# Study on Shear Rate and Particle Shape-dependency of Viscosity for Electrophotographic Liquid Toners

Joong-Hwan Choi and Kyung-Yol Yon Material Part, Project-C Team, Digital Printing Division, SamSung Eletronics Co. Ltd, Suwon, Kyungki-Do, Korea

## Abstract

In order to describe the liquid immersion development, electrophoretic mobility is important value because toner particles move in non-polar liquids when voltage is applied. Viscosity is known to influence the electrophoretic mobility, which effect is very considerable especially in high concentration and low shear rate. Generally speaking, viscosity of suspension is a function of various factors such as particle concentration, shear rate, temperature, and particle shape, etc. Even though temperature and concentration equal in liquid toner, viscosity of liquid toner is considerably influenced by shear rate and particle shape.

In development of liquid toner from developer roll to photoreceptor, toner particles experience shear flow resulting from velocity difference between developer roll and photoreceptor. However, most discussions about liquid toner development systems have concentrated on the effect of electrostatic force and ignored that of shear rate or particle shape.

In this work, three types of liquid toners with different particle shape were used to investigate the effects of shear rate and particle shape on the viscosity of liquid toners. From this work, it could be understood that the shear rate and particle shape of liquid toners influenced the viscosity of liquid toners under the same concentration and temperature. To describe the rheological behavior of the liquid toners quantitatively, modified Quemada equation, based on the hard sphere concept, was used. When  $\eta_0$  in the Quemada equation was used as a function of shear rate and particle shape, it could be observed that the modified equation well described the viscosity of the liquid toners for all shear rates and concentration.

### Introduction

Due to the smaller toner size and the feasibility of narrow development gap, development of electrostatic images with liquid toner has been gradually perceived to possess the potential of achieving the high image resolution demanded by high quality color prints.<sup>1</sup> In comparison with dry electrophotographic printing process, liquid toner, in which

toner particles are dispersed in non-polar liquids, is used in the liquid printing process.<sup>2</sup> Therefore, in order to describe the liquid immersion development, electrophoretic mobility and average charge-to-mass ratio (Q/M) for liquid toner are important values because non-polar liquids are used as carrier liquids.<sup>3</sup>

The charge q and the mobility  $\mu$  of colloidal particles are related by Stoke's law:

$$\mu = \frac{q}{6\pi\eta R} \tag{1}$$

where **R** is the particle radius and  $\eta$  is the coefficient of viscosity of the fluid. The average charge-to-mass ratio is obtained as follows:

$$\frac{Q}{M} = \frac{9\mu\eta}{2\rho R^2}$$
(2)

where  $\boldsymbol{\rho}$  is toner particle density.<sup>4</sup>

The parameters  $\rho$  and R in equation (2) are easily measured and they are constant independent of static or dynamic state. However, viscosity  $\eta$  depends on the volume fraction, temperature, shear rate, particle shape, etc.<sup>5,6</sup> Especially, the viscosity considerably changes as function of shear rate and particle shape under the same temperature and volume fraction.

In development of liquid toner from developer roll to photoreceptor, electrophoretic mobility for toner particles is, especially in high concentration, considerably influenced by viscosity of liquid toner which is dependent on the shear rate due to the shear flow resulting from velocity difference between developer roll and photoreceptor (see Figure 1).

Indigo N. V.<sup>7</sup> and Mitsubishi heavy industries (MHI) liquid toners<sup>8</sup> commercially available constitute similar component and have similar particle size. However, their toner particle shapes are very different, i.e., toner particles with plurality of fiber or tendrils for Indigo liquid toners and with nearly sphere for MHI liquid toners. For other liquid toner, core-shell type organosol was prepared to improve dispersion stability and erasure resistance because it surrounds pigment particles.<sup>9</sup> The different toner particle shapes may influence the liquid toner's viscosity and electrophoretic mobility. However, most discussions of liquid toner development systems have concentrated on the effect of electrostatic force and ignored that of shear rate or particle shape.<sup>10-12</sup>



Figure 1. Schematic diagram of liquid development

In this work, three types of liquid toners as mentioned above were used in order to confirm effect of toner particle shapes on viscosity of liquid toner. In addition to particle shape, we also investigate effect of shear rate on the viscosity of liquid toners, especially in high concentration region. For quantitative analysis of effects of particle shape and shear rate, Quemada equation<sup>13</sup> was modified.

