Superior Technology to Make the Advanced Full Color Toner for Fine Image Quality

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Abstract

It is effective to reduce the size of toner for fine image quality on electrophotographic system. But, in general, size production of toner is energy intensive. As its solution, the two technologies are proposed to make it possible to manufacture productively the full-color toners with smaller particle size in a dry process in the near future.

The mechanochemical method in a dry process of toner is introduced as the production of toner. This method is that the preground chips mixed with silica are ground using the pulverizer like a jet mill and is especially suitable to produce the color toners including high content of the wax. The size reduction of thus toners is especially hard in a dry process, but the specific energy consumption as grinding efficiency has been decreased up to half when using the mechanochemical method.

The grindability of the polyester resin as toner binder, which is main components of toner and controls the productivity of the toner, is also discussed. The specific energy consumption was decreased up to further half when using both high grindable resin and mechanochemical method.

It is proposed in this paper that both mechanochemical method and high grindable resin should be simultaneously applied as the process of size reduction of toner for fine image quality.

Introduction

The diffusion rate of electrophotographic color printer has been rapidly raised for a few years. Many end users have started to require the fine image quality, especially high definition such as photograph.

As the way to enhance the image quality, the size reduction of toner particle has been proposed. But the size reduction has been energy intensive and lessened its productivity in conventional dry process.

On the other hand, chemical toner or polymerized toner has been proposed as the answer of issue with size reduction. But several issues seem to exist in these methods, which are, for example, the disposal of wastewater after reaction and rinse, the requirement of thermal energy for drying, maybe the necessity of classification and then the disposal of substandard particles out of classifier.

We think it is not necessary to dare to select the chemical process for size reduction of toner particles because of including such issues. So it is significant to improve the conventional process and solve the issues of energy intensiveness and low productivity for size reduction of toner.

We firmly believe that it will be possible to manufacture the smaller size toner in a dry process.

Mechanochemical Method

It has been reported that the inorganic fine particles like silica were added as grinding aid [1]. But this method was auxiliary for grinding and classifying because the toner in the past did not include so much wax.

In this decade, the desire for oil-less (or oil-free) fusing has been rapidly raised by the various reasons, which were, for example, for size reduction of printers, for getting well the greasy touch of an OHP sheet after printing, for writing again on an OHP sheet printed, etc [2]. These reasons were caused by the necessity of oil for fusing. The full-color toner for oil-less fusing has been proposed that included much wax dispersed well by using open-roll kneader [3,4]. And above method was improved from auxiliary addition of silica for grinding to mechanochemical method (below MC-Method) for wax-rich full-color toner.

Experiments

Apparatus for Pulverization

Two types of jet mill and mechanical pulverizer were used in the experiments. One of jet mills was the type of collision of particle against target and another was the fluidized bed jet mill with opposed-nozzles that the particle impacted against each other. Mechanical mill was due to the percussion of high speed rotation of the wings against particles.

Preparation of Magenta Toner

The ingredients of the prepared toner for oil-less fusing are shown below.

The toner consisted of resin A (shown in Table 1) of 90wt%, the magenta pigment of 6wt%, negative type CCA of 1wt% and the wax of 6wt%. The individual components were premixed in a high-speed mixer and the pre-mixed raw materials were kneaded with the open-roll type kneader. The past toner mass was discharged into a cooling unit. The cooled mass toner was preground by a preliminary grinder to the size of the granules. In the case of applying the MC-Method, the toner granules were pre-mixed with silica, whose number mean particle diameter of primary particles was about 16 nm. The jet-mill or mechanical mill was used for the size reduction of this magenta toner granule and, if needed, the classifier was used to separate the fine particles from the ground product.

The particle size distribution was measured on Coulter Multi-Sizer II.

Preparation of Polyester Resins

Six kinds of polyester resins as toner resin were prepared with bisphenol A type alcohols and acid monomers.

