

Excellent Bistable Electrophoretic Displays with Contrast Ratio up to 81.9

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Abstract

The performance of electrophoretic displays is greatly dependent on the stability of the suspension. In this paper, the factors affecting the stability of electrophoretic colloids were well discussed, including the density difference between particles and solvents, system viscosity, solvation, and agglomeration. These above factors affected the dispersion stability of the system and the lifetime of the display. By optimizing these factors, the features of display panel were greatly improved, and exhibited excellent performance. Our work can be the guidance to the manufacturing of electrophoretic e-ink display industry.

Author Keywords

Electrophoretic colloid; Dispersion stability; Sedimentation; Diffusion; Spatial hindrance

1. Introduction

When the reflective display for electrophoresis was invented by Ota and co-workers^[1], electrophoretic display has attracted great interest from many researchers due to its unique performance. The display mechanism of electrophoretic display is to attach different charges to particles with different colors. When different voltages are applied to the electrodes, charged particles undergo electrophoresis in a low polarity system and accumulate at the top or bottom of the transparent electrode. Ambient light is reflected by the particles and enters human eyes, allowing the viewer to sense the color change. This display principle determines that e-ink screens have the advantages of high contrast, eye protection, and energy saving^[2-4].

Although the electrophoresis display possesses above advantages, it remains some challenges in this field, and one of the biggest challenge is the colloidal stability, which to be more specifically, is related to the suspension stability of the system. Reviewing the literature in this area, it is clear that both theoretical and experimental efforts are focused on aqueous media. In aqueous media, the main driving force for dispersing particles is the electrostatic repulsion between particles, which causes the particles to be positively or negatively charged through the dissociation of surface active agents or functional groups adsorbed on the particle surface. However, the electrostatic effect seems too small to stabilize the system in a non-polar solvents with low dielectric constant, which leads to unclear factors affecting the suspension stability of particles in hydrophobic media. Therefore, it is necessary to explore new strategies to stabilize charged pigment particles when use in hydrophobic media.

2. Experiment

2.1 Materials

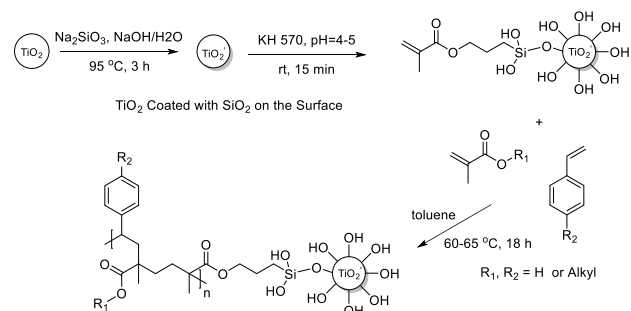
TiO₂ was purchased from was purchased from DuPont China Co., Ltd. Black particles, silane coupling agents (such as KH-570), acetic acid, ammonium hydroxide, sodium hydroxide, sodium silicate, acrylic resin, styrene, and 2,2'-azobis(2-methylpropionitrile) were purchased from Tansoole. Isopar L was purchased from Shanghai Huishuo Technology Co., Ltd. All the

other reagents and solvents were of reagent-grade.

2.2 Preparation of electrophoretic particles

The particle modification was refers to previous study^[5]. There are three steps in total, which are TiO₂ coated with SiO₂ on the Surface, silylation, polymerization and heat treatment as showed in Scheme 1. The silylation process introduced double bonds for polymerization; Polymerization can provide sufficient spatial hindrance for particles and make particles hydrophobic; Further heat treatment can make the particle surface smoother.

Scheme 1. Preparation of electrophoretic particles



2.3 Preparation of the electrophoretic test cells

First of all, the electrophoretic dispersions were prepared. Two-particle electrophoretic ink contained 21 wt% white particles, 7.0 wt% black particles, 1.5 wt% Charge control agent, 1 wt% thickener and mixed solvent, these was ball milled overnight for better dispersion.

