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Fabrication of Black/White Electronic Ink using High Mobility Particles

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Black and white electronic ink containing white nano particles with high mobility and organic black pigment particles dispersed in a dielectric fluid were prepared. A charge control agent affects the electrophoretic zeta potentials of the white particles, which show the maximum value of the zeta potential. The electronic ink panel fabricated with the charged white particles and the black particles exhibits a contrast ratio of more than 19:1 at 10 V.

Keywords: colloid; electrophoretic particle; electronic paper display

INTRODUCTION

Electronic paper that possesses reversibility, bistability, and flexibility with low manufacturing cost is of great interest to many researchers. Among electronic paper display technologies, an electrophoretic display functions as a non-emissive device based on the electrophoresis phenomenon of charged pigment particles suspended in a dielectric solvent. This was initially proposed by Ota et al. in 1969 [1]. Due to the passive quality of the display and the near-Lambertian scattering of the pigment, electrophoretic display devices exhibit excellent contrast over a wide range of viewing angles. In these systems, the particles displayed via electrophoresis should be maintained in a dispersive state extensively, and should clearly show the intended information on the display panel. Therefore, colloidal stability is of the utmost importance in the proper operation of an electrophoretic

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display device [2]. To overcome severe agglomeration between the primary pigment particles, a microcapsule as well as a micro-wall type of electrophoretic display mode have been introduced and developed [3]. The composition of the suspension determines the contrast ratio and response times of the device. The particles in the suspension acquire a surface charge due to the electrical double layer determined by the zeta potential [4]. The zeta potential can measure the stability of pigment particles in a suspension and then control the electrophoretic mobility. The electrophoretic mobility is determined by measuring the velocity of the particles in electronic ink under the influence of an electric field across this ink. The zeta potential is computed using the Hükel equation (for $\kappa a \gg 1$),

$$\varsigma = \frac{3\eta U}{2\varepsilon_0 \varepsilon_r} \tag{1}$$

where η is the viscosity of the liquid phase, ε_0 is the permittivity of free space, and ε_r is the dielectric constant of the liquid medium. The absorbed nonionic surfactant molecules develop resistance in the dispersed pigment particles to agglomeration in the low dielectric medium. They can either impart an electrical charge onto the particle surface and stabilize the suspension through an electrostatic mechanism or physically prevent the two surfaces from coming into adhesive contact through steric hindrance. Fundamental apprehensions for charging in the non-aqueous medium such as that by low dielectric hydrocarbon are lacking, primarily because the generation of stable ionic species in a low dielectric constant medium in not clearly understood. Due to the lack of ionic species, steric barriers are necessary to limit the maximum attractive force [5]. Although a limited number of studies have been conducted in this area, the concentration dependence of surfactants on the zeta potential in a low dielectric medium is examined in this study. The aims of this paper are to provide a molecular description of the surface charging actions of electrophoretic pigment particles in a low dielectric constant medium through the preparation of a rapid-response electrophoretic display device.

EXPERIMENTAL

Synthesis of Pigment Particles

For the white pigment particles, core/shell structured TiO_2/PS particles were synthesized by a dispersion polymerization method [3]. Styrene (Purity 99%), methacrylic acid (MAA), poly(vinylpyrolidone) (PVP, Mw = 55,000 g/mol), divinyl benzene (DVB), and 2,2′-azobis (2-methylpropiontrile) (AIBN) were purchased from Sigma-Aldrich Co. Ltd. Titanium dioxide (TiO_2) particles (Ti-Pure R-103) were obtained from DuPont Co. The TiO_2 particles used in this study had a rutile crystal structure and an average diameter of 230 nm. All chemicals used in this study were reagent grade without further purification steps.

In order to synthesize core/shell structured TiO_2/PS white pigment particles, 4 of PVP was dissolved in methanol in a 1l four-neck round-bottom flask equipped with mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen gas inlet and outlet. 8 g of TiO_2 was dispersed in a mixture of styrene (12 g) and DVB (0.6 g) for 5 min at room temperature. The TiO_2 dispersion in the monomer mixture was poured into a PVP methanol solution and emulsified with a sonicator for 1 h. A solution of AIBN (0.25 g) was then added to the flask reactor. The stirring speed was fixed at 250 rpm. Under a nitrogen atmosphere, polymerization was carried out at 65°C for 6 h. During the second stage, 1.2 g of MAA was slowly added to the reactor in order to be incorporated onto the surface of the core/shell structured TiO_2/PS composite particles, which brought the functional group to the surface of the composite particle. After adding the MAA, the reaction was carried out for 12 h at a constant temperature. After 12 h, the reaction was terminated and the TiO_2/PS composite particles were then isolated from the mixture by centrifugation. The final TiO_2/PS composite particles were obtained through freeze drying in a powder form.

The black particles were purchased from Soken Chemicals Co. (Japan) and were used without surface treatment.

