

Development of Spherical Polyamide Fine Powder

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A new synthesis and decoloring process has been developed for polyamide fine powder. The polyamide fine powder manufactured by this process have a spherical shape and pure white color, with narrow particle size distribution (5 to 10 μm in diameter). The powder is used mainly in cosmetic products. We granted a license for this technology to SH Chemical Co., Ltd. (Korea) and the company has started to manufacture the powder.

Other types of polyamide powder have been also studied. One example is a powder composed of spherical particles with diameters ranging from 20 to 100 μm . The new polyamide product will be commercialized for industrial use.

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Introduction

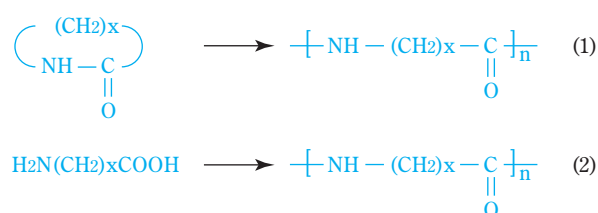
Polyamide resins are durable and have excellent friction/abrasion resistance and oil/solvent resistance. For these favorable characteristics, polyamide resins are widely utilized for industrial materials. In addition, polyamide fine powder is used for a variety of applications, including as an additive in paints and waxes, lubricants, adhesives and antitack agents. Although polyamide fine powder comes in various forms, spherical polyamide fine powder is attracting the most attention from industry for its smooth surface, soft texture and excellent extensibility on the skin, in addition to its generic polyamide resin properties. For this reason, demand for spherical polyamide fine powder is rapidly expanding in the area of cosmetics.^{1), 2)}

Because of this increasing demand, we have paid particular attention to spherical polyamide fine powder and have been conducting research on its manufacture. We have successfully developed a spherical polyamide fine powder that possesses a high degree of whiteness and a narrow particle size distribution. In this paper, we shall report our manufacturing method for spherical polyamide fine powder, and describe its characteristics.

Conventional Manufacturing Methods for Spherical Polyamide Fine Powder

Manufacturing methods for spherical polyamide fine

powder include ring-opening polymerization of lactam, and condensation polymerization³⁾ of aminocarboxylic acid monomer (Fig. 1). The manufacturing method for polyamide fine powder constituted of lactam is described in Japanese patent No. Sho-47-25157. However, as the above-mentioned method utilizes liquid paraffin for a reaction solvent, it is not easy to remove the liquid paraffin adhering to the polyamide particles. Japanese patent laid-open No. Hei-10-315750 outlines a method to disperse a produced polyamide into fine particles as follows: monomer is melted in a polymerizing solvent at a temperature higher than the melting point of the polymer, and the materials are stirred to achieve polymerization. Although this method allows us to produce polyamide particles of 10–100 μm in diameter, the particle size distribution is too wide and it is difficult to put the resulting polyamide fine powder to practical use.^{4), 5)}



(1) : Ring-opening polymerization

(2) : Condensation polymerization

Fig. 1 Schematic process of polyamide

Our Manufacturing Method for Spherical Polyamide Fine Powder

1. Synthesis Method

As a result of research on a variety of synthesis methods, we have developed a spherical polyamide fine powder that has a narrow particle size distribution. Fig. 2 outlines our manufacturing method. The procedures are as follows:

- ①, ② Lauro lactam or lactam having carbon numbers from 6 to 8, alkali catalyst, and dispersing agent such as fatty acid or fatty acid salt are added to inert solvent, then stirred and heated.
- ③ When the reaction solution temperature nears the melting point of polyamide resin, polymerization initiator is added to obtain spherical polyamide fine powder.
- ④ Once the polymerization is complete, the reaction liquid is cooled to the appropriate temperature, and solid-liquid separation is performed to obtain a polyamide fine powder cake.
- ⑤ Catalyst and reaction by-products are removed from the polyamide fine powder cake.
- ⑥ The cake is then dried to remove the wash solvent.

Through the above method, spherical polyamide fine powder having an average particle size of 5–10 μm and narrow particle size distribution is obtained.⁶⁾ Fig. 3 shows an electron microscope photograph of the polyamide fine powder manufactured using this method. Fig. 4 depicts its particle size distribution.

