

# Plastisol Based Liquid Electrophotographic Toners

*Eric Morrison, Julie Qian, Christopher Wolters, James Baker, and Kam Law  
Samsung Information Systems America; Digital Printing Solutions Laboratory  
Woodbury, Minnesota*

## Abstract

A plastisol is defined as a thermoplastic binder dispersion prepared by dispersing polymer particles in a liquid medium in which the polymer is insoluble. Plastisol based electrophotographic toners have been prepared with a novel composition that exhibits increased dispersion stability and improved chargeability. The plastisol based electrophotographic toners contain either a combination of acid functional binder resin plus base functional dispersant or base functional binder plus acid functional polymeric dispersant.

## Introduction

Liquid inks are widely used in a variety of imaging and printing processes, for example offset, bubble jet, ink jet, intaglio, rotogravure, electrographic, and electrophotographic printing. In electrophotographic applications, which includes devices such as photocopiers, laser printers, facsimile machines and the like, liquid inks are referred to as liquid toners or developers.

Generally, the electrophotographic process includes the steps of forming a latent electrostatic image on a charged photoconductor by exposing the photoconductor to radiation in an imagewise pattern, developing a temporary image on the photoconductor by contacting the photoconductor with a liquid ink, and finally transferring the temporary image to a receptor. The final transfer step may be performed either directly from the photoconductor or indirectly through an intermediate transport member. The developed image is usually subjected to heat and/or pressure to permanently fuse the image to the receptor.

Liquid electrophotographic inks typically comprise an electrically insulating liquid that serves as a carrier for a dispersion of charged particles, known as toner particles. These toner particles are composed of at least a colorant (e.g. pigment or dye) and a polymeric binder. A charge control agent is often included as a component of the liquid developer to regulate the polarity and magnitude of the charge on the toner particles.

New plastisol inks have been prepared from acrylic polymers by dispersing the polymer in the presence of pigment plus a functional dispersant. The dispersant acts to stabilize dispersed toner particles and to provide the correct charging characteristics to the dispersed toner particles.

## Experimental

### Preparation of Ink

A 0.5 liter vertical bead mill (Model 6TSG-1/4, Aimex Co., Ltd., Tokyo, Japan) was charged with 390 g of 1.3 mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, N.J.), 60.0g of resin, 8.14g of 6.15 weight percent Zr Hexcem solution (product of OMG Americas), 217g of Norpar 12, 10.0g of Cabot Monarch 120 black pigment, and 15.0g of 40% (w/w) Solsperse 13940 hyperdispersant in petroleum distillate. The mill was operated at 2,000 RPM for 2 hours with heating provided with a water/glycol mixture held at 70°C circulating through the cell jacket. The water/glycol mixture temperature was reduced to 35°C and milling was continued for an additional 2 hours to produce a black liquid electrophotographic toner.

### Evaluation of Ink

Percent non-volatile content of ink samples was determined gravimetrically using a halogen lamp drying oven attachment to a precision analytical balance (commercially obtained from Mettler Instruments Inc., Hightstown, NJ). Approximately two grams of sample were used in each determination of percent solids using this sample dry down method. Toner particle size distributions were determined using a Horiba LA-900 laser diffraction particle size analyzer (commercially obtained from Horiba Instruments, Inc, Irvine, CA). Toner samples were diluted approximately 1/500 by volume and sonicated for one minute at 150 watts and 20 kHz prior to measurement. The liquid toner conductivity (bulk conductivity,  $k_b$ ) was determined at approximately 18 Hz using a Scientifica model 627 conductivity meter (commercially obtained from Scientifica Instruments, Inc., Princeton, NJ). In addition, the free (dispersant) phase conductivity ( $k_f$ ) in the absence of toner particles was also determined. Toner particles were removed from the liquid milieu by centrifugation at 5°C for 1-2 hours at 6,000 rpm (6,110 relative centrifugal force) in a Jouan MR1822 centrifuge (commercially obtained from Jouan Inc., Winchester, VA). The supernatant liquid was then carefully decanted, and the conductivity of this liquid was measured using a Scientifica Model 627 conductance meter. The percentage of free phase conductivity relative to the bulk toner conductivity was then determined as: 100% ( $k_f/k_b$ ). Toner particle electrophoretic mobility (dynamic mobility) was measured

using a Matec MBS-8000 Electrokinetic Sonic Amplitude Analyzer (commercially obtained from Matec Applied Sciences, Inc., Hopkinton, MA). The electrostatic transfer properties of ink samples was evaluated using a 3-roll transfer tester. The 3-roll transfer tester consists of three stainless steel rolls approximately 2 inches in diameter which are separated by a gap of 0.15mm. A schematic drawing of the 3-roll tester is shown below.

