

Synthesis and Characteristics of Non-Spherical Toner by Polymerization Method

*Mikio Koyama, Kenji Hayashi, Tomoe Kikuchi and Kenji Tsujita
Business Machines Development Division, Konica Corporation, Tokyo, Japan*

1. Introduction

Recently, full-color copiers and printers employing an electrophotographic system have been introduced. This has increased the demand for fine image and high resolution in electrophotography.¹ For realizing fine images and high resolution in electrophotography, processes and materials involved in electrophotography are being improved. In particular, a technology for employing fine toner particles in terms of particle size is singled out as a powerful method for improving materials for enhanced image quality. The size of currently used toner particles generally ranges from 7 μm to 10 μm . These toner particles are currently produced through a crush method. In the crush method, it has been reported that the production cost becomes disadvantageous and difficulty increases on the aspects of both uniform charging on particles and control of particle size distribution as the particle size is reduced to 7 μm or less. As a method for overcoming this problem, production of toner using a polymerization method is attracting attention.

In general, methods such as a suspension polymerization method, an emulsion polymerization method and a dispersion polymerization method are known as the polymerization methods for producing toner.² Each of these polymerization methods has its own advantages and disadvantages, therefore, selection of the polymerization method depends on the performance expected for the toner particle. In the suspension polymerization method, it is difficult to synthesize particles having an average particle size of 7 μm or less and narrow particle size distribution. In the dispersion polymerization method, it is easy to synthesize particles having an average particle size of 7 μm or less and narrow particle size distribution, but it is difficult to cause inner additives to be contained in each particle. Particles produced by these methods are spherical in shape which makes it difficult for cleaning with a blade. On the other hand, those produced through the emulsion polymerization method are generally these polymer particles having the particle size of submicron or less. In addition, emulsion polymerization particles need to be increased to those having a particle size identical to that of toner particles, which is a problem. There are two methods for growing emulsion polymerization particles. One is (1) a seed polymerization method (a chemical method) and the other is (2) a coagulation method (a physico-chemical method). In the case of the seed polymerization method, it is possible to obtain particles having the particle size of 10 μm or less and with a narrow particle size distribution, which is an advantage. The disadvantages are that each particle is spherical in shape which is a problem for blade cleaning

and it is difficult to cause inner additives to be contained in a particle.

On the other hand, in the case of the coagulation method, it is effective for blade cleaning because it is possible to obtain any shape for the coagulated particle including a spherical one and a non-spherical one. Also in the case of the coagulation method, there is generally used a method wherein the inner additives are simultaneously coagulated during the coagulation operation. In this method, it is necessary to consider the influence caused by the position of the inner additives in the toner particle. For example, when inner additives and coloring agents are positioned locally on the surface of a toner particle, it affects the charging property. When inner additives enter the clearance between emulsion polymerization particles and are coagulated, fusion on this portion is insufficient. Also, there is a possibility that developability and durability are adversely affected by the crushed toner particles in the 2-component developing process. Keeping these problem in mind and focusing on the control of the shape of a toner particle, we selected a method to grow polymer particles produced through an emulsion polymerization method to the size of toner particles by a coagulation method. Our purpose was to prepare toner particles which can be cleaned by a blade and have a particle size of 7 μm or less. Now, emulsion polymerization technology in which polymer particles containing inner additives such as a pigment are produced through an emulsion polymerization method, and particle coagulation technology in which a particle size and a shape of emulsion polymerization particles containing inner additives and toner particles are freely controlled, along with the characteristics of the toner particles produced will be reported as follows.

2. Emulsion Polymerization Technology

An emulsion polymerization technology is a method in which monomers and radicals are diffused into a micelle where radical polymerization advances and polymer particles are produced.³ Even when inner additives such as a pigment exist together in monomers, the inner additives can not be diffused into a micelle. Therefore, the inner additives are not taken into the polymer particles. In such a system, pigments have an influence on the dispersion stability of emulsion polymerization and cause coagulation. In order to avoid these problems, we developed the following method.

