Electrophoresis of Polymer Particles Charged by Acid - Base Dissociation in Silicone Oil

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Abstract

A charge generation of particles due to an acid-base dissociation in non-polar solvent is essential for liquid toners used in electrophotography. In this paper, a charge generation and a dispersion stability of acrylic polymer particles including base groups by an interaction with acid / base dispersing polymers modified with silicone groups in silicone oil are discussed. The dynamic mobility and the dispersion stability of the particles are measured by electrokinetic sonic amplitude methods (ESA) and visually observed by a high-speed video camera. From these observations, it is suggested that the charge generation at the surface of particles is affected by the acid-base dissociation in the silicone oil. As evidence, the mobility of the particles increases responding to an increase in acid polymer concentration solved in silicone oil. In conclusion, a suitable concentration of the acid / base dispersing polymer which makes the particle higher mobility is presented.

Introduction

Basic technologies of the liquid toner using an electrophoresis has been used for a wide range of technical application so far and it is expected to be use for a digital paper or commercial printers.[1,2] For inks or liquid toners for those imaging device, a hydrocarbon solvents have been usually used. However, the solvents have problems such as an influence against a human bodies or uncomfortable smell. Because silicone oil has little effect on environmental pollution and wide range of boiling point, it is a potential candidate as a solvent replacing the hydrocarbon. However, the difficulty to disperse resin particles using the conventional dispersants in silicone oil has been preventing its application to liquid toners. In the charge generation and the dispersion stability in non-polar solvent, technique to dissolve metal soaps as a charge control agent (CCA) has been used with a toner for a conventional liquid development. [3,4] In the same as CCA, a technique of the charge generation by acid-base dissociation has been examined.[5,6,7] However, there are few papers described the stability and the charge generation of particles highly concentrated in the liquid. Therefore, a technique to control the charge generation by the ionic concentration is demanded in order to realize a high-speed response and highly concentrated toners and inks for the electrophotographic printer. The charge generation by an interaction between a surface of the mono-dispersing particle and acid / base polymers in solvent was examined by means of the observation of the electrophoresis and ESA. In this paper, we report a mechanism of the charge generation with the use of acid-base dissociation and the results of the examination on the fundamental electrophoresis properties.

Experimental

Solvent Soluble Polymer

A copolymer including methacrylic acid (MAA) in its components as a acid polymer soluble in silicone oil was synthesized.[9] The composition ratio of the copolymer with the acid group was MAA: silicone macromonomer = 0.275: 9.725. In the same way, the copolymer which included 2-(dimethylamino) ethyl methacrylate (DMMA) in component as base polymer soluble in silicone oil was synthesized. The composition ratio of the copolymer with the base group was DMMA: silicone macromonomer = 0.5:9.5. After the reaction finished, Silicone oil was removed by evaporation. Then, monomers remained in the liquid polymers were washed out by methanol. As a result, we obtained two liquid polymers having average molecular weight round 20,000. At the first we studied the ion dissociation mechanism of acid (n-Octanoic acid) / base (n-Octylamine) and this acid / base dispersion agent. The result is shown in Figure 1. In the ion dissociation mechanism of a weak electrolyte, a molar conductivity decreases as acid / base density increases usually. However, as for the acid / base in low viscosity silicone oil of 1 cSt, a molar conductivity looks increasing. As for this phenomenon, it is assumed that the aggregated formation such as a reverse micelle is generated by an ionization process of the acid-base dissociation in silicone oil. In addition, the acid / base interaction behaves like the ion dissociation in a weak electrolyte by the solvation when the polar component is dissolved in low viscous silicone oil.[5,8,9] Contrary, a molar conductivity decreases as the concentration of acid / base in high viscosity silicone oil increase. It was shown that ion generation by acid / base dissociation resembles the ion dissociate mechanism of a weak electrolyte. It is supposed

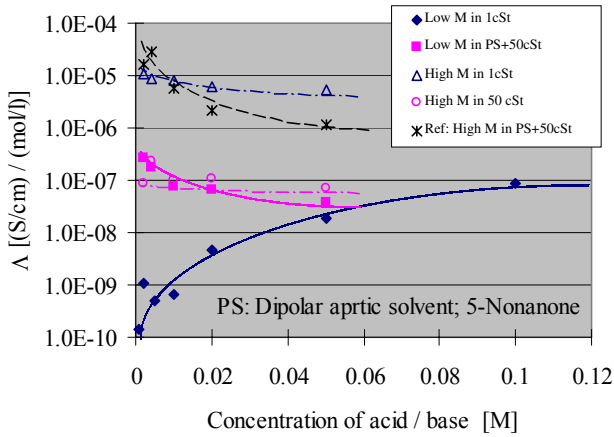that the dispersing agent (DA) behaves like the ion dissociation of a weak electrolyte.

