Toner Display Based on Particle Movements

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A novel electronic reflective display using conductive toners and dielectric white particles has been designed and constructed. The display cell consists of two indium−tin oxide (ITO) plates coated with a charge-transport layer (CTL) on the interior of the cell. The toner and white particles are placed in a small space formed by a spacer. In this display, toner movement is controlled by the action of an external electric field applied between the two ITO electrodes. The conductive toners in the vicinity of the CTL on the anode (lower electrode) are charged positively by hole injection from the CTL and then move to the cathode (upper electrode) to form a black image. The toner is held on the CTL of the cathode by an electrostatic force. A white image is formed by applying a reverse electric field that causes the toners to move back to the lower electrode. The reflection densities of the black and white images were determined to be 0.96 and 0.63, respectively. A response time of ca. 0.8 ms was obtained under optimal operating conditions. Observations of the image formation, optimization of particle-loading conditions, and investigation of the repetition characteristics of the display have been carried out.

Introduction

In the recent information society, many electronic documents have been distributed on the computer network. The displays for the information play important roles in understanding, thinking, and processing the electronic documents. The displays are divided into two types of media: one is a softcopy and the other a hardcopy. A liquid crystal[1] and a cathode ray tube[2] are representative of a softcopy. Though a great amount of information can be displayed by the softcopy medium, its long-time use is exhausting. On the other hand, the paper medium printed by a conventional printing and electronic printer is a typical example of a hardcopy. This medium is characterized by its thinness, lightweightedness, easy portability, and its not so exhausting use. However, much information cannot be displayed on the paper medium because of the lack of a rewritable feature. Additionally, a negative environmental impact is another serious problem with this medium. Thus, the development of an electronic analogue of paper has been an important and long-standing objective of much international research. Several candidates for rewritable and electronic papers have been reported.[3] Polymeric films containing dispersed long-chain molecules or leuco dyes have been investigated as thermal rewritable marking media. There is presently much fundamental and applied research being carried out on various methods for producing paper displays including a microcapsule-type electrophoretic display,[4,5] a twist ball display,[6] and a two-color dyes/liquid crystal type display.[7] In this paper, we report the principle and properties of a new reflection-type display based on the movement of electronically black conductive toner and white insulative particles.[8]

Principle of Display

General Characteristics. The mechanism of the new reflection-type display (toner display) is based on the electrostatic migration of black conductive toner particles[9] in a mixture containing white dielectric particles. Figure 1 shows the cross section of the toner display into which the toners and the white particles are loaded. The sandwich-type cell structure consists of two indium−tin oxide (ITO) coated glass plates separated by an insulating spacer. The inner surfaces of the ITOs are coated with charge-transport layers (CTLs).[10] The device displays a black or white pattern depending on the polarity of the applied voltage. When a positive bias voltage is applied to the lower ITO

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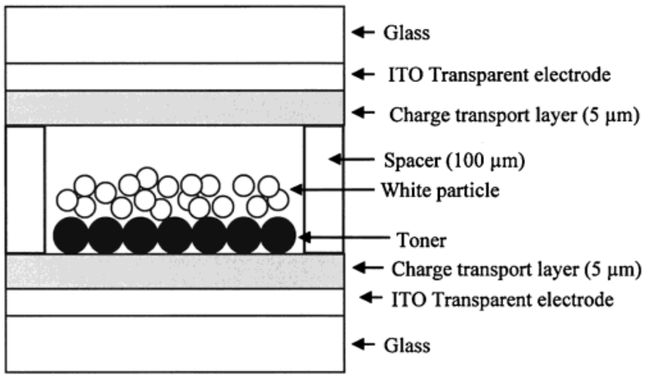

Figure 1. Cross section of a toner display using conductive toner and white particles.

electrode, the conductive toner particles move to the upper electrode because they are positively charged. When viewed through the upper electrode, the black toner particles adhere to the CTL of the upper electrode, and therefore, the indication of "black" is perceived by the human eye. The reverse (white image) is obtained when a negative bias voltage is applied to the lower ITO electrode. Even if the device is turned off, the conductive toner remains attached to the CTL by an electrostatic force. The display of white and black can be controlled by switching the polarity of the applied voltage.

