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# Imaging Parameters Influencing the Rewritable Process of Titanium Dioxide Electrophoresis

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**Abstract.** *The aim of the present research is to study the effects of titanium dioxide ($TiO_2$) and dye concentrations on the optical characteristics of the rewritable media. The influences of $TiO_2$ and dye concentrations on the optical characteristic and time response were investigated under various applied voltages and voltage cycles. The brightness change during each experiment was recorded in the motion JPEG mode and data analysis was done with a personal computer program. The optimal concentrations of $TiO_2$ and dye were found at 6 and* 0.2–0.3% w/w, *respectively, which yielded a good result of black-white contrast. The time response decreased when increasing the applied voltage, $TiO_2$, and the dye concentrations. The applied voltage also affected the optimal black-white contrast. The present work suggests that rewritable paper can be improved when the optimal conditions of the paper are achieved. © 2007 Society for Imaging Science and Technology.*
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## INTRODUCTION

As a result of rapid information technology developments in recent years, paper consumption for printing using electronic printers, such as electrophotographic printers and ink jet printers has increased dramatically. A certain amount of paper is used for data confirmation or document preparation. To decrease this paper consumption and preserve forests, an electronic paper technology has originated.[1] There are two main approaches to creating electronic paper, printer, and display technology, which can be seen in reversible coloring reactions of leuco dye,[2–4] liquid crystal,[5,6] twisting ball,[7,8] dry toner motion,[9–12] thermal magnetophoresis,[13] and gyricon.[14] The writing methods are divided into four main methods namely electrical, magnetic, light, and thermal writings, which are used with both categories of electronic paper (a paper-like display and rewritable paper). The advantages and disadvantages of each type of electronic paper depend on the writing method and the components in paper media.[15]

Electronic papers are prepared from a dye complex, which is composed of three main components, namely the coloring agent, the developing agent and the binder resin.[16] The major advantages of the dye complex system are the possibility of modulating the transition temperature at a wide range and the production of multicolored images. The number of writing and erasing cycles of some kinds of the dye complex material using a thermal head or bar capable of spotheating without affecting optical density could be only 100 times of usage.[17] The composition of liquid crystal rewritable recording media is based on smectic liquid crystal because of its bistability during a phase change between the opaque and transparent states.[18,19]

Recently, a new rewritable media has been proposed using electrophoresis and selected heating for which previous studies showing excellent visibility can be achieved. Hoshino and co-workers[20] have developed a rewritable media, which is composed of $TiO_2$ covered nylon particles as white particles, dye, and molten carnauba wax (under heating) as a medium. The mechanism of this rewritable media is shown in Fig. 1. At the initializing stage, when the rewritable media was heated and voltage was then applied, the $TiO_2$ particles moved to the upper side connected to a negative electrode. Thus, the upper side became white and the bottom side became black. At the imaging stage, after reversing the polarity of the voltage and heating a selected area, only the carnauba wax in the selected area was melted and the $TiO_2$ particles moved from the upper side to the bottom side resulting in a color difference which appeared as an image.

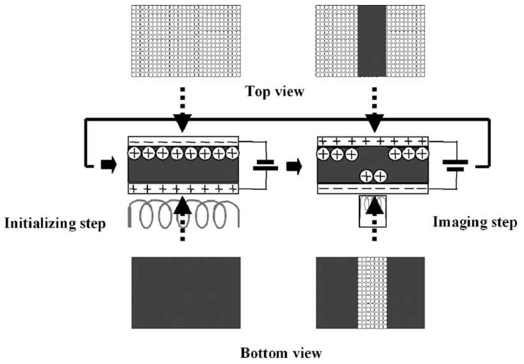

Figure 1. Mechanism of rewritable media by electrophoresis and selected heating.

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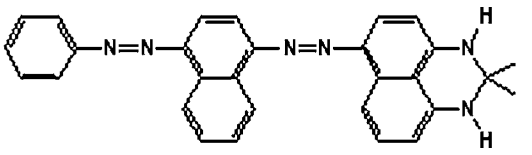

Figure 2. Chemical structure of HBB oil dye (Solvent Black 3 C.I. 26150).

