# The Advanced Color Toner for the Fine Image Quality II

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## Abstract
*As color printer becomes to be widely used, demand for fine image quality is also increasing. Therefore, toner with small and narrow size distribution for high-resolution development and small adhesion force to photoconductor for faithful transfer is required.*

*In this paper, design of pulverized toner with small and narrow particle size distribution for oil-less fusing system is reported. To pulverize toner to small size, the combination of fine wax dispersion and pre-condition method, or the pulverization in the existence of silica is important. This advanced pulverized toner using polyester resin also shows low-temperature fusing property, glossy image and fine durability. And an approach to the toner having small adhesion force to photoconductor is also reported. Both of control of the shape of toner and surface treatment by proper silica is effective.*

## Introduction
In recent years, as color printer has become to be widely used, the requirements of improvements for color printers have been also increasing. One of these demands is fine image quality. For fine image quality, both of development with high resolution and transfer without defects such as halo character is important. For the development with high resolution, the toner with small and narrow size distribution is required to develop latent image faithfully. And for the faithful transfer, the toner having small adhesion force to photoconductor is necessary. To meet these requirements, several chemical toners were developed and launched. It is said that the chemical toner is much better than the pulverized toner in the image quality.[1,2]

### *Small and Narrow Size Distribution*
In general chemical toner has an advantage in the small and narrow size distribution, because the chemical toner is directly polymerized.

On the other hand, technology to make pulverized toner with small and narrow size distribution was reported at NIP 20.[3] Mechanism of this technology named "pre-condition" is enhancing dispersibility of toner particles in pulverizer by pulverizing in the existence of silica, thus the efficiency of pulverizing is much improved (Fig. 1). Toner made by using this technology shows good dot image quality as well as typical chemical toner (Fig. 2).

We had found fine dispersion of wax in toner is also important to pulverize toner with small and narrow size distribution. This result is reported in this paper.

### *High Transfer Efficiency*
It is said spherical toner is proper to achieve high transfer efficiency because such toner comes in contact with photoconductor by a point area and it is easy to remove from that. The chemical toner is generally spherical, and it is possible to control the shape on the grounds of producing methods. On the other hand, it is said the transfer efficiency of pulverized toner is lower because of its irregular shape. In this paper, an attempt to improve the transfer efficiency of pulverized toner is reported.

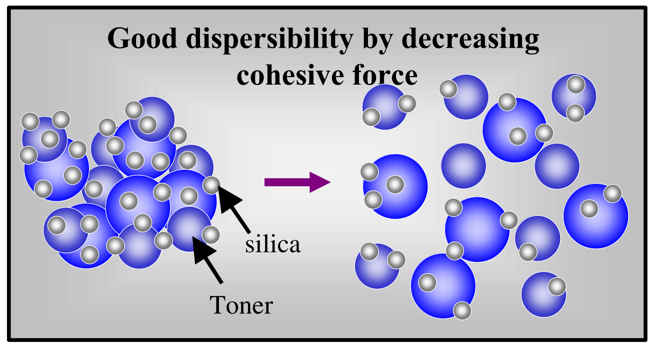



*Figure 1. The effect of the pre-condition silica*

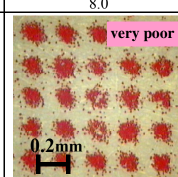
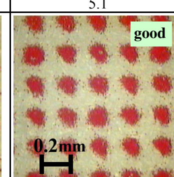
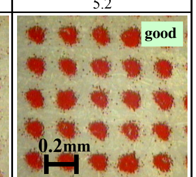
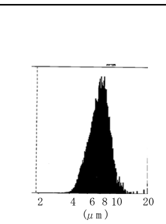
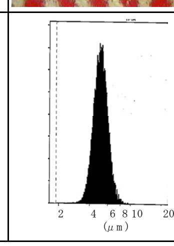
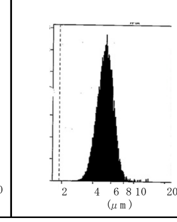
| | conventional pulverized toner | Pulverized with Silica | Typical chemical toner |
|---|---|---|---|
| D50(μm) | 8.0 | 5.1 | 5.2 |
| dot image (before fusing) |   |   |   |
| Particle size distribution (vol) |   |   |   |

*Figure 2. The comparison of image quality of conventional pulverized toner, typical chemical toner and the toner obtained by pre-condition method.*

## 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 the small amount of catalyst in a glass flask, which was equipped with a thermometer, a stainless steel stirring rod, a reflux condenser and nitrogen inlet tube.

