Grinding and Dispersion Equipment For Nano Scale Applications

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INTRODUCTION

Ever since Tokyo University of Science professor Norio Taniguchi coined the term, “nano-technology” in 1974, we have heard much about nanoparticles and what can be done with them. What has received less attention is the material science of reducing particles to nano size, and the machines and processes that achieve that result. This article will discuss this facet of nanotechnology and, the author hopes, provide some insight into efficient and repeatable methods of particle reduction.

Many industries and markets have benefited from advances in nanotechnology, and the ink industry is certainly among them. The quality of printing inks, inkjet inks, pigments and dyes continues to increase as smaller and smaller particles contribute to greater color saturation, consistency, and stability.

Most pigments used in inks and coatings have a primary particle size from at least 0.02 microns (μm), or 20 nanometers, up to 200 nanometers. There are certain materials, like carbon black or ultrafine titanium dioxide, that begin as nanoparticles but become agglomerated during the manufacturing process or in storage. The goal is to disperse these particles to their primary particle size.

For this article, we will assume that the desired particle size is less than 200 nanometers. The question we will address is: What equipment most effectively grinds and disperses particles to less than 200 nanometers, and how does it work?

PRODUCING NANOPARTICLES: BOTTOM-UP OR TOP-DOWN

Two basic process types are presently used to produce nanoparticles: one is known as “bottom-up” and the other is called “top-down.” Bottom-up processes may begin with either a gas or a liquid, and the desired particles are extracted or fabricated by means of evaporation, precipitation, or the action of various solvents. The top-down process consists of grinding or dispersing solids or suspended particles to specific size distributions by controlling shear force, impact rate of the grinding media, and other factors. This article addresses the top-down process because of Netzsch’s expertise in the development and production of grinding and dispersing equipment.

With the top-down process, the aim of the operation must be defined before beginning: Is it to deagglomerate nanoparticles that already exist but are “stuck together,” or is it to produce nanoparticles by reducing larger primary particles? The first involves separating larger particles into smaller units; the second involves breaking larger particles into smaller ones.

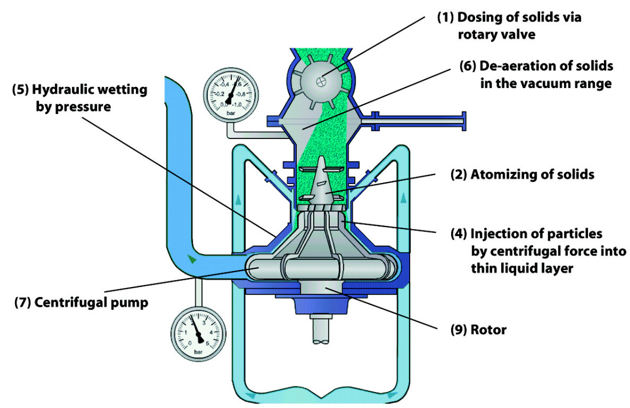


Figure 1 –
Process stages in the Netzsch PSI-Mix inline disperser

In both operations, it is important to know what effect the separating or breaking-up may have on the integrity of the particles. In deagglomeration, the separation process may destroy particle morphology or the coating (if any) that covers the primary particles, because they may not break away “clean” as the agglomerates are dismantled. When reducing large primary particles to smaller particle size, the grinding operation will, because of the nature of the process, destroy particle morphology and any coating that may be present.

DISPERSION EQUIPMENT – A NEW IDEA

An ideal dispersion is achieved when finely dispersed powders come in contact with a large liquid surface and are wetted under shearing. At optimum, the wet surface equals the specific dry surface of the particles before dispersion begins.

NSTI-Nanotech 2007, www.nsti.org, ISBN 1420063766 Vol. 4, 2007

The barrier has always been that, because of surface forces, dry solid particles with a fineness of less than 10µm form extremely cohesive agglomerates with interspaces that are filled with air. Optimum dispersion must overcome the linkage forces between particles and replace the entrained air with binding agent solution. Until recently, the effort to achieve this objective had been stalled for decades, but one recent innovation offers a significant improvement to the process.

The Netzsch PSI-Mix inline disperser mixes fine powders with liquids by creating a vacuum that causes the capillary air in solid agglomerates to expand, breaking them up through internal gas expansion. A cutting rotor boosts the distribution of solid particles as they move into the acceleration chamber. The mixing and wetting occurs in the compression zone where liquid is forced into the capillary paths of the agglomerates.

Figure 1 shows details of the process. The rotary valve (1) attached to the solids feeding station seals off the dispersion chamber from the atmosphere and doses the powder. In the feeding tunnel (6) that is under vacuum, the dry agglomerate is de-aerated and fed to the atomizer (2). The vacuum in the chamber causes the capillary air in the solid agglomerates to expand, and this internal gas expansion breaks apart the agglomerates. The vacuum is produced by a hydrocyclone effect, similar in concept to a liquid ring vacuum pump.

The pump (7) transports a liquid stream tangentially to a ring-shaped acceleration chamber where it is hydraulically accelerated into rotation. A “free-falling liquid curtain” is created and leveled by centrifugal forces. After about 100 mm, this liquid layer merges with the rotor to form a seal, and then is discharged at high speed.

