This article explains how nanoparticles are produced in suspension using an agitator bead mill. It also describes methods of separating the resulting nanoparticles from the grinding media.

In recent years, more companies have begun using nanoparticles — that is, particles that are smaller than 200 nanometers, sometimes a mere fraction of that — in various applications. In fact, the list of products that benefit from nanosize particles is large and growing each day. For example:

- Crop protection companies are now manufacturing herbicides and other products in the range of 10 to 100 nanometers. A nanoparticle herbicide contains trillions of particles of active ingredient per liter. The increased surface area resulting from the particle fineness improves the product’s potency, accelerates the plant’s absorption of the product, and can significantly reduce the amount of active ingredient needed for the same effectiveness, thereby reducing potential toxicity and negative environmental effects.

- Active pharmaceutical ingredients also benefit from reduction to nanosize. Many potentially effective drug discoveries are abandoned because the ingredients are insoluble. By reducing the particles to nanosize, we can dramatically increase their surface area and solubility. Other known benefits are improved dissolution rate, increased bioavailability, and higher activity, leading to lower dosages and a lower risk of patient side effects.

- Another example is the growing field of reusable energy products, especially lithium ion batteries. Battery manufacturers are always looking to increase overall efficiency by improving conductivity, lengthening charge life, and shortening recharge time. All three are needed to make a commercially viable battery for advanced technologies like cell phones, laptops, and cars. Second-generation lithium ion batteries require a precise and repeatable manufacturing approach that relies on nanotechnology advances. Anode and cathode coatings made with nanoparticles help manufacturers produce a better-performing, more efficient battery.

The agitator bead mill

Reducing particles to nanosize involves one or both of these processes: mild dispersion (disaggregating or deagglomerating — that is, separating particles from one another without changing their primary size or structure) and real comminution (reducing particles below their primary size by grinding and fracturing). Reducing particles to nanosize is challenging and is most efficiently done with the coarse particles in a suspension. Not every mill can do this job. The mill commonly used to reliably reduce coarse particles to nanosize — whether by dispersion or comminution — is the agitator bead mill, as shown in Figure 1.

![Figure 1](image-url)
An agitator bead mill consists of a grinding chamber, an agitator consisting of a rotating shaft equipped with agitator elements, a drive motor, and a media separator (located at the mill’s discharge). The agitator elements are typically disks or pins. The grinding chamber is filled with 9-micrometer to 30-micron grinding media up to 95 percent of the mill volume. The grinding media can be made from materials such as stainless steel and glass as well as advanced ceramic materials such as yttrium-stabilized zirconium oxide and cerium-stabilized zirconium oxide.

In operation, the suspension containing the coarse material is pumped into the mill from a feed tank. The material flows into the grinding chamber and downward into the spaces between the grinding media. As the agitator rotates (at typical tip speeds between 4 and 20 m/s), the media move around the chamber and impart compression and shear forces to the suspended particles, fracturing or dispersing them. Particles reduced to the required fineness discharge through the media separator to a product tank.

The milling process is conducted in one of four modes, as shown in Figure 2. In the single-pass mode the suspension passes through the mill once and is collected in a product tank (Figure 2a). In the pendular (or multipass) mode the suspension passes through the same mill multiple times, traveling from feed tank to product tank repeatedly (Figure 2b). In the cascade mode the suspension passes through two connected mills (Figure 2c). In the circulation mode the suspension can be continuously pumped through the mill multiple times, each with a short residence time, until the desired particle size is reached (Figure 2d).

Each mode has advantages and disadvantages. The main advantage of the single-pass mode is simplicity for those applications where the end particle size can be reached in a single pass. However, there’s no guarantee that every particle passes through the mill’s highest-energy zones; therefore the final particle size distribution (PSD) may be wider than desired.

The pendular mode ensures that more of the particles pass through the mill’s highest-energy zones. Using a high flowrate and two or more passes, the required particle size and a steeper PSD may be reached with a lower total residence time. This mode’s higher flowrate also results in less material heating, but the material is handled two or more times, which is undesirable in some applications.

The cascade mode allows the use of two mills with different grinding media sizes — a larger size in the first mill takes a coarse feed material to a size that allows the next mill to use finer media to reach the final desired particle size. In this way two-step grinding is accomplished in a single process.
The circulation mode’s high flow rate also gives the material a short residence time, keeping both the material and the mill cooler and allowing accurate control of the material temperature.