**Table 1: Properties of the Experimental Polyester Resin**

| Resin | Acid Value[a] (mg KOH/g) | T1/2[b] (°C) | Tg[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 (Tg) was measured by a differential scanning calorimeter "DSC Model 200" manufactured by Seiko Instruments Inc., at a heating rate of 10/min.

### Preparation of Toner Samples

#### *Toner Samples to Investigate Relationship of Wax Dispersion and Pulverizing Efficiency*

Toner samples were comprised of the resin described above, wax, charge control agent and colorant. The colorant was Quinacridone (Pigment Red 122) and a melting point of the wax was 80°C. A content of the colorant was 6.5wt%. A content of the wax is 2.0% for Toner A and 6.0% for Toner B and C.

The materials were premixed in a batch mixer, then they were kneaded. We used two types of kneading machines, twin extruder (Toner A and B) and open-roll type kneader (Toner C). And before pulverizing, this toner chip was mixed with 1.0wt% of the hydrophobic silica, or pre-condition process. And then, it was pulverized and classified. The target size was 5 μm.

**Table 2: Toner Samples (1)**

| Toner No. | Wax | Kneading | Pre-condition |
|---|---|---|---|
| Toner A | 2.0% | Twin Extruder | Silica=1.0% |
| Toner B | 6.0% | Twin Extruder | Silica=1.0% |
| Toner C | 6.0% | Open-roll | Silica=1.0% |

#### *Toner Samples to Investigate an Influence of Shape of Toner on Transfer Efficiency*

Toner D and E were obtained by thermal treatment to be spherical shape based on Toner C. Toner was passed through thermal atmosphere for a split second. The temperature of thermal atmosphere for toner D was 250°C, and toner D was 400°C.

**Table 3: Toner Samples (2)**

| Toner No. | Thermal treatment to be spherical shape |
|---|---|
| Toner C | None |
| Toner D | 250°C atmosphere |
| Toner E | 400°C atmosphere |

#### *Toner Samples to Investigate an Influence of Silica Addition on Transfer Efficiency*

Toner C was blended with fumed silica by mixer to investigate an influence of surface additives on transfer efficiency. We used several kinds of silica described below.

**Table 4: Silica Used for Surface Addition**

| Toner No. | Primary particle size |
|---|---|
| Silica A | 8nm |
| Silica B | 16nm |
| Silica C | 40nm |

### Measurement of Wax Dispersion

The dispersed size of wax was observed by TEM. For convenience of evaluation, the TEM photograph was taken over the toner before pulverizing.

### Measurement of Particle Size Distribution

The particle size distribution was measured by Coulter Multisizer Ⅱ with the 100 μm size aperture.

### Measurement of Image Quality

Toner was developed by a non-magnetic single component printer. The resolution was 1200dpi, and the size of one dot was about 0.1mm. The dot image on paper before fusing was observed by microscope.

### Measurement of Transfer Efficiency

The transfer efficiency was defined as an amount of the residual toner on photoconductor after transfer process. M/A on the photoconductor was controlled at 0.40-0.45mg/cm$^2$. The residual toner was removed by clear tape and placed on a white paper. The amount of the residual toner is defined as the difference of hue (ΔE) between blank tape on the same paper.

### Measurement of Circularity

Circularity was measured by FPIA 2100 (Sysmex).

## Result and Discussion

### The Influence of Wax Dispersion on Pulverizing Efficiency

Figure 3 shows wax dispersion in the toner before pulverizing. The dispersed size of wax of toner A is about 0.2-0.5μm. But the dispersed size of wax of toner B is about 1.0-1.5μm. This indicates it is difficult to disperse a plenty of wax by conventional kneader. On the other hand, toner C shows fine dispersed size of wax as well as toner A in spite of the same amount of wax with toner B. Thus open-roll type kneader is suitable for kneading a plenty of wax finely because of the low temperature in the kneading process (Fig. 4). And from the viewpoint of oil-less fusing, toner should contain a plenty of wax inside because the resin of color toner has low and narrow molecular weight distribution, and such resin cannot give wide non-offset range in fusing.

