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Dependence of Rewritable Characteristics on Dye and TiO_2 Concentrations in Wax-Based Electrophoretic Thin Media

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Abstract. *Wax-based electrophoretic rewritable media have been investigated since they potentially have good preservation characteristics. Reducing the thickness of rewritable media is critical for reducing the writing/erasing energy of wax-based rewritable media. The present study investigates the effect of rewritable media thickness. Samples of with dye concentrations of 0, 0.03, and, 0.07 wt. % and TiO_2 concentrations of 2.5, 5, and 10 wt. % with respect to wax were prepared with media thicknesses of 0.05, 0.1, and 0.2 mm and their rewritable characteristics were evaluated. The Kubelka-Munk equation was applied to investigate the dependence of the reflection of the dyed side on the dye and TiO_2 concentrations and the absorption coefficient of the dye was estimated. It was found that a TiO_2 concentration of 5 wt. % and a dye concentration of 0.07 wt. % give suitable display characteristics for cells with thicknesses of 0.1-0.2 mm. A preliminary rewrite experiment was performed on an enlarged dot cell. © 2011 Society for Imaging Science and Technology.*
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INTRODUCTION

With the rapid increase in information traffic associated with the development of computer and network technologies, the demand for hard copy information has increased rapidly. Electronic paper technology has been investigated as a means for reducing the paper consumption associated with hard copy printing and thereby reducing the environmental impact.[1] There are two main approaches for realizing electronic paper. One approach has its origins in printer technology. In this approach, like printed media, the display medium has no addressable circuit. The other approach is based on the display technology. In this approach, like display devices, the medium has an addressable circuit. Printer-based technologies are primarily rewritable media that utilize the reversible coloring reactions of leuco dye, e-ink, liquid crystal, dry toner motion, thermal magnetophoresis, and gyricon.[2–14] Writing methods are classified into four main types: electrical, magnetic, light, and thermal writing. These are used with both kinds of electronic paper: paper-like displays and rewritable paper. The advantages and disadvantages of each type of electronic paper depend on the writing method and the components in the paper media.[15]

A wax-based electrophoretic rewritable paper has been proposed. The major advantage of this wax system is the possibility of modulating the melting temperature over a wide range and of realizing good preservation properties.[16–19] Such paper is expected to have a very high number of write/erase cycles because it employs an electrophoretic process. This rewritable mechanism involves melting the wax when writing or erasing.[16] The energy consumed during writing and erasing is considered to be relatively high. Therefore, it is very important to make rewritable media thin. However, the thickness characteristics of wax-based electrophoretic rewritable paper have not been sufficiently investigated.

The purpose of the present study is to clarify the thickness characteristics of these rewritable media. The dependence of the rewritable characteristics on the dye and TiO_2 concentrations is measured and the thickness characteristics are discussed. Rewritable mechanisms are tentatively confirmed by preparing an enlarged rewritable dot cell.

EXPERIMENTAL

Sample Preparation

Samples were prepared by mixing dye, surfactant, and TiO_2. Two waxes (carnauba and rice waxes) were investigated. Carnauba and rice waxes have melting points of approximately 80 and 44 °C, respectively. Oil Black HBB (Orient Chemical Industries Co., Ltd.) was used as the dye and an anionic surfactant was used as the surfactant. The mean size of the TiO_2 particles was about 250 nm. If the particles are smaller than 250 nm, then their whitening ability will be weak, whereas if they are larger, sedimentation due to gravity cannot be ignored.

The materials were prepared using the ratios shown in Table I. Mixing was performed as follows: wax, dye, TiO_2, surfactant, and a 9.5-mm-diameter nylon ball were bottled and the bottle was placed in a temperature-controlled box (Koyo Thermo System, KL-45M) that was maintained at 120 °C for 10 min. With the exception of the ball, the content of the bottle melted. The bottle was removed from the oven and was shaken by hand for 2 min. The bottle was then placed in the oven for a further 10 min. It was then removed from the oven and shaken using a paint shaker (Red Devil Inc.,) for 10 min.

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Table 1. Mixing ratios of materials.

