Journal of Imaging Science and Technology® 51(5): 407–412, 2007.

Advanced Color Toner for Fine Image Quality[1]

Akihiro Eida, Shinichiro Omatsu and Jun Shimizu
Performance Chemicals Research Laboratories, Kao Corporation, Wakayama, 640-8580 Japan
E-mail: eida.akihiro@kao.co.jp

Abstract. *Application of full color printers has spread rapidly in the office environment, and demands on the full color printer have been also increasing; especially, high-speed printing, oilless fusing and fine image quality are strongly requested. Recently, several types of chemical toner have been launched. Because they have small and narrow particle size distributions, they have an advantage in fine image quality. However, the resin of chemical toners are usually styrene-acrylic, which is not suitable for high-speed printing and glossy images for pictorial applications because the styrene-acrylic has to be high molecular weight to make toner have sufficient durability. On the other hand, polyester has better properties for high-speed printing than styrene-acrylic because of the existence of a polar group that enhances a compatibility with the cellulose of paper. Polyester has good durability even if it has a low molecular weight and thus can provide a glossy image. Thus polyester has several advantages over styrene-acrylic. In general, it is difficult to use polyester as the binder resin of chemical toner. On the other hand, it is easy to make polyester color toner by the pulverization method, but it is difficult to make pulverized toner having small and narrow particle size distribution for fine image quality, and it is also difficult to make pulverized toner having both oilless fusing ability and sufficient durability. In this article, design of oilless fusable, pulverized color toner with small and narrow particle size distribution was investigated. This advanced color toner named "MC toner" can provide high-speed printing, oilless fusing, and also fine image quality. © 2007 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.(2007)51:5(407)]

INTRODUCTION

In recent years, as color printers have become widely used, demands on the color printer have also been increasing: for instance, high image quality, high speed, and low cost performances are required for the toner. These properties imply, for example, small particle size, narrow particle size distribution, good transfer property, low temperature fusing, etc.

To achieve these requirements, several types of chemical toner were developed and launched. It is said that performance of chemical toner is better than pulverized toner with respect to various points of performance.[1,2]

Demands on color printing and requirements for color toner in order to achieve these demands are listed below. Comparison of typical chemical toner and pulverized toner and a comparison of styrene-acrylic and polyester resins with respect to these requirements are also discussed.

Fine Image Quality

For fine image quality, faithful dot reproduction of latent image, faithful transfer property, glossy image for pictorial image, wide color gamut, are required.

Faithful Dot Reproduction

Figure 1 shows a dependency of raggedness of line defined as TEP on toner particle size. This indicates that the raggedness increases in proportion to toner particle size. Thus, for faithful dot reproduction, toner is required to be a small size. From this point of view, chemical toner has an advantage because chemical toners are made by a buildup method. Figure 2 shows toner size distribution of conventional pulverized toner and typical chemical toner. The toner size distribution of the chemical toner is smaller and narrower.

Faithful Transfer

In general, it is said that a spherical toner shows a good transfer efficiency.[3,4] Indeed, Figure 3 shows transfer efficiency of chemical toner having a spherical shape (circularity=0.98) is much better than irregular-shaped toner (circularity=0.92), where, transfer efficiency is represented by ΔE, which is the color difference between blank tape on paper and tape removing residual toner from the organic photoconductor (OPC). (For more detail, see Experimental section.) On the other hand, scatter of spherical toner is much worse than for irregularly shaped toner, which indicates that spherical toner tends to roll in the transfer process because of high flowability. Moreover, cleaning properties of spherical toner are also bad. Thus, it is not clear whether spherical shape is beneficial for fine image quality. Recently, some chemical toners have adopted moderately spherical shape (i.e., circularity is ~0.96; for example, potato shape, spindle shape, or dimple shape). Transfer efficiency,

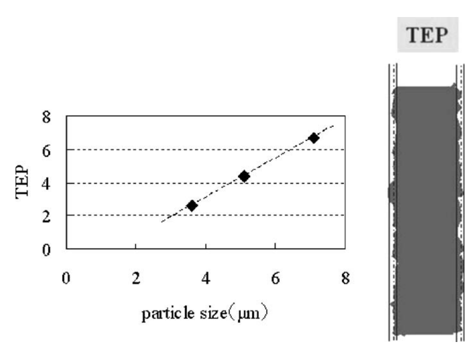


Figure 1. Dependency of image quality (TEP) on toner particle size.

