Properties of Polymerized Toners

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Abstract

The electrophotographic properties of mono- and dual-component toners produced by the polymerization method, which is an *in situ* polymerization technique, were studied. The effects of different production methods were also described. For the dual-component type toner, the effects of different production methods for the fundamental particle properties were not observed, except for the powder fluidity. Enhancement of the fluidity was introduced by the spherical shape of the polymerized toner particles. The image quality with this toner was also enhanced in the reproduction of fine lines and small dots. The powder fluidity of the monocomponent polymerized toner was not improved over that of the conventional melt-mixed toner. The spherical particles of the polymerized toner may introduce a smooth and efficient agitation on the magnetic brush, so that the toner particles form a very uniform triboelectric charge. Accordingly, the developed toner image has a smooth profile with low background fog. The polymerization method can reduce the number of manufacturing processes involved in making small-particle toner. The main advantages come from cost reduction. It is shown that the polymerized toner has some desirable properties, which can enhance its potential for use as electrophotographic toner.

Introduction

Since toners were introduced in the mid-1950s, there has been a steady trend toward smaller particle size. The average particle size of toners before 1980 was over 13 µm. Around 1990, the particle size was reduced to approximately 11 µm, and if predictions hold, most toners will have particle sizes from 3-8 µm by the end of this decade.

Most toners currently manufactured are produced by a melt-mixing method. With this method, charge-controlling agents (CCAs), colorants, modifiers, and other additives are dispersed in a toner resin matrix. Melt mixing is followed by cooling, crushing, pulverizing, and classifying. With this method, the toner particle size has a significant effect on the total manufacturing cost of the toner. The reduction in toner particle size cited above has caused a sharp increase in production costs. The reasons for the sharp rise in cost are the exponential increase in energy needed for pulverization, and the decrease in collection efficiency during classification.

A second problem associated with smaller particle-size toner is related to proper melt mixing. To obtain a uniform formulation of toner with small-size toner particles, a good pigment and additive dispersion in the binder resin is necessary. Such a minute pigment dispersion in a resin matrix is difficult when standard toner manufacturing methods are employed.

High image resolution copying and printing, along with color copying, are certainly the trends of the 1990s and beyond. These trends are intensifying the driving force for reduced particle-size toner. Subsequently, the technology for producing small particle-size toner has attracted considerable attention from equipment manufacturers and toner-producing companies.

Alternative toner-production methods, which can generate well- dispersed, fine particle toners, are now of great interest. One such method is an *in situ* polymerization technique, which produces what is commonly referred to as *polymerized toner.* In this method, small particle-size toners with good dispersion are easily produced. The good dispersion is a function of the liquid (monomer) system employed to form the polymer particle. Thus given the same toner formulation as a typical melt mixed toner, a small-particle-size toner having good pigment and additive dispersion can be prepared.

In this study, the properties of polymerized mono- and dual-component toners are described and are compared with those of conventional melt-mixed/crushed toner having similar formulations.

Experimental

Preparation of Polymerized Toner (General Method)

We have proposed a unique suspension polymerization system known as a single-stage-dispersion system (SSD),[1,2] which produces small-size particles having a narrow particle-size distribution. In the SSD system, the disperse phase component and the continuous phase component are supplied by independent passageways into a shear-force-generating field. The two components do not mix until they are in the shearing field. In the field, the components are instantly dispersed, using a high-speed mill.

In the SSD system, we have generated polymerized toner for both mono- and dual-component toners.[3] The formulas for the disperse phase and operating conditions for each are given in Table I and Table II, respectively. The CCA and carbon black, which is used as a colorant, are dispersed in the monomer mixture with the aid of a dispersing agent. The continuous phase used was a 5% aqueous tricalcium phosphate dispersion. The resulting mixture of disperse and continuous phases was heated at 60°C for 4 hr. then at 80°C for an additional 3 hr.

The resulting polymer particles were washed with 1 N nitric acid, followed by a thorough washing with deionized water. This process removes the residual tricalcium phosphate from the particle surface. The polymer particles were then isolated by centrifugation and dried overnight in a vacuum oven at ca. 35°C/20 mm Hg.