Samples number	Dye wax (wt%)	wt% ratio Wax : Dye	TiO_2 (wt%)	Surfactant (wt%)
1	97	100 : 0	2.5	0.5
2	97	100 : 0.03	2.5	0.5
3	97	100 : 0.07	2.5	0.5
4	94.5	100 : 0	5	0.5
5	94.5	100 : 0.03	5	0.5
6	94.5	100 : 0.07	5	0.5
7	89.5	100 : 0	10	0.5
8	89.5	100 : 0.03	10	0.5
9	89.5	100 : 0.07	10	0.5

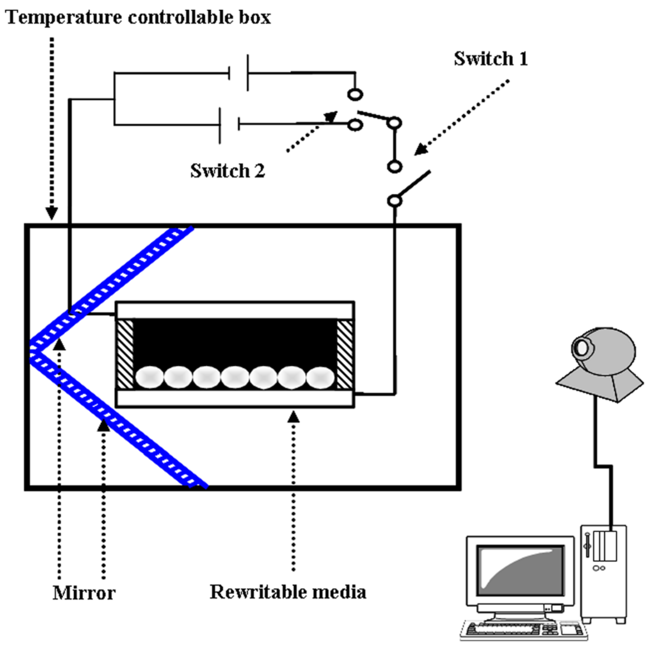

Figure 1. Schematic diagram of experimental system.

To determine the optimum shaking time, mixing times using the paint shaker of 1, 2, 5, 10, and 15 min were trialed. The TiO_2 side of the cell had good uniformity at a mixing time of 10 min. Thus, a mixing time of 10 min was used in subsequent experiments.

Measurement Methodology

Figure 1 shows a schematic diagram of the experimental method. Switch 1 was used to turn the dc power supply (Kenwood, PA500) on and off and switch 2 was used to change the polarity of the voltage applied to the measurement cell. The sample was kept in a temperature-controlled box (Koyo Thermo Systems, KLΦ-45M). The temperature was raised from room temperature to 100 °C. After the wax had melted sufficiently, switch 1 was turned on. A dc voltage of 100 V was applied to the lower electrode. This electric potential was applied to move the negatively charged

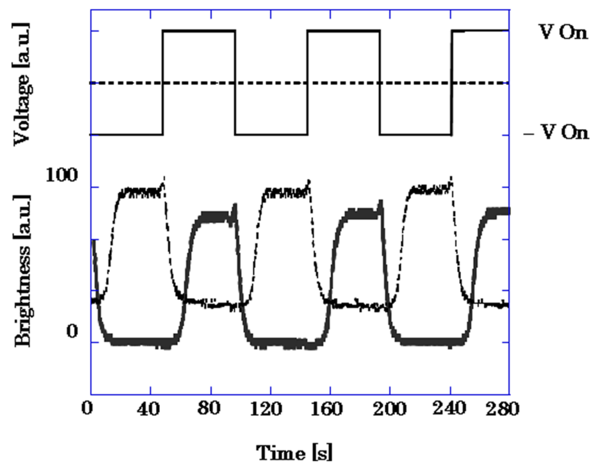

Figure 2. Time response of reflection when a rectangular voltage is applied.