# **Experimental**

#### Materials

As mentioned above, three types of liquid toners<sup>7-9</sup> (black) were used. The black liquid toners consist of carbon black, resin, dispersants (or organosol), and charge control agent. Toner A (Indigo) and Toner B (MHI) were diluted or concentrated by a non-polar liquid, Isopar<sup>®</sup> L (Exxon Chem.) and Toner C using core-shell organosol was diluted or concentrated by Norpar<sup>®</sup> 12 (Exxon Chem.). To disperse toner particles and fuse pigment on printing media, the liquid toners were made by using ethylene vinyl acetate/acid terpolymer, saponified ethylene-vinyl acetate copolymer, and organosol (core-shell type Lauryl Methacrylate/Ethyl Methacrylate polymer), respectively. Toner A and Toner B may have a certain degree of particle-particle or particleliquid interactions at room temperature. The organosol used in Toner C consists of core and shell part. The core part is compatible with Norpar<sup>®</sup> 12 but the shell part isn't. Volume average toner particle sizes for the three liquid toners are 5.7, 4.4, and 2.87  $\mu$ m, respectively, which were measured by laser scattering particle size distribution analyzer (Horiba<sup>®</sup> LA-910).

#### **Rheological Measurements**

The steady shear viscosity measurement of the three liquid toners was carried out on an Advanced Rheometric Expansion System (ARES-100FRT) with couette geometry.

The steady rate sweeps from 0.01 to 200 rad/s were carried out at  $25^{\circ}$ C.

# **Results and Discussion**

The steady sweep rate tests for three liquid toners (black) were carried out at 25°C and their results are shown in Figures 2 to 4. Apparently unbounded viscosity data at low shear rate were observed for Toner A and Toner B. It is known that agglomeration of particles or interaction at particle/fluid interface generally results in substantial increase of viscosity, mainly at low shear rates due to disturbance of fluid flow and formation of transient network at high concentration.<sup>14,15</sup> However, as shear rate increases, particles dispersed in fluid can be more easily separated each other and then the effect mentioned above decreases because they experience stronger shear flow around themselves. Therefore, the viscosity of the liquid toners decreases as shear rate increases. However, unbounded viscosity data at low shear rate were not observed below 6.0% for Toner C in Figure 4. From this observation, it may be stated that the degree of dispersion for Toner C is better than those of Toner A and Toner B. That may be due to the core-shell type structure for organosol in Toner C. It is also observed that the viscosity of Toner A is highest and that of Toner C is lowest for same volume fraction. However, the viscosity difference between the Toner A and Toner C decreases as shear rate increases. In consideration of the above results, the viscosity for three liquid toners depends on shear rate and volume fraction. In other words, the viscosity for three liquid toners increases as shear rate decreases at a certain volume fraction and it also increases as volume fraction increases at a certain shear rate.

To understand and manipulate concentrated colloidal dispersions in both practical and academic fields, hard spheres dispersed in fluid have provided a convenient model because hard spheres feel no interparticle force except an infinite repulsion at contact. Up to now, various equations have been proposed for the description of viscosity data as a function of volume fraction. Quemada<sup>13</sup> also proposed a equation which is frequently used to describe the viscosity of concentrated hard sphere dispersions and the exponent of -2 in it has also been proposed in theoretical work by Brady.<sup>17</sup>

$$\eta = \eta_o \left( 1 - \frac{\phi}{\phi_m} \right)^{-2} \tag{3}$$

Here  $\eta$  and  $\eta_0$  is the viscosity of suspension and dispersionmedium fluid, respectively, and  $\phi$  and  $\phi_m$  are solid particle volume fraction and that where  $\eta$  diverges, respectively.



Figure 2. Plots of viscosity of Toner A as a function of shear rate for various volume fraction at  $25 \,^{\circ}C$ 



Figure 3. Plots of viscosity of Toner B as a function of shear rate for various volume fraction at  $25 \,^{\circ}C$ 



Figure 4. Plots of viscosity of Toner C as a function of shear rate for various volume fraction at  $25 \,^{\circ}C$ 

Figure 5 represents the variation of  $\eta$  with particle volume fraction for Toner A. It is observed that the viscosity depends on shear rate and volume fraction. The solid line represents Quemada model prediction and the values of parameters used to calculate the equations are summarized in Table I. In case of using constant  $\eta_0$ , the Quemada prediction well describes the experimental data from experimental data *only* at 100 rad/s, but it starts to deviate below 100 rad/s.

 Table 1. The values of parameters used in calculating the

 Quemada equations in Figure 5

Parameters in Eq. (4)	$\eta_{_0}$ (poise)	$\phi_{ m m}$
Value	0.02	0.160



Figure 5. Comparison of viscosity measured by experiments with the model predictions for Toner A

The above results indicate that equations induced from hard sphere concept cannot be used to describe the viscosity of three liquid toners for wide range of shear rate region except for high shear rates. The phenomena can be ascribed to the fact that particles dispersed in fluid for the liquid toners can be easily separated each other over 100 rad/s because they experience much stronger shear flow around themselves. Therefore, since particle-particle interaction and fluid entrapment by particles may be nearly eliminated over 100 rad/s, Quemada equation based on hard sphere concept can well describe the experimental data for the liquid toners. However, at low shear rates, theoretical predictions fail to describe the experimental viscosity data because the particle-particle interaction and fluid entrapment isn't negligibly small.