TABLE I. Recipe for Dual-Component Toner

Disperse phase	
Monomers	
Styrene	85 parts
n-Butylacrylate	15
CCA (Metal bisazo complex)	2
Carbon black	5
Initiator (Azobisdimethylvaleronitrile)	2
Additives	3.5
Dispersion conditions	
Monomer flow	3.6 L/hr
Water flow	14.4 L/hr
Agitation speed	35.0m/sec

TABLE II. Recipe for Monocomponent Toner

Disperse phase	
Monomers	
Styrene	85 parts
n-Butylacrylate	15
CCA (Metal bisazo complex)	2
Magnetite	35
Initiator (Azobisdimethylvaleronitrile)	2
Additives	3.5
Dispersion conditions	
Monomer flow	3.6 L/hr
Water flow	14.4 L/hr
Agitation speed	28.0m/sec

Preparation of Melt-Mixed Toner (General Method)

The toner matrix resin (85% styrene/15% butylacrylate) was polymerized by suspension polymerization in a similar fashion to that reported in Tables I and II. The base resin was then crushed and mixed with colorant, CCA, and additives. The coarse mixture was then kneaded. The resulting melt mixture was cooled, crushed, pulverized, and classified in the same fashion as in conventional toner-manufacturing operations.

Particle Size

Particle size and distribution were determined on a TAII Coulter device (Coulter Electronics, Inc., Nikkaki KK, Tokyo, Japan). The aperture of the tube for the Coulter analysis was 75 µm in diameter.

Electron Microscopy

Electron microscopic analysis was performed on a JEOL JSM-T22A scanning electron microscope (Tokyo, Japan).

Molecular Properties of Polymer Particles

Molecular weights were determined, using a Waters M600 chromatograph (Nippon Waters Ltd., Tokyo, Japan) with a UV detector and a System Instrument Company data processor (Tokyo, Japan). The detection wavelength was 268 nm, which corresponds to the absorption maximum of polystyrene. The column used was a Shodex GPC KF-80 M (Showa Denko, Tokyo, Japan) packed with polystyrene gel. The separation range of the column was 4×10^7 (molecular weight of polystyrene) at 25°C. Calibration of the column was performed with standardized polystyrene supplied by Showa Denko. The solvent used for elution was THF, with a flow rate of 1 mL/ min.

Determination of Particle Charge Distribution

Particle charge distribution of the toners was measured with an Epping q-meter (Epping GmbH, München, Germany).

Determination of Fluidity

Dual-component toner (20 g) or monocomponent toner (30 g) is charged in the hopper with a knurled roller (2-cm diameter and a 1-mm gap on the surface) at the bottom. The toner is discharged by the rotation (3 rpm for 5 min) of the knurled roller. The fluidity is estimated from the weight of discharged toner.

Results and Discussion

Dual-Component Toner

The polymerized toner particle size and distribution are shown in Figure 1. The toner size can be controlled within the range 2-10 µm by modification of the operating parameters of the SSD system. The particle size of our experimental toner was kept at around 7 µm. The reason for selecting this toner-particle size is the lack of commercial copy machines that can accommodate toner with <7 µm toner.

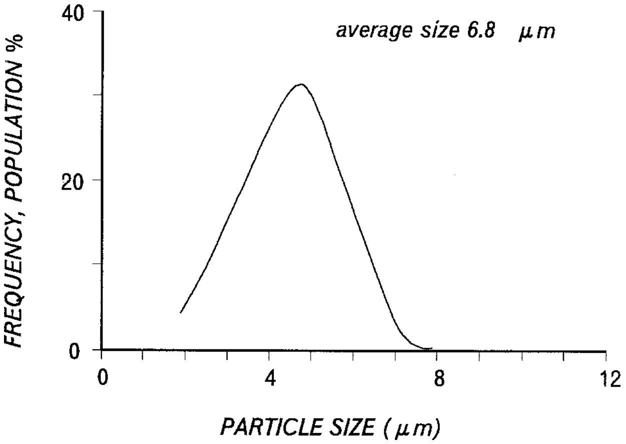


Figure 1. Size distribution of polymerized toner.

In Table III, the properties of the polymerized toner and the conventional melt-mixed toner are compared. The particle size of the melt-mixed toner was regulated at approximately 7.0 µm during the classification process. The formulations of both toners are essentially identical, except that the polymerized toner has some minor additives, such as initiator and dispersing agents. Both production methods, polymerization and melt mixing, have similar effects on the fundamental particle properties. The only notable exception is the fluidity of the toners. The polymerized toner has a higher flow rate, which may be because of the spherical shape of its particles.