TiO_2 particles to the lower side initially. Switch 2 was then turned on to move the TiO_2 particles from the lower side to the upper side. The voltage was applied for 1 min and the reflectance of the upper side of the sample was measured. Subsequently, the polarity of the voltage applied to the sample was reversed. The polarity was reversed several times. Figure 2 shows the changes in the reflectance. After several polarity changes, the sample was cooled to room temperature while applying a voltage. Both sides of the sample were measured using a spectrophotometer (Minolta, CM-2022). Three points on the sample were measured and the three values obtained were averaged.

A dot cell was prepared, as shown in Figure 3. The dot cell is 3 mm in diameter and the rewritable medium is 0.1 mm thick. The cell contains rewritable medium with 5 wt. % TiO_2 and 0.07 wt. % dye. Writing and erasing were performed at an applied voltage of 100 V and a temperature of 100 °C. The voltage was applied to the indium tin oxide (ITO) conductive surfaces indicated in Fig. 3.

RESULTS AND DISCUSSION

Figure 4 illustrates the reflectance dependence on the wavelength for dye concentrations of 0, 0.03, and 0.07 wt. % with respect to wax for a TiO_2 concentration of 5 wt. %. For comparison, Figure 5 shows the reflectance obtained with no TiO_2. From Figs. 4 and 5, it is found that the reflectance decreases in nearly all visible wavelength as dye is added. At the dye concentration 0.07 wt. %, the reflectance of the dyed wax side is less than 5%. The color of the dyed wax side is accordingly considered black which agrees with our visual impression. Concerning with the function of TiO_2, Fig. 4 shows that reflectance of all cases increases as TiO_2 is added. It is proposed that the reflectance increase of even the dyed side is owing to a small amount of TiO_2 remaining dispersed in wax and also attached to the ITO surface.

Figure 6 shows the dependence of the reflectance at a wavelength of 550 nm (to which the human eye is highly sensitive) on the dye concentration. The reflectance decreases with increasing dye concentration and increases with increasing TiO_2 concentration. The difference in the

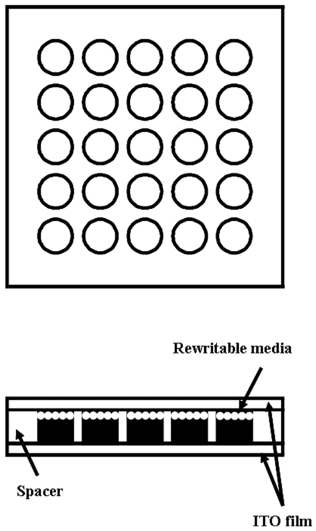

Figure 3. Experimental cell structure of rewritable media.

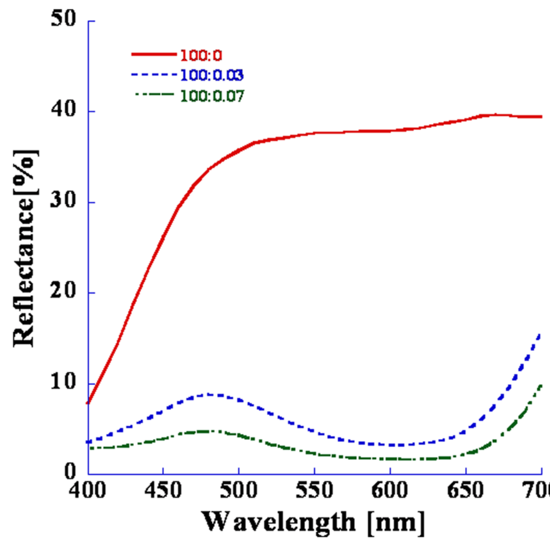

Figure 5. Reflection spectra of wax for dye concentrations of 0, 0.03, and 0.07 wt. %. The wax contains no TiO_2. Wax is carnauba wax and thickness of the media is 0.2 mm.

