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A Review In Preparation of Electronic Ink for Electrophoretic Displays

S. Kholghi Eshkalak*, M. Khatibzadeh†

Department of Polymer Engineering and Color Technology, Amirkabir University of Technology P.O. Box 15875 Hafez Street, Tehran, Iran

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Electrophoretic displays attracted a lot of attention recently due to its low cost, low weight, low power consumption and reliability. Based on these characteristics, they are going to replace the conventional paper. Electrophoretic displays are called non- emitting displays based on light particle suspensions. They behave as motion of charged particles in a dielectric fluid towards the electrodes with the opposite charge. Electrical and optical properties of electrophoretic displays suspension composition are dependent on the electronic ink that is called E- ink. Thus, key factors in determining image quality depended on electrophoretic particle properties. Enhancing the great image quality for accurate image control and faster response to the voltage applied is dependent on the very small particle size, narrow size distribution and high surface charge of particles. So a lot of research has been done on the modification of particles, surface morphology, surface charge and their stability in media. Therefore, this article reviews the studies of these topics.

Keywords: Electrophoretic display, Microcapsules, E-ink, Electric response.

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1. INTRODUCTION

Electrophoretic displays have been one of the greatest interest to researchers in the past decade due to its low power, paper-like, flexibility, response to the driving applied voltage and image memory [1-3]. The electrophoretic displays potential applications are in different devices for example E-reader, E-book, wearable computer screens, electronic signs and smart identity cards (Fig. 1) [4, 5].

Fig. 1 – Commercially available electrophoretic displays and some prototypes [6]

The image quality of the electrophoretic displays is highly dependent on the quality of suspension particles, which are called electronic ink [E-ink]. The electrical and optical properties of the suspended particles are very important in a dielectric fluid. There are a few important parameters which can be affected in E-ink as particle size, size distribution, surface charge of particles and response to the applied electric field dependent [7-9].

2. EXPERIMENTAL

2.1 Electrophoretic Displays

The term electrophoresis is a composition of electro and phoresis, two words that are derived from the Greek words for charge and the act of carrying. In that way, the name electrophoretic display (ED) already gives a hint about its basic working principle. As shown on the picture below an ED is made of an ink layer, sandwiched between two layers that can be plastic, glass or even paper. The total thickness of the layer structure is between 0.5 mm on glass and 0.1 mm on plastic which is in the order of a sheet of paper.

In the simplest case of a black and white display, the top substrate is covered with a single transparent electrode, while the bottom substrate contains a complex pattern of line-electrodes. Using active matrix driving, a single pixel can be addressed, meaning that the bottom electrode can be made either positive or negative compared to the top-electrode. The electrophoretic ink between these electrodes is a mixture of transparent liquid and microscopic charged pigment particles. The usual choice is negatively charged black particles [carbon black] and positively charged white ones (TiO_2). When a voltage is applied over the top- and bottom of the electrode, the charged pigments will move due to an electrostatic force to the attracting electrodes. For instance, when the bottom electrode is positive, it will attract black particles and repel white ones. These white particles gather at the top-electrode, where they reflect incident light in all directions. This is the white state. In the opposite case, a negative bottom electrode pushes the black particles to the surface, where they absorb the light. This is the black state (Fig. 2). This basic principle is different than most displays by the fact that it is reflective. So, an ED is a type of display that reflects or absorbs ambient light in contrast to transmissive displays such as the CRT or LCD.

* S.kholghi@aut.ac.ir
† Khatib@aut.ac.ir

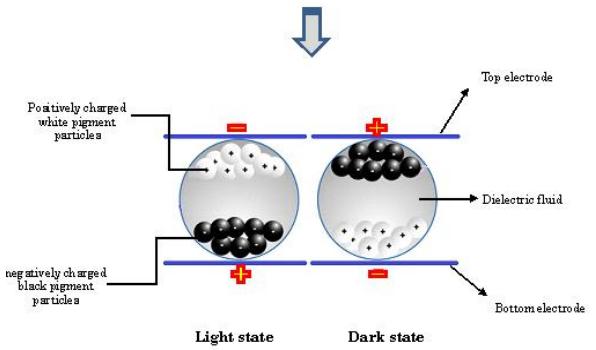

Fig. 2 – Schematic illustration of microcapsule-type electrophoretic display

2.2 Advantages of Electrophoretic Displays

The major advantages of the electrophoretic technology are:

