

# Phase Change Developer for Liquid Electrophotography

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## Abstract

A phase change developer can reversibly change from a solid state to a liquid state at its melting/crystallization temperature. This phase change developer is solid in storage and before imaging development. During image development, it melts at a temperature above its melting point to form a liquid developer which then undergoes the process of liquid electrophotographic development to produce toned images. These unique characteristics of the phase change developer were achieved using a binder which contains a polymerizable crystallizable component (PCC).<sup>1,2</sup> The resulting images exhibited high gloss, high resolution, good transparency, and superior blocking and erasure resistances.

## Introduction

Imaging developing methods can be classified into liquid type<sup>3</sup> and dry type.<sup>4</sup> Dry developers were generally prepared by mixing and dispersing colorant particles and a charge director into a thermoplastic binder resin, followed by milling and micropulverization. The resulted developer particle sizes are usually in the range of 4 to 10 microns. These fine size particles are considered to be a pollutant when they are scattered, therefore pose an environmental problem. However, the dry particles provide excellent ease of handling and stability. Liquid developers are prepared by dispersing colorant particles, a charge director, and a binder in an insulating liquid (i.e., a carrier liquid). The resulting developer particle size can be in the range of submicron to 3 microns, which is significantly smaller than the dry developer particle. Therefore, liquid developers are capable of producing higher resolution and better transparent images. The major drawbacks of liquid developer are (1) the emission of the liquid carrier from liquid developers to the environment during the drying and transfer process; (2) the need and difficulty in disposing the waste liquid; (3) the inconvenience of using and handling of liquid developers; (4) the aggregation and sedimentation instability of liquid developer. Therefore, it is desirable to provide a novel phase change toner which provides the advantages of both the dry and liquid developer. The phase change developer is stable, easy to handle, poses no environmental problems, and provides high resolution images.

## Experimental

### Preparation of Developer

#### 1) Binder Synthesis

The binder (also called organosol) was prepared using a dispersion polymerization technique, which allows better custom tailored polymer properties for charging, colloidal stability and durability.

A reaction flask was charged with a mixture of a carrier liquid (e.g. Norpar<sup>TM</sup> 12), a PCC, BHA (behenyl acrylate), HEMA (2-hydroxyethyl methacrylate), and an initiator, V-601 (dimethyl 2, 2'-azobisisobutyrate). While stirred and purged with dry nitrogen, the mixture was heated to 70°C for 12 to 16 hours, at which time the conversion was quantitative. A catalyst, DBTDL (dibutyl tin dilaurate) and TMI (dimethyl-m-isopropenyl benzyl isocyanate) were added to the mixture and the mixture was further allowed to react at 70°C for 6 hours, and thus formed a graft copolymer stabilizer. Into this graft stabilizer mixture, monomers such as EMA (ethyl methacrylate), EA (ethyl acrylate) and initiators such as V-601 (dimethyl 2, 2'-azobisisobutyrate) were combined and the resulting mixture reacted at 70°C for 12 to 16 hours to complete polymerization which resulted in an organosol dispersion. The organosol polymer is referred to as having a core shell structure where the shell is composed of graft stabilizer and the core is formed from monomers added in the second step polymerization. The residual monomers were stripped from the organosol dispersion using a rotary evaporator equipped with a dry ice/acetone condenser and operating at a temperature of 90°C and a vacuum of approximately 15 mm Hg. The resulting organosol was capable of reversibly undergoing phase transformation at its melt/crystallization temperatures.

#### 2) Pigment Milling

The above organosol, pigments and charge control agent such as, Zirconium HEX-CEM, were combined and milled in a vertical bead mill (Model 6TSG-1/4, Amex Co., Ltd., Tokyo, Japan) charged with 390 g of 1.3 mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at 2,000 RPM for 1.5 hours with water circulating through the jacket of the milling chamber at 70°C.

### Evaluation of Developer

For characterization of the developers, the following were measured: (1) size-related properties (particle size) were determined using a Horiba LA-900 laser diffraction particle size analyzer (Horiba Instruments, Inc., Irvine, Calif.). Toner samples were diluted approximately 1/500 by volume and sonicated for one minute at 150 watts and 20 kHz prior to measurement. Toner particle size was expressed on a volume-average basis in order to provide an indication of the fundamental (primary) particle size; (2) charge-related properties (bulk phase conductivity) were determined at approximately 18 Hz using a Scientifica Model 627 conductivity meter (Scientifica Instruments, Inc., Princeton, N.J.). (3) dynamic mobility and zeta potential were measured using a Matec MBS-8000 Electrokinetic Sonic Amplitude Analyzer (Matec Applied Sciences, Inc., Hopkinton, MA). Unlike electrokinetic measurements based upon microelectrophoresis, the MBS-8000 instrument has the advantage of requiring no dilution of the toner sample in order to obtain the mobility value. Thus, it was possible to measure toner particle dynamic mobility at solids concentrations actually preferred in printing. The MBS-8000 measures the response of charged particles to high frequency (1.2 MHz) alternating (AC) electric fields. In a high frequency AC electric field, the relative motion between charged toner particles and the surrounding dispersion medium (including counter-ions) generates an ultrasonic wave at the same frequency of the applied electric field. The amplitude of this ultrasonic wave at 1.2 MHz can be measured using a piezoelectric quartz transducer; this electrokinetic sonic amplitude (ESA) is directly proportional to the low field AC electrophoretic mobility of the particles. The particle zeta potential can then be computed by the instrument from the measured dynamic mobility and the known toner particle size, liquid dispersant viscosity, and liquid dielectric constant.