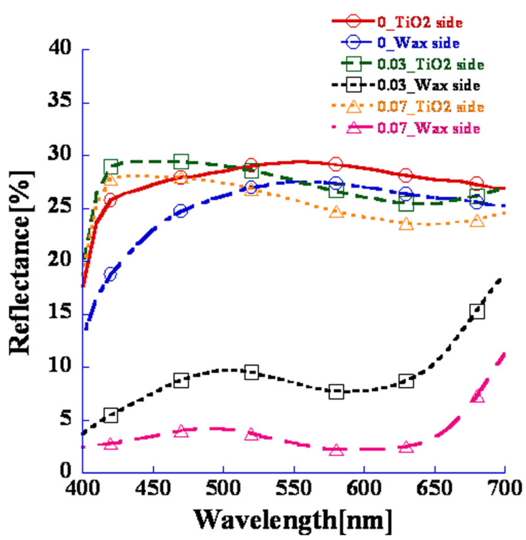

Figure 4. Reflectance spectra from the TiO_2 and dyed wax sides of test media for dye concentrations of 0, 0.03, and 0.07 wt. %. Wax is carnauba wax and thickness of the media is 0.2 mm.

reflectances of the white side (i.e., the TiO_2 side) and the black side (i.e., the dye-wax side) increases with increasing dye concentration because the dye absorbs light, whereas TiO_2 reflects light. Figure 7 schematically illustrates the light reflection model and the variable definitions.

The reflection dependence on cell thickness and dye concentration is discussed in terms of the Kubelka-Munk (KM) equation,[20] which is a fundamental equation for the optical properties of mixed systems. The KM equation is expressed as

$$\frac{dI}{dz} = -(S+E)I + SJ, \qquad -\frac{dJ}{dz} = SI + (S+E)J, \tag{1}$$

where I is the light intensity incident on the bottom side, J is the light intensity incident on the top side, S is the scattering coefficient, and E is the absorption coefficient.

The scattering coefficient S is considered to be low since the dye is highly absorbing and is well dispersed in the wax. If S is neglected, the KM equation is simplified. The ratio of the reflectances of the white side (i.e., the TiO_2 side) and the black side (i.e., the dye-wax side) is given by

$$R_b = R_w \exp(-2EL), \tag{2}$$

where R_b is the reflectivity when TiO_2 moves to the bottom of the cell and R_w is the reflectivity when TiO_2 moves to the surface.

Figure 8 shows a plot of $\ln(R_b / R_w)$ versus L. It shows that $\ln(R_b / R_w)$ is a linear function of L at a constant dye concentration. This indicates that applying the simplified KM equation does not give rise to a contradiction. The slope of the plot, E, depends on the dye concentration. The slope is nearly horizontal when no dye is added, which implies that the absorption arises mainly from dye. Figure 9 shows the relation between the slope and the dye concentration. It is found that E is proportional to the dye concentration; i.e.,

$$E = kC_{\text{dye}}, \tag{3}$$

where k is a coefficient, dependent on the dye state in the wax, and C_{dye} is the dye concentration (dye gram/media gram).

The values k are obtained as $k = 1.4 \times 10^4$ [1/mm] and 7×10^3 [1/mm] for carnauba and rice waxes, respectively.