The solidified wax after cooling to room temperature caused the image to be of high stability and wide view-angle visibility. However, $TiO_2$ covered nylon particles do not show adequate whiteness due to the mixing method at the sample preparation stage. The aim of the present study is therefore to develop a rewritable medium using $TiO_2$, dye as a color generator, and a surfactant. In addition, mixing and heating sequences are able to influence image visibility so the effects of the $TiO_2$ concentration, the dye concentration, the applied voltage, and voltage cycles on image visibility have been investigated.

## EXPERIMENT

The materials used in the rewritable medium were carnauba wax (Hayashi Chemical, Japan), HBB oil black dye or another name of Sudan Black 3 (Solvent Black 3 C.I. 26150, Orient Chemical Industries Ltd. Japan, its chemical structure is presented in Fig. 2 as indicated as a type of azo dye), and $TiO_2$ (particle size of 0.25 $\mu$m, Ishihara Sangyo Kaisha, Ltd. Japan). First, the carnauba wax was melted and mixed with the black dye. Next, $TiO_2$ and 2.5% w/w of the surfactant (SAT, its IR spectrum is shown in Fig. 3 to indicate some possible functional groups as follows: $\nu_{\text{-OH}}$, 3471 $\text{cm}^{-1}$, $\nu_{\text{-NH}}$, 3308 $\text{cm}^{-1}$, $\nu_{\text{=CH}}$, 3085 $\text{cm}^{-1}$, $\nu_{\text{-CH}}$, 2916 and 2856 $\text{cm}^{-1}$, $\delta_{\text{-NH}}$, 1647 or $\nu_{\text{-C=C}}$, $\text{cm}^{-1}$, $\nu_{\text{-C-N}}$, 1466 $\text{cm}^{-1}$, $\nu_{\text{-C-O-C-}}$, 1221 $\text{cm}^{-1}$, $\nu_{\text{-O-C,-C-O-C}}$, 1022 $\text{cm}^{-1}$; its functional groups imply that it may be a cationic surfactant) were added to the dyed carnauba wax at a temperature of 120 °C. After cooling, this mixture was cut and placed on an indium tin oxide (ITO) glass. Another piece of ITO glass was assembled with the first ITO glass separated by a piece of polycarbonate spacer with a thickness of 200 $\mu$m as shown in Fig. 4. This sample cell was put in an oven, and a specific voltage was applied when the temperature had reached 100 °C. The brightness change during the experiment was then recorded with a digital camera (Minolta: DiMAGE Z1, Tokyo, Japan). After cooling to room temperature, the reflectance spectra were measured by colorimetry (Minolta: CM-2022, Tokyo, Japan). For the voltage cycle experiment, the experiment was done in similar conditions as described above but the voltage polarity was reversed after the voltage had been applied at 3 min/cycle. Details of the material components and setup conditions of the experiments are shown in Table I.

The time response of the reflectance ($t_{1/2}$) of both sides of the sample cell was measured using the same digital camera for recording the brightness change during each experiment in a motion JPEG mode. Then the motion JPEG data were analyzed using a personal computer program. More details of the measurement have been described elsewhere.[20]

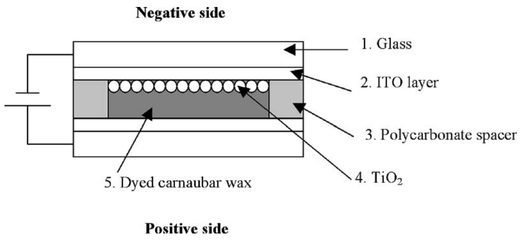

Figure 4. Sample cell.