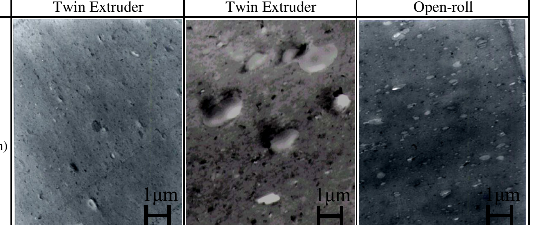
| | Toner A | Toner B | Toner C |
|---|---|---|---|
| Wax | 2.0% | 6.0% | 6.0% |
| Kneading | Twin Extruder | Twin Extruder | Open-roll |
| Wax dispersion in ther toner (TEM investigation) |  | | |
| Dispersed size of wax | 0.2～0.5μm | 1.0～1.5μm | 0.2～0.5μm |

*Figure 3. The dispersion of wax in each toner sample*

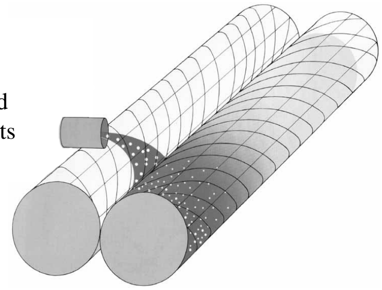



*Figure 4. Open-roll type kneader*

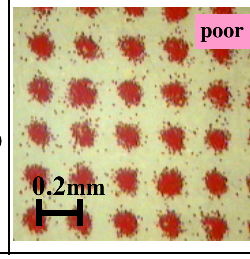
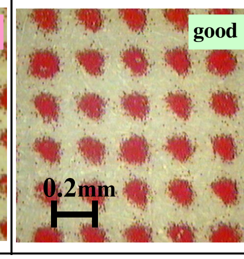
| | Toner B | Toner C |
|---|---|---|
| dot image (before fusing) |   |   |

*Figure 6.The comparison of dot image*

Figure 5 shows the result of pulverizing of each toner. The condition of pulverizing and classifying is same. This data indicates toner with poor wax dispersion cannot be pulverized to small and narrow particle distribution even when pre-condition method is applied. And when wax dispersion is good, the efficiency of pulverizing is also good regardless of the amount of wax. It is considered that the large domains of wax disturb efficient pulverizing, because they tend to exist on the surface of toner after crashing and adhere to the inside of pulverizer or each toner particles. In this way, to obtain the oil-less fusable toner with small and narrow size distribution, the fine wax dispersion is also important as same as pre-condition method for efficient pulverizing and classifying.

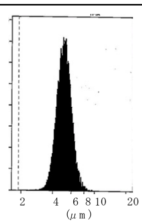
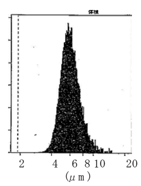
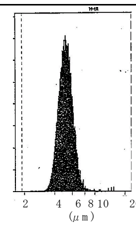
| | Toner A | Toner B | Toner C |
|---|---|---|---|
| Wax | 2.0% | 6.0% | 6.0% |
| Kneading | Twin Extruder | Twin Extruder | Open-roll |
| Dispersed size of wax | 0.2～0.5μm | 1.0～1.5μm | 0.2～0.5μm |
| Particle size distribution (vol) |   |   |   |
| D50(μm) | 5.1 | 5.9 | 5.2 |
| 3μm>(%) | 0.2 | 0.2 | 0.2 |
| 8μm<(%) | 0.6 | 10.2 | 1.0 |
| CV | 18 | 25 | 19 |

*Figure 5. The comparison of the particle size distribution*

Figure 6 shows dot image of toner B and toner C. The image quality of toner B is poor, because toner scattering is marked. It is considered the cause of such poor image quality is the existence of extra-size particles. Thus, to obtain the toner for fine image quality, small size of toner and less extra-size particles is also important.

As a result, total performance of toner C is very good. Because of using polyester binder resin, low-temperature fusing property is better than the toner using styrene-acrylic resin, and glossy image is possible. And by virtue of a plenty of wax, oil-less fusing is possible. In addition, in spite of such amount of wax, the durability is very good. Because this toner has very narrow size distribution and the fine particles with loose wax particles are removed.