The resin A was typical polyester resin, which was the linear type. The terephtalic acid was used as the main acid monomer. The resins from B to E were prepared with trivalent monomer to introduce branch structure into the polymer based on resin A. The resin F was the linear type like resin A and included fumaric acid not terephtalic acid.

Number-average molecular weight (below Mn) of each resin was varied by adjusting monomer ratio and reaction condition. Tm of all resins was adjusted to around 110 degree C in order to eliminate the effect from Tm on resin grindability. Tm of resin F was reduced to 101 degree C because of the investigation of the affect of Mn in the linear type. The properties of all resins are summarized in Table 1.

Table 1: The Properties of Polyester Resins

Resin	Acid value	Mn	Type	Tm (C)
A	<5	4700	Linear	110
B	21	2800	Branch	107
C	31	2400	Branch	109
D	35	2000	Branch	111
E	25	2500	Branch	108
F	20	4000	Linear	101

Grinding Efficiency

The grinding efficiency was described with the specific energy consumption (below SEC). The equation (1) shown below was used for the calculation of SEC.

$$SEC = GE / MF \quad (1)$$

In general, the jet energy is lead from the equation (2), which was used as grinding energy GE in the case of jet-mill. MF means the raw material feed (kg/h) into pulverizer.

$$GE = C\, d^2 P_0\, n\, (1-(P_1/P_0)^{(\gamma-1)/\gamma})(T)^{1/2} \quad (2)$$

$C = (2R/M)^{1/2}\, \phi_{max}\, \gamma / (\gamma - 1)\, \pi / 4$
$\phi_{max} = (\gamma / (\gamma - 1)\, ((P_c/P_0)^{2/\gamma} - (P_c/P_0)^{(\gamma+1)/\gamma})^{1/2}$
$P_c/P_0 = (2/(\gamma+1))^{\gamma/(\gamma-1)}$: critical pressure ratio
d : the orifice diameter of jet nozzle (m).
P_0 : the absolute pressure of jet air (Pa)
P_1 : the absolute pressure in chamber (Pa)
n : the number of jet nozzle
T : absolute temperature in chamber (K)
γ : ratio of specific heats
R : universal gas constant (J/kg mol K)
M : molecular weight

The equation (3) was used as grinding energy GE in the case of mechanical mill.

$$GE = Pgr + Pca \quad (3)$$

Here Pgr, which was actually measured, means the electrical power requirement of grinding rotor and Pca, which was calculated using the equation (4), means the electrical power requirement of cooling air.

$$Pca = SH \times MA \times \Delta T \quad (4)$$

Here SH is specific heat, MA is mass flow rate of air and Δ T is the difference of air temperature between before cooling and after cooling

Results and Discussion

Effect of Mechanochemical Method on Grinding Efficiency

The prepared magenta toner was ground by two types of jet-mill. As in Figure 1, the closed circles and opened squares show the relationship between SEC and the volume median particle diameter (below dv50) of ground products with the MC-Method. The closed diamond shows the data without the MC-Method using fluidized bed jet mill. The effect of the MC-Method on pulverization is shown in Figure 1.

The SEC of the ground product at the size of 5.5-micron without the MC-Method (closed diamond shape in Figure 1) was required about two times as much as with the MC-Method.