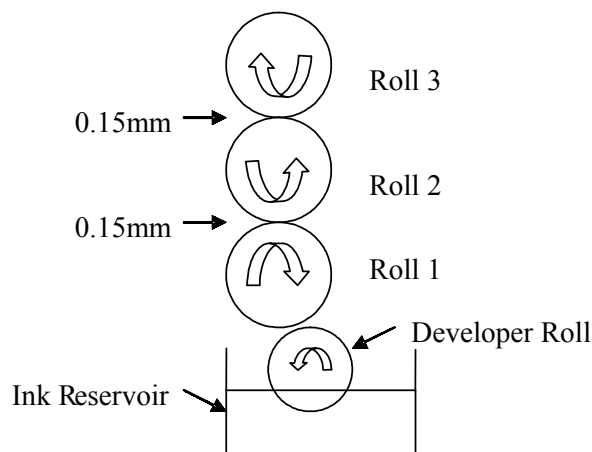


Figure 1. Three Roll Transfer Tester

According to the three roll test method, the transfer of toner particles from one roll to another is tested as a function of the bias voltage.

## Results

Acrylic polymers with glass transition temperatures between approximately 35 and 60C were selected for evaluation. The criteria for polymer selection includes sufficiently high glass transition temperature for image durability (no blocking of printed sheets) and sufficiently low glass transition temperature for fusing. The following table lists commercially available Elvacite and Joncryl acrylic resins (available from Ineos Acrylics and Johnson Polymers, respectively).

### Yield of Ink

The yield of ink was determined by dividing the actual % non-volatile material by the % non-volatile material expected on the basis of formulation. In the case of Elvacite resins, it was found that the yield is dependent on the molecular weight of the resin. Polymers with relatively lower molecular weight gave relatively higher yields of dispersed ink particles as shown in Figure 2. Although Elvacite 4004 with high intrinsic viscosity (0.32) gave an acceptable yield of ink, in this case the ink particle size was unacceptably high (volume average particle size = 26 microns, compared to 0.4 microns to 5 microns for other polymers).

Table 1. Properties of Commercial Acrylic Resins

Polymer	Glass Transition, C	Polymer Acid Number, mg KOH/g	Inherent Viscosity
Elvacite 2016	50	3.5	0.25
Elvacite 2550	36	17	0.32
Elvacite 2697	50	2	0.24
Elvacite 2776	45	80	0.10
Elvacite 2823	50	3.5	0.23
Elvacite 2927	50	3.5	0.12
Elvacite 4004	52	117	0.32
Elvacite EDP 296	50	0	
Joncryl 586	60	108	
Joncryl 587	45	4	
Joncryl 611	50	52	
Joncryl 804	60	15	
Joncryl 815	55	35	
Joncryl 819	57	75	
Joncryl 835	50	53	

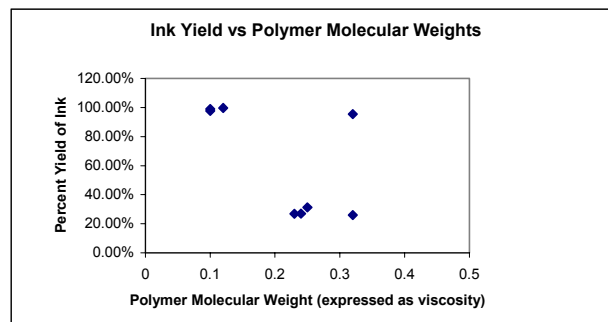


Figure 2. Graph of Ink Yield vs Polymer Molecular Weight

### Ink Electrical Properties

Ink conductivity showed poor correlation with the acid number of the polymer as shown in Figure 3.