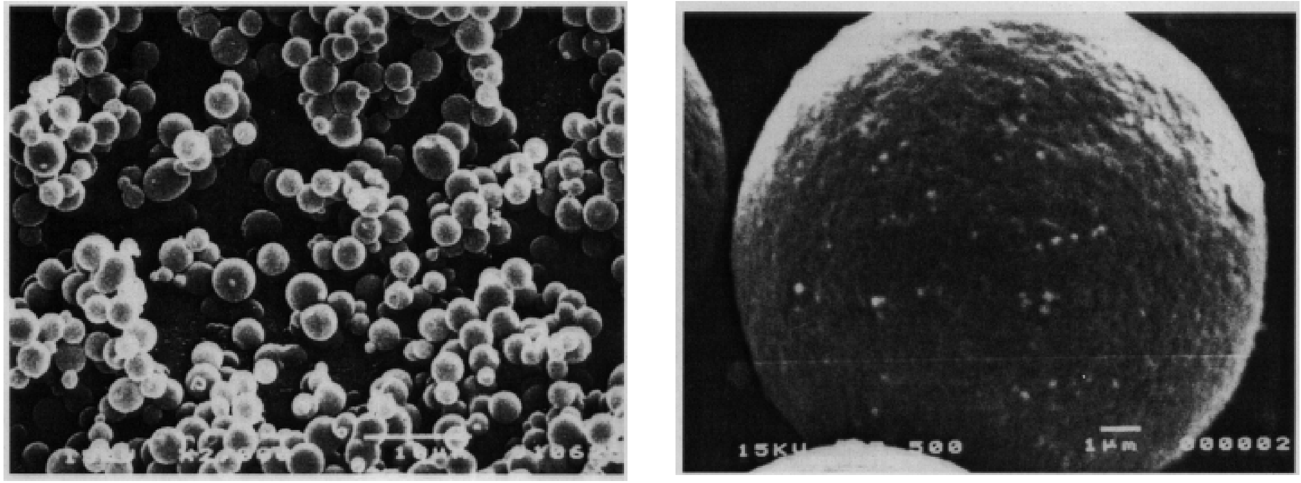


Figure 2. Scanning electron micrographs of polymerized dual-component toner.

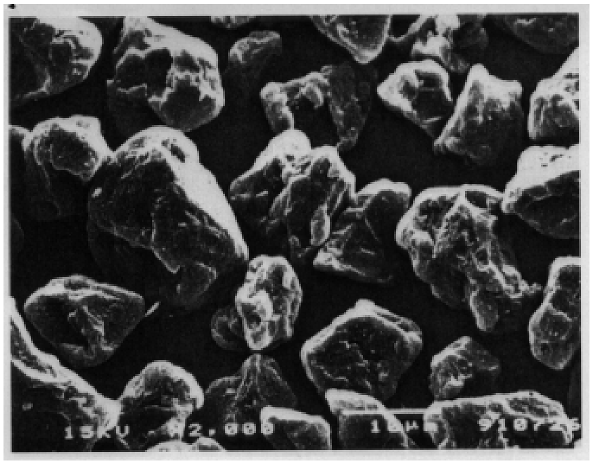
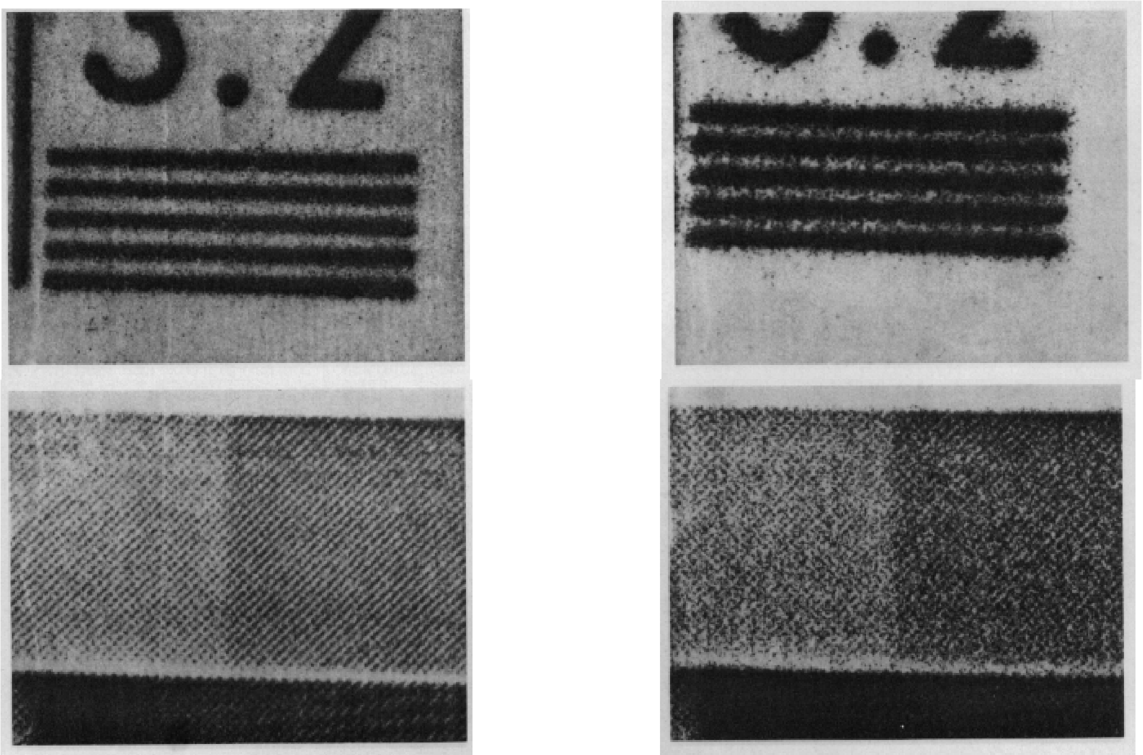