In concentrate dispersion system, fluid flow around a solid particle at low shear rates is different from that at high shear rates because disturbance of fluid flow, fluid's entrapment, and transient network formation are extremely generated at low shear rate. Therefore, it was assumed that different  $\eta_0$  in Eq. (3) had to be used for different volume fraction in order to incorporate the effect of flow disturbance, entrapment and/or transient network formation into the Quemada equation. In other words, environmental fluid flows around particles change when volume fractions are different.

Based on the above argument, different value of  $\eta_0$  in Eq. (3) is used for each shear rate to fit the model prediction to experimental viscosity data for liquid toners. The modified Quemada equation and experimental viscosity data are compared in Figures 6 to 8 for various shear rates.



Figure 6. Comparison between viscosity data measured by experiments and those calculated by the Quemada equation using different  $\eta_a$  for Toner A



Figure 7. Comparison between viscosity data measured by experiments and those calculated by the Quemada equation using different  $\eta_a$  for Toner B



Figure 8. Comparison between viscosity data measured by experiments and those calculated by the Quemada equation using different  $\eta_{c}$  for Toner C

It is observed that the modified Quemada equation using different values of  $\eta_0$  well describes the viscosity of the three liquid toners for various shear rates and volume fractions. On the other hand,  $\eta_0$  of Toner A is the highest value among the three liquid toners. It can be explained by the fact that the amount of flow entrapment or transient network formation for Toner A is the greatest among those of the three toners due to the difference of toner particle shape. In addition, it can be recognized that values of  $\eta_0$  is proportional to the amount of flow entrapment or transient network formation.

# Conclusions

In concentrate dispersion system, fluid flow around a solid particle at low shear rates is different from that at high shear rates because disturbance of fluid flow, fluid's entrapment, and transient network formation are extremely generated at low shear rate. In addition, although the core particle size and particle concentration are equal, formation of transient network and the strength of the transient network may be different for liquid toners with different particle shape because the degree of particle connections between adjacent particles are very different. In fact, it can be observed that viscosity of liquid toner depends on shear rate and particle size in this work. However, the Quemada equation cannot describe the experimental data for the liquid toners, especially at low shear rates since it based on hard sphere concept. In order to incorporate the effect of flow disturbance, entrapment and/or transient network formation into the Quemada equation,  $\eta_0$  or exponent in it was used as a function of shear rate. As a result, it was observed that the modified Quemada equation well describes the viscosity of the liquid toners for various shear rates and volume fractions except for low volume fraction.

## References

- 1. R. M. Schaffert, *Electrophotography*, Focal Press, London, 1975.
- 2. A. S. Diamond (Ed.), *Handbook of Imaging Materials*, Marcel Dekker, New York, 1991, Chapter 6.
- 3. V. Novotny and M. L. Hair, J. Colloid Interface Science, **71**, 273 (1979).
- 4. M. D. Croucher, S. Drappel, J. Duff, K. Lok and R. W. Wong, *Colloids and Surfaces*, **11**, 303 (1984).
- P. J. Carreau, D. C. R. De Kee and R. P. Chhabra, *Rheology* of *Polymeric Systems: Principles and Applications*, Hanser Publisher, Munich, 1997.
- 6. C. D. Han, *Multiphase Flow in Polymer Processing*, Academic Press, New York, 1981.
- 7. B. Landa, P. Ben-Auraham, J. Hall and G. A. Gibson, *US Pat.* 5,407,771, 1995.
- 8. Y. Suda, H. Kawamura and H. Kuno, US Pat. 5,876,896, 1999.
- 9. J. A. Baker, W. Hudson, J. Venkatesan, W.-S. Li and G. L. Herman, *US Pat.* 5,652,282, 1997.
- L. B. Schein, G. P. Gee, M. H. Lee and C. I. Dodds, J. Imaging Sci. Technol., 38, 409 (1994).
- 11. I. Chen, J. Imaging Sci. Technol., 43, 270 (1999).
- 12. I. Chen, J. Imaging Sci. Technol., 39, 473 (1995).
- 13. D. Quemada, Rheol. Acta, 16, 82 (1977).
- 14. H. C. Brinkman, J. Chem. Phys., 20, 571 (1952).
- 15. R. Roscoe, Br. J. Appl. Phys., 3, 267 (1952).
- 16. I. M. Krieger, Adv. Colloid Interface Sci., 3, 111 (1972).
- 17. J. F. Brady, J. Chem. Phys., 99, 567 (1993).