Mechanistic Aspects. When a positive voltage is applied to the lower electrode, the conductive toners are charged positively by hole injection from the CTL and move to the upper electrode because of the coulombic force acting on the toner charge by the electric field across the cell. The movement of the particles by switching the polarity of the bias voltage is shown in Figure 2a,b. In this process, the positive charge at the ITO can be injected into the CTL because of the ohmic characteristics for holes at the interface and then transported through the CTL by hopping conduction.[10a,11] The conductive toner is then charged positively by hole injection from the CTL at the toner/CTL interface. Therefore, the toner moves through the white particle layer toward the upper electrode (Figure 2a). The use of hole injection for toner charging was made to secure constancy of the toner charge, which should be stably maintained during the operation even when the toner is discharged. More rapid transport of the toner requires a lower friction coefficient and a smaller occupation volume of the white particles in the cell space. As a result of this transport, the toners reach the CTL coated on the upper electrode, and a black pattern is observed when viewed from the top of the cell (Figure 2b). The CTL involves hole-transport molecules, and accordingly, negative charges on the ITO electrode cannot be injected into the CTL; the CTL serves as an insulating layer under this condition. Even if the power supply is turned off, the toner remains fixed at the upper CTL by the electrostatic image force between the positive charge of the toner and the conducting upper ITO electrode. Next, when the polarity of the upper electrode is switched from negative to positive, the toner is moved through the white particle cloud toward the lower electrode by a reversal coulombic electrostatic force. As a result, the toners are positioned below the white particles and hence a white pattern is observed when viewed from the top of the cell (Figure 2d). Note that the CTL functions in two ways depending on its operation conditions. First, it injects holes into the conductive toner in the initial stage, making the toner charged positively. Second, it functions as an insulating layer when biased negatively and attracts the toners electrostatically to form a black pattern image.

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Experimental Section

A mixture of conductive toner and white particles was loaded into the toner display cell consisting of transparent ITO electrodes coated with a CTL. The thickness of the spacer is 100 μm, and the electrically addressable size for one pixel is 10 mm × 10 mm.

Magnetic conductive toner (Hitachi Metals, Ltd.) and carbon fluoride (Nippon Carbon Co.) were used for the black and white particles, respectively. Carbon fluoride is a derivative of graphite denoted as $-(-CF-)-_n$ in which a fluorine atom is attached to each carbon atom in the graphitic sheet. Figure 3 shows their scanning electron microphotographs. The toner particles are almost spherical in shape with a median diameter of ca. 15 μm and a size range from 5 to 30 μm. In this study, magnetic toner particles were chosen for the experiments because the toner stationary layer can be formed on the lower ITO by attracting them with a magnet in the initial stage of the experiments (see Figures 1 and 2a). The carbon fluoride is flake-shaped with a smaller size of 1−2 μm (Figure 3b) and high resistivity.

A mixture of 4-(dibenzylamino)-2-methylbenzaldehyde-1,1-diphenyl hydrazone (Figure 4; Anan Co., Ltd.) as the charge-transport molecule and polycarbonate (PC; Teijin Chemicals Ltd., Panlite k-1300) dissolved in 1,2-dichloroethane in a 1:1 weight ratio was coated on the ITOs by the spin-coating method to form the CTL with a thickness of 5 μm.

The response of the display to switching of the applied voltage was monitored with an optical microscope (Olympus Optical Co., Ltd., BH2-UMA), and the optical reflection density of the image was measured with a reflection densitometer (Ihara Electronic Ind. Co., Ltd., Ihac-11). The image contrast, C, was calculated as follows: $C = (D_B - D_W)/(D_B + D_W)$, where D_B and D_W are the reflection densities of the black display and the white display, respectively.

The response time of the toner display was measured by a photon counting technique. The light from a He−Ne laser (632.8 nm) was irradiated on the upper ITO surface, and its reflection was introduced into a photomultiplier (Hamamatsu Co., R943-02). The change in the photon number with time was monitored by a signal processor (Hamamatsu Co., C2550-01). The response time is defined as the period during which a steady number of photons per unit time reflected from the black image completely changes to that from the white image or vice versa.

Results and Discussion

Observation of Black and White Image Formation. A 6 mg mixture consisting of conductive toner and white particles was mixed in a 1:1 weight ratio and enclosed in the display cell. The toners were placed in contact with the CTL on the lower ITO electrode by stirring the mixture with a magnetic stirrer. Figure 5 shows the photograph of the toner display with four pixels: Two cells on the diagonal line display black and the others white.