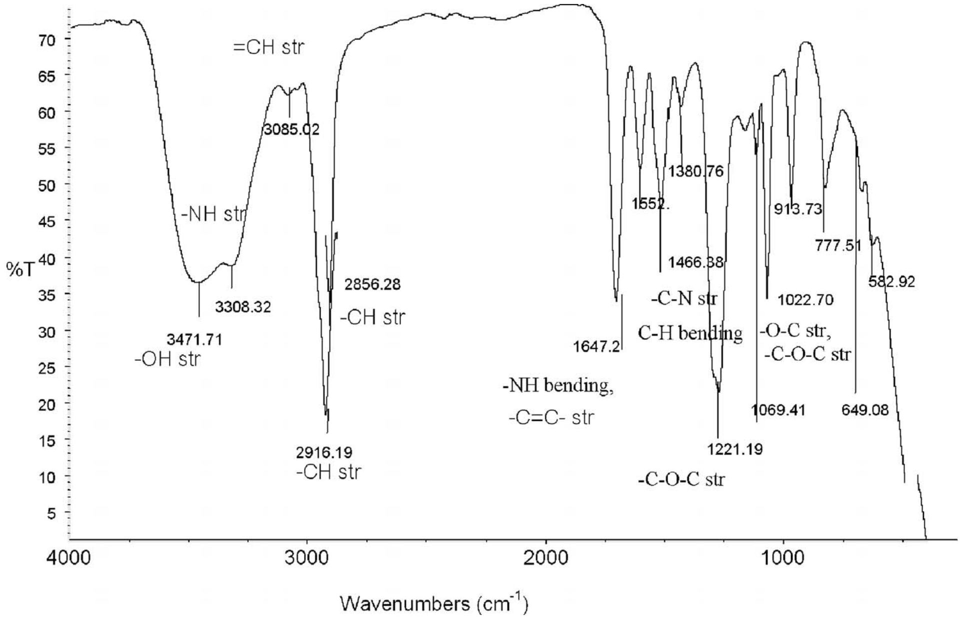

Figure 3. IR spectrum of SAT.

## RESULTS AND DISCUSSION

### *Effect of $TiO_2$ Concentration*

When the sample cell was heated, the dyed carnauba wax melted and the $TiO_2$ particles, possessing positive charges, moved from the ITO glass connected to the positive side of the applied voltage to the negative side. The movement of $TiO_2$ resulted in the reflectance difference between the ITO glasses. As shown in Fig. 5, the result shows that the percentage reflectance of the negative side (the white side, *W*) increases with increasing $TiO_2$ concentrations caused by increases in the amount of $TiO_2$ on this side. On the other hand, the percentage reflectance of the positive side (the black side, *B*) was comparably low when 1, 2.5,

**Table I.** Components and conditions of the experiment.

| | Condition | | |
|---|---|---|---|
| Experiment | $TiO_2$ (% wt) | Carnuaba wax: Dye (100: X) | Voltage (V) |
| 1. $TiO_2$ concentration | 1, 2.5, 6, 10 | 0.3 | 100 |
| 2. Dye concentration | 6 | 0.1, 0.2, 0.3, 0.6, 1 | 100 |
| 3. Voltage cycle at | | | |
| gravity falling | 6 | 0.2 | 10, 20, 50, 100, 200 |
| voltage falling | 6 | 0.2 | 50, 100, 200 |
| 4. Dye concentration and voltage cycle | 6 | 0.05, 0.1, 0.2, 0.5, 1 | 100 |

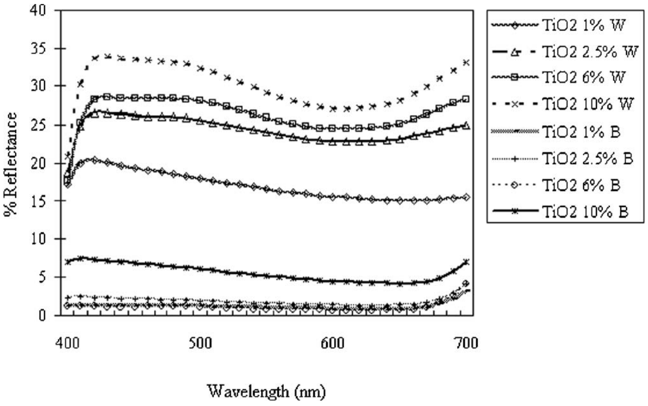

Figure 5. Reflectance spectra of various $TiO_2$ concentrations (both the positive (*B* for black) and the negative (*W* for white) sides).