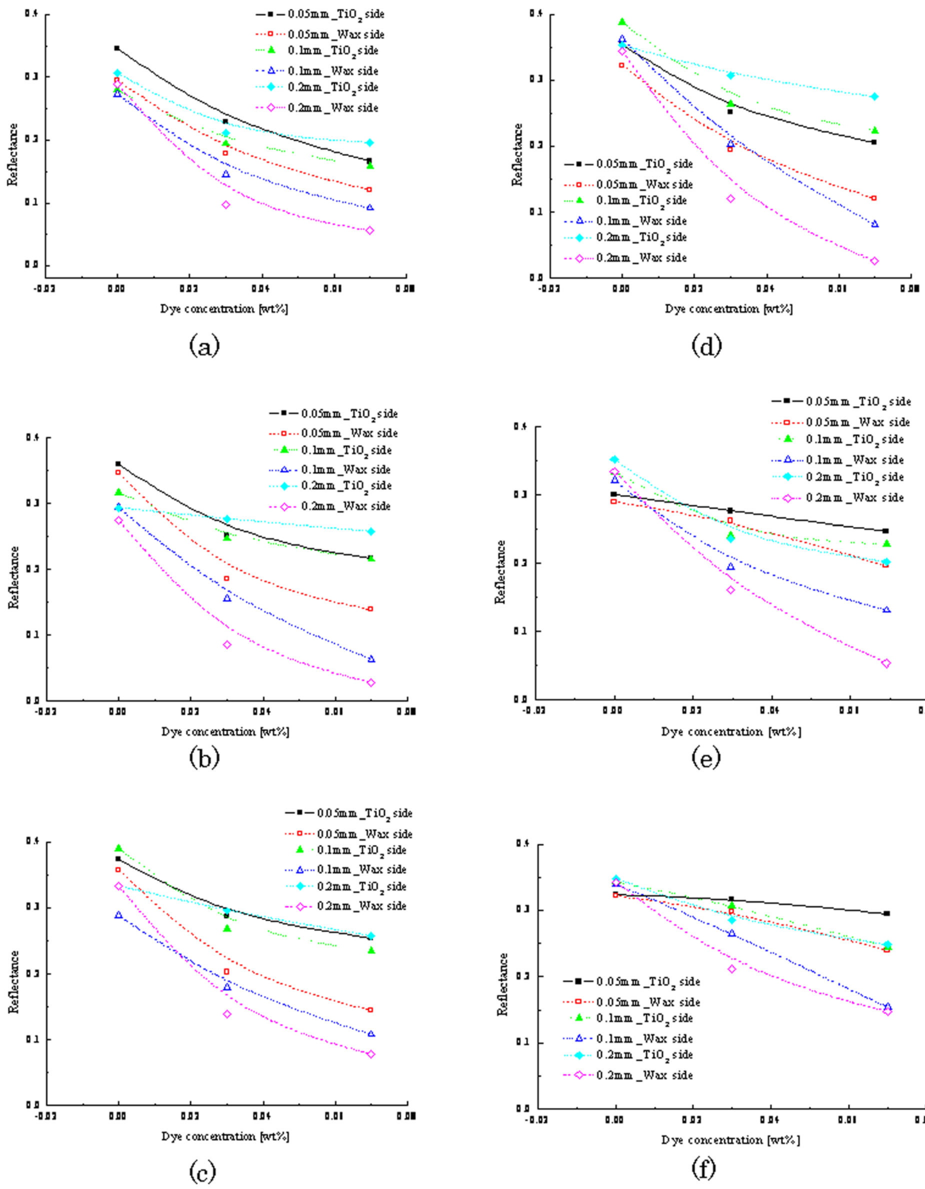

Figure 6. Plots of reflection at 550 nm on the TiO_2 and dyed wax sides as a function of dye concentration. (a) TiO_2 2.5 wt. %, carnauba wax; (b) TiO_2 5 wt. %, carnauba wax; (c) TiO_2 10 wt. %, carnauba wax; (d) TiO_2 2.5 wt. %, rice wax; (e) TiO_2 5 wt. %, rice wax; (f) TiO_2 10 wt. %, rice wax.

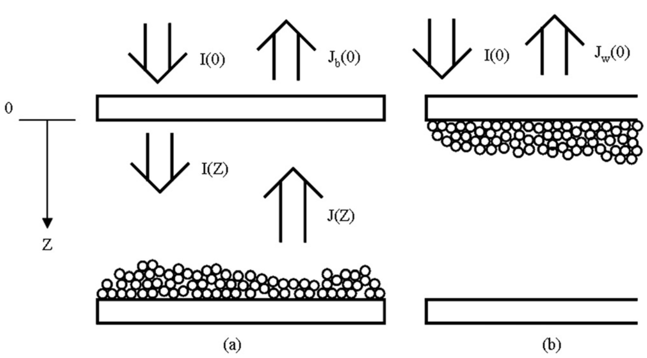

Figure 7. Light reflection model and definitions of the variables. (a) When TiO_2 moves to upper side and (b) when TiO_2 moves to bottom side.

This difference in k may be due to dye dispersion properties. These values are useful for predicting the display characteristics of rewritable media made from these mixed systems.