## *Attempt to Improve Transfer Efficiency of Pulverized Toner*

### *Influence of Toner Shape on the Transfer Efficiency*

In general, it is said spherical toner shows good transfer efficiency because such toner contact with photoconductor by small adhesion force. So, the influence of controlling pulverized toner shape on the transfer efficiency is investigated. Figure 7 shows SEM photograph of toner after thermal treatment to be spherical shape. As the thermal condition become higher, the shape of toner becomes round and spherical. The value of circularity also increases. (It is thought the reason why the value of circularity of toner E is not so high contrary to appearances by SEM is the existing of coupling of toner particles generated in the thermal process.) The transfer efficiency becomes well as the shape becomes round. This indicates the adhesion force to photoconductor decreases as the shape of toner round. Especially the transfer efficiency of toner E is comparable with spherical chemical toner. Thus the transfer efficiency of pulverized toner can be improved by control of the shape of toner.

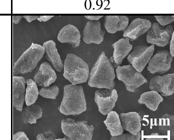
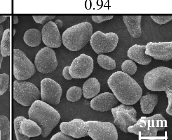
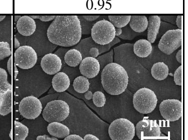
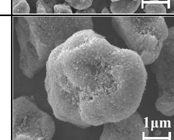
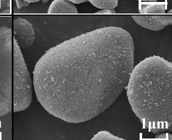
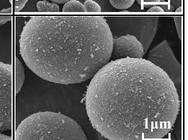
| | Toner C | Toner D | Toner E |
|---|---|---|---|
| Thermal treatment | none | 250°C atmosphere | 400°C atmosphere |
| Circularity | 0.92 | 0.94 | 0.95 |
| SEM (x2000) |   |   |   |
| SEM (x10000) |   |   |   |
| Residual toner of transfer (ΔE) | 15.3 | 7.8 | 2.0 |

*Figure 7. The influence of the toner shape on the toner performance*

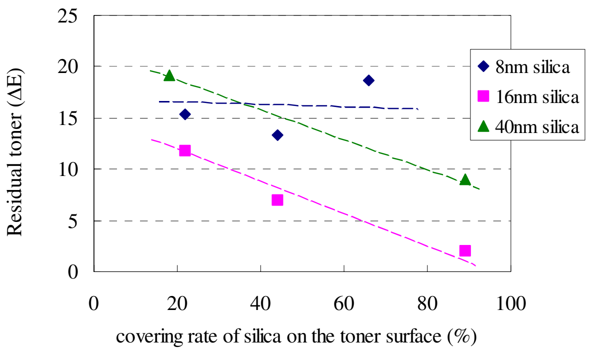



*Figure 8. The effect of surface treatment on the transfer efficiency*

### *Attempt to Improve the Transfer Efficiency by Surface Treatment*

The attempt to improve transfer efficiency by surface treatment of silica to irregular shape toner was also investigated. In general surface treatment makes adhesion force of toner decrease. It is effective to reduce the adhesion force for improvement of transfer efficiency. Figure 8 indicates the relationship of covering rate of silica on the surface of toner C and transfer efficiency in case of several particle size of silica. This data shows the effect for transfer efficiency is not determined by only covering rate, and there is an optimal size of silica. In this case, a combination of toner C and 16 nm size silica shows good transfer efficiency. Thus when proper silica for each type of toner is chosen, it is possible to improve transfer efficiency as well as chemical toner even if the toner shape is irregular.

## Conclusion

For fine image quality, both of development with high resolution and transfer without defect such as halo character are necessary. To obtain pulverized toner with small and narrow particle size distribution, wax in toner should be dispersed with fine domain. And the combination of fine dispersed size of wax and pre-condition method is suitable for efficient pulverization and classifying. For high transfer efficiency, toner having small adhesion force to photoconductor is appropriate. To decrease the adhesion force, both of spherical shape of toner and surface treatment by proper silica is effective.

## References

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## Author Biography

*Akihiro Eida received his master degree in physics from Hokkaido University in 1996. Since 1996 he has been working for Kao Corporation in the Performance Chemicals Research Laboratories in Wakayama, Japan. His work has primarily focused on the development of toner and toner binding with polyester resin, including the design of color toner regarding wax, colorant, CCA and surface treatment agent.*