The conductive toner was moved to the upper electrode by applying a positive voltage to the lower

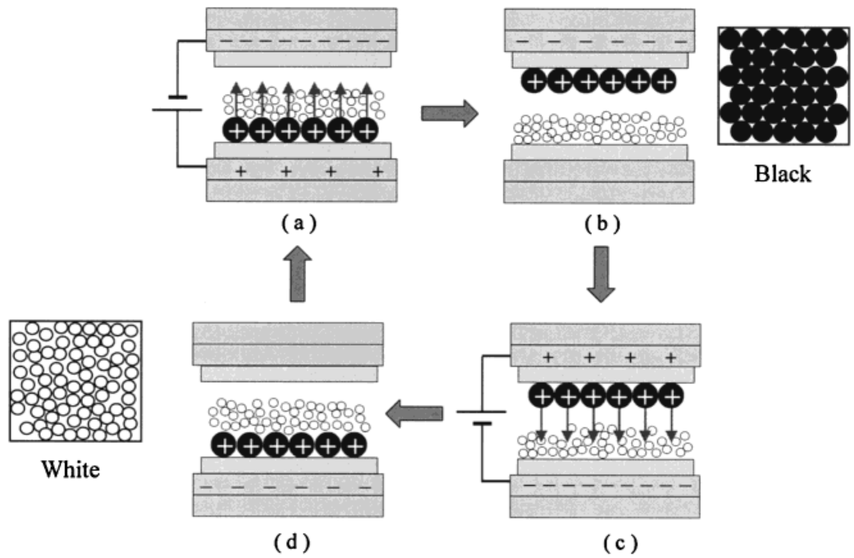

Figure 2. Principle of black and white images by switching the polarity of the bias voltage.

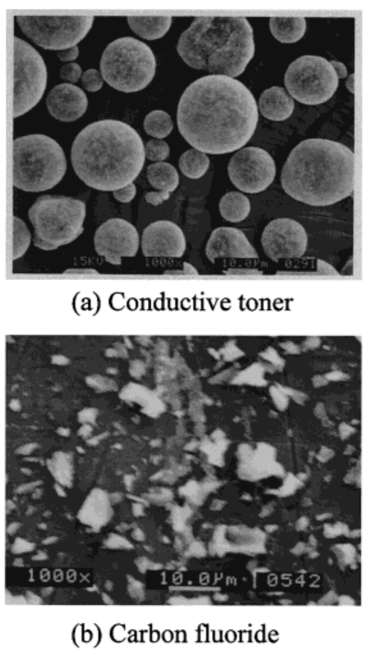

Figure 3. Scanning electron microphotograph of conductive toner (a) and white particles (b). Scale bars: 10 μm.

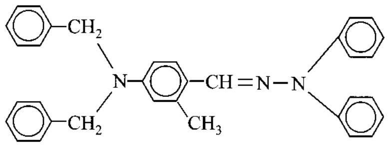

Figure 4. Chemical structure of the charge-transport material.

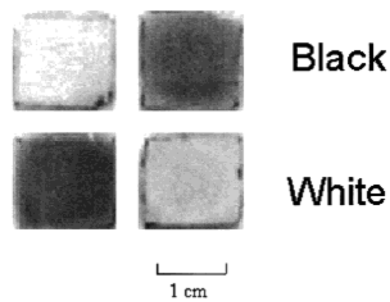

Figure 5. Photographs of a display cell with four pixels showing black and white images.

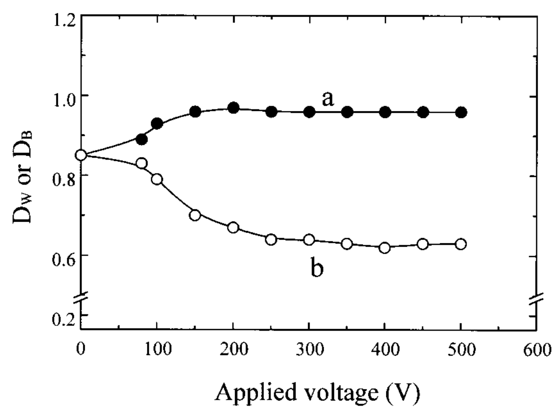

Figure 6. Relationships between optical reflection density and applied voltage. D_B and D_W stand for the density for the black (a) and white (b) images.