In this method, inner additives are dispersed in water phase using an emulsifying agent, and a false micelle is formed by an emulsifying agent adsorbed on the surface of

a pigment, as shown in Fig. 1. Monomers added to the system and radicals produced through heat decomposition of the radical initiator enter the false micelle through molecular diffusion, thus, in the false micelle, polymerization advances on the surface of an inner additive at the polymerization speed higher than that in water phase in accordance with the polymerization mechanism of the emulsion polymerization, and polymer particles containing inner additives are produced. In this case, it is possible to obtain polymer particles having the submicron particle size by limiting the dispersed particle size of the inner additives to submicron or less. By using the particles produced by this method, it is possible to solve the above-mentioned problems of charging trouble and mechanical strength caused by the position of the inner additives. In this method, it is also possible to design and control molecular weight and molecular weight distribution, glass transition temperature, softening point and viscoelasticity of the polymers without being affected by the inner additives.

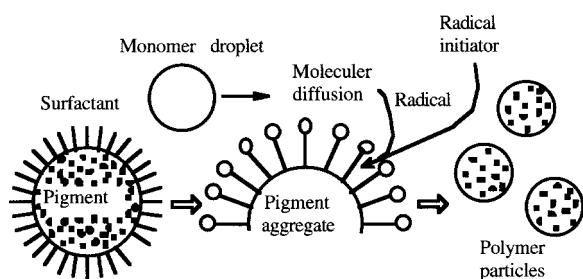


Figure 1. Mechanism of emulsion polymerization.

3. Particle Coagulation Technology

In general, dispersed particles start their coagulation when their dispersion stabilizing factor is rapidly hindered. This phenomenon is generally called rapid coagulation. In the case of the rapid coagulation, it is difficult to control particle size, particle size distribution and the particle shape of the produced coagulation particles. We, therefore, gave repulsive force between particles to the surface of a polymer particle for the purpose of avoiding the rapid coagulation condition and of changing it to a slow coagulation condition thus making it easy to control the particle size and particle size distribution. As a result, it was possible to control the particle size to 7 μm or less and to further control the particle size distribution. Coagulated polymer particles showed a strong fusion between particles through heat treatment in the water phase, thus the polymerization toner was produced. This polymerization toner can be used as toner after being filtered and dried like conventional polymerization toner. It is possible to control the particle size of the toner within a range from about 2 μm to about 30 μm by adjusting the hindrance level of the dispersion stabilizing factor of emulsion polymerization particles and adjusting the repulsive force between emulsion the polymerization particles.

By changing the reaction condition as already described, it is possible to change the average particle size while keeping the extremely narrow particle size distribution. Further, Fig. 2 shows particle size distributions of polymerization toner and toner made from a crushing

method. Compared with the toner from a crushing method in which classification is repeated after crushing and particle size distribution shown in the figure is achieved, toner of a polymerization method does not require classification operation at all, and toner particles having the narrow particle size distribution can be produced.

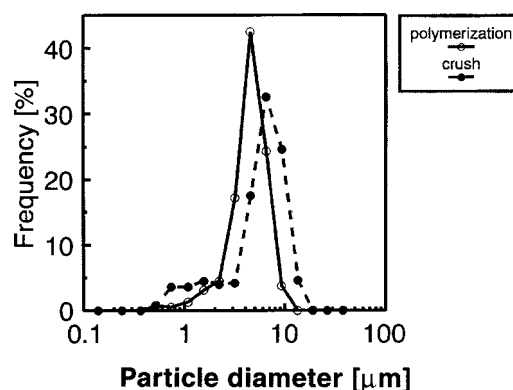


Figure 2. Particle size distribution.

In Table 1, toner shapes were changed by changing reaction conditions and SEM photograph of the polymerization toner in that case and its shape factor are shown. For the shape factor (SF), a value calculated by the following equation (1) was used.

$$SF = 0.9 PM^2/4\pi (A - PM/2) \quad (1)$$

PM = Circumference length [μm] of projected particle image

A = Area [μm^2] of projected particle image

In the case of the polymerization toner produced using this method, it is possible to freely control the particle shape by changing reaction conditions.