[1]Presented, in part at IS&T NIP21 Baltimore.

Received Jan. 9, 2005; accepted for publication Jun. 10, 2007.
1062-3701/2007/51(5)/407/6/$20.00.

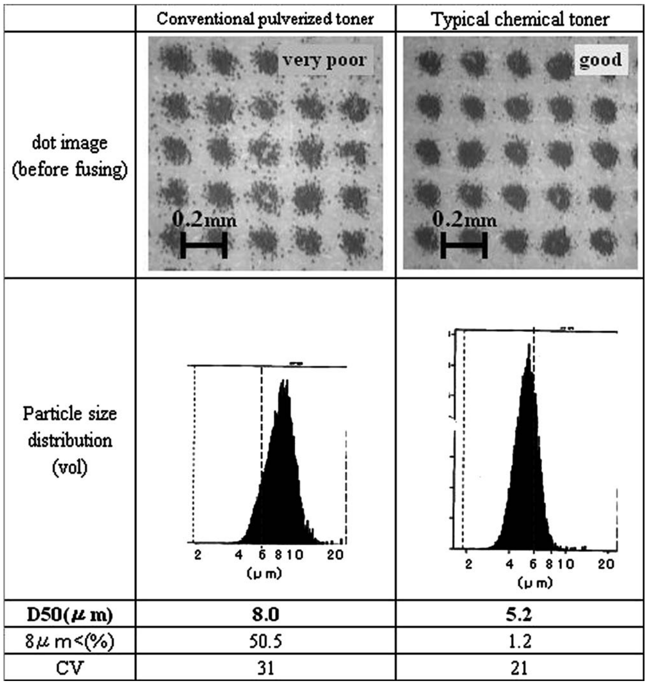


Figure 2. Comparison of particle size distribution and image quality of conventional pulverized toner and typical chemical toner.

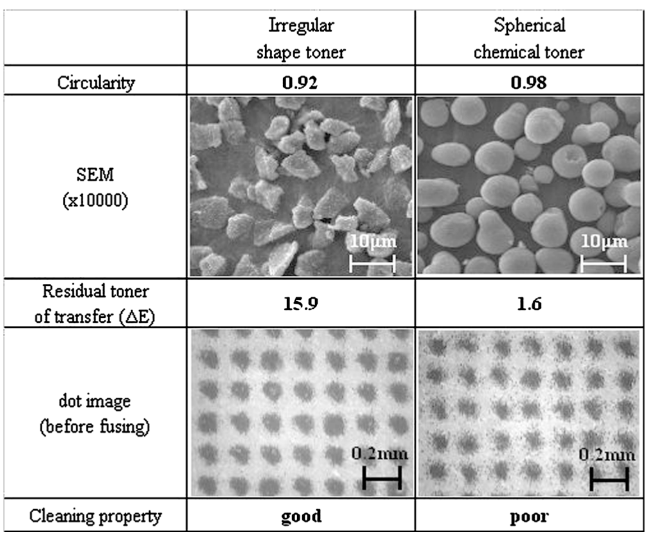


Figure 3. Comparison of performance of spherical shape toner and irregular shape toner.

scattering property, and cleaning property of toner with such a moderately spherical shape are well balanced.

Glossy Image

For pictorial image printing, a glossy image is preferable. To print an image with high gloss, it is necessary that a toner resin have a low molecular weight, because in the fusing process, viscosity of the resin having low molecular weight is low and the surface of fused image becomes smooth, and the image having such smooth surface specularly reflects light well and shows high gloss.

From this point of view, polyester resin has an advantage over styrene-acrylic resin. Polyester resin has sufficient durability owing to hydrogen bonded polar groups, while styrene-acrylic resin has poor durability for the same low molecular weight distribution as polyester.

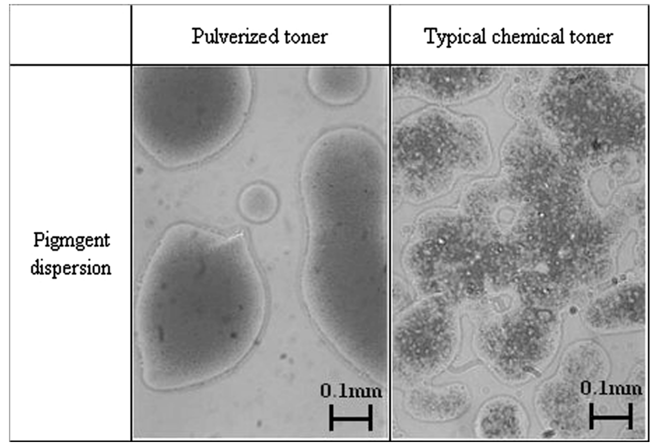


Figure 4. Comparison of pigment dispersion of pulverized toner and typical chemical toner.