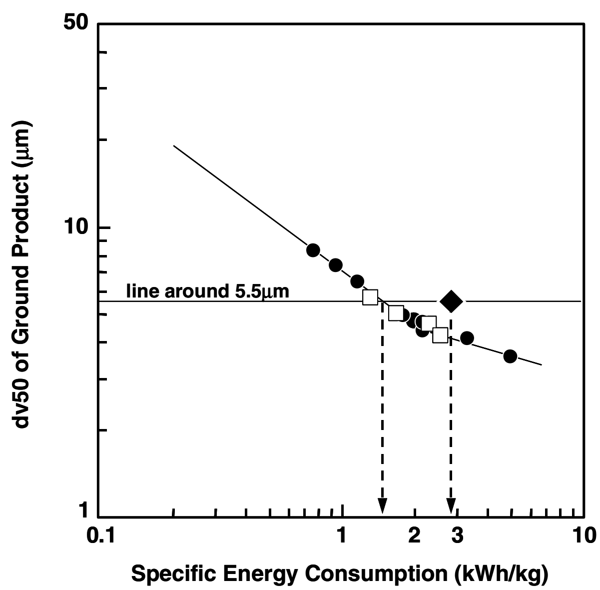

Figure 1. The effect of the MC-Method on SEC. The closed circles and the opened squares are the data from two types of jet-mill under the MC-Method. The closed diamond is the data without the MC-Method.

This result is guessed that the dispersion of particles got well because of lessening cohesive force among particles under the MC-Method and silica moderately embedded in the surface of particles (see Photo 1) prevented them from making cohesiveness again.

The activity on the particle surface newly generated by collision, which caused the cohesive force, would be counteracted by the embedment of silica on the particle surface.

It is also expected that the MC-Method will be able to improve the classification of ground product and the pulverizing.

In the pulverizing or grinding apparatus, the small portion of ground particles is drawn off out of equipment through the classifying zone and the large portion of them falls back to grinding zone.

It is thought that many independent particles dispersed under the MC-Method will be efficiently separated in the classifying zones. Further, cohesive particles must play a role of buffer against impact and independent particles must be easily ground with utilizing the power of jet energy efficiently.

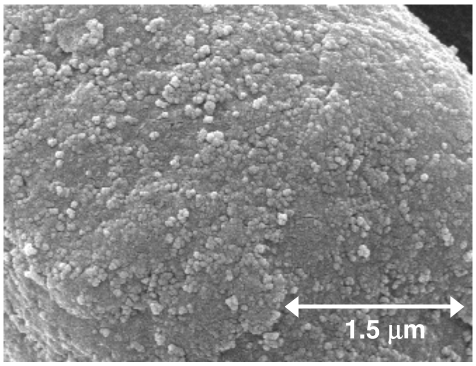

***Photo 1**. The SEM of toner surface with the MC-Method.*

Grinding Efficiency of Different Types of Pulverizer

In the three types of pulverizer, relationship between the SEC and dv50 of ground products from magenta toner mass, which were not classified, was evaluated to investigate which pulverizer was advantageous to the size reduction.

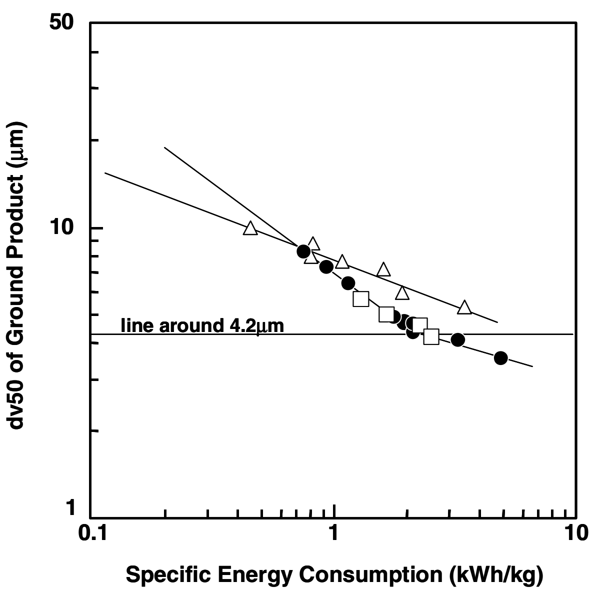

***Figure 2**. The relationship between the volume median diameter and the specific energy consumption. The closed circles and the opened squares are the data from two types of jet-mill. The opened triangles are the data from mechanical mill.*

The result is shown in Figure 2. The points of two types of jet mill are almost on the same line. This result indicates no difference between fluidized bed jet-mill and target type jet-mill has been found in the grinding efficiency. But, the clear difference between jet mill and mechanical mill has been found.