The influence of the dye concentration on the display characteristics has been mentioned above. We next discuss the influence of the TiO_2 concentration. When the TiO_2 concentration increases, the reflectances of the white and black sides increase for both waxes. This is because TiO_2 has strong scattering properties. On the black side, a small amount of TiO_2 is considered to attach to the surface of the ITO glass. The TiO_2 layer is considered to be thicker on the white side. In carnauba wax, the difference in the reflectances of the white and black sides starts to increase from 2.5

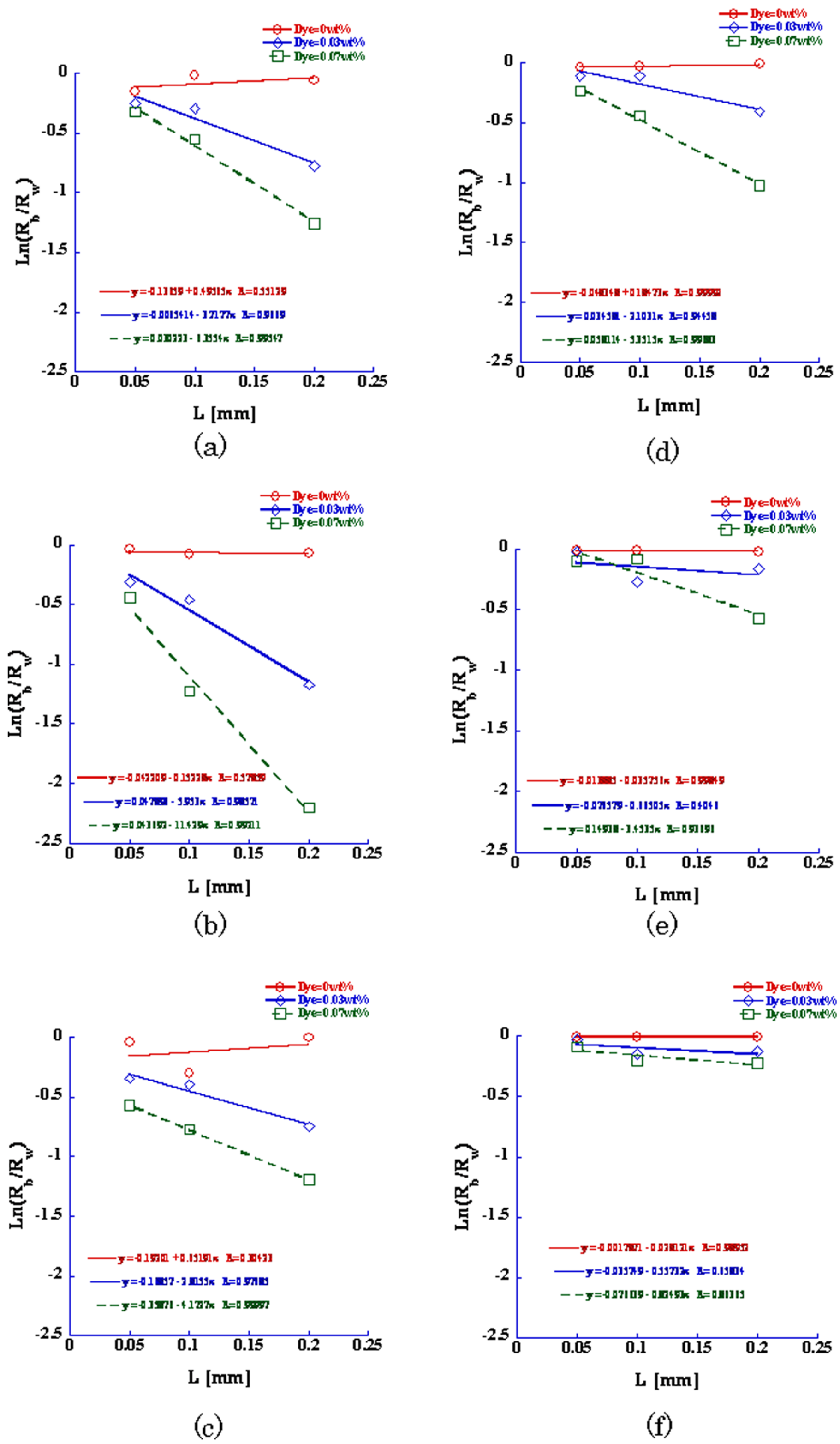

Figure 8. $\ln(R_b/R_w)$ dependence on L. (a) TiO_2 2.5 wt. %, carnauba wax, (b) 5 wt. % TiO_2, carnauba wax, (c) 10 wt. % TiO_2, carnauba wax, (d) 2.5 wt. % TiO_2, rice wax, (e) 5 wt. % TiO_2, rice wax, (f) 10 wt. % TiO_2, rice wax.

wt. % and saturates at around 5-10 wt. % with increasing TiO_2 concentration. In rice wax, the reflectance difference between the two sides decreases gradually from around 2.5-5 wt. %. The variation with the type of wax is due to TiO_2 having different dispersion properties in different waxes. In these mixed systems, carnauba and rice waxes are found to have suitable display characteristics at wax concentrations of about 5-10 and 2.5-5 wt. %, respectively.

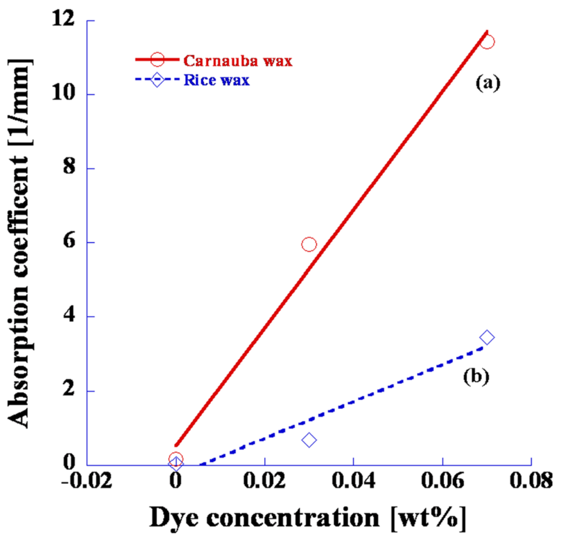

Figure 9. Absorption coefficient dependence on dye concentration for 5 wt. % TiO_2; (a) carnauba wax and (b) rice wax.