Secondly, the test cells were prepared. The parallel plate electrode is made of two pieces of ITO with a thickness of 30 um, which is controlled by OCA adhesive. After injecting ink, it is sealed with photosensitive acrylic adhesive.

3. Proposed Mechanism

It is generally believed that hydrophobic particles in solution are mainly influenced by the combined effects of van der Waals forces, electrostatic forces, gravity, and spatial hindrance (Figure 1). For monodisperse systems, the greater the electrostatic force, the better the stability of the entire system; For polydisperse systems (particles of different colors carrying different charges),

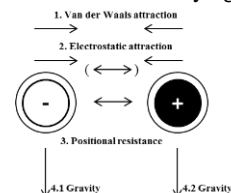


Figure 1. Force analysis of particles in dispersed systems excessive electrostatic forces seem to cause different particles to attract and aggregate with each other, but insufficient particle

charge will affect particle migration speed, which leads to complex electrostatic effects in multi particle electrophoretic colloids. Therefore, it requires a suitable value to balance the tradeoff performances.

Sedimentation is the process in which particles in a multiphase dispersed system sink due to gravity. The settling velocity is derived from Stokes' law as shown in equation (1). Among these, “ v_0 ” represents the settling velocity, “ d ” represents the apparent particle size of the particle, “ $\Delta\rho$ ” represents the density difference between the pigment and the solvent, and “ μ ” represents the viscosity of the solvent.

$$v_0 = 54.5d^2 \frac{\Delta\rho}{\mu} \quad (1)$$

Diffusion force is the directional migration of particles due to Brownian motion, which can promote a more uniform system and can be adjusted by controlling the spatial hindrance of particles. It can be calculated by the Einstein Stokes equation as shown in equation (2). Among these, “ D ” is the diffusion coefficient, which describes the rate at which substances diffuse in a medium, “ k ” is the Boltzmann constant, “ T ” is the absolute temperature, “ μ ” is the dynamic viscosity of the fluid, “ r ” is the radius of the spherical particle.

$$D = \frac{kT}{6\pi\mu r} \quad (2)$$

From a kinetic perspective, when the sedimentation force acting on the particles in the solution reaches equilibrium with the diffusion force caused by Brownian motion, it can be considered that the particles can remain stably suspended in the solution. (Figure 2), this paper describes the process of coating polymer with low density and polarity on the surface of particles to reduce the density difference with dispersing solvents; Secondly, it can also increase the spatial hindrance of particle surfaces, which can slighten the agglomeration caused by excessive surface energy, thereby reducing sedimentation force and increasing diffusion and achieving a balance between sedimentation and diffusion.

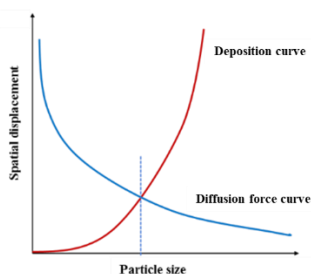


Figure 2. Sedimentation and diffusion forces in hydrophobic media.

4. Results and Discussion

4.1 Reduce the impact of sedimentation

According to Stokes' law, reducing particle density difference and increasing system viscosity is effective in reducing the influence of gravity. We synthesized particles of different densities by regulating the amount of polymerization monomers. As shown in the Table 1, the particle density difference decreases with the increase of polymer coating amount. Unfortunately, particles with lower density difference did not exhibit better dispersion, which we attribute to excessive polymer content causing particle adhesion as showed in Figure 3 (a) and (b), which is not

conducive to particle dispersion. Therefore, 1.1 equivalents of polymer is most economical and effective.

In addition, by adding 1 wt% thickener to the electrophoretic colloid, the pigment sedimentation rate has been significantly reduced, from 28% sedimentation within 3 days to only 6%, as showed in Figure 3 (c).