**Media separator types**

Once the particles have reached the desired size, they’re discharged from the mill while being separated from the grinding media. The media separator can be any of several types: a rotating separator gap, a screen cartridge, a classifying rotor, or either of two variations of the classifier rotor.

The simplest is the *rotating separator gap* (Figure 3a), which uses an annular gap between a rotating inner ring and a stationary outer ring made from hard ceramic materials. The gap is smaller than the grinding media diameter, allowing the product to flow through the gap but retaining the grinding media in the mill.

The *screen cartridge* is normally a stationary screen located at the mill outlet. The screen’s openings are smaller than the grinding media, so the product flows through the screen, but the media is retained in the mill.

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**Figure 3**

**Media separators**

- **a. Rotating separator gap**
- **b. Classifying rotor (stationary screen)**
- **c. Classifying rotor (rotating screen)**
- **d. Screenless classifying rotor (open dynamic classifier)**
The classifying rotor, also called a dynamic classifying cartridge (Figure 3b), is attached to the mill’s rotor and contains a stationary slotted screen. The classifying rotor uses centrifugal force and is similar to an air classifier. The mill agitator disk nearest the mill’s outlet side pumps the media back toward the mill’s inlet side, while the centrifugal forces generated by the revolving rotor and disks force the media away from the outlet. The slotted screen prevents media from exiting the mill during the rotor’s startup, before it reaches operating speed, and on shutdown, while it decelerates. The screen also prevents broken media, which may be light enough to be carried by the suspension during normal operation, from exiting the mill. The screen opening size depends on the grinding media size: Normally each screen opening is one-half to one-third the media diameter. Therefore, if the media size is changed, the screen must also be changed.

With very small grinding media, the separation process becomes more critical. Some background: As a rule of thumb, the final nanoparticle median size \(D_{50}\) will be approximately \(1/1,000\) the media diameter. So, to reach a median particle size of 100 nanometers, a media diameter of 100 microns is used. Media as small as 30 microns is sometimes used to reach a median particle size less than 30 nanometers.

When using media smaller than 200 microns coupled with a suspension whose viscosity may increase as the particles are dispersed or comminuted, the media can be transported all the way to the separator screen by the suspension’s flow forces though the mill, causing screen blockage. In such a case, the best media separator is the classifying rotor with a stationary screen. Generally, the centrifugal forces it generates ensure media separation from the suspension.

One classifying rotor variation further increases the centrifugal forces by rotating the separator screen with the agitator shaft (Figure 3c). This guarantees media separation even if the viscosity rises during the dispersion or comminution process. It’s especially useful when using the very fine media and low agitator tip speeds typical in mild dispersion processes.

Another classifying rotor variation can be used for low-viscosity suspensions, in which grinding media is less likely to be transported with the suspension. This separator is a screenless classifying rotor, known as an open dynamic classifier (Figure 3d). It has several obvious advantages: variable media sizes can be used without having to change the screen size; grinding media size reduction from wear during long operation isn’t a problem; screen plugging is impossible; significantly lower pressure increase in the mill leads to higher throughput rates; and the device is easily disassembled and cleaned.

Mild dispersion versus real comminution

The bead mill reduces material to nanoparticles in one of two ways — mild dispersion and real comminution. The difference between mild dispersion (disaggregation or deagglomeration) and real comminution (reducing particles below their primary particle size) is a matter of energy input. This energy input is largely a function of the peripheral speed of the agitator shaft that drives the grinding media. The media diameter and density are also factors.

In mild dispersion, particle strings and agglomerates are merely separated into discrete particles, dispersed by lower shear, pressure, and impact forces. The surface air is also removed and the particle surface is wetted. Typical agitator tip speeds are in the range of 4 to 6 m/s. Selection of the smallest and densest media is based on the media separator used and the lowest tip speed that will provide effective media separation. The tip speed can be increased as long as the specific energy (kilowatts per kilogram) doesn’t increase.

In real comminution, the primary particles are ground in a liquid phase by high shearing, pressure, and impact forces. Typically the agitator tip speed is in the range of 13 to 16 m/s. Grinding media size and density selection is based on optimal efficiency. The tip speed is maximized for motor power and product temperature requirements. Particles are deagglomerated but also crushed, which can destroy the particle structure.