Figure 3. Scanning electron micrographs of melt-mixed toner.

TABLE III. Toner Properties

	Polymerized toner	Melt-mixed toner
Density (g/mL)	0.398	0.359
Powder flow (g/5 min)	4.06	2.93
Electrical resistance (10^{-10} ohm/cm)	4.88	5.90
Mol . weight (10^{-4})		
Mn	0.9	0.6
Mw	3.6	3.1
Charge (µC/g)	–25.0	–20.3
Fusibility		
nonoffset range (°C)	130-220	130-210
Particle size (µm)	6.8	7.2



POLYMERIZED TONER *MELT/CRUSHED TONER*

Figure 4. Copied images of toner (×8.2).

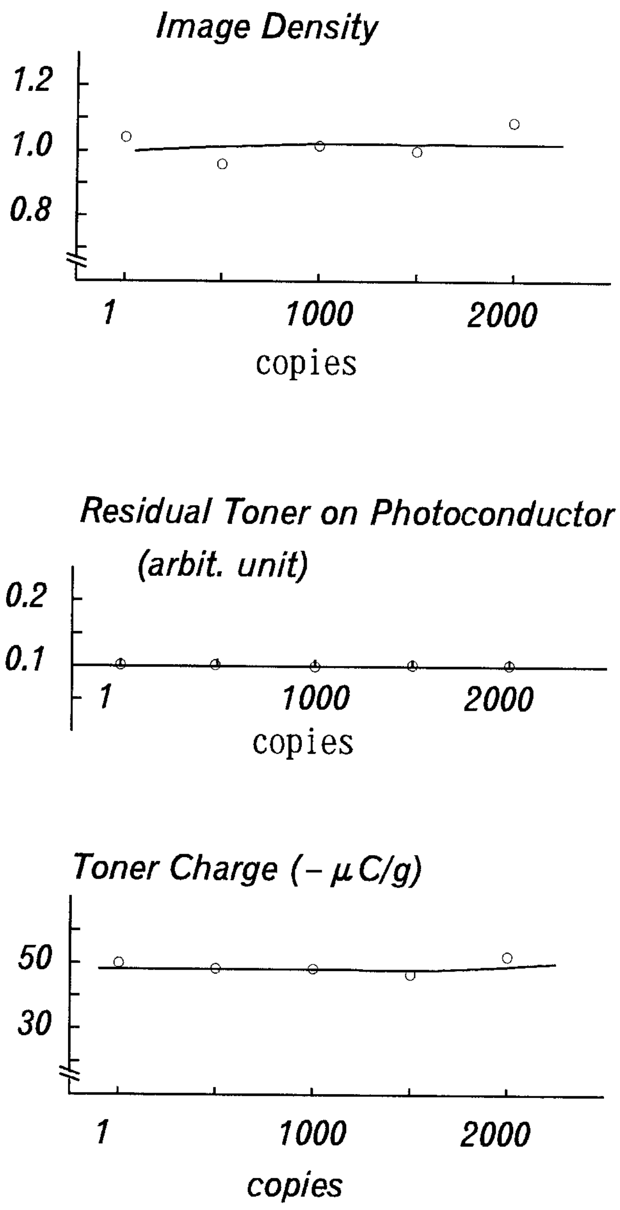


Figure 5. Durability of polymerized toner.

Table IV. Toner Properties

	Polymerized toner	Melt-crushed toner
Magnetization (emu/g)		
Saturation	33.970	32.300
Residual	3.340	2.000
Coercive force (Oe)	87.080	64.700
Density (g/ mL)	0.613	0.518
Powder flow (g/5 min)	5.030	4.630
Electrical resistance (10^{-10} ohm/ cm)	0.520	6.300
Mol. weight (10^{-4})		
Mn	1.7	0.5
Mw	16.9	17.6
Charge (μC/g)	18.5	20.4
Size (μm)	8.8	10.3

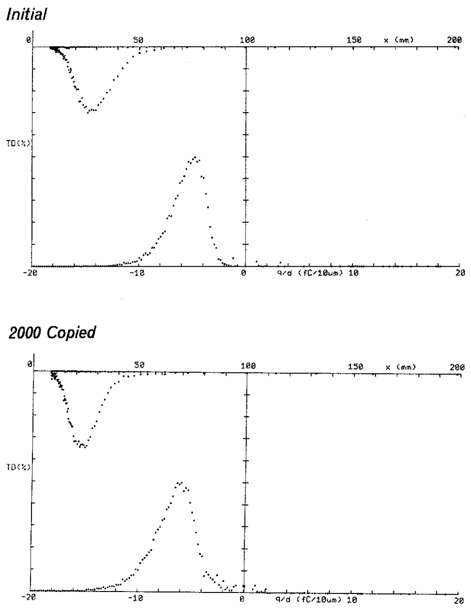


Figure 6. Toner charge distribution.

Scanning electron microscopy (SEM) images of the polymerized and melt-mixed toners are shown in Figures 2 and 3, respectively. The shapes of the particles are quite different. The polymerized toner particle is spherical with a smooth surface, whereas the melt-mixed toner particle has an irregular shape and a ragged surface. The spherical nature is advantageous in view of the powder fluidity. Also, the smoother particles may increase the durability or life of the metal carrier particles, through the reduction in mechanical impact. Finally, the spherical shape has an advantage for the secondary treatment of toners. Toners are often treated with fine inorganic powders, which improve the toner's powder fluidity and other minor properties. The spherical shape and smooth surface of the polymerized particles intensify the effects caused by the after treatment of toners, most likely through the uniform deposition of the fine additives on the toner surface.

The image qualities of the polymerized and melt-mixed toners were examined on a commercial copy machine. Magnified copy images of both toner types are shown in Figure 4. Comparison of the copy samples shows that the polymerized toner reproduces thin lines and fine dot images with much less raggedness and line fattening. The difference in this reproducibility may come from the tightness of the toner charge distribution. The charge distribution in the developer unit should be much narrower, because of the uniform contact between the spherical toner and the carrier particles. Also, the uniformity of the formulation may have a positive effect on particle charge distribution.

Because the dual-component toner needs a developer the polymerized toner was tested for durability with carrier. The toner was blended with a silicone-coated magnetite carrier (5% by weight). The developer was tested for two thousand copies for image density, toner charge, and residual buildup of toner on the photoconductor drum (see Figure 5). The general parameters that reflect the stability of the polymerized toner were good after two thousand copies. The diagrams of the particle charge distribution of the initial and 2000-copy samples are shown in Figure 6. The