Table 1. Sedimentation rates corresponding to different equivalent monomers

Entry	Equiv	Density difference between particles and solvent (g/mL)	Sedimentation rate (%)
1	0	2.6	100%
2	1.1	2.0	~20%
3	2	1.5	~30%
4	3	-0.3	100%

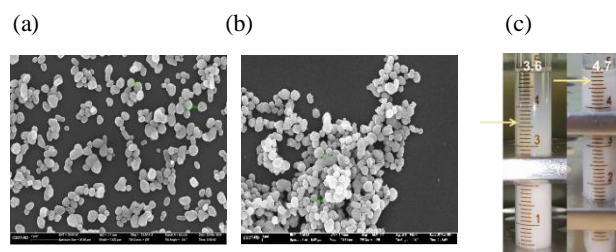


Figure 3. (a) 1.1 equiv polymer monomer, the surface of the particles is clean; (b) 3 equiv polymer monomer, visible polymer adhesion on the surface of particles; (c) After adding thickener, the settling rate decreased by 22%.

4.2 Enhance diffusion

As shown in equation (2), the key to increase diffusion force lies in controlling the particle size. Because the current particle size is determined, all we can do is minimize the agglomeration between particles, which can be achieved through good coating of polymers.

4.2.1 Optimization of polymer coating.

The spatial hindrance between particles is the key to maintaining the stability of the entire system. There are usually two requirements to achieve high spatial hindrance in modified particles. Firstly, the polymer coating rate of the particles should reach 100% and be smooth, Lower coating rate <50%, which will cause the particle attraction and sedimentation. In addition, the rough surface of particles is not conducive to relative motion between particles; Secondly, the soft polymer coated on the surface may cause entanglement and bridging, leading to particle aggregation. Therefore, introducing rigid structures for copolymerization during free radical polymerization is a good solution (Figure 4).

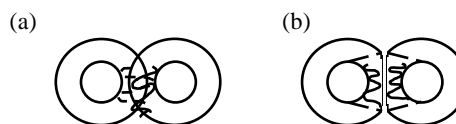
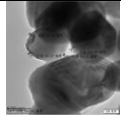
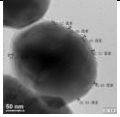
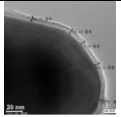


Figure 4. (a) Agglomeration, polymer winding; (b) Dispersion, Polymer compression.

The study of influence of polymer coating on particle was listed

in table 2. We characterized the first modified particles **W1** with poor coating conditions, it can be learned from TEM data that most of the polymer's coating rate is not reach 50% and not smooth, which leads to the uneven charging and agglomeration of the ink. We coated a thin layer of silica on the surface of titanium dioxide to provide more hydroxyl groups, this enabled more silane coupling agents to be grafted onto the pigment surface, thus achieving a 100% coating rate of the **W2** after polymerization. On the basis of achieving a 100% coating rate, in order to achieve smoother polymer coating on the particles, we carried out a copolymerization reaction using styrene with rigid benzene ring and lauryl acrylate, and performed heat treatment on the coated particles at the 120°C. This enabled us to successfully obtain the final form of particle **W3**.

Table 2. **W1**, first edition; **W2**, increase the SiO₂ in TiO₂; **W3**, increase the SiO₂ in TiO₂, add rigid monomers for copolymerization and heat treatment

Entry	W1	W2	W3
TEM			
Thickness / nm	5.9	5.4	6.9
Coating rate	<50%	100%	100%
Uniformity	★	★★★	★★★★★

4.2.2 Selection of good solvents

In addition to having a complete coating layer, whether the polymer chains can stretch well in the dispersed system is also a key factor. So, we tested the affinity of modified particles for water, alkanes, and iodomethane separately. The particles powder was fabricated to film, and different solvent was dropped onto the particle film to measure the contact angles, and the results was shown in table 3. Under the microscope, we can observe that the particles have significantly changed from their original hydrophilicity to almost non hydrophilicity after modification (the contact angle of water on their surface is close to 130 °), and the affinity of modified particles for iodomethane is significantly better than isopar L, which is consistent with our actual sedimentation experiment results were shown in table 4 and Figure 5. We obtained a minimum sedimentation rate of 40% in a single tetrachloroethylene solution. Therefore, it can be concluded that halogenated hydrocarbons have better wetting properties for particles and better dispersion of their systems.