Figure 1. Equivalent conductivity versus acid / base dispersing polymers concentration. Low M; acid (n-Octanoic Acid) / base (n-Octylamine), High M; acid / base dispersing agent, PS; Dipolar solvent.

Mono-Dispersing Colored Particle

Various particle sizes of mono-dispersed colored acrylic particles with the basic group insoluble to silicone oil were prepared. These particles and the liquid polymers were dispersed in silicone oil. Then we observed the toner charge generation. The concentration of base per unit area on the surface of the particle was measured by a pH-stat. It was about 1.0×10^{16} [unit/m^2].

Dynamic Mobility

Dynamic mobility and the dispersion stability of the particles were measured by electrokinetic sonic amplitude methods (ESA; Matec Applied Sciences ESA-9800).[10, 11] Figure 2 shows the schematic diagram of ESA sensor. Parameters of the solvent used for measurement of ESA are shown in the following table 1.
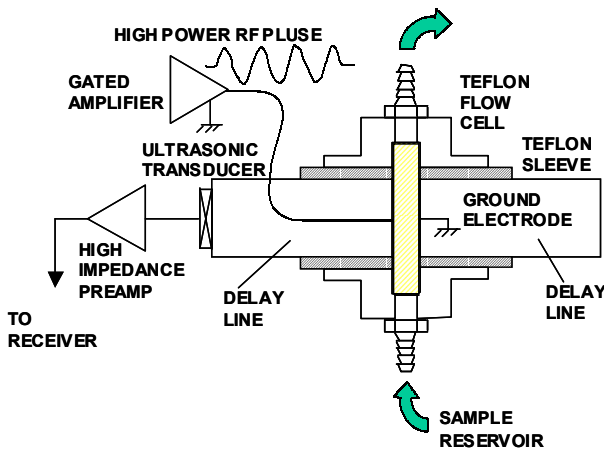

Figure 2. Schematic diagram of ESA sensor

Table 1. Physical property of particles and solvent

Mono-dispersing colored particle	*Density*	*1.0 g/cc*
	Diameter	*1.9, 3.9, 5.8 μm*
	Volume Percent	*19.4 vol%*
	Weight percent	*20.0 wt%*
Solvent (Dimethyl Silicone 50cSt)	*Weight percent*	*75 – 80 wt%*
	Density	*0.960 gm/cc*
	Viscosity	*52.083 cp*
	Visc. Temp. Coeff.	*-5.90 % / C*
	Dielectric Constant	*2.710*
	Speed of Sound	*982 m/s*
Dispersion	*Weight percent*	*0 – 5 wt%*

As a solvent, silicone oil of 50 cSt, was used. The concentration of samples was adjusted to 20 wt % solid contents dispersed by ultrasonic wave for 60 minutes.

High Speed Video Camera

An observation device of electrophoresis of polymer particles is illustrated in Figure 3. Indium Tin Oxide (ITO) electrode of 100 μm gap is deposited on the top of a glass substrate. The insulation glass (thickness: 25 μm) is pasted on the electrode. High-speed video camera system is installed so that the motion of the particles in the gap can be observed directly. A sample toner is dropped at the gap. After it, surplus fluid is removed by rubber blade. Applying pulse voltage described in Figure 3 at the gap, the motion of the dispersed particles is recorded by video camera with 1/5000 second per 1 frame.
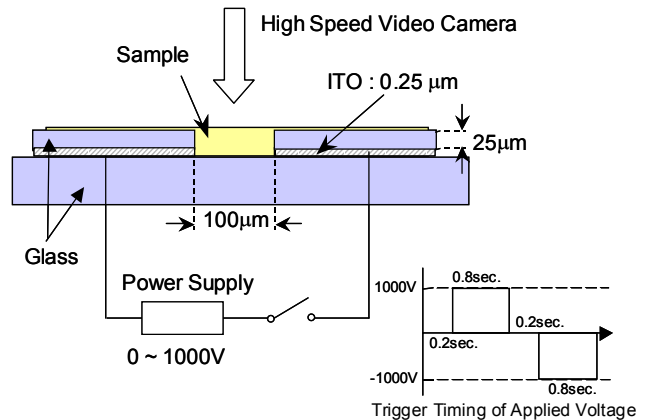