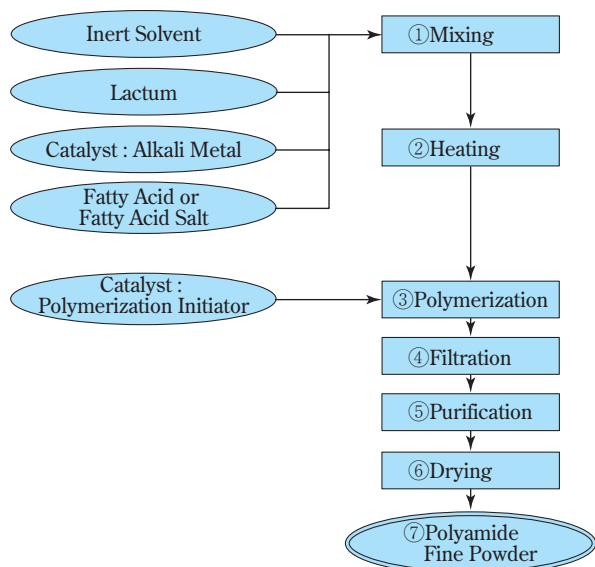


Fig. 2 Flow chart of polyamide fine powder

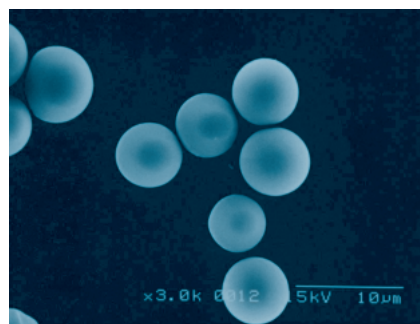


Fig. 3 Spherical polyamide fine particles (scanning electron microscope)

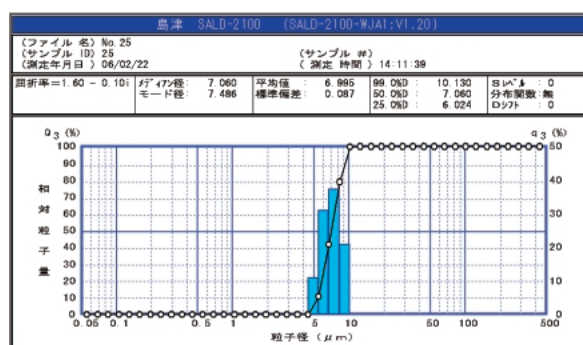
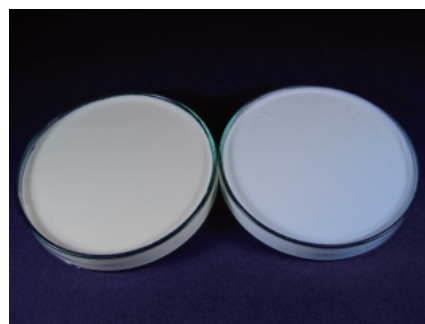


Fig. 4 Particle size distribution of spherical polyamide fine powder with 5 to 10 μm in diameter

2. Decoloring Process

Polyamide fine powder manufactured using the conventional method and spherical polyamide fine powder produced through our method can be slightly discolored/yellowed. This discoloration is caused by impurities contained in the raw material and in a reaction to high temperature. Discoloration is a problem when using polyamide fine powder as a raw material for cosmetics. We have conducted research on improving polyamide fine powder whiteness, and have developed the following method:



Left : Before decoloring Right : After decoloring

Fig. 5 Polyamide fine powder

A spherical polyamide fine powder cake is stirred in a hydrogen peroxide solution at a temperature of 70–80°C for a period of 20–30 minutes. The liquid is cooled down to the appropriate temperature, and solid-liquid separation is performed. After a washing process (i.e.: rinsing with water), a spherical polyamide fine powder with the desirably high degree of whiteness is obtained.⁷⁾ Fig. 5 compares the spherical polyamide fine powder before and after the decoloring process.

3. Characteristics of Our Product and Its Applications

The spherical polyamide fine powder obtained through the above manufacturing method has excellent whiteness and a narrow particle size distribution. Therefore, it is superior to our competitors' products. Table 1 shows the characteristics of our products.

Table 1 Characteristics of Shinto Fine's polyamide fine powder

Item	Characteristics	Test Method
1) Description	Pure white powder	JCIC
2) Identification	Recognize the	JCIC
Infrared Absorption Spectrum	characteristic absorption	
3) Heavy Metals Content	10ppm (Max.)	JCIC
4) Arsenic Content	1ppm (Max.)	JCIC
5) Residue on Ignition	0.5% (Max.)	JSCI-II
6) pH	6.0 – 8.0	JSCI-II
7) Water-Soluble Substances	0.2% (Max.)	JSCI-II
8) Apparent Density	3.0 – 6.0mL/g	JIS K-5101
9) Average Particle Diameter	6.0 – 9.0µm	Laser Diffraction Particle Size Analyzer
10) Particle size	20µm (Max.)	Laser Diffraction Particle Size Analyzer
11) Melting Point	165 – 180°C	Differential Thermo Analysis
12) Color	85% (Min.)	Chroma Meter
13) Water Content	1.0% (Max.)	JSCI-II

JCIC : Japanese Cosmetic Ingredients Codex

JSCI-II : The Japanese Standard of Cosmetics Ingredients, Second Edition

JIS : Japanese Industrial Standard

In general, spherical polyamide fine powder is more expensive than other polymer based fine powder. However, our spherical polyamide fine powder is a popular choice for many purposes because of its high quality and consistent particle size distribution.