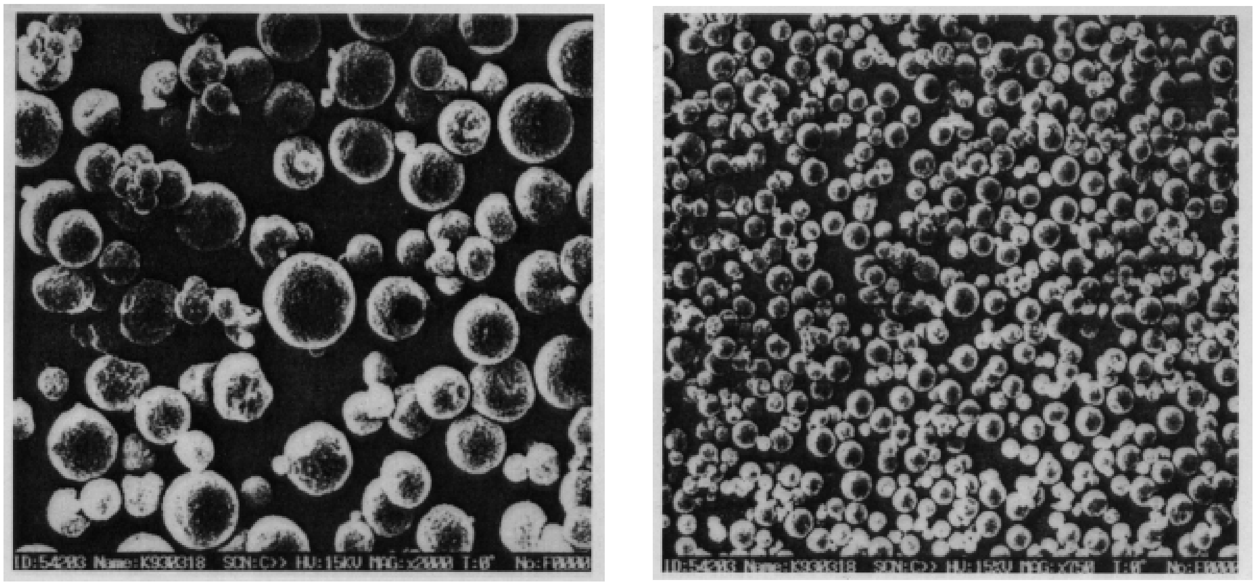


Figure 7. Scanning electron micrographs of polymerized monocomponent toner (×8100, left; ×304, right).

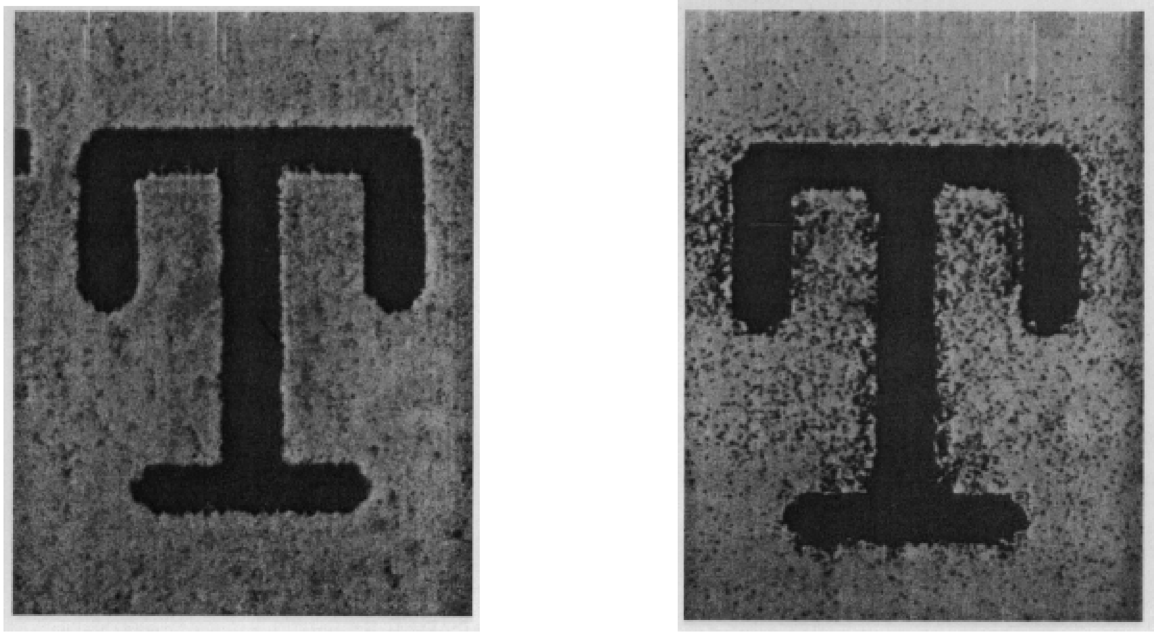


Figure 8. Toner images on photoconductor (×12).