or 6% w/w of $TiO_2$ were used. The low percentage reflectance was caused by the black color of the dyed carnauba wax on this side, which obstructed the $TiO_2$ reflectance. However, $TiO_2$ concentration 10% w/w yielded an increase in the reflectance on the positive side. This result indicates that a high concentration of $TiO_2$, inducing a thick $TiO_2$ layer in the negative side, adversely affected the percentage reflectance of the positive side by increasing the percentage reflectance due to the inherent whiteness of $TiO_2$. In this case, the optimal concentration of $TiO_2$ was found to be 6% w/w, because it gave a high reflectance of the negative side and a low reflectance of the positive side. This difference in the percentage reflectance could provide a better image contrast. The $t_{1/2}$ of the particles moving to the negative side (the increase direction) decreased when $TiO_2$ concentration increased as shown in Fig. 6. However, the effect of $TiO_2$ concentration was not observed for $t_{1/2}$ on the opposite side, which is the positive side (the decreasing direction). In the presence of a high $TiO_2$ concentration, the distance between the $TiO_2$ layer on the positive side and the ITO glass on the negative side decreased. The movement of $TiO_2$ to the negative side was faster due to the shorter distance. This caused the time response ($t_{1/2}$) to decrease.

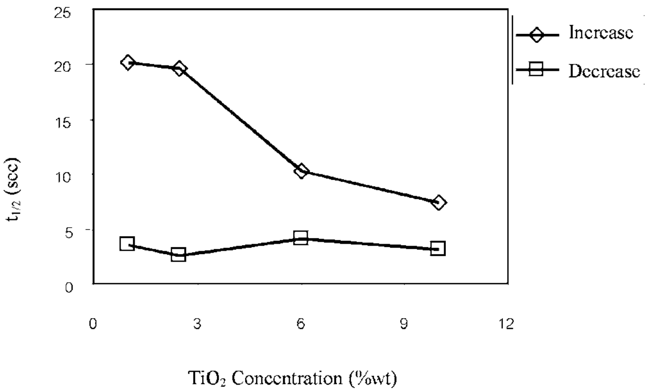

Figure 6. Time response ($t_{1/2}$) as a function of $TiO_2$ concentration (both the positive (increasing) and the negative (decreasing) sides).

### *Effect of Dye Concentration*

When the dye concentration was increased, the percentage reflectance of both the negative and positive sides decreased as shown in Figs. 7 and 8. The reflectance of the positive side was only affected by the dye because $TiO_2$ would move from the positive side to the other side by the applied voltage. On the other hand, the percentage reflectance of the negative side was a summation of $TiO_2$ and dye reflectance. It was found that when a dye concentration of as high as 0.6 or 1% w/w was used, the reflectance of the negative side was also very low and led to low contrast images. At 0.1% w/w dye concentration, the result shows insufficient black density on the positive side. When dye concentrations were 0.2 and 0.3% w/w, they gained a high percentage reflectance on the negative side and still maintained a low percentage reflectance on the positive side. The big difference between the black and white reflectances produced high contrast images. Thus, the optimal dye concentration could be either 0.2 or 0.3% w/w.

### *Effect of Voltage Cycle*

#### *First Cycle with $TiO_2$ Falling by Gravity*

The first cycle was started by letting the $TiO_2$ particles in the sample cell come under normal gravitational force for 20 min, and then the voltage was applied to the sample cell, in order to investigate the combination of the voltage and gravity effects. The results indicated that the optimal black-white contrast, crossover between the increasing and the decreasing brightness of the positive side and negative side when $TiO_2$ moves, was obtained when applying 100 or 200 V, whereas no crossover was observed at 10 or 20 V. This indicated that $TiO_2$ could not reach the negative side when the applied voltage was low at 20 V (Fig. 9). Figure 10 illustrates the brightness contrast at 100 V.