The incline of the mechanical mill is clearly gentle compared with the incline of jet mill and each line crosses at around the 0.7kWh/kg- 9-micron point. This result shows the efficiency of mechanical mill is advantageous when producing 9-micron particles and over, however, jet mill is suitable to produce smaller particle size toner.

Figure 2 also shows the line consisting of jet mill has a kink at around 4.2-micron and its incline becomes gentle toward the side of small size. It is guessed that the grinding energy will remarkably increase from that point.

Investigation of Grindability and Productivity of Resins

All the resins from A to E in Table 1 not including another components of toner were ground to evaluate the productivity of resin. These five resins with different Mn were ground up to dv50 = around 5.0 microns to evaluate the productivity with the fluidized bed jet-mill. The ground products were separated to both the required coarse particles and the fine particles by the classifier. In addition, these experiments were practiced under the MC-Method to except the bad influence, which was cohesiveness of particles, on pulverization and classification and investigate the real grindability of resins.

The grinding efficiency parameters, the feed rate of raw material "a", the yield ratio of ground product "b" and the resin grindability "b× a", of the ground products are summarized in Table 2.

In general, it is known that the grindability of resins depends on Mn. Table 1 and Table 2 also show that resin with low Mn is more grindable than high Mn. As shown in Figure 3, the resin grindability is clearly related to Mn.

Table 2: The Grindability Data of Each Ground Product Discharged from Pulverizer

Raw Material Resin	Volume Median Diameter dv50 (μm)	Feed Rate of Raw Material a (kg/h)	Yield ratio of Ground Product b (%)	Resin Grindability b× a (kg/h)
A	5.1	3.6	90.3	3.3
B	4.9	4.9	95.9	4.7
C	4.9	6.8	90.4	6.1
D	4.7	9.0	84.8	7.6
E	5.0	5.9	90.4	5.3

The classified required coarse particles were made from above ground products using the classifier with classifying rotor. The result of classifying efficiency is summarized in Table 3. The each coarse particle stayed at the dv50 of about 5.3 μm and the volume CV-value of around 20%.

The feed rate of ground product into the classifier "c", the yield ratio of coarse particles "d" and the yield per hour of classifying "d× c" are summarized in Table 3. The value of "d× c" described in Table 3 was able to be estimated the amount of fine particles generated in grinding. It was guessed that high grindable resin was very fragile and easily generated fine particles

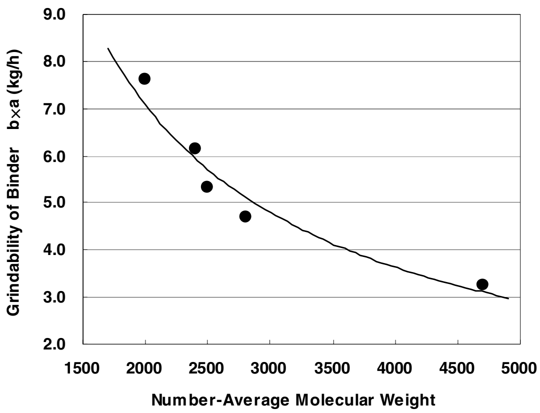

***Figure 3**. The relationship between the number-average molecular weight and the grindability of resin.*

Table 3: The Productivity Data of Each Classified Coarse Particles Discharged from Classifier

Raw Material Resin	Volume Median Diameter dv50(μm)	Feed Rate of Ground Product c (kg/h)	Yield ratio of Coarse Particles d (%)	d× c (kg/h)
A	5.3	8.3	79.0	6.6
B	5.3	7.7	65.9	5.1
C	5.5	8.3	61.0	5.1
D	5.3	7.0	60.8	4.3
E	5.4	8.3	70.6	5.9

As shown in Table 4, the value of "Yt× a" was defined as the final productivity in this test. The "Yt", "b× d" described in Table 4, was the total yield ratio through both ground products and coarse particles.