Figure 3. Schematic diagram of high-speed camera

Consideration

Adding Acid Dispersing Agent

Figure 4 shows dependency of the dynamic mobility measured by ESA on the concentration of acid DA. The concentration of DA is defined by the number of MAA components added in the liquid per unit area of the particle surface. In the experiment, three particle sizes, 1.9, 3.9 and 5.8, were examined. With adding the acid DA, the dynamic mobility of particles of all sizes are increasing, and peaks almost equally appears at $1.2x10^8$ [unit/m^2]. This peak corresponds to the concentration of base on the particle surface. In the less concentration range under the peak point, (a) to (b), it is supposed that the charge of the particles are affected by the acid-base dissociation. However after the peaks appeared, the dynamic mobility of the particles behaves sudden decrease. It is supposed that a part of particles get charged to opposite polarity by the excess acid DA.
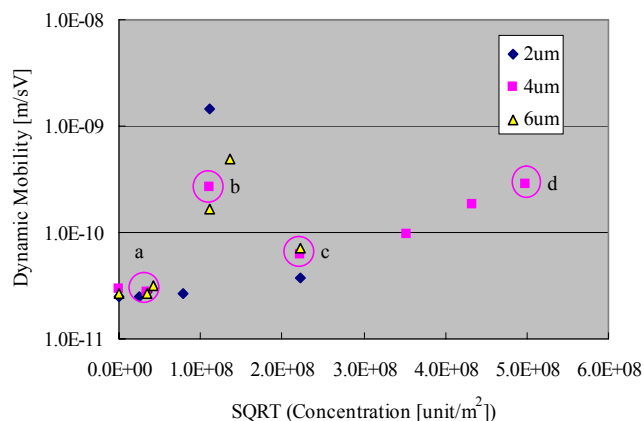

← *Electric Field*

Figure 5. Observation of high-speed video (Still picture of the movie after 0.5 sec. from time of an applied voltage)

Figure 4. Dynamic mobility versus acid dispersing agent concentration

Figure 5 shows images of high-speed video movie after 0.5 sec. from a trigger. (a), (b), (c) and (d) in Figure 5 correspond to the same as in Figure 4. (a) shows the case of the liquid without the DA. A lot of aggregated particles are observed in the gap. And the particle movement from right electrode toward left electrode does not finish while DC voltage is applied. For the case (b), almost all particles deposit on the left electrode from the right electrode. It means that the mobility of the particles is become faster. And also it means that the polarity and the charge of the particles are optimized. For the case (c), the particles which returns to electrode of the right-hand side form left-hand side are observed It is supposed that the particles which move to opposite direction were charged negatively by the excess acid DA. For the case (d), comparing with (c), the particles behave reciprocated motion in the gap, even though DC voltage is applied It is supposed that the particles are charged negatively accelerated by an adsorption of the excess acid DA onto the particles.
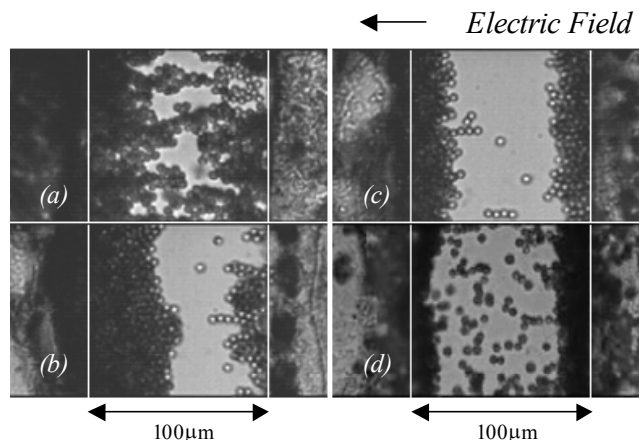
In the range between (a) and (b), the dynamic mobility increases as the concentration of the acid DA increases because the particles become well dispersed in the liquid by the DA. On the other hand, in the range between (b) and (c), a part of the particles are charged negatively. Because the concentration of the acid DA at the interface of the particle surface and the DA become high enough to adsorb, silicone chains of DA begin to be fixed on the surface of the particles. And the number of the particles increase and the dynamic mobility decreases as the concentration of the acid DA increases. The high-speed video shows that the particles irregularly moving in the DC electric field applied in the gap increase as the concentration of the DA increases. Then, an average of the dynamic mobility measured by ESA decreases. It also suggests that the decrease of the dynamic mobility is caused by electrostatic interactions and physical collisions between those particles.