electrode, and the reflection density of the black display (D_B) was measured. In addition, the white display was prepared by switching the polarity of the bias voltage, and the reflection density of the white display (D_W) was measured. Figure 6 shows the relationships between the reflection density and applied voltage. A voltage was applied to the device, resulting in a black image. The reflection density was then measured using the densitometer. This was followed by reversal of the voltage polarity and the reflection-density measurement of the resulting white image. It can be seen from Figure 6 that the onset voltage at which the toner moves is ca. 80 V because the difference in the reflection density between the black and white displays, $D_B - D_W$, is clearly observed above ca. 80 V. A definite increment in bias voltage, 50 V, was selected for the measurements. The reflection densities for the black and white images were constant at 0.96 and 0.63, respectively, above 200 V. No threshold voltage was observed in Figure 6 because the density changed gradually with voltage below ca. 200 V. This may be due to the wide distribution of the toner size (see Figure 3a), and therefore, only the smaller toners may be movable below ca. 200 V. The lack of a threshold voltage and the gradual change in C in the

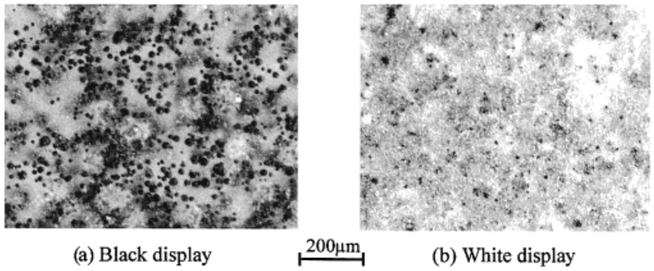

Figure 7. Microphotographs of black (a) and white (b) displays when viewed through the upper ITO electrode.

voltage region of ca. 80−200 V permitted gray scaling. The reflection density of the display in which only the toner was enclosed was 1.7. This value is larger than that for the black image in Figure 6 (closed circles), which shows a reflection density of 0.96. The reason for the low reflection density may be due to the low coverage of the toner on the upper electrode. On the other hand, the reflection density of the display containing only the white particles was 0.3. The fact that this is smaller than the 0.63 reflection density for the white image in Figure 6 suggests the existence of residual toner particles on the upper electrode.

To obtain further information on the adhesion properties of the particles, optical microscopic observations were carried out. Figure 7 shows the top views of the display cell for the black (a) and white images (b). The cell contained a mixture of toner and white particles (1:1 in weight, 6 mg) in which the two electrodes were separated by a 100 μm thick spacer. The bias voltage was 300 V. The coverage of the black toner in Figure 7a was about 26%. This coverage was nearly constant above 200 V and did not increase with increasing applied voltage. The cross-sectional view of the cell revealed that many toner particles were still confined in the bulk of the white particle layer. Careful observation indicated that the white carbon fluoride particles were absorbed on the toner surface and the lower CTL. The adsorption should prevent the toner from being charged enough to move to the upper electrode: The adsorbed white particles should not allow hole injection from the CTL to the toner particles. The white display in Figure 7b exhibited a toner coverage of about 5%, which is the background of the image formation by the toner display. We believe that the problem with stiction of the white flakes to the toner particles, as well as the toner particles and flakes to the CTL, should be solved by the use of spherical toner and white particles of approximately equal size. The finding of white spherical particles and their classification, as well as the classification of the toner particles, are the subject of ongoing research in our laboratory.