According to electrophoresis theory,[21] the $TiO_2$ particles feel a force pushing them in one direction. The force involved due to the electric field acting on the charge of the $TiO_2$ particle is represented as

$$F = QE, \tag{1}$$

where $F$ is the force, $E$ is the electric field, and $Q$ is the net charge. However, when the $TiO_2$ particles move, frictional

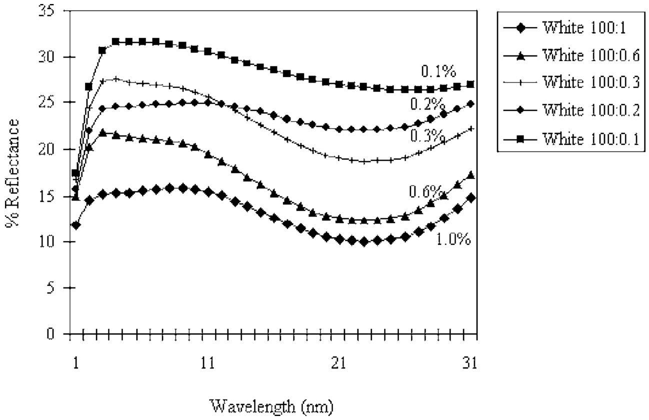

Figure 7. Reflectance spectra of various dye concentrations on the negative side.

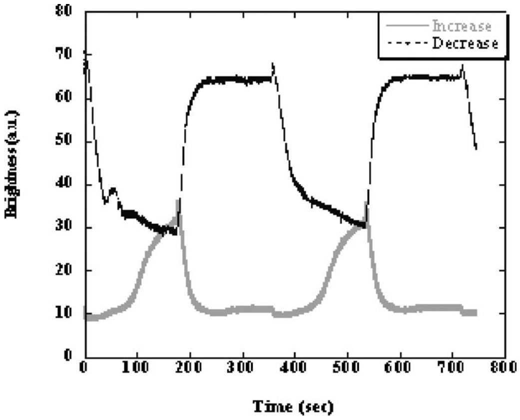

Figure 9. Brightness crossover between the increasing and the decreasing at 20 V (the first cycle fallen with gravitational force 20 min).

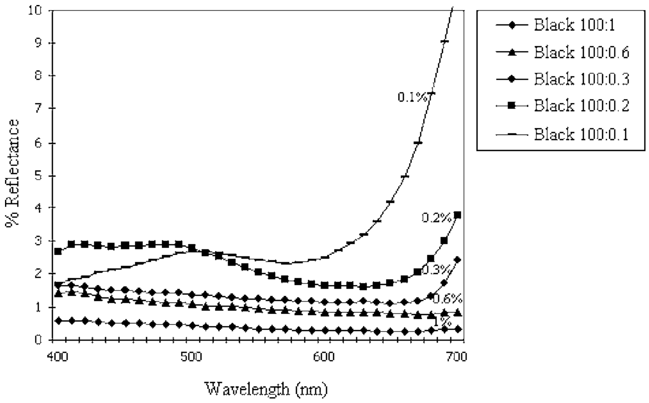

Figure 8. Reflectance spectra of various dye concentrations on the positive side.