4. Application Fields of Spherical Polyamide Fine Powder

Spherical polyamide fine powder was originally developed as an additive for cosmetics. Thus, it is most widely utilized in this area, as shown in Table 2. By adjusting the amount of spherical polyamide fine powder added to cosmetic products, different levels of dryness or moistness can be achieved. As well, spherical polyamide fine powder has high oil/solvent resistance, and is particularly resistant toward alcohol. As neither expansion of particles nor cohesion among particles occurs in spherical polyamide fine powder, it demonstrates a high miscibility with other cosmetic components. Fig. 6 depicts examples of applications for spherical polyamide fine powder.

Table 2 Use of polyamide fine powder⁸⁾

Use	Market (%)	Examples
Cosmetics	96	Foundation cream, Face powder, Eye shadow, Hair care products, Body shampoo
Others	4	Ink additives, Lubricating oil additives
Total	100	



Fig. 6 Example of final products using polyamide fine powder

International Expansion and Licensing of Technology

1. International Expansion

Our company's polyamide fine powder has excellent whiteness and a narrow particle size distribution. Because of these qualities, it is expected that international demand for our products will continue to

increase. Based on this expectation, we considered the overseas export of our production technology. A Korean company, Shinho Petrochemical Co., Ltd. (present name: SH Chemical Co., Ltd.), expressed an interest in manufacturing and distributing our product (Fig. 7) in space left vacant after part of their production plant was moved to China. Their manufacturing technology and quality control were found to be excellent, and we decided to license our technology to Shinho Petrochemical Co., Ltd. The company's plant is in the city of Kunsan, located along the Huang Hai coast in central Korea. This location was satisfactory for a manufacturing plant, as it is only a three hour drive from Seoul and the Incheon International Airport.



Fig. 7 Headquarter of SH Chemical Co., Ltd.

2. Technology License

Our company signed a technology license agreement with Shinho Petrochemical Co., Ltd. Based on this agreement we disclosed our polyamide fine powder manufacturing technology and provided a basic design for their plant. As well, we have continued to meet with Shinho Petrochemical Co., Ltd. to discuss project details. Shinho Petrochemical Co., Ltd. refurbished their Kunsan Plant based on the information we provided (Fig. 8). Although in the original plan all raw materials required for manufacturing would be procured within Korea, some components were unavailable. We decided to import these raw materials from Japan. We visited the plant when construction was complete to provide Shinho Petrochemical employees with instruction and training in our manufacturing method. Although there were some initial complications, we duly established their ability to manufacture products compliant with our standards. Following this confirmation, we completed the technology export process.



Fig. 8 Manufacturing plant of polyamide fine powder

This project provided our first experience with the technology export process. Complex aspects of the project included license agreement negotiation, basic plant design, and the development of quality control testing in the new manufacturing facility. Our project succeeded with a great deal of support from the Legal Department of Sumitomo Chemical Co., Ltd. and Sumitomo Chemical Engineering Co., Ltd. This experience will prove invaluable in the development of our company's future global strategy.

Development of New Polyamide Particles

1. Development of Spherical Polyamide Particles Having Average Particle Size of 20–100 μ m

(1) Conventional Manufacturing Methods

The ideal particle size distribution of polyamide powder required for a specific product varies depending on its application. Generally, for applications in cosmetics and ink additives, polyamide powder having an average particle size of 5–10 μ m is desirable. This is the major application for our current polyamide fine powder product. For rotational molding, polyamide powder having a larger particle size is preferable.¹⁾ Several manufacturing methods already exist for larger particle size polyamide powder (average particle size ranging from 20–100 μ m). In general, polyamide powder manufactured using conventional methods has the following disadvantages:

- 1) Porous particles
- 2) Uneven spherical condition in particles
- 3) Uneven particle size distribution

Previously, there was no manufacturing method capable of directly producing non-porous polyamide