Effect of Loading Conditions on Image Contrast. The features of the toner display depend on the mixing ratio and the total mixture amount placed in the cell. Figure 8 shows the relationship between the toner concentration (weight percent) and the contrast in the reflection density (*C*) between the black and the white images. The total amount of the mixture was fixed at 6 mg. The bias voltage was 500 V. The contrast increased with increasing toner concentration in a range lower than 50 wt %. On the other hand, the contrast decreased with an increase in the toner concentration above 50 wt %, showing a peak at 50 wt %. This decrease suggests that significant amounts of uncharged toner particles still exist after the application of bias voltages and that they prevent transport of the charged toner particles in the cell. As described above, lower contrast values below 50 wt % can be explained by the increased adsorption of the white particles on the toner and CTL surfaces with an increase in their concentration. Further addition of the white particles beyond 50 wt % may result in a decrease in the hole-injection efficiency and thereby an increase in the number of the uncharged toner particles. Though not shown here, at applied voltages of 100, 200, 300, and 400 V, the contrast also showed a peak at a toner concentration of 50 wt %. Figure 9 shows the plot of *C* vs applied voltage at cell loadings of 4−8 mg, in which the weight ratio of the toner to the white particles was 1. The value of *C* increases with the applied voltage below 200 V and assumes a steady value above 200 V, except in the case of a 8 mg loading, where the contrast shows a monotonic increase with applied voltage. Additionally, a maximum contrast was obtained with the 6 mg loading that was independent of the bias voltage. This implies the importance of particle-free space in the cell, and it was found that the transport of the toner was hindered beyond the loading of 6 mg (see Figure 10 in which the contrast was replotted as a function of the loading at a bias voltage of 500 V). This was supported by the study on the dependence of *C* on the spacer thickness (d). The value of *C* for $d = 50$ μm was ca. a quarter of those for

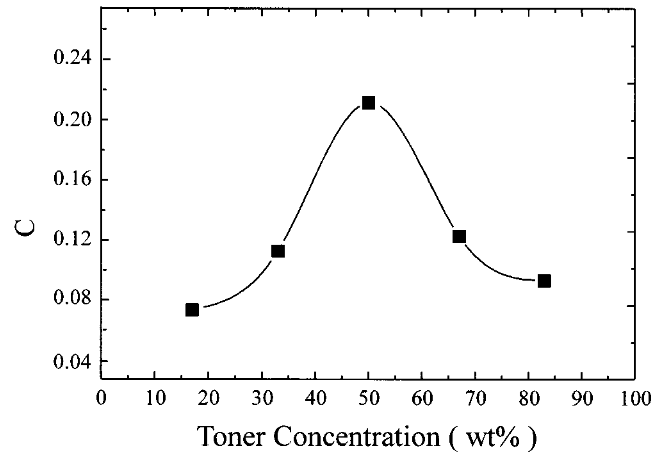

Figure 8. Change in the image contrast, *C*, with the toner concentration in the particle mixture.

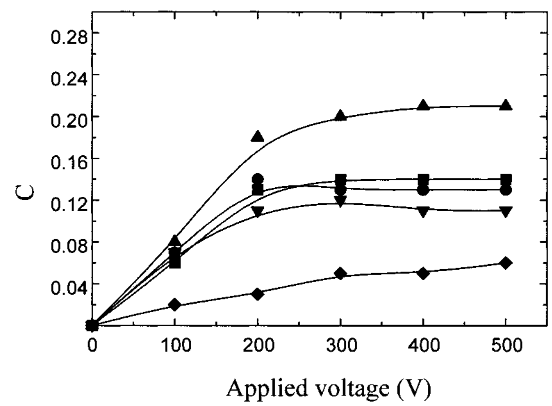

Figure 9. Dependence of *C* on applied voltage. Total amount of the mixture: ●, 4 mg; ■, 5 mg; ▲, 6 mg; ▼, 7 mg; ◆, 8 mg.

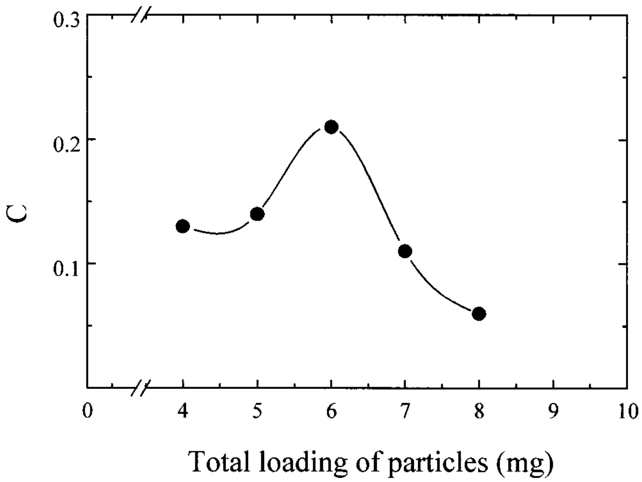

Figure 10. Dependence of *C* on the total loading of the mixture. Externally applied voltage: 500 V.