In both processes appropriate additives are used to stabilize the suspension and prevent reagglomeration.

Mild dispersion and real comminution — practical examples

Dispersing titanium oxide. Mild dispersion techniques were compared in tests using titanium dioxide (TiO\(_2\)). \(^1\) The objective was to deagglomerate the TiO\(_2\), without degrading the particle surface as measured by X-ray diffraction analysis. Since the raw material’s primary particle size was already 6 nanometers, further size reduction wasn’t a consideration. The agglomerated feed material’s size was 0.6 microns. Agitator tip speeds of 4, 6, 10 and 13 m/s were compared, using 0.1-millimeter-diameter yttrium-stabilized zirconium oxide grinding media. The tests were conducted in an agitator bead mill in circulation mode with 3-liter product batches.

Figure 4 shows how the median particle size changed as specific energy input and circulation time changed. In both comparisons, the lower tip speed proved to be more effective in providing a finer dispersion at a lower specific energy input.
More important, however, is the advantage the lower tip speed gives in the material properties. X-ray diffraction analysis showed that after mild dispersion the TiO₂ maintained quality much closer to the raw material, while the sample processed at high tip speed was significantly different (Figure 5).

**Real comminution of titanium dioxide.** In another study, of functional coating production, titanium dioxide with the particle size distribution $D_{50} \sim 200$ nanometers and $D_{99} \sim 375$ nanometers was to be ground as fine as possible. The TiO₂ was in a water-based suspension with a solids content of 48.5 percent by weight, stabilized by an appropriate additive. Two grinding tests were carried out in a 4-liter agitator bead mill.

During test A, 0.2- to 0.3-millimeter-diameter yttrium-stabilized zirconium oxide grinding media was used. The mill used a classifying rotor with a rotating screen to separate the nanoparticles from the grinding media. Test B was run with 0.1-millimeter-diameter yttrium-stabilized zirconium oxide grinding media. To prevent a pressure increase in the mill, the open dynamic classifier separator was used. All other operating parameters were constant, with a 12-m/s tip speed and 420-kg/h throughput. The test results are shown in Figure 6.

During test A, particle sizes $D_{50} \sim 60$ nanometers, $D_{90} \sim 92$ nanometers, and $D_{99} \sim 125$ nanometers were obtained after a specific energy input of 1.83 kWh/kg and a grinding time of 6 hours. By using smaller grinding media (test B), significantly better results were obtained with one-third of the specific energy input (0.61 kWh/kg) and after a grinding time of only 2.5 hours. The particle size results were $D_{50} \sim 45$ nanometers, $D_{90} \sim 76$ nanometers, and $D_{99} \sim 110$ nanometers.

**Conclusion and outlook**

These results aren’t atypical. In the case of TiO₂ dispersion, mild dispersion at a low tip speed was more effective and preserved the material’s desirable characteristics. In the case of real comminution of TiO₂, smaller-diameter grinding media provided much better results in terms of specific energy and processing time.

As the trend toward finer products continues, the challenge is to use smaller grinding media and techniques suited to the application, whether mild dispersion or real comminution. As the previous examples demonstrate, it’s not always a matter of using the highest energy input, largest media, or highest tip speeds. Indeed, using more energy than necessary results in unnecessary wear on the mill and grinding media, increasing costs and downtime, and decreasing product quality by adding contamination.
Mill designs will continue to evolve to meet the demands of the bulk solids industry. Process engineers should consult with the mill manufacturer’s engineers early in the process. Often this will involve conducting product trials at the mill manufacturer’s facility to learn about mill capabilities and limitations. This relationship allows the mill manufacturer to tailor equipment to the user’s application.

Reference
1. Tests were conducted at a NETZSCH testing laboratory.

Figure 6
Effect of grinding media size on TiO₂ real comminution

For further reading
Find more information on this topic in articles listed under “Size reduction” and “Nanotechnology” in Powder and Bulk Engineering’s comprehensive article index (in the December 2010 issue and at PBE’s website, www.powderbulk.com) and in books available on the website at the PBE Bookstore. You can also purchase copies of past PBE articles at www.powderbulk.com.

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