- High reflectivity of the white state and high contrast:
- High resolution:
- Very low energy consumption
- Possibility of thin, mobile and flexible displays

2.3 E-ink Microcapsules

Microcapsules process is said to be very fine particles or droplets which are surrounded by a capsule of small useful features. The tiny sphere microcapsules with uniform wall have to be put simply around its core. The microcapsules are formed of the core, internal phase or filled, and the walls of the shell, coating, or membrane [10].

Several different technologies are used in the electronic display such as a microencapsulated electrophoretic display (MC-EPD), a twisting ball display, an electrochromic display and an electrowetting display. Among them, MC-EPD is a reflective device based on the electrostatic migration of suspended particles in a dielectric fluid [11]. The disadvantages of electrophoretic displays is the lack of stability of the electrophoretic particles that obtained by agglomerate, clustering and delayed migration in a long time thus microcapsules are the solution to fix this problem [10, 12]. In 1997, Chomsky et al., produced the first MC-EPD by using electrophoretic particles [13].

Various materials have been used as the shell materials of microcapsules such as melamine-formaldehyde [10, 14, 15], urea–formaldehyde [16-18], gelatin [19], polyurethane [20] and wax. For electrophoretic displays, the wall of the microcapsules requires not only the properties of a solid to retain its interior materials but also transparency such that the core can be observed during the migration of particles and be relatively inexpensive to produce. The UM/F resin was chosen as a wall material, which was prepared by an in situ polymerization [21], occurring at the interface formed by dispersed core materials and a continuous phase [10].

On the other hand, wall materials of the microcapsule not only should be strong enough to keep its internal phase but also be transparent enough to have an observable change through the migration of internal particles. Melamine-formaldehyde (MF) resin has been regarded to be useful as wall materials [16,17]. The choice of emulsifier, suitable pH after dissolving and good adsorption into the wall materials is very important parameters to gain the stability during microcapsulation process.

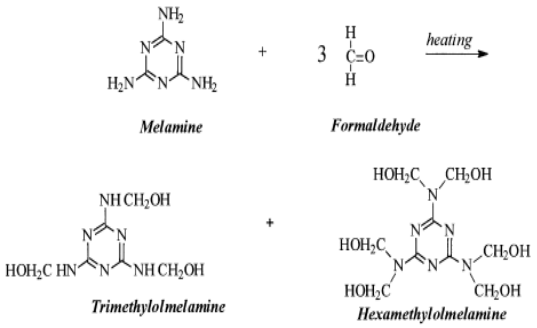

Fig. 3 – Mechanism for polymerization of MF resin [14]

Thus several microencapsulation techniques have been developed including the chemical method*in situ* and interfacial polymerization, the physical-chemical method coacervation and the mechanical-physical method spray encapsulation. Among these, in situ and interfacial polymerization methods have become the most commonly used methods for the preparation of microcapsules [22].

3. CHEMICAL APPROACH

In 1997 a hardware researcher at the MIT Media lab tech began to produce the electronic paper display (EPD) as a result of E-books which was called the Amazon Kindle. Joseph Jacobson and Barrett Comiskey were listed as inventors on the original patent filed in 1996 [23].

Fig. 4 – An example of Amazons Kindle

In a study conducted by Comiskey et al., E-ink microcapsule with white particles dispersing in the blue fluid was reported by providing *in situ* urea/ formaldehyde polymerization. Titanium dioxide with a density of 2.4 was used because of high color purity reflection as white particles. Polyethylene was used as a coating on titanium dioxide to reduce the density and surface modification of charged particles and the response to

applied electric field. In this study, 0.1 sec was reported as the response time [13].

In 2002, for the first time the E-Ink Corporation, Boston (Massachusetts) showed a prototype of a full color electronic ink display at the "Symposium, Seminar and Exhibition of the Society for Information Display (SID)" [24].