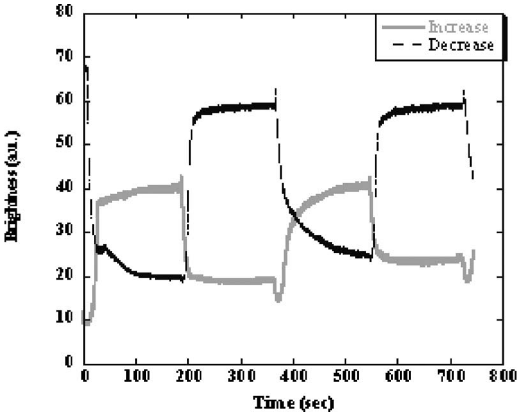

Figure 10. Brightness crossover between the increasing and the decreasing at 100 V (the first cycle fallen with gravitational force 20 min).

forces are generated in the opposite direction. The frictional forces slow the $TiO_2$ particles traveling through the medium depending on the size of the $TiO_2$ particles. The speed at which the $TiO_2$ particles go through the medium is determined by the point at which the forces driving them forward are just balanced by the frictional forces. In this case, the driving force for $TiO_2$ movement in the increasing direction i.e., forwards the positive side of the cell (the increase cycles Nos. 1 and 3 as shown in Fig. 11) is the electric force, but the total opposing force is the sum of the gravity and frictional forces. When the applied voltage was low, the driving force was small and then the gravitational force dominated the $TiO_2$ movement. Thus a longer time response was obtained when the applied voltage was as low as 50 V. On the other hand, when the applied voltage was 200 V, the driving force was so large that the response time was the shortest. For $TiO_2$ movement in a decreasing direction i.e., forwards the negative side of the cell (the increase cycles, Nos. 2 and 4), the total driving force is a resultant of the electric and gravitational forces. When the applied voltage was high, the effect of the gravitational force was no longer dominant. The time response at 50 V was not so different from those at 100 and 200 V. These results indicated that the effect of gravity dominated the $TiO_2$ movement in both directions at 50 V, whereas the effect of voltage dominated it at 100 and 200 V where $t_{1/2}$ was more-or-less stable over the increase and decrease directions. The current rewritable systems can write/erase/write for more than ten cycles without any image degradation.

### *First Cycle with $TiO_2$ Falling by Voltage*

The movement of the $TiO_2$ was controlled to fall during the first cycle with a lower applied voltage. The longest time response was obtained when the applied voltage was 50 V (Fig. 12). In contrast, the time response was shortest for the applied voltage of 200 V in order to move the $TiO_2$ particles in the increasing direction. When the voltage of 100 or 200 V was applied, the gravitational force was not the dominant effect. The result was similar to that of the first cycle for $TiO_2$ particles moving towards the decreasing direction under gravity. This suggests that at the low applied voltage of 50 V, the particles still moved under the gravitational effect. At the high voltage of 100 or 200 V, the time responses of the increase and decrease directions were not much different in each cycle. This indicated that the voltage effect dominated at 100 and 200 V.

When comparing the movement in the decreasing direction under gravity and under applied voltage, the time response of the first cycle movement at 50 V under gravity

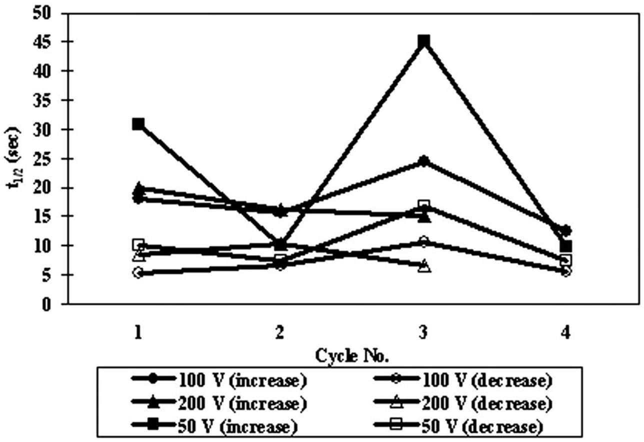

Figure 11. Time response of $TiO_2$ movement at 50, 100, and 200 V (the first cycle fallen with gravitational force for 20 min).