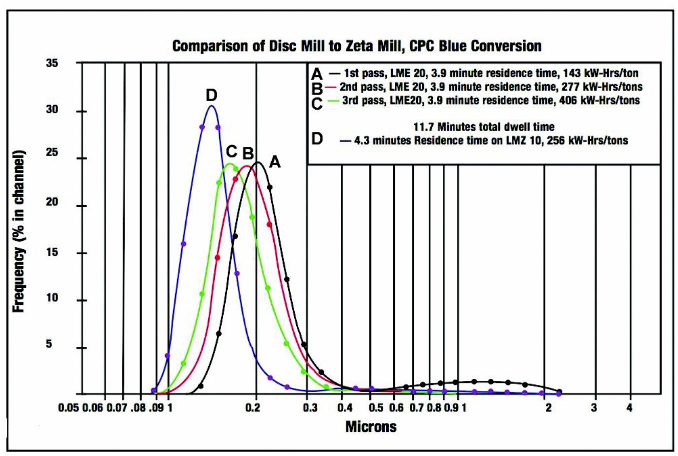
The finely atomized solids falling from above are spun towards the outside by the rotor (9) and onto the liquid layer. Wetting occurs during the immersion of the individual solids (4) and is assisted by the immediate increase in pressure (7). Another aid to optimum wetting is the quickly flowing liquid, which creates a surface area of more than two square meters per second. Creating this large liquid surface in relation to the specific surface of the atomized solid agglomerates is the essential principle of the PSI-Mix.

BEAD MILLS, GRINDING AND PARTICLE SIZE CONTROL

There are two types of bead mill that are effective in grinding to the nano range, but we favor the high-energy pin mill over the disc mill for a number of reasons. First, because a 20-liter disc mill has 25 or 30 hp, as does a 10-liter pin mill, which makes the lower-capacity pin mill capable of running at higher tip speeds. Higher tip speeds increase the centrifugal compression of the media, which decreases the gaps between beads. The result is an increased filtration effect and a tighter, finer particle size distribution.

The second point in favor of the pin mill is that the higher-capacity disc mill requires a larger volume of grinding media, which increases the likelihood of product contamination. Also, charging a 20-liter mill with 125µm YTZP (yttria tetragonal zirconia polycrystals) beads would cost around $43,000 – about the same price as the mill.

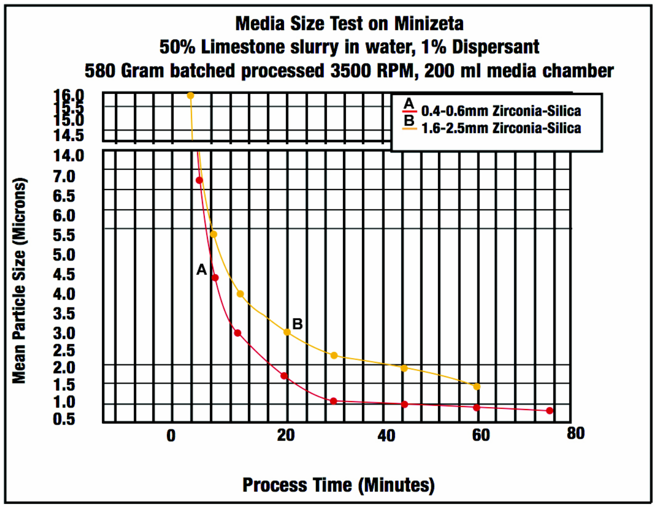
Graph 1 illustrates the increase in grinding efficiency and bead compression of the high-energy pin mill while grinding phthalo blue pigment. The same slurry is processed using 250µm steel beads in a disc mill and a pin mill. Three passes through the disc mill at a total residence time of 11.7 minutes and a specific energy consumption (Espec) of 406 kilowatt hours per ton do not produce as fine a particle size as circulation grinding on a pin mill at 4.3 minutes of residence time and 256 kWhrs/ton Espec. The pin mill’s larger separation system allows much higher flow rates than the disc mill.



Graph 1:
Disc mill vs. Zeta mill, grinding phthalo blue pigment

Unlike deagglomeration, in which primary particle size is already largely determined, grinding brings into play a number of variables that all have some effect on final particle size. Lab tests show that the particle size achieved from a bead mill is a direct function of the media size used in grinding. One rule of thumb is that the average particle size quickly achievable in a bead mill is about 1/1000th the size of the grinding media. Graph 2 illustrates this point:

We see that rapid particle size reduction occurs and the curve plateaus at around 0.5µm for the 0.5mm nominal media, and the curve starts to plateau around 1.5 to 2µm for the 2mm nominal media.