Particles of titanium dioxide (TiO2) was used as a white particle electrophoretic ink [25-27]. In order toreduce thesurfacedensity and particles chargeability, surfactants and other modifiers was applied as modification or other treatments [28, 29]. In a study, the internal phase, TiO2 nanoparticles was coated with poly(methyl methacrylate)(PMMA) to enhance the surface modification and dispersion stability via dispersion polymerization [30, 31]. The investigation which was conducted by B.J. Park et al., dodecylbenzensulfonic acid (DBSA) was used for pretreatmentto change the surface characteristics of TiO_2. Moreover, microencapsulation of the modified TiO_2 nanoparticles suspended in the medium was carried out with amino precondensates as a wall material and poly(ammonium styrenesulfonic acid) (PASA) asan emulsifier. As the resultsare showed in Figure 5, it can be noticed that the PMMA and TiO_2 are combined with each other [29].

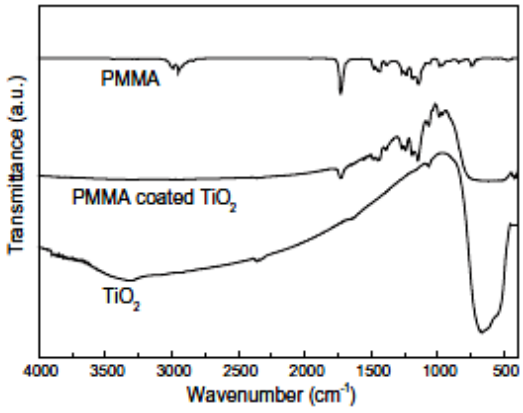

Fig. 5 – FT-IR spectra of PMMA, TiO_2, and TiO_2-coated PMMA nanoparticles [29]

H.L. Guo and his colleagues in 2004 reported an encapsulated electrophoretic ink. In this work Scarlet pigment powder was used because of brightness, small size and low density. They prepared modified pigment suspension in tetrachloro ethylene. E-ink Microcapsules was provided by *insitu* polymerization method using urea/formaldehyde shell materials. It was shown that the presence of polyethylene surface modification leaded to increased spread and stability of pigment particles.It also caused the particles tended to be negative electrode.The response time of this study was 3.2 seconds (Fig. 6), when the microcapsules were placed under zero electric field thepigments were placed randomly inside the capsule (Fig. 6a). However, the electric field immediately responded directly $E = 120$ V/mm (Fig. 6b) and was oriented towards the negative pole, and vice versa in the reverse electric field, are pushing back [32].

J.P. Wang et al., produced blue E-Ink particles from phthalocyanine blue BGS (PB15 : 3) due to the high brightness and low prices.Actually the urea and formaldehyde polymer was used as the core and shell materials, respectively. Modified particles in tetrachloroethylene (TCE) were prepared by insitu polymerization. In this work, the effects of the various factors such as the type of modifier, the reaction conditions and the concentration of surfactant in TCE were experimentally investigated to study the dispersibility of PB15 : 3 particles in TCE, the capsule morphology and the adsorption of PB15 : 3 particles on internal surface of capsule wall. Table 1 shows the fundamental characteristics of prepared electronic ink microcapsules at different experimental conditions.

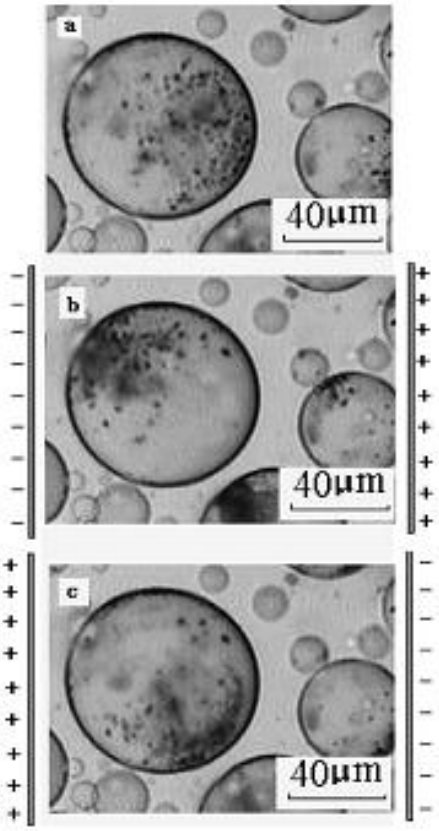

Fig. 6 – Microcapsules in the electric field ((a) $E = 0$, (b) $E = +120$ V/mm, (c) $E = -120$ V/mm) [32]