Table 3 Manufacturing process of polyamide powder

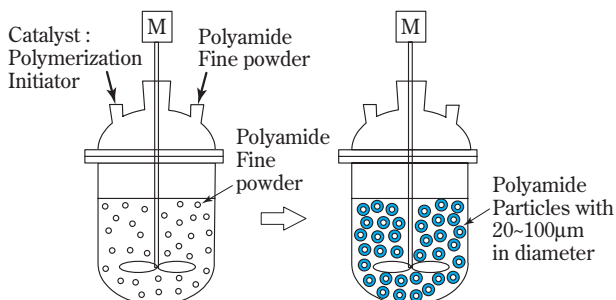
Classification of process	Characteristics	Reference
Chemical grinding method	Dissolve or disperse polyamide in solvent, and cool it or add poor solvent therein to be precipitated as fine particles. Grind polyamide by a grinder.	1), 9), 10) 1)
Mechanical grinding method	Pour fused polyamide on a disc rapidly rotated, and splash it to get fine particles.	11)
Polymerization method	Polymerize monomers in solvent directly, and disperse the reacted polyamide as fine particles.	4), 5), 12)

powder of relatively even particle size. **Table 3** shows existing manufacturing methods.

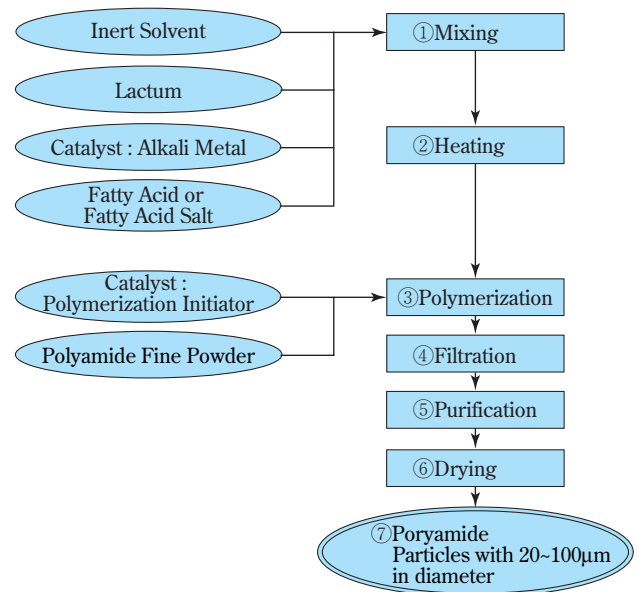
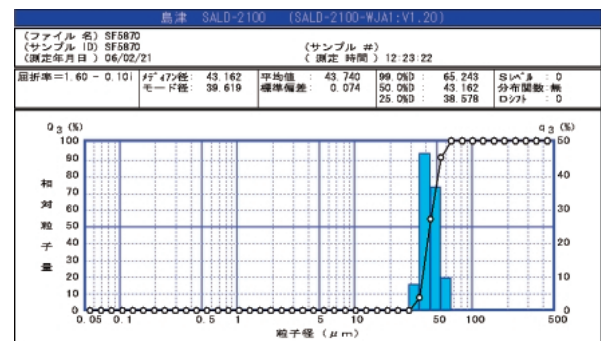
(2) Our Method for Manufacturing Larger Particle Size (20–100 μm) Spherical Polyamide Particles

As a result of our research, we have developed an excellent method of synthesizing spherical polyamide particles having both an average particle size of 20–100 μm and narrow particle size distribution. This new method is shown in **Fig. 9** and **10**. Lactam is polymerized under the presence of spherical polyamide fine powder serving as seed in the inactive solvent. The seed spherical polyamide powder can be produced through the procedures described in the previous section entitled “Our Manufacturing Method for Spherical Polyamide Fine Powder.” Thus, the desired larger particle size polyamide particles were obtained by adding a polymerization initiator and spherical polyamide fine powder seed to the process described above (number 3 of **Fig. 2**) when the temperature of the reaction liquid reached the melting point of the polyamide resin.¹³⁾ **Fig. 11** shows a scanning electron microscope photograph of the polyamide particles manufactured by our method. **Fig. 12** shows its particle size distribution.

As the polyamide particles manufactured through

**Fig. 9** Outline of the process

this method have a spherical shape and a narrow particle size distribution, we expect to utilize them in molding materials, cosmetic components, surface-treating agents, etc.

**Fig. 10** Manufacturing process of polyamide particles with 20 to 100 μm in diameter**Fig. 11** Spherical polyamide particles (scanning electron microscope)**Fig. 12** Particle size distribution of spherical polyamide particles with 20 to 100 μm in diameter

Conclusion

In this paper we have described our method for manufacturing spherical polyamide fine powder for various applications. Our production process and products are not only used domestically; they have also been exported into the Korean market through SH Chemical Co., Ltd. and we intend to continue expanding into broader international markets. We have recently established a manufacturing method for spherical polyamide particles having large particle size, and are currently researching silicon treated polyamide fine powder in the interest of increasing our range of available products and technologies. Our polyamide business can be expected to thrive.

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