It is expected that acid groups pendant on the toner particle binder resin can ionize to give negatively charged toner particles. Several US patents describe the use of ethylene/methacrylic acid copolymers as binder resins for negatively charged electrophotographic inks<sup>1-3</sup> Charge additives for negatively charged toner particles can include quaternary ammonium block copolymers<sup>4</sup> and zwitterionic block copolymers.<sup>5</sup>

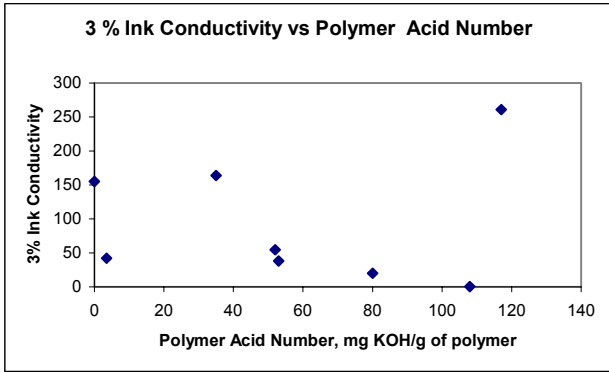


Figure 3. Ink Conductivity vs Polymer Acid Content

Although ink conductivity showed poor correlation with the acid number of the polymer binder, the properties of ink conductivity, ink free phase conductivity, and ink electrophoretic mobility all showed a smooth dependence upon the ratio of dispersant amine groups to polymer acid groups. These relationships are shown in Figures 4 and 5.

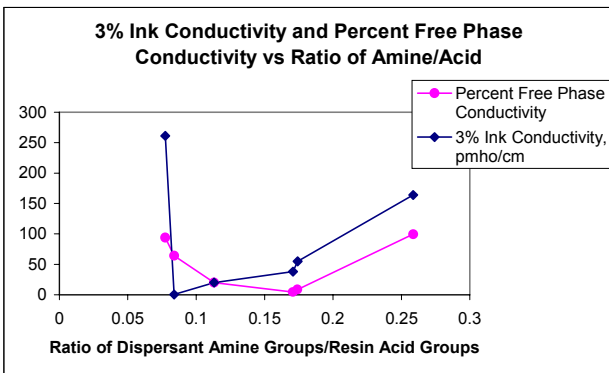


Figure 4. Graph of Ink Conductivity and Free Phase Conductivity vs Ratio of Dispersant Amine Groups to Polymer Acid Groups

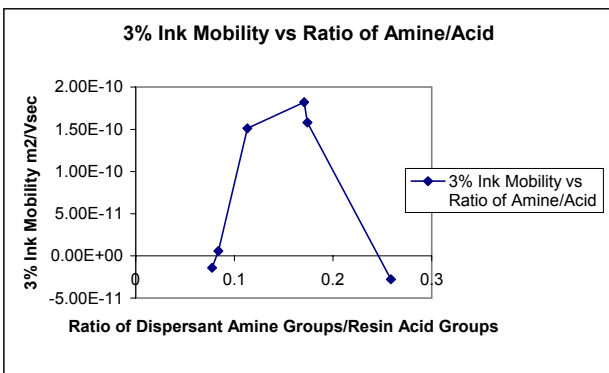


Figure 5. Graph of Ink Electrophoretic Mobility vs Ratio of Dispersant Amine Groups to Polymer Acid Groups

### Electrostatic Transfer Properties

Positively charged inks with electrophoretic mobility between  $1E-10$  m<sup>2</sup>/V•sec and  $2E-10$  m<sup>2</sup>/V•sec showed good electrostatic transfer properties. For example, a positive bias voltage of between 100V and 200V is sufficient to prevent movement of toner particles from the developer roll to roll 1 in the 3 – roll testing jig (a 100V to 200V bias voltage is sufficient to prevent background development).

Toner particles transferred from roll 1 to roll 2 completely (100% transfer in one roll revolution) using negative bias voltages of between 500V and 750V (destination roll voltage is 500V to 750V more negative than source roll voltage). Toner particles were capable to be repetitively transferred (do not fail to respond to a voltage bias if transferred multiple times).