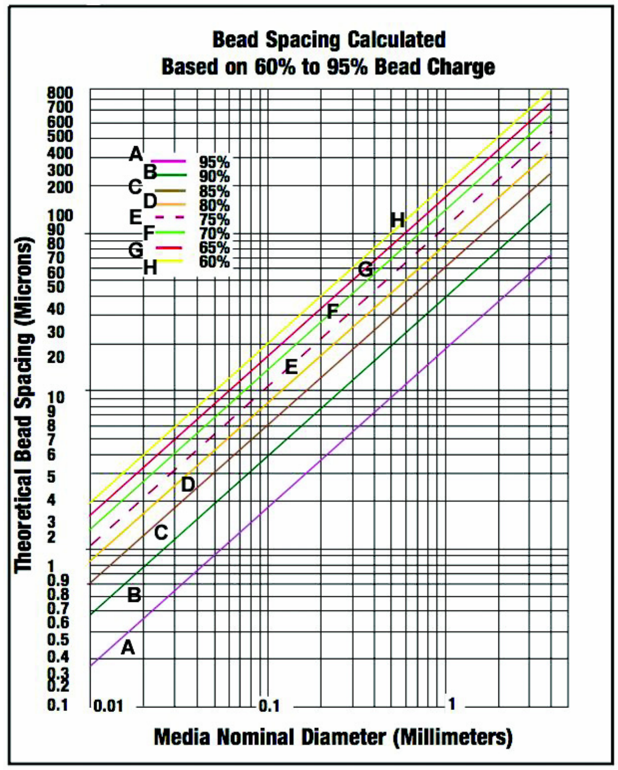
Graph 2:
Two different media sizes in Mini-Zeta, grinding limestone slurry

Another factor that affects final particle size in the grinding process is bead charge. ("Bead charge" indicates the percent of total volume of the material in the grinding chamber that is occupied by the grinding media) Graph 3 shows the calculated interstitial space between grinding media at various charge levels. For example, if a 2mm bead is used at 60 percent bead charge, the calculated space is approximately 400µm. If we use 100µm beads at a 95 percent bead charge, the space is about 1.5µm. As might be expected, tighter bead spacing results in higher filtration, because the frequency of contact between particles and grinding media increases as the gaps between them narrow.

The primary challenge in using small media at a high flow rate in a bead mill is bead separation – removing the grinding media from the final product. In the "classic" bead mill design, the beads are filtered from a slurry using some type of screen inserted into the chamber or mounted in the end or wall of the chamber. The main shortcoming of this design is that the screen often becomes blocked with layers of media, pressure in the vessel rises to an unacceptable level, and the overpressure safety device shuts down the mill.

In the modern bead mill, like Netzsch's ZETA system, removing the grinding media from the slurry is achieved by centrifugal separation. This method is far more efficient, and allows continuous operation of the mill. We achieve this by making sure that the separation force created by the centrifuging of the rotor exceeds the flow force of the product traveling through the mill. This concept is covered in US patent #4,620,673, and its efficacy is attested to by the more than 1,000 Zeta machines installed worldwide.

Bead density is also very important for efficient media separation. High viscosity slurries require beads of greater mass to increase the centrifuging force and overcome the drag force of the product flow. For example, using a 1mm YTZP bead that has a density of 6 gm/cm3 will more than double the separation force created by 1mm glass bead with a density of 2.6 gm/cm3, given a constant rotor speed.



Graph 3:
Interstitial space between grinding media at various bead charge levels

Screen open surface area is another key issue. For example, a 20-liter disc mill using a 100µm screen has about 12 cm2 screen open surface area, or about the same open surface area as a 1" pipe. The 10-liter pin mill has about 30 cm2 open surface area, or about the same area as a 2" pipe.

To synopsize, we highly recommend the following features when selecting a mill for efficient grinding of materials to the nano range:

- Low mill volume with high energy input for high rotor speed
- Low volume of media required
- Large separation system
- High centrifugal force for effective bead separation
- Greater screen open surface area for reduction in flow-through velocity
- Low length-to-diameter ratio
- Reduction in hydraulic compression
- Lower drag force on media

One more consideration – Input power is almost completely transformed into heat, so there must be a cooling mechanism in place to ensure that the temperature of the product does not exceed the recommended maximum.

SUMMARY

When dispersing nanoparticles, a fully enclosed process chamber promotes safe handling of very low density powders and solids. Other important considerations include a good premixing system for initial wetting, and proper formulation, not only for particle stabilization, but to control viscosity to allow efficient bead separation. In the dispersion process, lower density beads might be the better choice of media, to prevent breaking particles beyond their primary size and destroying surface coating. Conversely, grinding may require high-density beads for particle fracturing.

Grinding can be a very cost-effective means of particle reduction. Production costs per kilogram are typically in the \$0.02 - \$0.10 range, which compares favorably to chemical processes. Grinding equipment also costs less to install and operate than most chemical processes. Also, with fewer chemicals present in the process, there is less potential for hazardous waste, so the workplace environment is safer.

In the interest of full disclosure, we know of two disadvantages to the use of bead mills in grinding operations. First, minute particles may break away from some grinding media and contaminate some products. The mass deposited in the product may be as low as one part per million, or approach 1,000 parts per million, but the potential exists. Second, some materials simply cannot be ground by a bead mill, given the current technology. Polymers like PTFE and Nylon, for example, pose challenges because they are not “friable.” Particle reduction for materials like these is a very expensive venture, as it requires some sort of cryogenic process.

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