It was shown that using octadecylamine (ODA) to modify PB15 : 3 particles resulted in a significant increase of the dispersing extent (D.E) [about four times more than that of unmodified]. The response time of particles to 0.1 V/μm DC electric field improved from 2.6 s to 0.6 s. Figure 8 showsthe relation between concentration of Span80 and the interfacial tension. The concentration of Span80 in TCE was not less than 0.062 mM, the adsorption of PB15 : 3 particles on internal surface of wall were restrained [33].

In a study conducted by HouXin-Yan et al., in 2012, the conventional organic pigment PR2, Permanent Red F2R, was used as colored electrophoretic particles. Surface charge and surface modification was carried out in an organic media to increase the stability of the dispersions. So the spherical shape of particles as well as increasing the electrical charge of surface leads to increasing of dispersity in media. According to the results

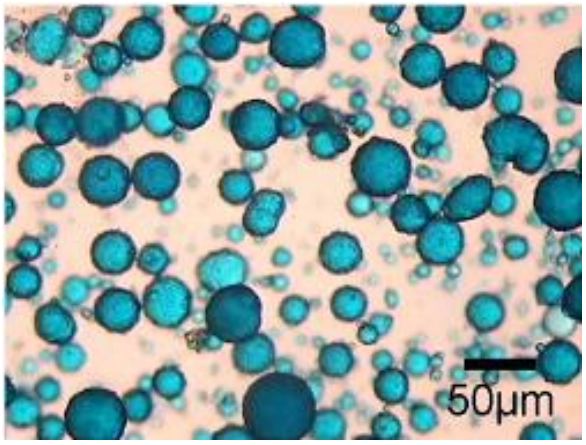

Fig. 7 – The micrography of prepared blue E-ink microcapsules [33]

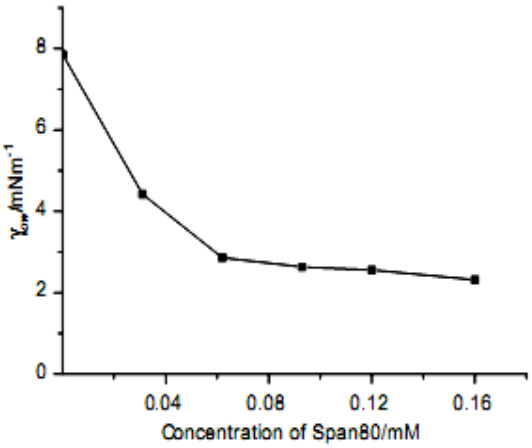

Fig. 8 – Relation between concentration of Span80 and the interfacial tension [33]

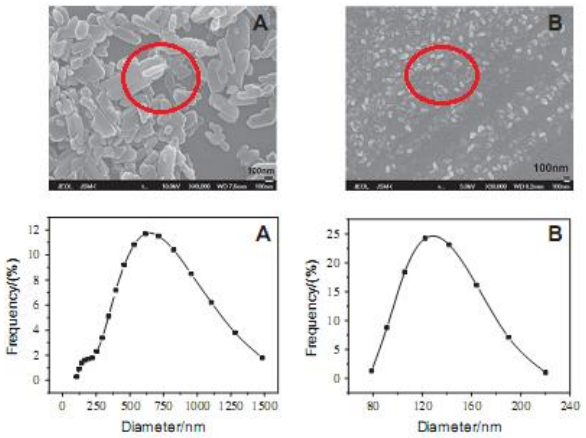

Fig. 9 – SEM and particle size distribution before and after modification. (A) Raw materials. (B) Modified by ODA [9]

of SEM images, the average particle size obtained. The particle size distribution of raw materials which was modified with ODA is shown in Figure 9. The distribution of particle sizes was from 100 to 1500 nm in the unmodifiedconditions while the extent of 80 to 220 nm in the modified particles could often be found. In this work, the average size of particles was 105 nm and they had a very narrow dispersion index equal to 0.068.