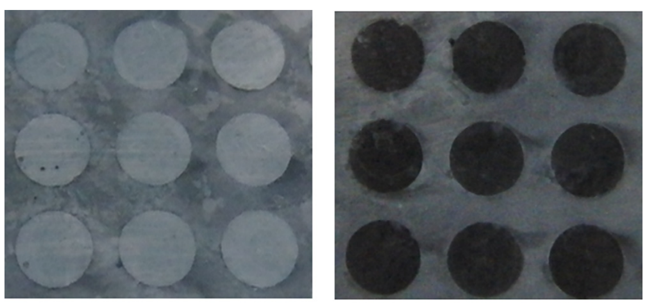

Figure 10. Photographs of written and erased dots: (a) TiO_2 side when TiO_2 moved to the upper side; (b) dyed side when TiO_2 moved to the bottom side.

The write and erase processes are carried out at an applied voltage of 100 V and a temperature of 100 °C. The photographs of written and erased dots are shown in Figure 10. It is confirmed that rewriting is possible on an enlarged dot cell.

SUMMARY

The effect of dye and TiO_2 concentration on rewritable characteristics was investigated to determine the optimum dye and TiO_2 concentrations for realizing a thin rewritable layer. With increasing dye concentration, the reflectance of the dyed side of the medium decreases exponentially. This decrease is explained by in terms of the Kubelka–Munk equation. This equation is used to estimate the absorption coefficient of the dye in the wax. The optimum dye concentration can be estimated from the absorption coefficient based on the expected thickness of the medium. In these mixed systems, good display characteristics are obtained for 5 wt. % TiO_2 and 0.07 wt. % dye. A preliminary experiment was performed on an enlarged dot cell and rewriting was confirmed to be possible by heating while applying a voltage. This investigation was undertaken to provide potentially useful for the engineering of wax-based rewritable media.