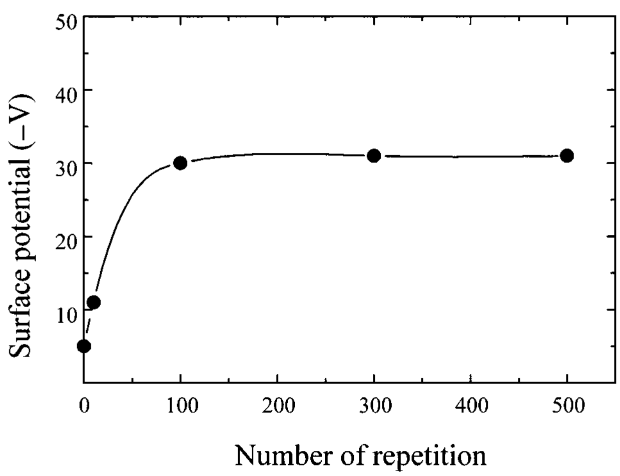

Figure 11. Surface potential of the mixture plotted against the number of repeated operations.

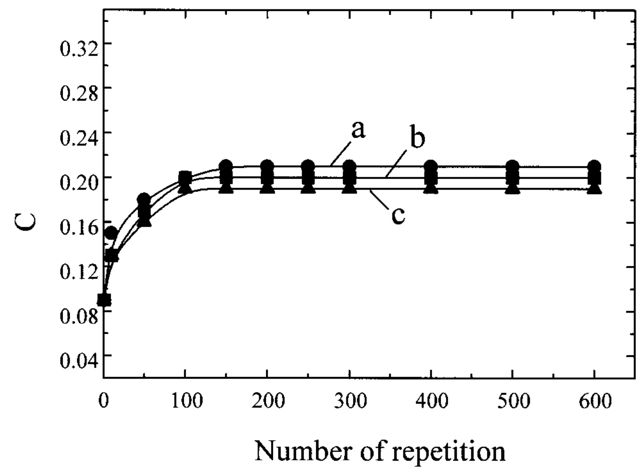

Figure 12. Repetition characteristics of the toner display. The ratio of the toner to the white particles: a, 1; b, 3/2; c, 2/3. Total amount of loading: 6 mg.

$d = 100$, 150, and 200 μm, being another demonstration of the importance of particle-free space.

Display Repetition Characteristic. The white particles are charged triboelectrically by the movement of the toner. Figure 11 shows the change in the surface potential of the mixture with the repetition of switching of the bias voltage under the following conditions: bias voltage, 500 V; particle loading, 6 mg; weight ratio of the toner to the white particles, 1. The measurements were carried out by repeating the switching procedure, which was terminated by application of a negative voltage (−500 V) to the upper electrode. The resulting display was black (see Figure 2b), and toner particles adhered to the top electrode. After a power supply was turned off, the top electrode was removed and the surface potential of the mixture remaining on the lower electrode was measured. The mixture was charged to −5 V only by mixing in the initial stage of operation, and the surface potential increased at first but then tapered off after the number of repetitions reached 100. A final steady value of −30 V decayed to half upon storage for 1 week. This finding indicates that the white particles are negatively charged during the initial operations and that their contribution to the operation of the toner display should be taken into account for the elucidation of the mechanism. This is the subject of ongoing research in our laboratory.

To investigate the repetition characteristics of our display, stability tests were conducted. Figure 12 shows the dependence of the contrast on the number of repetitions. The weight ratios of the toner to the white particles were 3/3 (a), 3/2 (b), and 2/3 (c) for a mixture loading of 6 mg and a bias voltage of 300 V. The curves were quite similar in shape to that in Figure 11, indicating that the triboelectric charging of the white particles is one of the keys to the operation of the display. As described in Figures 7 and 8, it is suggested that the adsorption of the white particles on the toner and CTL surfaces prevents the toners from charging, and accordingly many toner particles are still uncharged in the initial stage of the operation. However, the initial operations (ca. 100 times) may induce friction between the toner and the white particles, leading to positive and negative charging of the former and the latter particles, respectively. Their tribocharging should enhance the efficiency for their electrostatic separation under the action of an electric field, and hence, the value of *C*. Note that the contrast remained constant even after the operation was repeated 600 times. Also notable is the memory effect of the display device. The device retained the toner images formed previously even after it was switched off, during which the CTL blocks the electron injection from the ITO to the toner, making possible the fixation of toner particles on the upper electrode. Such an ability to store the display with no sustaining power, which is also an important characteristic of electrochromic[12] and electrophoretic displays,[13] can be an advantage from the point of view of energy conservation.