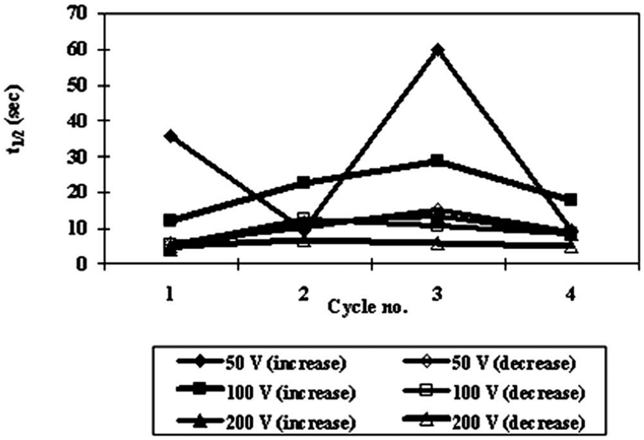

Figure 12. Time response of $TiO_2$ movement at 50, 100, and 200 V (the first cycle fallen with applied voltages of 20, 50, or 100 V).

was shorter than that under applied voltage. This is because the $TiO_2$ particles fell only with the gravitational force and formed a loose packed $TiO_2$ layer. The distance between the top $TiO_2$ layer and the negative side was accordingly short. On the other hand, in the case of applying voltage, the combination effect of the electric force and gravitational force induced a close packing of the $TiO_2$ layers. In this case, the distance between the top of the $TiO_2$ layer and the negative side was longer. Thus, a shorter time response was obtained in the case of movement under gravity due to the shorter distance.

When the applied voltage was increased from 50 to 100 or 200 V, the $TiO_2$ formed more closely packed layers. The relationship between the applied voltage, ions and distance between ions can be expressed as follows:

$$E = \frac{V}{r} = \frac{kq_1q_2}{r}, \tag{2}$$

where $E$ is the electric field which is in direct proportion to voltage $V$, $r$ is the distance between the positive and negative ions, $q_1$ and $q_2$ of the titanium dioxide, and $k$ is a constant. When a high voltage is applied, the distance between the ions, $q_1$ and $q_2$ is reduced and thus the ions can pack more closely to each other, leaving a larger distance for the ions to travel back to the opposite side during the reverse voltage. This is in agreement with the longer $t_{1/2}$.

The distance between the top $TiO_2$ layer and the negative side was longer than that at 50 V. However, the driving force of the electric force was also increased when increasing the applied voltage. In the case of 100 or 200 V, the time response was more affected by the driving force than the difference in distance. Thus, for $TiO_2$ falling by voltage, the time responses of 100 and 200 V in the first cycle were shorter than those of $TiO_2$ falling by gravity. The different distance between the cycle numbers also caused different time responses in cycles 1 and 3, where the $TiO_2$ particles move in the same direction, as with those of cycles 2 and 4.

### *Effect of Dye Concentration and Voltage Cycle*

The voltage was applied to the sample cell for several cycles and similar time responses between the cycles in the same direction of movement were obtained. The time response of the third cycle in the increasing direction was found to be close to those of the fifth and of the seventh cycles. It was shown that cycle numbers 3, 5, and 7 provided the most steady state in which increasing applied voltages resulted in an increase of the $1/(t_{1/2})^2$ as shown in Fig. 13. When the $TiO_2$ particle moves in the increasing direction by electrostatic force in the viscous medium, the equation for the $TiO_2$ particle movement can be written as

$$F_E - F_\eta - F_{mg} = ma, \tag{3}$$

$$q\frac{V}{d} - 6\pi\eta\nu - mg = ma, \tag{4}$$

where $V$ is the potential difference (voltage), $d$ is the distance between electrodes, $q$ is the net charge of the $TiO_2$ particles, $m$ is the mass of the $TiO_2$ particles, $g$ is the gravitational constant, and $\eta$ is the viscosity of the carnauba wax. From Eq. (4) when the terms of the $F_\eta$ and $F_{\mathrm{mg}}$ were negligible and the high voltage controlled the movement of the particle, $V$ is then simply proportional to $(t_{1/2})^2$. The results are shown in Fig. 13. It was indicated that the higher the voltage is, the faster the mobility of the $TiO_2$ particles becomes. Thus, when the applied voltage increases, the time response decreases.