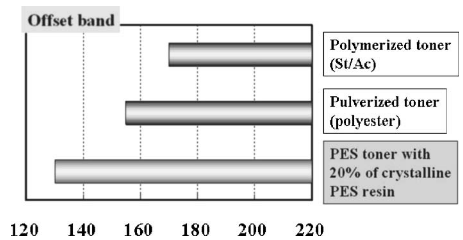


Figure 5. Offset band of St/Ac toner, polyester toner, and crystalline polyester containing toner.

Wide Color Gamut

For wide color gamut, fine dispersion of the pigment is necessary. Figure 4 shows dispersion of the pigment of pulverized toner and chemical toner. In general, dispersion of a pulverized toner pigment is better than for a chemical toner, because the kneading process enhances dispersion of the pigment. In general polyester resin has better pigment dispersability than styrene-acrylic resin, because the polar groups of polyester resin enhance dispersion of the pigment. Therefore, for a wide color gamut, pulverized toner and polyester resin have advantages over chemical toner and styrene-acrylic resin.[5]

High-Speed Printing

For high-speed printing, low-temperature fusing ability is required for color toner. As described above, polyester resin has sufficient durability with low molecular weight. Moreover, polyester has polar groups that enhance compatibility with cellulose of paper. Thus, polyester resin has an advantage for high-speed printing over styrene-acrylic resin. Recently a crystalline polyester resin that has ideal viscoelasticity for low-temperature fusing has been proposed (Figure 5) for higher speed printing.[6–8]

Oilless Fusability for Low Cost Machine

For low machine cost, oilless fusing ability is required for color toner, so that the oil applying unit can be removed

Table I. Properties of the experimental polyester resin.

Resin	Acid Value[a] (mg KOH/g)	$T1/2$[b] (°C)	T_g[c] (°C)
Polyester	20	115	63

[a]The acid value was measured according to ASTM D1980-67.
[b]The softening point ($T1/2$) was measured according to ASTM E-28-67.
[c]The glass transition temperature (T_g) was measured by a differentital scanning calorimeter "DSC Model 200" manufactured by Seiko Instruments Inc., at a heating rate of 10°C/min.

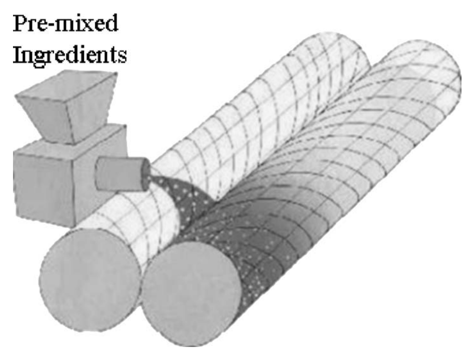


Figure 6. Open-roll-type kneader.

from the printer system. Generally, a resin for color toner has a low and narrow molecular weight distribution for glossy image and high transparency, but such a resin cannot give a wide nonoffset range in fusing because elasticity of such resin fusing conditions is low and offset problems tend to occur. Therefore, to prevent offset problems, under a conventional oil applying unit may be attached to the fuser unit, which is costly. Thus, oilless fusable toner is described for design of a low cost machine. To achieve oilless fusing, it is necessary to add wax to the toner. In the fusing process, the wax melts and diffuses out from inside the toner and works as a releasing agent instead of oil applied to the fusing roller. However, it is difficult to disperse sufficient wax by a twin-screw extruder, such as is conventionally used in the kneading process. Also, thereby the dispersed size of wax domains in the toner becomes very large, and such poor dispersion of wax causes poor durability of the toner.[9,10] On the other hand, chemical toner can include plenty of wax, which does not exist on the toner surface; thus, chemical toner is oilless fusable without a durability problem.