diagrams show no change in the particle charge distribution. The corresponding melt-mixed toner was tested for 2000 copies, and the diagrams of the charge distribution also presented no change. From the durability tests above, the polymerized toner shows no problem that would originate from the manufacturing method.

Monocomponent Toner

SEM images of the monocomponent polymerized toner are given in Figure 7. The toner shape is spherical, as with the dual-component type toner. The particle surface is smooth, and no magnetite pigment is observed on the surface. In this case, the surface of the polymerized monocomponent toner is considered to be a magnetite-free layer. This type of magnetite-free surface might inhibit the liberation of magnetite pigments during the movement of bulk toner. Free magnetite can cause contamination of the photoconductor and the developer.

The toner properties of the polymerized monocomponent toner are shown in Table IV, along with those of the reference sample produced by the melt-mix method. The magnetic properties of the two toners are comparable because of the total magnetite content in each sample. The electric resistivity of the polymerized toner is approximately one-tenth that of the melt-mixed toner. This variation may arise from the degree of magnetite dispersion in the two types of toner. Typical kneading techniques cannot accomplish very fine magnetite dispersion in a toner resin matrix. The magnetite particles tend to coagulate and stay as islands within the resin matrix. In polymerized toner manufacturing, the magnetite particles are well dispersed in the liquid monomer system. Thus a fine dispersion is achieved by the appropriate equipment and procedures. The well-dispersed magnetite may then provide a good electrical network within the resin matrix. This shows up in the reduced electrical resistivity of the toner. The attempt of direct observation of the dispersion degree by transmission electron microscopy failed, however, because the magnetite in high content prevents the slicing of the particles to transparent sections.

The powder fluidity is not significantly improved in the polymerized monocomponent toner, as was the case for the dual-component type toner. Normally, monocomponent toner particles tend to behave as small particulate magnets and stick to each other. This characteristic is very pronounced, and it offsets any small gain in fluidity caused by spherical particles.

Figure 8 shows the developed toner images on the photoconductor of an electrophotographic system. For the melt-mixed toner, the image shows background fog and raggedness. The polymerized toner shows virtually no distortion of the image. However, when the images are transferred to the paper, almost no difference is found in image quality. The reason for this could be that the melt-mixed toner contains toner particles that have low charge. This low-charge toner is picked up by the photoconductor, but is not transferred to the paper by the electric field. The polymerized toner, therefore, is more efficiently and uniformly triboelectrically charged than the melt-mixed toner. The toner particles are charged by rotating on the magnetic brush. This process is much more efficient with the spherical particles. The spherical shape can assist in the effective rotation of the toner particles on the brush.

Summary and Conclusion

The electrophotographic properties of mono- and dual-component toners produced by the polymerization method were studied. The effect of different production was also described.

For the dual-component type toner, the effects of different production methods on the fundamental particle properties were not observed, except for the powder fluidity. The enhancement of the fluidity was introduced by the spherical shape of the polymerized toner particles. The image quality with this toner was also enhanced in the reproduction of fine lines and small dots.

The powder fluidity of the monocomponent polymerized toner was not improved over that of the conventional melt-mixed toner. The raggedness of the developed toner images on a photoconductor seen with the melt-mixed toner is not present when the polymerized toner is used. The spherical particles of the toner may introduce a smooth and efficient agitation on the magnetic brush, so that the toner particles form a very uniform triboelectric charge. Accordingly, the developed toner image has a smoother profile with less background fog.

The polymerization method described above can reduce the number of manufacturing processes involved in making small particle toners. The main advantages come from the reduction of cost. In this study, the properties of the polymerized toner are characterized and compared with those of the conventional melt-mixed toner. It was shown that the polymerized toner has some desirable properties, which can enhance its potential for use as electrophotographic toner. In the future polymerized toners will have a substantial position in the field of electrophotography.

References

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