Fabrication of an Electrophoretic Ink Panel

The electrophoretic suspensions were prepared by suspending the TiO_2/PS composite particles, as the charged white pigment, and the black pigment particles in a clear dielectric fluid. Suspensions were prepared by ball-milling using ceramic grinding balls. The procedure involved initially dissolving the charge control agent in the suspending liquid. The white pigment was then added, and the mixture was ball-milled for several hours to make a stock solution type of suspension. The concentrated black suspensions were also prepared using this method. To create the electrophoretic ink suspension, the concentrated white stock solution and the black stock solution were mixed, and this was diluted to a fixed concentration and was exposed to sonication. Routine testing of the suspensions was conducted in simple test cells, and measurements of the contrast, response times, and

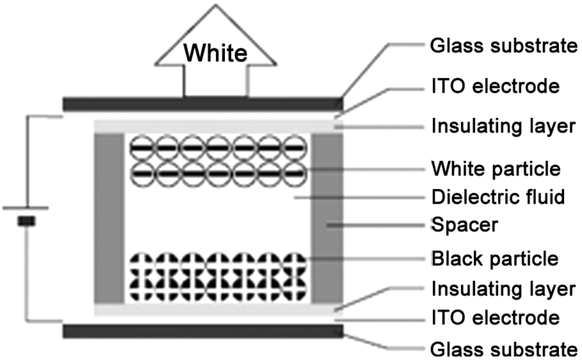

FIGURE 1 Black particle and white particle movements by the applied voltage.

conductivity were performed. The electrophoretic cells structured onto two 4 cm × 4 cm transparent plates with electrodes placed opposing each other, leaving a 150 μm distance between each electrode using spacers. The structure of the testing cell using the black and white particle suspension is shown in Figure 1.

RESULTS AND DISCUSSION

Figure 2 shows the surface morphology of pristine TiO_2 and the TiO_2/PS composite particles. The pristine particles exhibit an irregular plate-like shape that is heterogeneously distributed, which is a characteristic that is usually associated with conventional nano sized TiO_2 particles. When bare TiO_2 particles were introduced in the polymerization medium, investigation of the morphology of the resulting

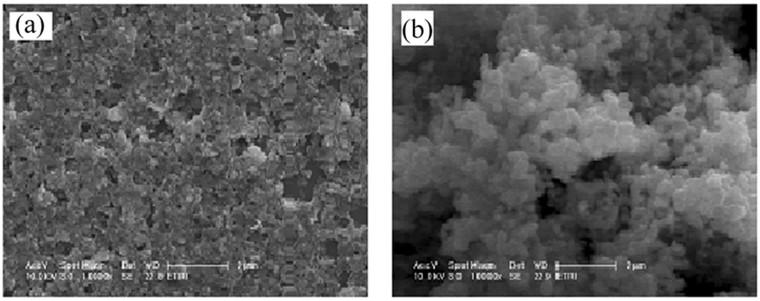

FIGURE 2 SEM images of (a) pristine TiO_2 and (b) PS-coated composite particles.

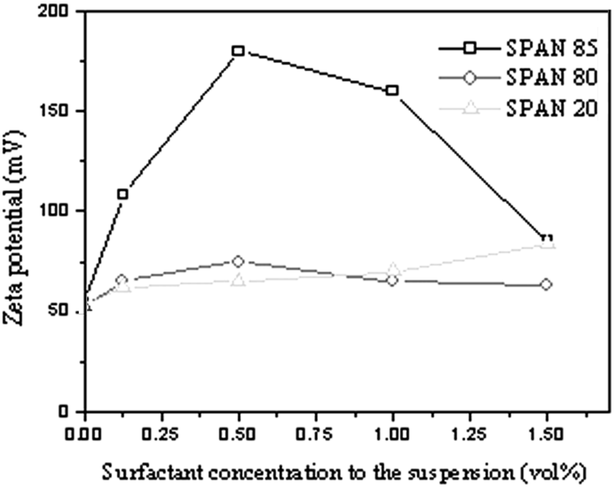

FIGURE 3 Zeta potential of the TiO_2/PS electrophoretic particle suspension with three different surfactants.

composite particles by FE-SEM revealed that small pure TiO_2 particles were covered with polymer. The surface of the composite particles was smooth with a less irregular spherical shape. Bare TiO_2 particles were not detected over the entire surface of the sample.

In order to determine the surface charge of the composite particles, the zeta potentials of the electrophoretic white TiO_2/PS composite pigment particle suspensions composed of the white pigment and the dielectric fluid were measured using a Zetasizer 2000 (Malvern Instruments). Figure 3 represents the surface charge characteristics of the TiO_2/PS. The particles were dispersed in isoparaffin oil with different types of the oil soluble surfactant Span as a charge control agent. Span-grade surfactants showed different hydrophile-lipophile balance (HLB) values. The HLB values for Span 20, Span 80, and Span 85 were 8.6, 4.3, and 1.8, respectively. The HLB of Span 85 was the lowest among the three different grades. The zeta potentials of the particle suspension were affected by the HLB value of the surfactant. A lower HLB value for a suspension represented a higher degree of hydrophobicity. In addition to the electrostatic mechanism for the colloidal stability in the non-aqueous suspensions, the hydrophobicity induced by the exposed hydrocarbon tails of the adsorbed surfactant molecules will render the particles more compatible with the non-aqueous phase and enhance the suspension stability. Therefore, the highest hydrophobic surfactant of Span 85 results in the best the stability of