Various modifiers were tested such as: SDS, CTAB, CH-6 and D-655.D-655 was thebest commercial dispersant according to the results of Figure 10. Sedimentation rate of the particles which was prepared at tetrachloroethylenewas less than 5 % in 12 days. Red particles which was obtained with white electrophoretic particles were used in this work to show the good contrast in electrophoretic display which had 200 ms recovery time [9].

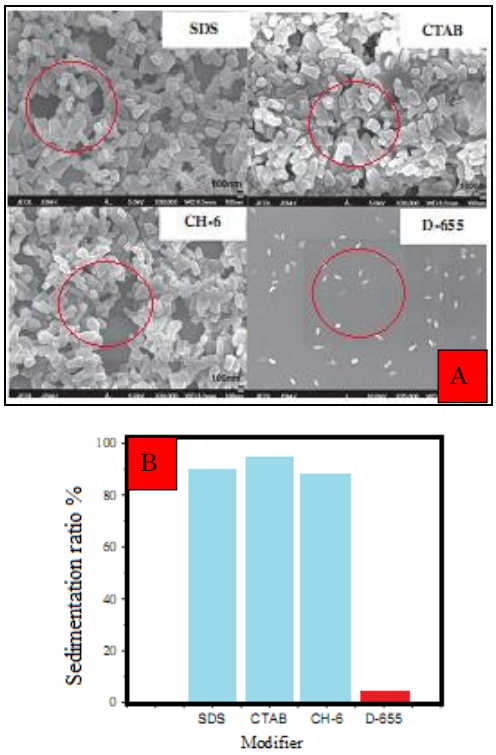

Fig. 10 – Effect of different dispersant on modified P.R.2 particles (A) SEM images (B) Sedimentation ratio within 12 days [9]

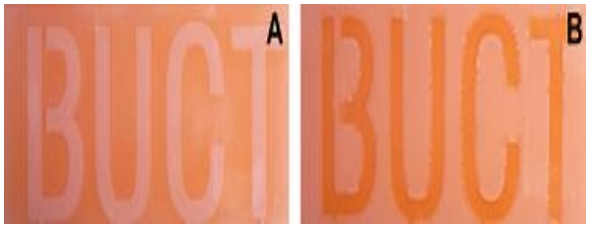

Fig. 11 – Electrophoretic display suspension in the electric field. (A) Negative field is applied to the upper plate.(B) Positive field is applied to the upper plate [9]

4. CONCLUSION

As reviewed in this paper, composition of the E-inkmicrocapsules were contained of materials, colored electrophoretic particles, media of dielectric, charge control agent and dispersant. Thus, a key factor in determining image quality will electrophoretic particle properties. The Increaseimage quality requires high surface charge and responds faster to voltage applied to make exact image control. So a lot of researchhas been studied on themicroencapsolation process, modification of particles, surface morphology, surface charge and stability of the steric.

Table 1 – The characteristics of electronic ink microcapsules prepared by different reacting conditions

Experiment condition*	Situation of encapsulation	Particle size distribution	Topography	Transparency	Mechanical strength	Quantity of resin generated in water phase
a	Encapsulated	Homogeneous	Smooth	Good	High	Little
b	Encapsulated	Unhomogeneous	Rough	Poor	Higher	Rather
c	Encapsulated	Unhomogeneous	Rough	Poor	Higher	Much
d	Encapsulated	Unhomogeneous	Rough	Better	Higher	Mass

*[a] According to condition of preparation of the electronic ink microcapsules in this paper; [b] to substitute 0.3 mol/L of the citric acid-sodium hydroxide buffer solution by 10% of HCl solution; [c] reaction was performed for 1.5 h at room temperature directly; [d] volumes of the prepolymer were increased to 20 mL [33]

Although, black and white electrophoretic displays microcapsules was produced with commercial success but itmay notmet monochromeEPDdisplay market-requirements. Thus purpose of the progresses and technologies is produce color displays.

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