Table 1. The toner shape control

shape	spherical \longleftrightarrow non-spherical			
SEM Photograph				
Shape factor	1.059	1.216	1.288	1.664

\longleftrightarrow 2 μm

4. Toner Characteristics

Polymerized toner having an average particle size of 5 μm and crushed method toner of styrene/acrylate resin binder for comparison were used. For the evaluation, 2-component developing agents and carriers prepared by coating styrene/acrylate resin on a ferrite core were used.

Polymerization toner with an average particle size of 5 μm having different shape factors shown in Figure 1 was used, and apparent density, that is an index for fluidity of

powder, was measured. The results are shown in Figure 3. Broken lines indicate the apparent density of the crushing method toner having a particle size of 5 μm . Polymerization toner shows an extremely high fluidity compared with crushing method toner. This is because it is possible to smooth the particle surface as shown in the SEM photograph and to change particle shapes freely in the polymerization toner.

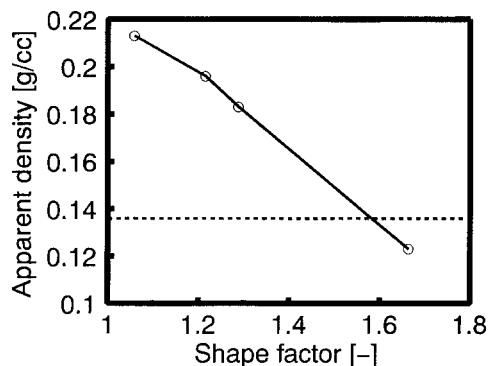


Figure 3. Relationship between shape factor and fluidity.

Triboelectric charge for polymerization toner is determined by the amount of functional groups giving a charging property to the polymerization toner surface. It is possible to change the triboelectric charge freely through copolymerization by changing the copolymerization rate of the monomer having functional group that gives the charging property of the particle surface. Figure 4 shows that the triboelectric charge of toner can be controlled from $-5 \mu\text{C/g}$ to $-30 \mu\text{C/g}$ using the above-mentioned method.

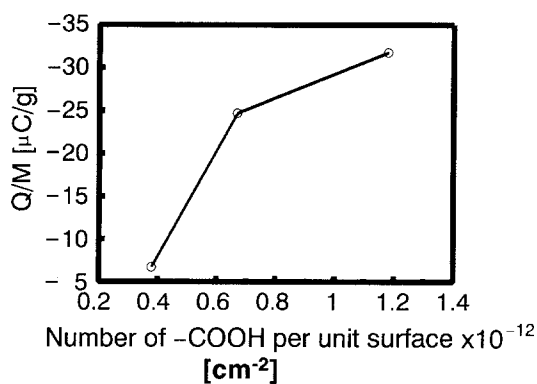


Figure 4. Relationship between the number of $-\text{COOH}$ on toner surface and triboelectric charge.

With regard to charging behavior, the period of time for polymerization toner to arrive at a saturated triboelectric charge is shorter than for crushing method toner.

In addition, the triboelectric charge distribution for polymerization toner is narrower than that for the crushing method toner as shown in Figure 5. The reason for this is thought to be that the uniformity of charging group distribution of each emulsion polymerization particle is high and therefore the uniformity of the charging group distribution on the surface of the polymerization toner where emulsion polymerization particles are coagulated is also high.

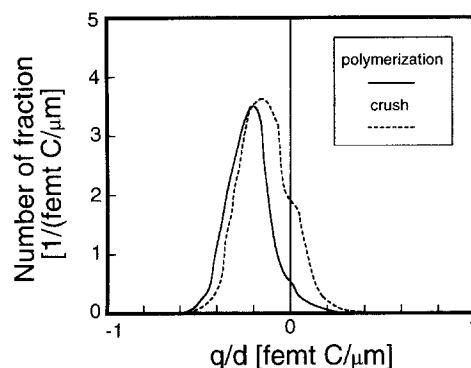


Figure 5. Charge distribution.

In the case of polymerization toner, there is generally a possibility that the charging property will be adversely affected by the remaining dispersant used for reaction. Figure 6 shows how the environmental dependency of the triboelectric charge is affected by the difference in washing. In the figure, “with washing” means that filtration and drying were carried out after the reaction and then pure water in a quantity 5 times that of toner was used for washing, while “without” washing means that filtration and drying were carried out after the reaction but no washing was carried out. Polymerization toner, which has been washed, shows stable charging properties under conditions of high temperature and high humidity as well as conditions of low temperature and low humidity. Polymerization toner, which has not been washed, on the other hand, shows a big difference of triboelectric charge between high temperature/high humidity and low temperature/low humidity conditions. However, it is possible to obtain toner having a stable triboelectric charge for an environment where a surfactant has no influence, if an appropriate washing method is devised.