It is shown in Table 4 that the final productivity becomes high when the total yield ratio was low. The final productivities of each resin were plotted versus Mn in Figure 4. This is very interesting result. This result indicates that the small size toner will be able to be satisfactorily produced in the final productivity if the high grindable resin is used.

Table 4: The Total Yield Ratio and Final Productivity of Each Resin

Raw Material Resin	Total Yield Ratio(Yt) b× d (%)	Final Productivity Yt× a (kg/h)
A	71.3	2.6
B	63.2	3.1
C	55.1	3.7
D	51.6	4.6
E	63.8	3.8

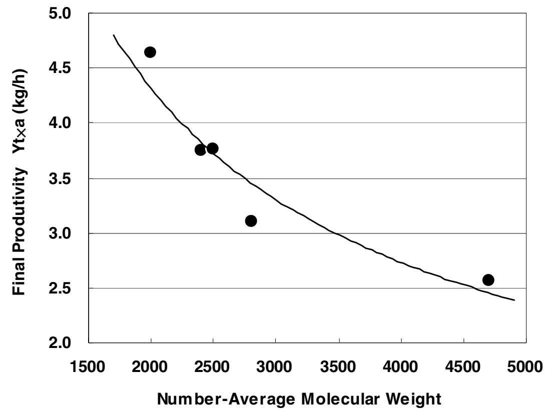

***Figure 4**. The relationship between the number-average molecular weight and the final productivity of resin.*

Boost in Grinding Efficiency with High Grindable Resin

It was already mentioned that the resin with low Mn was high grindability. Then, the magenta toner was made from the resin F at the same formulation as the one from the resin A and its grinding efficiency was investigated.

As shown in Figure 5, under the MC-Method, the line formed by SEC of the ground product made from the resin F was parallel with the line formed by another products with normal grindable resin A and shifted to the low energy side.

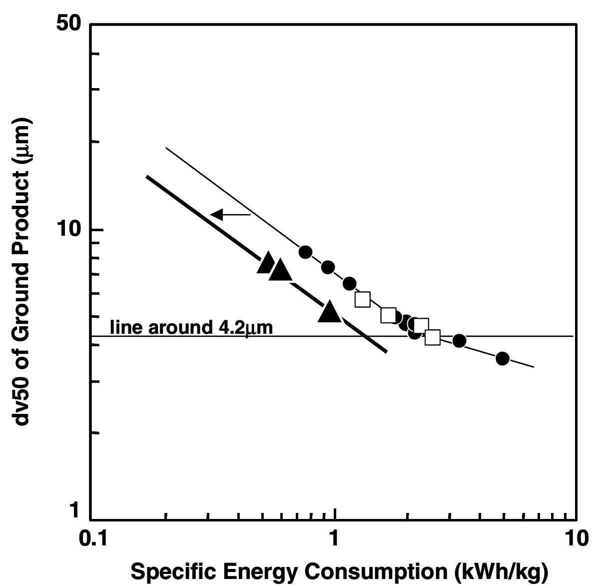

***Figure 5**. The effect of both high grindable resin and the MC-Method on SEC. The closed triangles are the data of using high grindable resin under the MC-Method.*

SEC of the ground product with high grindability was from two thirds to half as much as the one with normal grindability. And only a fourth of energy will be needed to make the particles as compared with generally well-known method without both the MC-Method and high grindable resin (closed diamond shown in Figure 1).

Challenging More Size Reduction of Current Toner with Normal Grindable Resin

The current product, which was the magenta toner with the particle size of dv50=8 microns, made from normal grindable resin A was made smaller in size up to dv50=4.5 and 5.6 microns under the MC-Method.

One parameter “e”, which was the feed rate of raw material into the fluidized bed jet-mill, was estimated as toner grindability. The other parameter “f ”, which was the yield ratio coarse particles discharged out of the classifier, was estimated as classifying efficiency. And, the each total productivity was calculated as the “e× f”.