DSC was used to measure the melting points of the organosols. The measurements were performed using a TA Instruments Model 2929 Differential Scanning Calorimeter (New Castle, Del.) equipped with a DSC refrigerated cooling system (-70°C, minimum temperature limit), and dry helium and nitrogen exchange gases. The calorimeter ran on a Thermal Analyst 2100 workstation.

The erasure resistances of the images were tested according to the ASTM Test Method F 1319-94. The images were generated on a printing device developed internally. The reflected optical densities (OD) of the images were maintained at approximately 1.3 for cyan, magenta and black and 0.8 for yellow. The erasure resistance of printed images was evaluated using a Crockmeter (available from Atlas Electric Devices Co., Chicago, IL). By this method, a test cloth (available from Testfabrics Inc., Middlesex, NJ) was mounted over the end of the finger and passed over the image twenty times. The reflected OD of the image was recorded before and after the erase. The erasure resistance (ER) of the image was calculated using the following formulation:

$$ER = 100 \times OD_{(\text{image before erase})} - OD_{(\text{after erase})} / OD_{(\text{image before erase})}$$

The blocking resistances of the images were tested according to the ASTM Test Method D1146-88. "Blocking" refers to second degree blocking, as defined in the test method, i.e. "an adherence of such degree that when the surfaces under tests are parted one surface to the other will be found to be damaged." All the blocking tests reported herein are to be interpreted as thermoplastic adhesive blocking tests as defined in the test. The adhesive blocking tests are determined by superimposing three sheets of standard (1.5 inch square) paper on the adhesive face of a (1.5 inch square) conditioned imaged receptor, aligning the resulting test specimen on a glass plate such that the edges are flush, and placing a one pound weight on top of the aligned specimens in the center of the 1.5 inch square area. The above test assembly is placed in a desiccator at 58°C and 75% RH for 24 hours, and then cooled to room temperature prior to testing.

The phase change developer was printed on an apparatus developed internally<sup>2</sup>, as shown in Figures 1 to 3. Heating element 1 heats a thin layer of developer 8 at the top to a melting temperature of the developer that allows the toner particles to have the correct mobility and conductivity to be able to plate to the surface of an image-wise charged photoreceptor 10 in the presence of a positive or negative electric field which is established by placing developer roll 26 near the surface of photoreceptor 10 and imposing a bias voltage on developer roll 26. The image developed on the photoreceptor 10 is then transferred, either indirectly by way of transfer rollers 38 and 40, or preferably directly to the receiving medium 36 to be printed.

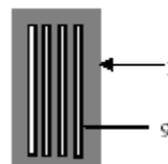


Figure 1. A diagram of a heater used for melting the developer. 1-heating element; 9-opening

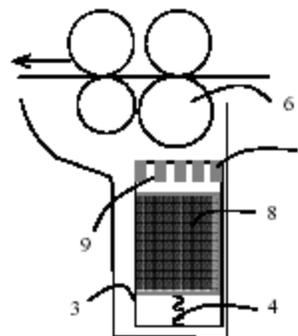


Figure 2. A diagram of a developer storage and deliver system wherein a phase change developer is placed in a developer tank fitted with a heater near the top. 1-heating element; 3-developer tank; 4-indexing unit; 6-develop roll; 8-developer; 9-opening

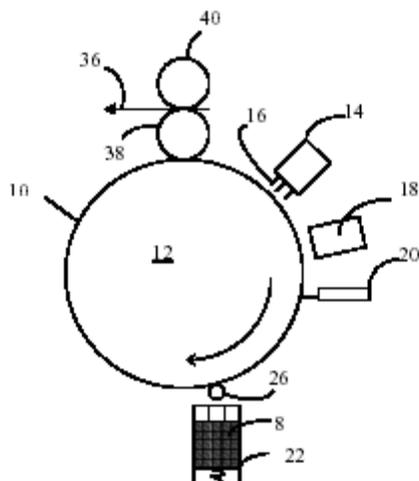


Figure 3. A diagram of an apparatus of a basic liquid electrophotographic process. 8-heated developer; 10-light sensitive photoreceptor; 12-drum; 14-erase lamp; 16-radiation; 18-charging device; 20-laser imaging device; 22-deliver system; 26-developer roll; 36-receiving medium; 38,40-transfer roll.

### Results and Discussion

The compositions of the phase change developers are listed in Table 1. BHA, ODA, and two types of silicon waxes were used as the graft stabilizers due to their proper melting temperatures and good solubility in the carriers. Three types of carriers (i.e. Norpar™12, Eicosane and Microcrystalline Wax) were compared in terms of their melting temperatures and viscosities. A DSC curve of a typical organosol containing BHA, as shown in Figure 4, indicates that the binder undergoes a sharp transformation from solid to liquid at its melting point (i.e. approximately 58°C).