As described above, both chemical toner and pulverized toner have good points and bad points. But polyester resin has a certain advantage over styrene-acrylic resin. In general, it is difficult to use polyester resin in chemical toner. On the other hand, it is easy to make polyester color toner by the pulverization method, but it is difficult to make pulverized toner with small and narrow particle size distribution for fine image quality. To summarize, the ideal toner is expected as follows:

- to use polyester for glossy image and high-speed printing
- to be small and narrow size distribution, for fine image quality
- to contain plenty of wax with high durability, for oil-less fusing

Table II. Toner samples.

Toner	Wax (%)	Kneading Machine	Preconditioning	Target Size (μm)
A	7.0	Twin-screw	None	8
B	7.0	Open-roll	None	8
C	6.0	Open-roll	None	5
D	6.0	Open-roll	Silica=1.0%	5
E	6.0	Twin-screw	Silica=1.0%	5

In this article, the design of an oilless fusable polyester pulverized color toner with small and narrow particle size distribution is presented. Factors that enable toner to be pulverized with a small and narrow particle size distribution were investigated in detail.

EXPERIMENTAL

Preparation of Polyester Resin

Bisphenol-A propylene oxide adducts, ethylene oxide adducts, terephthalic acid, C12-succinic anhydride, and trimellitic anhydride were allowed to react for condensation polymerization at 230°C with a small amount of the catalyst in a glass flask, which was equipped with a thermometer, a stainless steel stirring rod, a reflux condenser, and nitrogen inlet tube. Physical properties of this polyester resin are listed in Table I.

Preparation of Toner Samples: For Investigation of a Factor of Oilless Fusable Toner

Toner samples A and B comprised the resin described above, wax, charge control agent, and colorant. The colorant was Quinacridone (Pigment Red 122); the melting point of the wax was 80°C. Content of the colorant was 6.5 wt. %; content of the wax was 7.0%, which is the amount that enables oilless fusability. The materials were premixed in a batch mixer, and then they were kneaded. We used two types of kneader, a conventional twin-screw extruder for toner A and an open-roll-type kneader (Figure 6) for toner B. The toners were pulverized and classified to 8 μm. Toner samples are listed Table II.

Preparation of Toner Samples: For Investigation of a Factor of Efficient Pulverizing

Toner samples C, D, and E also comprised the resin described above, wax, charge control agent, and colorant. The colorant was Quinacridone (Pigment Red 122); the melting point of the wax was 80°C. Content of the colorant was 6.5 wt. %, and content of the wax was 6.0%, which is the amount that enables oilless fusability.

The materials were premixed in a batch mixer, and then they were kneaded. Toners C and D were kneaded by the open-roll-type kneader, and toner E was kneaded by the twin-screw extruder. Before pulverizing, toner chips for tonners D and E were mixed with 1.0 wt. % of hydrophobic

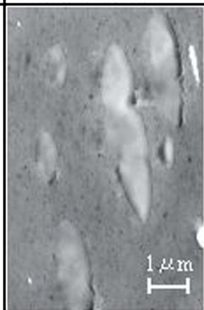
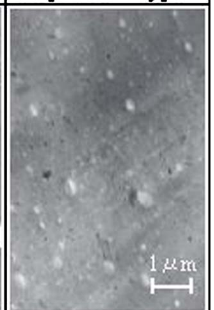
Toner No.	Toner A	Toner B
Kneader	Twin-screw	Open-roll Type
The wax dispersion in the toner (TEM investigation)		
Offset band	125℃ - over 200℃	125℃ - 200℃
Durability	less than 30min	over 180min

Figure 7. Comparison of wax dispersion and durability.

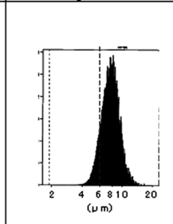
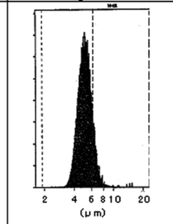
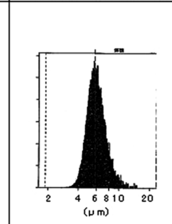
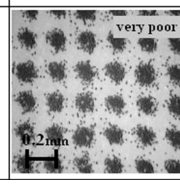
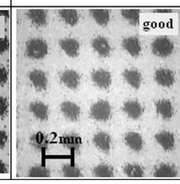
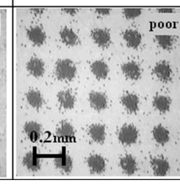
	Toner C	Toner D	Toner E
Pre-conditioning	None	Silica=1.0%	Silica=1.0%
Kneading	Open-roll	Open-roll	Twin Screw Extruder
Particle size distribution (vol)			
D50(μm)	7.6	5.2	5.9
3μm>(%)	0.3	0.2	0.2
8μm<(%)	40.5	1.0	10.2
CV	23	19	25
dot image (before fusing)			

Figure 8. Result of pulverizing of toners C, D, and E.

silica; we call this process "preconditioning." Then, they were pulverized and classified. The target size was 5 μm. Toner samples are listed Table II.