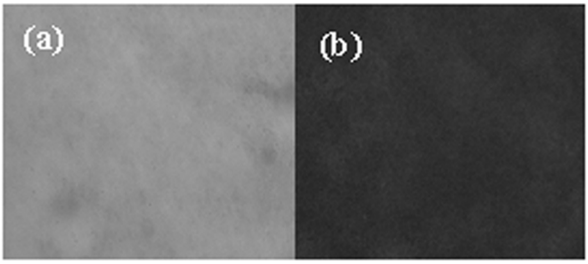

FIGURE 4 Photomicrographs of the black/white electrophoretic ink suspension cell in a power-on state: (a) shows $+10\,\mathrm{V}$ applied to the front electrode while (b) shows $-10\,\mathrm{V}$ applied to the front electrode.

suspension. The zeta potentials increased with surfactant concentrations at a low concentration range but this showed a maximum value and then decreased. Surfactant concentrations for the maximum value depended on the HLB value of the surfactant.

Based on the result of the zeta potential measurement, an electrophoretic ink suspension for use with a display device was prepared with Span 85. 20 vol% of white particles dispersed in 0.5 vol% of Span 85 concentrated isoparaffin oil was blended with 5 vol% of the black particle suspension. This was then sonicated for 1 h. The contrast ratio of the electrophoretic ink suspension was calculated using the reflectivity value in $+10\,\mathrm{V}$ versus that at $-10\,\mathrm{V}$ through a test cell with a thickness of $150\,\mu\mathrm{m}$. Figure 4 shows the performance of the black/white electrophoretic ink suspension in the cell after 10 V was applied. The reflectivity values of the black/white electrophoretic suspension cell were measured using a chromameter (CS-100, Minolta Co.). The white state showed a value of $211\,\mathrm{cd/m^2}$ while the black state showed $11\,\mathrm{cd/m^2}$. The contrast ratio (CR) of the black/white electrophoretic suspension in the cell was measured to be 19:1 with an operating time of nearly 5 sec. This CR value is the highest CR ever announced for electrophoretic display panels. Therefore, a gelatin microcapsule containing a charge pigment particle suspension was formulated. The approximate size of the sieved gelatin microcapsules ranged from 43 to $65\,\mu\mathrm{m}$. These microcapsules were blended with a 10 wt% aqueous urethane binder. A monolayer of the close-packed microcapsules was formed on a flexible transparent electrode using a knife coating. The state of the close-packed microcapsule layer was confirmed through an optical microscopic photograph of the layer of microcapsules. Figure 5 shows a completed sheet of an electronic ink panel (total thickness is approximately 0.5 mm with a contrast ratio of nearly 4:1). The reduction of the contrast ratio with a

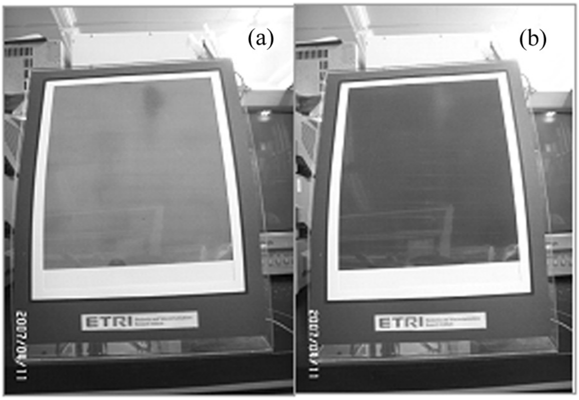

FIGURE 5 Photographs of an A4-sized electronic ink panel with an electrophoretic ink microcapsule diameter of $50 \pm 10\,\mu$m in a power-on state: (a) shows $+10$ V applied to the front electrode while (b) shows -10 V applied to the front electrode.

microencapsulated electronic ink panel may come from the microscopic small voids among the microcapsules or from inactive microcapsules which cannot operate. The zeta potential of the black and white concentrated electrophoretic ink was measured. The value of the zeta potential was found to be approximately 70 mV. Compared to the dilute solution in Figure 3, this value is decreased by half. Therefore, it is surmised that this reduction of the zeta potential represents a reduction of the charge amount per particle, which contributes to the instability of the electrophoretic suspension and to the reduction of the CR value. At present, the authors are trying to recover this decrease in the zeta potential.

CONCLUSIONS

This study shows the development of an electrophoretic ink suspension with a high contrast ratio. This suspension can be used with high-visibility electronic paper displays. The effects of the charge control additives on the zeta potential were significant. The appropriate addition of charge control additives results in an increase in the electrophoretic mobility. Monolayer panels of close-packed microcapsules containing the proposed very high quality electrophoretic ink resulted in a decrease in the contrast ratio. The reduction in the contrast ratio in the microencapsulated electronic ink panel is attributed to various factors, including microscopic voids among the microcapsules, inoperative microcapsules, and a decrease of the electrophoretic mobility. Therefore, in order to fabricate electrophoretic ink display panels with a high contrast ratio, the reflective CR should be above 10:1.

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