In the range between (c) and (d), the dynamic mobility increases again as the concentration of the acid DA increases. And from the observation of the high-speed video, the particles move in high speed but reciprocally, and the higher the concentration of the acid DA the better the dispersion stability. It is suggested that as negative ion species dissolved in the solvent increase by adding the excess acid DA, a steric stabilization by elements of the DA becomes more effectively, and an interaction between the particles and the ions, e.g. adhering and leasing of the ions, is activated. Thereby, the dynamic mobility increases.

Adding Base Dispersing Agent

Figure 6 shows a dependency of dynamic mobility measured by ESA on the concentration of the base DA. The concentration of DA is defined as the number of DMMA components added in the solvent per unit area of the particle surface. At the points where the concentration exceeds the equilibrium point, around $1.5x10^8$ [unit/m^2], the polarity of the particles changes from positive to negative. This

phenomenon suggests that an interaction of the base DA and a residual acid or H^+ on the particle surface makes the particles negative. To make the particle positive, it is necessary to fix the base component to the surface of the particle. In addition, the same as the acid DA, a dispersion stability of the particles is improved by steric repulsion as the concentration of the base DA increases.
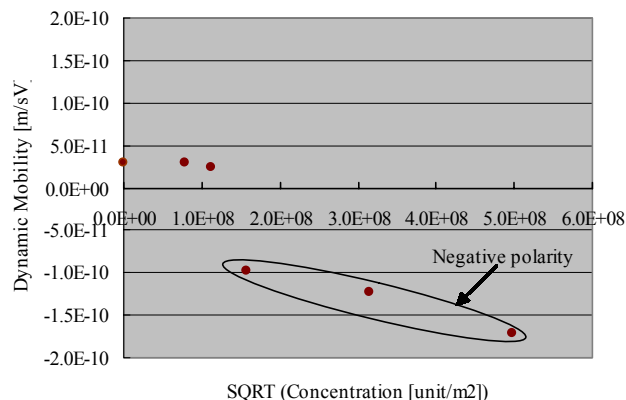

Figure 6. Dynamic mobility versus base dispersing agent concentration (particle diameter size is 3.9 μm)

It is found that these acid-base dissolutions at the interface between the base polymer particle and the solution containing the acid (or base) group generate an electric double layer around the particles and make all particles charge positively (or negatively), and that the charge on the particles can be controlled by ionic concentration at the surface. Therefore, it is supposed deductively that the charge on the acid polymer particles can be controlled by ionic concentration.

Conclusion

1. The dispersion stability of particles becomes better proportionally to the DA concentration by steric repulsion.

2. In case the concentration of the acid DA is smaller than that of the base on the particle surface, as the acid-base dissociation by the solvation occurs at the surface of the particle, the particle charge and also the mobility become higher.

3. In case the concentration of the acid DA is larger than that of the base on the particle surface, the dynamic mobility of the particle becomes faster. However, the polarity of the particle charge changes reciprocally.

4. The charges of the base particle build-up negatively as the concentration of the base DA increases.

Acknowledgements

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Biography

Tsutomu Teraoka received his Dr. Eng. in Applied Material Science and Engineering from the Muroran Institute of Technology, Japan in 1994. Since 1994 he has worked as a researcher on the applied inorganic material in research and development group of Ricoh Co., Ltd.. He then is working on a research of charging and dispersing mechanism of polymer particle in non-polar solvent for liquid toner.