Response Time. The response time of a display device is a parameter of obvious importance, and so it was determined by using three types of toners with different resistivity but the same size (ca. 15 μm). Figure 13 shows the plot of response time vs applied voltage for the display: The curves a−c show the data for the

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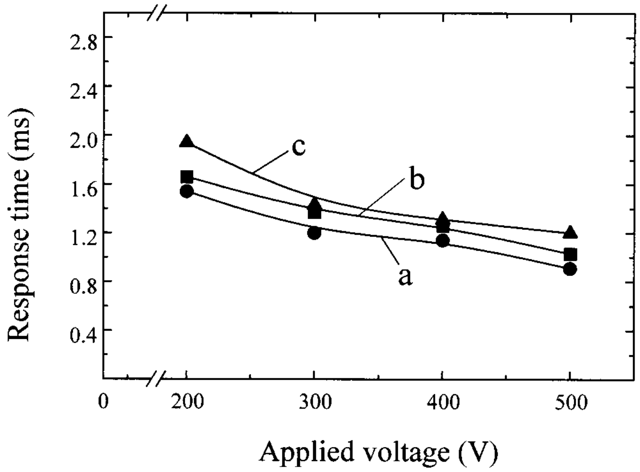

Figure 13. Dependence of response time on applied voltage. The resistivity value: a, 1×10^8 Ω·cm; b, 1×10^{10} Ω·cm; c, 5×10^{11} Ω·cm.

toner resistivity of 1×10^8, 1×10^{10}, and 5×10^{11} Ω·cm, respectively. The total loading of the mixture and the weight ratio of the toner to the white particles were 6 mg and 1, respectively. The response time was dependent on the applied voltage and toner resistivity and ranged from 0.8 to 2.0 ms. These values are smaller than the response time for a liquid crystal display (milliseconds to 0.1 s), an electrochromic display (0.1 s), and an electrophoretic image display (10 ms) but larger than that of a cathode ray tube (microseconds), a light-emitting diode (microseconds), a plasma display panel (10 μs), and an electroluminescence display (0.5 μs).[14] The response time decreased with a decrease in the toner resistivity. The toner charge will depend on its adhesion to the CTL because the adhesion controls the field at which the toner particle is detached. If we assume that the adhesiveness increases with a decrease in the toner resistivity, the lower resistivity should lead to a larger amount of toner charging and, therefore, to the more rapid transport of the toner particles. However, the question of a resistivity−adhesion relation remains open.

Conclusions

Conductive toner and the white insulative particles were loaded in a sandwich-type cell to form black and white images by applying and switching bias voltages. In the image formation process, the toner is positively charged by hole injection from the CTL and moves through the white particle layer to the counter electrode. On the other hand, the white particles, which are negatively tribocharged by the friction with the toner particles, move in the opposite direction. The response time of this process was ca. 0.8 ms, which is much faster than that of the eye (~0.1 s).[14] The reflection densities of the black and white displays were 0.96 and 0.63, respectively. The maximum contrast was obtained when the total amount of loading was 6 mg and the weight ratio of the toner to the white particles was 1. This process makes possible rewritable toner imaging based on image recording and erasing by the action of an electric field. In addition, the memory effect exhibited by this display should be noted: When viewed through the upper transparent electrode, the toner image was retained even under an open circuit condition. Though not shown here, also notable is the fact that our toner display can be made flexible by the use of flexible ITO plastic sheets. A real electronic paper display requires not only a flexible ITO sheet but also a flexible drive circuitry. The toner image will be displayed by the application of pulse voltage to the strive pair electrodes which fall at right angles with each other. The pulse time for the display of a pixel is about 1 ms. We are beginning to prepare such flexible devices, the details of which will be reported elsewhere. While the mechanism of the image formation has not been fully understood, the fact that the combination of magnetic toner and carbon fluoride particles allows the fabrication of a display device should open new avenues for both fundamental and applied research.

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