### Discussion

The generation of positive charge from metal carboxylate charge control additives is influenced by the presence of amine compounds such as tertiary amine groups found in dispersants such as Solsperse 13940. Dispersant and charge director can complex to toner particles via ionic bonds between protonated quaternary ammonium groups on the dispersant and carboxylate groups on the polymer binder, thus imparting a positive charge to the toner particle:

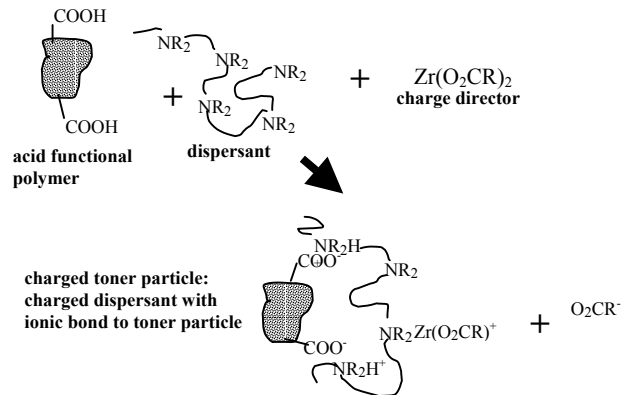


Figure 6. Generation of Toner Particle Electrophoretic Mobility by Interaction of Binder, Dispersant and Charge Control Additive.

In the absence of carboxylic acid groups in the polymer binder, the dispersant and charge director remain soluble in the aliphatic hydrocarbon solvent, thereby giving conductivity to the solvent rather than the toner particle.

In these experiments, the concentration of Solsperse 13940 hyperdispersant remained constant from sample to sample. In this case, high ratios of dispersant amine groups to polymer binder acid groups are indicative of a small concentration of carboxylic acid groups on the resin. The diagram above is the limiting case where there are no carboxylate groups. As the concentration of carboxylate groups increases, the positive charge on the toner particle

increases giving positive electrophoretic mobility to the particle. As the concentration of carboxylate groups increases further, the positive charge of the ionically bonded dispersant plus charge control agent is increasingly offset by negative charge resulting from ionization of the polymer carboxylate groups. In this case, as the ratio of amine groups to acid groups increases, a maximum for electrophoretic mobility is observed as shown in Figure 6. The optimum ratio of amine groups to acid groups was not unity but was between about 0.15 and 0.20. This is most likely due to the fact that the majority of the resin carboxylate groups are occluded within the toner particle and are inaccessible to the dispersant.

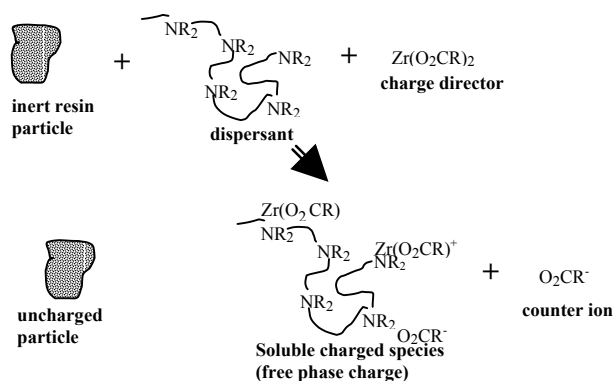


Figure 7. Generation of Soluble Phase Conductivity in the Absence of Interaction Between Binder and Dispersant

## Conclusion

Novel plastisol based electrophotographic toners can be prepared by milling acid functional acrylic binder resins with positive charge control additives and amine functional dispersant in aliphatic hydrocarbon solvent. Electrophotographic toners with stable positive charge and useful levels of electrophoretic mobility are obtained. These show good transfer properties in the presence of an electrostatic bias voltage.

Useful electrophoretic mobility is obtained by interaction between amine groups in dispersants and acid groups in the binder resins. An amount of amine functional dispersant much less than stoichiometric gives the best results, most likely because the majority of polymer acid groups are occluded within the polymer.

## References

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## Biography

**Eric Morrison** received his Ph.D. in Chemistry from Penn State University, University Park, PA in 1985. Dr. Morrison worked for 3M Company from 1985 - 1997 and for Imation Corp. from 1997-2000. He is currently a research group leader with Samsung Information Systems America, Digital Printing Solutions Lab, Woodbury, Minnesota. Dr. Morrison's main research activities involve the development and scale-up of novel materials for electrophotographic applications. Correspondence on this paper should be e-mailed to [emorrison@mn.sisa.samsung.com](mailto:emorrison@mn.sisa.samsung.com)