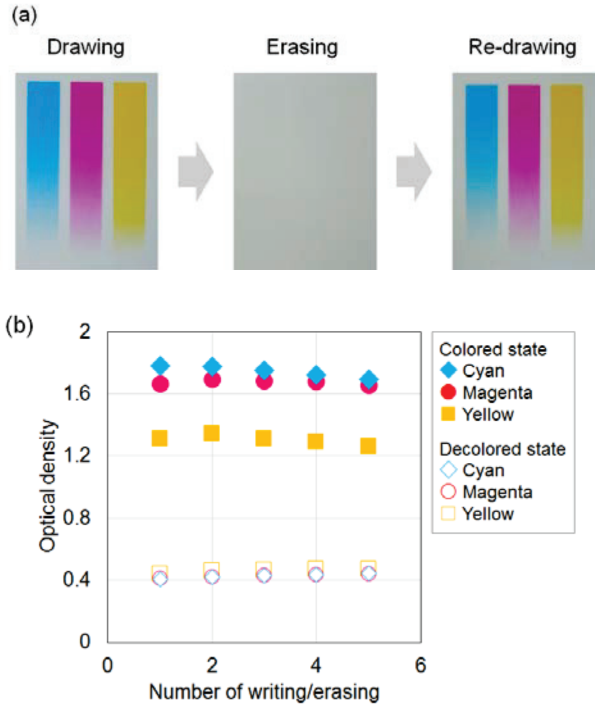


**Fig. 9 (a) Demonstration of rewritability of gradation pattern images during cyclic writing/erasing test and (b) stability of OD during cyclic writing/erasing test.**

### 4.4 Application

Noncontact and on-demand laser addressing have the respective advantages of (1) writing an image through a transparent cover film such as glass or a transparent film with a decorated surface structure and (2) free form factor. Therefore, various applications can be achieved, such as designing images on surfaces of varying shapes while promoting scratch tolerance and texture feelings. We demonstrated such applications as shown in Fig. 10.

**Fig. 10 High-resolution full-color images on sheets of various shapes under transparent cover film.**

## 5 CONCLUSIONS

We developed a single pixel full-color rewritable sheet based on a thermochromic system with leuco dyes. The sheet is composed of a vertically stacked C/M/Y-thermochromic system with unrecognized parallax and achieves photographic-quality images with a high resolution of 426 ppi, a wide color gamut of 70% coverage of SWOP standards, and wide viewing angle over 60°. The sheet was manufactured by a R2R process. Writing and erasing were performed by scanning with NIR laser light, and rewritability was confirmed for a whole range of the gradations. We also demonstrated that noncontact laser addressing has other advantages in its high form factor flexibility and that it promotes scratch tolerance. Thus, this technology will create new applications for on-demand rewritable image design while saving power and reducing the use of paper, contributing to a sustainable society.

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