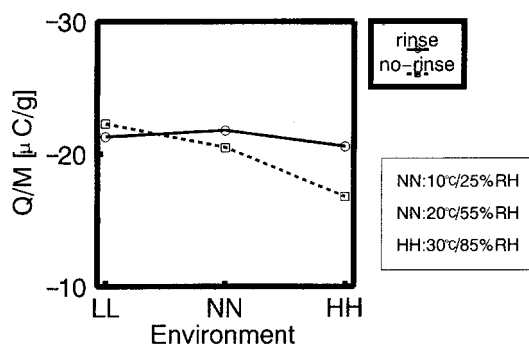


Figure 6. Effect of emulsifier on triboelectric charge.

The blade cleaning property of the polymerization toner having different particle shapes was studied. Polymerization toner shown in Table 1 was loaded in a Konica U-Bix 9028 equipped with a blade cleaner, and exposure, developing and cleaning were carried out. The cleaning efficiency was then calculated from the ratio of toner weight on a photoreceptor after developing to that on a photoreceptor after cleaning. The results are shown in Table 2 which shows that the cleaning efficiency is lowered as the particle shape approaches that of a sphere. This implies that the particle shape of polymerization toner needs to be non-spherical for insuring a high blade cleaning property.

Table 2. Relationship between shape factor and cleaning efficiency

Shape factor	1.059	1.216	1.288	1.664
Cleaning Efficiency	65	95.8	94.9	91.8

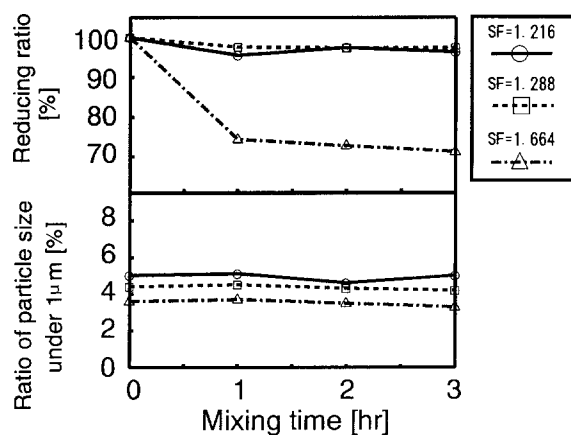


Figure 7. Relationship between shape factor and mechanical toughness.

Further, the relation between the shape of a toner particle and its mechanical strength was studied. Four types of polymerization toners each having a different particle shape, were used for preparing developers in such a manner as to mix each type of toner with a carrier to realize a toner concentration of 7%. This developer was forcibly agitated in a developing unit, and samples were picked up once an hour to measure the average particle size and amount of fine particles having a size of 1 μm or less. The results of the measurement are shown in Figure 7. When the particle has

a large shape factor, particle split takes place in the early stage of agitating. On the other hand, when the particle has a small shape factor, a change in average particle size is not observed at all. Further, even when the shape of a particle is changed, no occurrence of fine particles having the average particle size of 1 μm or less is observed. From this phenomenon, it was confirmed that polymerization toner will not be crushed provided that the shape of the toner particle is not excessively non-spherical.

5. Summary

As a means for achieving an electro-photographic process for fine images and high resolution, we studied fine-grained toner particles and developed nonspherical fine particle toner produced through an emulsion polymerization method. In this method, it is possible to inhibit dispersion stability of the emulsion polymerization particle wherein inner additives are compounded. Thereby it is possible to control the particle size so that a narrow particle size distribution is obtained. Since the shape of a toner particle can be freely changed, blade cleaning can be used. In addition, due to the use of emulsion polymerization particles wherein inner additives are compounded, excellent toner particles characteristics such as excellent charging property, fluidity and mechanical strength are displayed.

Reference

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