As shown in Table 5, the size reduction finally caused the decrease of the total productivity. The feed rate of raw material when making 5.6μm toner was down to 59% as compared with 8.0μm toner and its value in the case of making 4.5μm toner was more down to 25%. These were very understandable results.

Table 5: The Comparison Between the Productivity of 8μm Toner and the Productivity of 4.5μm Toner under MC-Method

dv50 of Toner (μm)	Feed Rate of Raw Material e (kg/h)	Yield ratio of Coarse Particles f (%)	Total Productivity e× f (kg/h)
8.0	17.6	73	12.8
5.6	10.4	75	7.8
4.5	4.4	73	3.2

Here, it should be noted that each yield ratio of coarse particles was almost equal though feed rate of raw material was decreased as size reduction. This result is guessed that the MC-Method has enhanced the accuracy of classification in the classifier.

In above mentioned, SEC without the MC-Method was large. But it was the result in the case of making ground product and therefore, the lessening of classifying efficiency was not included. In real process of toner, the final productivity was calculated from the efficiencies of both pulverizing and classifying and it has been confirmed that the yield ratio of classification became about half if not using the MC-Method (result not shown). So it is sure that the MC-Method made the classifying efficiency improved in a classifier.

The production of the smaller size toner, for example dv50=4.5 μm, will be possible if only the feed rate of raw material into the pulverizer is boosted. The further remarkable improvement of the grinding efficiency was very difficult and not expected even if using the MC-Method. But the high grindable resin will make it possible to improve the grinding efficiency in size reduction under the MC-Method.

In above mentioned, SEC with high grindable resin was about half as much as SEC with normal grindable resin. In other words, if using high grindable resin under the MC-Method, it will be expected that the grinding efficiency will increase maximum two times and it is not incredible that the feed rate of raw material in the case of making the 4.5μm toner may achieve up to 8.8kg/h.

As shown in Table 4, under the MC-Method, the final productivity of the most grindable resin D was about 1.8 times as much as the normal A. If the toner of dv50=4.5μm is made from the resin D, its total productivity will be estimated 5.8 kg/h. Then, its total productivity may be recovered up to 74% of the one of 5.6μm toner listed in Table 5.

In addition, the full-color toners of dv50=5.6μm were recently developed by us and its productivity was satisfactorily realistic.

It is no doubt that the high grindable resin like D is needed to be more improved. But all of these results firmly indicate that toner in size of level of 4.5μm could be productively manufactured in the near future if using high grindable resin under the MC-Method.

Conclusion

The conclusion was reached below.

It was indicated that high grindable polyester resin as toner binder had high final productivity with lower energy though its yield ratio did not get well because of generating many fine particles.

The MC-Method was able to enhance the grinding and classifying efficiency and was integral technology to make the smaller size toner.

In classical theory, for example in Kick’s law, the grinding energy of a 4.5μm toner is only 1.2 times as much as an 8μm toner. But, in the real process of toner, the former energy was four times as much as the later (estimated as the feed rate).

Because the critical kink point existed at around 4.2μm in grinding with normal grindable resin, it is very difficult to make the ground product having less than 4.2μm particle size. But if fine particles are removed from 4.2μm ground product, the 4.5μm toner will be able to be obtained. Therefore, the size of smaller toner should be aimed to be 4.5μm. And the productivity will be improved by using higher grindable resin like D or F.

In the near future, the both technologies, the MC-Method and high grindable resin, could make it possible to manufacture productively the full-color toners for oil-less fusing in size of level of 4.5μm in a dry process.

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Author Biography

Shinichiro Omatsu was granted Master of Science from Hokkaido University in 1987 and has begun to work for Kao Corporation in the same year.

He is working in the Performance Chemicals Research Laboratories in Wakayama, Japan during 17 years. After development of toner, he has started current job, which is manufacturing technique and process of toner.

His mission is mainly the continuous evolution of pulverized toner based on the process technology.