MEASUREMENTS

Durability was tested by using a toner cartridge of a color laser printer for which the developing system was a single component. Toner was put into the cartridge, and the developer roll was rotated at 60 rpm without developing the toner to the organic photoconductor. Durability was defined as time when filming of the toner to the doctor blade occurred and a streak appeared in the toner layer on the developer roller.

The particle size distribution was measured by a Coulter Multisizer II with a 100 μm size aperture. The size of dispersed wax domains was observed by TEM. For convenience of evaluation, a cross section of the toner chip before pulverizing was observed.

Toner was developed in a nonmagnetic single-component printer whose resolution was 600 dpi. A dot image on the paper before fusing was observed under the microscope. Dispersion state of silica and free silica rate were measured by Particle Analyzer FT-1000 (Horiba). Circularity was measured by FPIA 2100 (Sysmex).

Transfer efficiency was defined as the amount of residual toner on the photoconductor after the transfer process. Areal density on the photoconductor was controlled at 0.40–0.45 mg/cm^2. The residual toner was removed by clear tape and placed on white paper. The amount of the residual toner is defined as the difference of hue (ΔE) between the residual toner sample and the blank tape on the same paper.

RESULTS AND DISCUSSION

Wax Dispersion and Durability

Figure 7 shows wax dispersion in toners A and B. The size of the dispersed wax domains in toner A that was kneaded by conventional twin-screw extruder is very large. This indicates the twin-screw extruder cannot disperse wax finely enough. On the other hand, the dispersed size of wax of toner B was very small. Toner B was kneaded by an open-roll-type kneader, and this type of kneader can knead toner at a lower kneading temperature, which means toner is kneaded more strongly at a higher resin viscosity compared to the twin-screw extruder.

Durability of toner B is over six times that of toner A, and is enough for practical use. This result indicates that large domains of wax decrease durability of toner because, it is thought, that such a large wax domain tends to (i) exist on the toner surface after pulverizing and (ii) stick to the doctor blade and developer roller. To avoid this problem, it is necessary to disperse wax finely in the toner; thus, toner kneaded by the open-roll-type kneader can contain plenty of wax with finely dispersed size and can yield both efficient fusing ability and durability for oilless fusing.

Result of Pulverizing of Toners C, D, and E

Figure 8 shows the result of pulverizing. Toner D was pulverized to 5 μm size with narrow distribution successfully. Toner C, which was not preconditioned, was not pulverized to a small size, and it contains large-size particles. Toner E, which was preconditioned but kneaded by the twin-screw extruder, also was not pulverized to 5 μm size. Dot image quality with toner D is as good as with typical chemical toner shown in Fig. 2. On the other hand, the dot images with toners C and E are worse because of toner scatter. These results indicate that small and narrow size distribution is necessary for fine image quality. The reason why toners C and E were not pulverized successfully is discussed below.

Difference between Toners C and D

In general, as toner particle size in the pulverizer becomes smaller, the adhesion force between particles increases; small toner particles tend to agglomerate. Such agglomerated particles cannot be given pulverizing energy efficiently, and it is difficult to pulverize toner to small size, as was observed for toner C. But in the case of toner D, silica is present in the

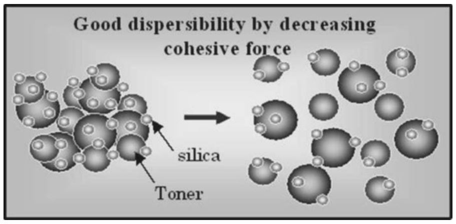


Figure 9. Effect of the preconditioning silica.

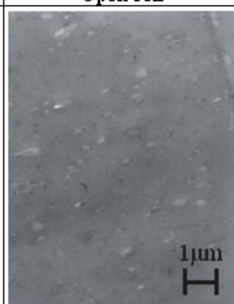
	Toner D	Toner E
Wax	6.0%	6.0%
Kneading	Open-roll	Twin Screw Extruder
Toner wax dispersion (TEM investigation)		
Dispersed size of wax	0.2~0.5μm	1.0~1.5μm

Figure 10. Wax dispersion in toners D and E.