When the dye concentration was changed, the time response was also affected. Observed results generated from the third cycle in the increasing direction at 100 V were that an increase in the dye concentration decreased the $t_{1/2}$ as shown in Fig. 14. The longest time response was obtained when the dye concentration was 0.05% w/w.

The dye concentration did not affect the movement time of $TiO_2$ particles because they were moved by their electric charges. On the other hand, the dye concentration did affect $t_{1/2}$ of the system in that the low dye concentration increased $t_{1/2}$ and vice versa. At the lower dye concentration, the dye molecules diffused at a slower rate compared with those at a higher concentration. After the $TiO_2$ particles had

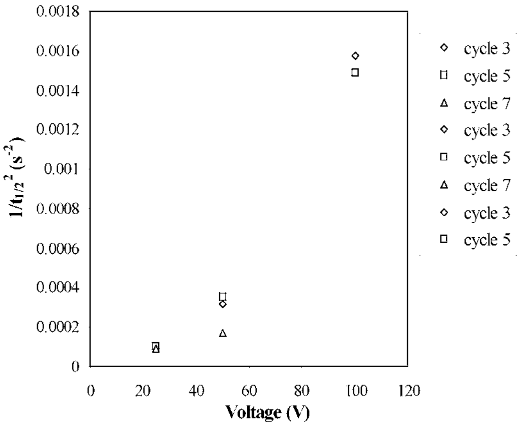

Figure 13. Time response of $TiO_2$ movement on the increase at 25, 50, and 100 V.

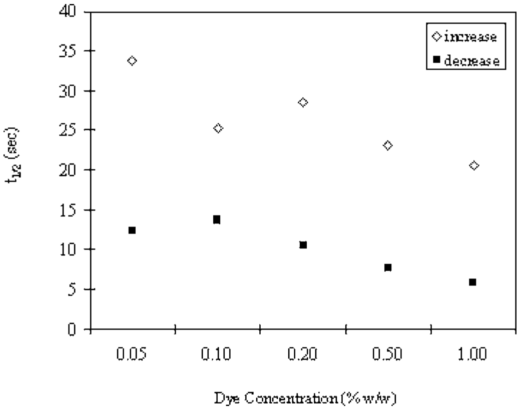

Figure 14. Time response of $TiO_2$ movement on the increase vs dye concentration at 100 V.

been moved by the applied voltage, the dye molecules took a longer time, or a longer $t_{1/2}$, to replace the $TiO_2$ particles to achieve complete blackness on one side. At the higher dye concentration, the dye molecules would spontaneously diffuse to replace the $TiO_2$ particles in a shorter time ($t_{1/2}$) producing a better contrast between the white and black sides.

## CONCLUSIONS

A new rewritable medium by electrophoresis with selected heating was invented using $TiO_2$ particles for its smaller particle size and higher whiteness. The effects of the $TiO_2$ and the dye concentrations on the optical characteristics and time response of this rewritable medium were investigated. The optimal concentrations of $TiO_2$ and dye were 6 and 0.2–0.3% w/w, respectively, which gave good black-white image contrast. Increasing the concentrations of $TiO_2$ or dye resulted in a decrease in the time response. Time response also decreased when increasing the applied voltage. Using an applied voltage of 100 or 200 V, the optimal black-white contrast could be obtained. Several cycles of the $TiO_2$ movement under the applied voltage had shown similar time responses in cycles Nos. 3, 5 and 7 where the $TiO_2$ moved in the same direction. One of the advantages of a rewritable medium by the electrophoresis and selected heating mechanism is that this modified method can be optimized easily by changing the components of the medium. It is possible to improve the quality of the medium for a new rewritable paper in the future.

## ACKNOWLEDGMENTS

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