REFERENCES

[1] M. Omodani, J. Imaging Soc. Jpn. **38**, 115 (1999) [in Japanese].
[2] K. Tsutsui, T. Yamaguchi, and K. Sato, J. Appl. Phys., Part 1 **33**, 5925 (1994) [in Japanese].
[3] K. Naito, S. Takayama, and T. Sasaki, US Patent 6,010,808 (2000).
[4] K. Tsutsui, "Rewritable printing system using leuco dyes," *Proc. IS&T's NIP20: Int. Conference on Digital Printing Technologies* (IS&T, Springfield, VA, 2004) p. 214.
[5] J. M. Jacobson, US Patent No. 7,106,2961 B1 (2006).
[6] H. Yoshikawa, M. Omodani, K. Nakamura, and Y. Takahashi, J. Imaging Sci. Technol. **47**, 304 (2003).
[7] T. Z. Kosc, K. L. Marshall, A. Trajkovska-Petkosha E. Kimball, and S. D. Jacobs, Displays **25**, 171 (2004).
[8] T. Kitamura, H. Nakamura, N. Mizuno, S. Nakamura, and K. Hoshino, "Movement of Triboelectrically Charged Particles in Toner Display," *Proc. IS&T's NIP19: Int. Conference on Digital Printing Technologies* (IS&T, Springfield VA, 2003) p. 902.
[9] H. Mizuno, and K. Yogome, *Proc. Imaging Society of Japan Electrophotography Meeting* (ISJ Tokyo Japan, 2004) IDY2004-37, p. 17.
[10] T. Kitamura G. Jo, and K. Hoshino, "Response Time for Toner Display by Electrical Particle Movement," *Proc. IS&T's NIP16: Int. Conference on Digital Printing Technologies* (IS&T, Springfield VA, 2000) p. 110.
[11] T. Kitamura N. Mizuno S. Nakamura, and K. Hoshino, "Improvement of Image Contrast in Toner Display," *Proc. IS&T's NIP20: Int. Conference on Digital Printing Technologies* (IS&T, Springfield, VA, 2004) p. 1005.
[12] O. Majima, *Proc. Imaging Society of Japan, Electrography Meeting* (ISJ, Tokyo, Japan, 2004), IDY2004-36, p. 1.
[13] D. A. Hays J. Electrost. **51**, 57 (2001).
[14] N. K. Sheridon, "The Gyricon as an electronic paper medium," *Proc. Society of Electrophotography of Japan, Pan-Pacific Imaging Conference/Japan Hardcopy '98* (Soc. Electrophotography of Japan, Tokyo, Japan, 1998) p. 83.
[15] H. Arisawa and K. Shigehiro, "Photo-addressable E-paper and toner display," *Proc. IS&T's NIP20: Int. Conference on Digital Printing Technologies* (IS&T, Springfield, VA, 2004) p. 922.
[16] Y. Hoshino M. Ogura and T. Sano, Jap. J. Appl. Phys. **43**, 7129 (2004).
[17] S. Noppakundilograt S. Phattanarudee S. Kiatkamjornwong R. Kumekawa M. Ogura, and Y. Hoshino, "Imaging Parameters Influencing the Rewritable Process of Titanium Dioxide Electrophoresis," J. Imaging Sci. Technol. **51**, 190 (2007).
[18] R. Kumekawa T. Hasegawa Y. Hoshino, and T. Sano, "Estimation of TiO_2 particle electrophoresis by measuring reflectance response," *Proc. IS&T's NIP 21: Int. Conference on Digital Printing Technologies* (IS&T, Springfield, VA, 2005) p. 56.
[19] T. Hasegawa R. Kumekawa Y. Hoshino, and T. Sano, "Electrophoretic Characteristic of TiO_2 Particle in Melted Wax," *Proc. IS&T's NIP 22: Int. Conference on Digital Printing Technologies* (IS&T, Springfield, VA, 2006) p. 477.
[20] K. Kubelka and F. Munk, "Ein Beitrag zur Optik der Farbenstriche," Z. Tech. Physik. **12**, 593 (1931).