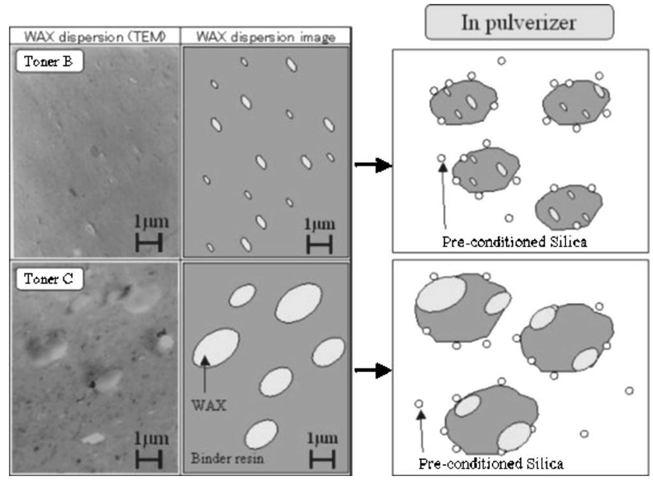


Figure 11. Difficulty of pulverizing in case of large domain of wax.

pulverizer, and the silica decreases the cohesive force of the toner particles (Figure 9). Such dispersed particles can be pulverized efficiently, and the efficiency of classifying is also improved. Thus, the preconditioning method is suitable for pulverizing toner to a small and narrow size distribution.

Difference between Toners D and E

Figure 10 shows wax dispersion in toners D and E. Wax domain size in toner E is much bigger than in toner D because of the difference of kneader, as described above. It is thought that this difference of wax dispersion also affects pulverizing efficiency. Figure 11 illustrates the influence of wax domain size on pulverizing. When the wax domain is small, the effect of preconditioned silica is sufficient. On the other hand, in the case of large wax domains, such as toner E, the toner chip tends to be pulverized at the surface of a wax domain. Consequently, the large domains of wax exist at toner surface and cause decreasing flowability and sticking to the pulverizer, even if silica preconditioning is employed. Thus, such large domains of wax disrupt efficient pulverizing. These results indicate that both preconditioning and fine wax dispersion are necessary to pulverize toner to small size with narrow distribution.

Effect of Silica Preconditioning

Toner pulverized by the preconditioning method already has silica added during the pulverizing process. Thus, the preconditioning method is a technique of both pulverizing and surface treatment. The properties of silica added by the preconditioning method are analyzed by a particle analyzer

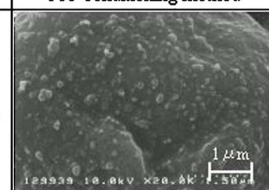
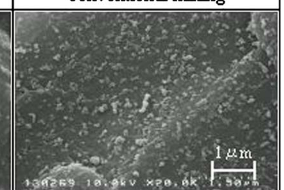
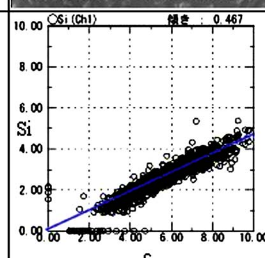
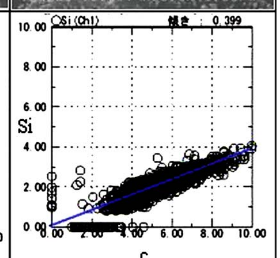
	Silica added by Pre-conditioning method	Silica added by conventional mixing
SEM of the toner surface		
Si dispersion		
SD of the Si dispersion	0.061	0.092
free Si rate	0.39%	1.02%

Figure 12. Comparison of silica dispersion of toner surface.

(Horiba). Figure 12 shows a comparison of the state of silica on the toner surface. Silica dispersion of toner added by the preconditioning method is better than conventional silica dispersion by addition in the mixer, and free silica rate is less. It is supposed that silica added in the pulverizing process is strongly bound to the particles, and extra free silica agglomeration is avoided or eliminated on classification. In general, free silica agglomeration is a cause of filming; thus, toner made by the preconditioning method has good durability.