Table 3. Contact angle between particles and solvents


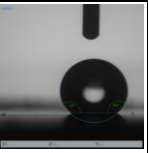
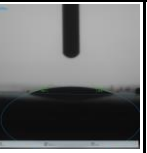

Unmodified	Modified		
Water	Water	Isopar L	CH ₃ I
			
0°	130°	20°	6°

Table 4. Particle sedimentation rates corresponding to different solvents

Entry	Solvent	Sedimentation rate (%)
1	C ₂ Cl ₄	~40%
2	C ₂ Cl ₄ / Isopar L=1:1	~50%
3	Isopar L	~70%

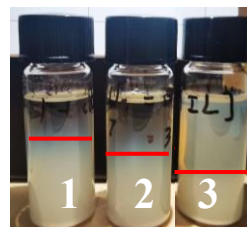
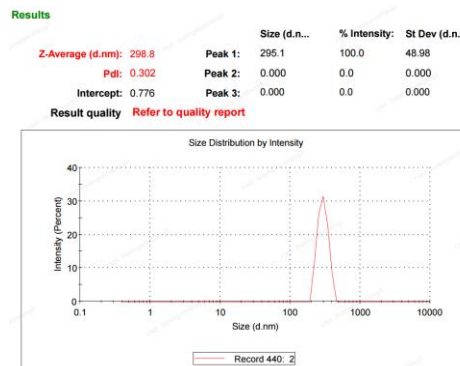


Figure 5. Particle sedimentation rates corresponding to different solvents.

5. Performance characterization

We used the Malvern Panalytical ZetaSizer Nano ZS90 to test the particle size and Zeta potential of the white ink. The test results was showed in Figure 6. The particle size of white ink is mainly distributed at 298.8 nm, which is in line with the target particle size (half of the visible light wave length). The Zeta potential reaches -81 mV, which is far exceeding the ± 30 mV that required for the stability of the colloid system.

(a)



(b)

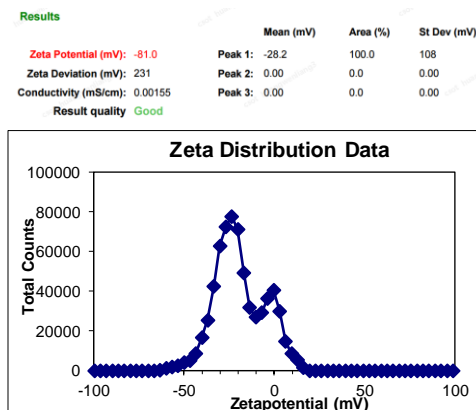


Figure 6. (a) particle size distribution data; (b) Zeta distribution data

The ink with particle ratio of 3:1 of white and black were mixed and packaged into a box using the experimental method described in section 2.2. The demo picture of the test cell is shown in Figure 7. The key performance of electronic ink screen test cell was listed in table 5. The contrast of the test box can reach 81.9 (CR of reference is 6.6), which far exceeds the level of all electrophoretic e-papers on the market.

Table 5. Reflectivity of electronic ink screen

Item	CSOT	Ref.
White state (SCE)	51.6%	44.43%
Black state (SCE)	0.63%	6.63%
Contrast ratio	81.9	6.6

To drive the target image, the electronic ink display exhibiting good contrast and resolution, and the brightness of the image remained almost unchanged within 72 hours.



Figure 7. Test cell of 3-inch badge

6. Conclusion

In summary, by adjusting the particle density difference and

system viscosity, the sedimentation of ink has been effectively reduced. In addition, the particles exhibited good fluorine coating efficiency through optimization of the synthesis method, with the particle size mainly well dispersed at 298.8nm, and the zeta potential of the mixed white ink reaching $\pm 81\text{mV}$. Meanwhile, our excellent bistable electrophoretic test units also demonstrated performance with contrast ratio up to 81.9, which is approximately 12 times that of market - reference products.

7. Acknowledgements

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8. References

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