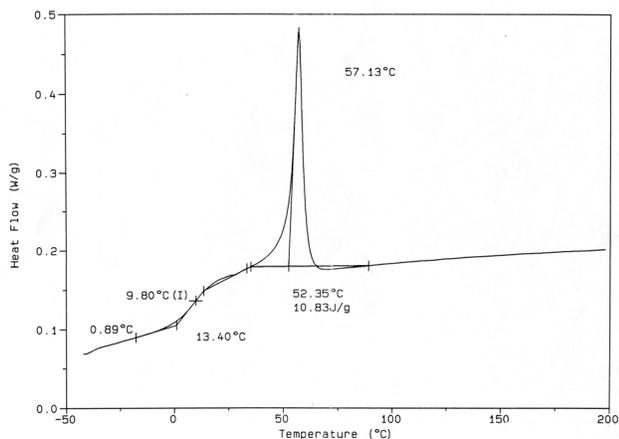


Figure 4. A DSC curve of a BHA Organosol

The properties of the phase developer such as particle sizes (i.e. volume and number average diameters  $D_v$  and  $D_n$ ), bulk conductivities and mobility of the developer particles when they are melted are listed in Table 2. The diameters of the particles ranged from 0.4 to 2.1  $\mu\text{m}$ , which is desirable for producing high resolution and transparency images. The conductivities and mobility of the developer particles when they were molten were within the require range for electrophotographic printing. Both the conductivities and mobility decreased significantly as the viscosities of the carrier increased. When a high viscosity carrier (microcrystalline wax) was used, the mobility of the developer particles was too low to produce a good image. The high viscosity of the melted developer is believed to be the main limitation factor for developer particle plating.

Table 1. The Compositions of Phase Change Developers

ID	Binder		Carrier		
	PCC Composition	Tm (°C)	Composition	Tm	[ ]
1	BHA	58	N12	<RM	Low
2	BHA	58	Eicosane	36	Med
3	BHA	58	Microcyatalline Wax	75-80	High
4	ODA	45	Eicosane	36	Med
5	Silicone Wax Exp628*	62	Eicosane	36	Med
6	Silicone Wax Exp61*	43	Eicosane	36	Med

\*From Genesee Polymers Corporation, Flint, MI, 48507

Table 2. Typical Properties of Phase Change Developers

ID	$D_v$ ( $\mu\text{m}$ )	$D_n$ ( $\mu\text{m}$ )	Conductivity (pMho/cm)	Mobility ( $\text{m}^2/\text{V}\cdot\text{s}$ )
1	1.7	0.6	174	1.4E-10
2	1.5	0.5	103	5.8E-11
3	2.1	0.7	17	2.9E-12
4	1.5	0.6	156	5.2E-11
5	0.8	0.4	264	3.3E-11
6	0.8	0.5	277	2.1E-11

An advantage of the phase change developer is that it provides a superior blocking and erasure resistance to images, as shown in Table 3. The liquid developer, which contained no PCC and had a  $T_g$  of  $-1^\circ\text{C}$  failed the blocking and gave a poor erasure resistance around 82%, while the phase change developer which also had a  $T_g$  of  $-1^\circ\text{C}$ , passed the blocking tests, and yielded an erasure resistance as high as 99%. It is believed that crystalline property of the PCC materials in the binder of phase change developer plays the crucial role in improving blocking and erasure resistance of the final images.

**Table 3. Blocking and Erasure Resistance of Liquid vs. Phase Change Developer**

Developer	Organosol core T <sub>g</sub> (°C)	Erasure Resistance (%)	Blocking Resistance (58°C, 75% RH)			
			Adhesion		Cohesion	
Liquid	-1	82	No	-	2	High
BHA	-1	98	No	-	No	-
ODA	-1	91	No	-	No	-
Silicone Wax Exp-628	-1	99	No	-	No	-

### Conclusion

A phase change developer that reversibly undergoes phase transformation within a temperature range of 1 to 2°C was successfully developed. Various PCC materials were identified as the binder, and low dielectric hydrocarbons that have 12 to 40 carbons can be used as a carrier, and a higher viscosity of the medium limits the plating speed of the developer particles.

High quality images, such as high resolution, gloss, and transparency, were produced by the phase change developers. The crystalline properties of the binder also provided a superior blocking and erasure resistance to the final images.

### Reference

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### Biography

**Dr. Julie Qian** received her Ph.D. in Polymer Science and Engineering from Lehigh University, Bethlehem, PA in 1995 and did postdoctoral research at the Emulsion Polymer Institute, Lehigh University under Professor Mohamed El-Aasser from 1995-1996. Dr. Qian worked for Binney and Smith Inc. from 1996-1997 and Imation Corp. from 1997-2000. She is currently a research specialist with Samsung Information Systems America, Digital Printing Solutions Laboratory, Woodbury, Minnesota. Dr. Qian's main research activities involve the development of liquid and dry toners for electrophotographic printing.

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