In summary, toner pulverized by the preconditioning method has a small and narrow size distribution that is suitable for fine image quality and also has good silica dispersion on the surface for uniform charging ability and good durability. Accordingly, we named the preconditioning method “MechanoChemical” technology, and we call toner made by mechanochemical technology, “MC toner.”

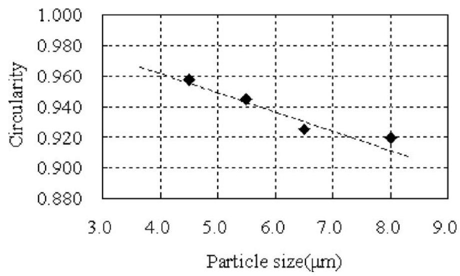


Figure 13. Dependency of circularity on toner particle size.

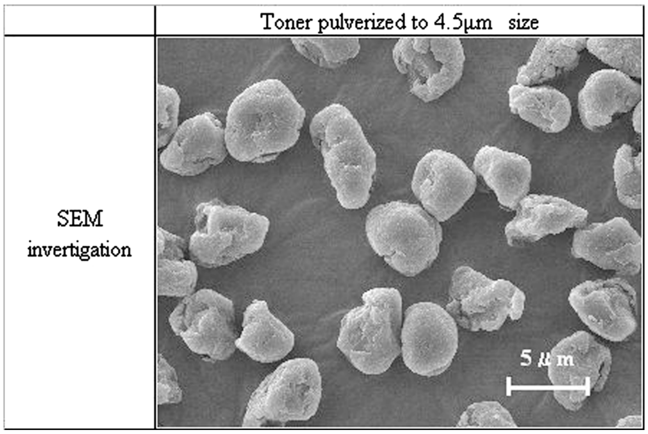


Figure 14. SEM photograph of small-size toner made by preconditioning method.

Tendency of Toner Shape on Particle Size

Figure 13 shows circularity of toner pulverized by the preconditioning method. Circularity increases as toner particles become small. This indicates that small particle size toner tends to be rounded by frequent collision in the pulverizer (Figure 14). Transfer efficiency (ΔE) of this potatolike shape toner (4.5 μm) was 5.2.

CONCLUSIONS

The present investigation leads to the following conclusions:

1. To achieve both oilless fusability and high durability, fine wax dispersion is necessary. An open-roll-type kneader is suitable for kneading the requisite amount of wax because low kneading temperature is possible.
2. To pulverize toner to small size with narrow distribution, both preconditioning and fine wax dispersion are necessary.
3. Distribution of silica added to toner surface by preconditioning is uniform, and the resulting toner has less free-silica agglomerations.
4. Shape of toner pulverized to small size become rounded because of frequent collisions in the pulverizer.

REFERENCES

1. Y. Matsumura, P. Gurns, and T. Fuchiwaki, *Proc. IS&T's NIP17* (IS&T, Springfield, VA, 2001) p. 341.
2. M. Yamazaki, M. Uchiyama, and K. Tanigawa, *Proc. of Japan Hardcopy 2000 Fall Meeting* (Imaging Soc. Japan, Tokyo, 2000) p. 1.
3. C. Suzuki, M. Takagi, S. Inoue, T. Ishiyama, H. Ishida, and T. Aoki, *Proc. IS&T's NIP19* (IS&T, Springfield, VA, 2003) p. 134.
4. T. Aoki, *Proc. IS&T's NIP19* (IS&T, Springfield, VA, 2003) p. 2.
5. A. Eida, S. Omatsu, and J. Shimizu, *Proc. IS&T's NIP20* (IS&T, Springfield, VA, 2004) p. 102.
6. E. Shirai, K. Aoki, and M. Maruta, *Proc. IS&T's NIP18* (IS&T, Springfield, VA, 2002) p. 258.
7. E. Shirai, K. Aoki, and M. Maruta, *Proc. IS&T's NIP19* (IS&T, Springfield, VA, 2003) p. 119.
8. T. Kubo, E. Shirai, and K. Aoki, *Proc. IS&T's NIP20* (IS&T, Springfield, VA, 2004) p. 73.
9. A. Eida and J. Shimizu, *Proc. IS&T's NIP16* (IS&T, Springfield, VA, 2000) p. 618.
10. J. Shimizu, S. Omatsu, and Y. Hidaka, *Proc. IS&T's NIP19* (IS&T, Springfield, VA, 2003) p. 130.