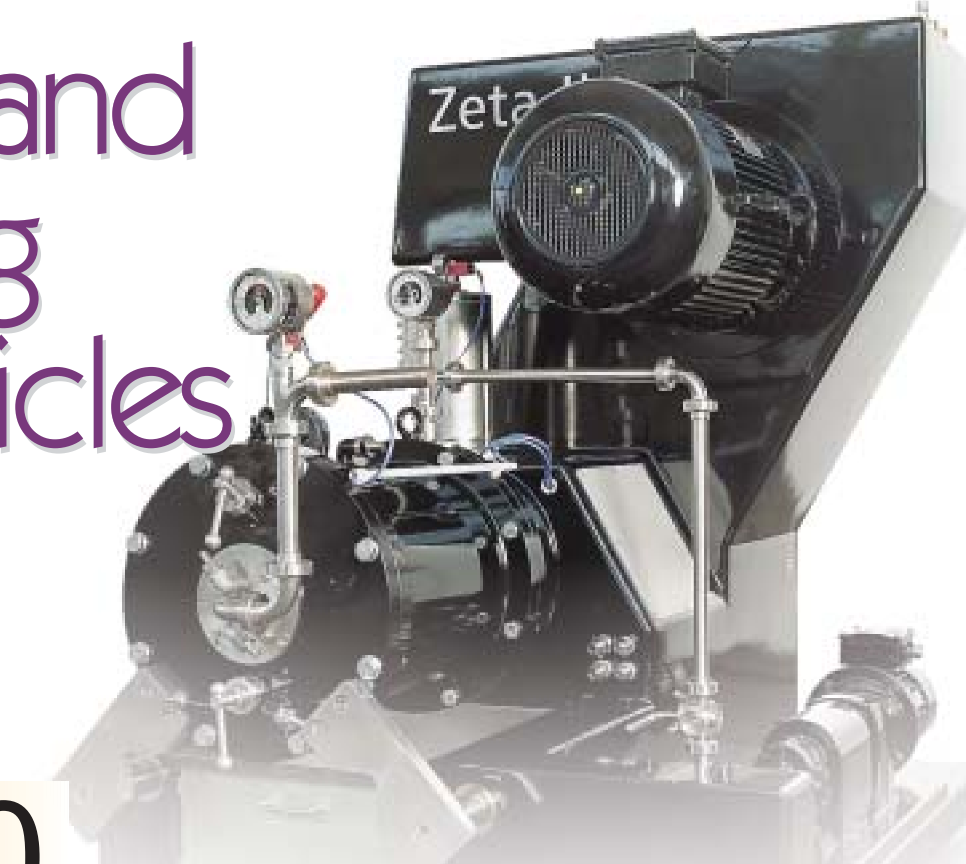
Grinding and Dispersing Nanoparticles



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Over the past few years we have observed an increase in the desire to use bead mills for grinding and dispersion of "nanoscale" particles. The objective of this paper is a general discussion of how this process works in a bead mill, the parameters required to successfully produce these nanoscale dispersions, and some experience in grinding or particle size reduction of solids to the nanoscale.

According to a report released by the National Science and Technology Council (NSTC), "Nanoscience and Nanotechnology generally refer to the world as it works on the nanometer scale, say, from one nanometer to several hundred nanometers."[1] If we interpret this to mean that the particle size referred to as a nanoparticle means something that ranges from a few nanometers up to 700 nanometers, most of the components currently processed on a bead mill fall into the area of nanotechnology.

Most pigments used in inks and coatings, for example, have primary particle size from at least 0.02 μm or 20 nanometers up to 200 nanometers. With the particle size analysis technology available today, we can easily learn that many operators of bead mills are grinding and dispersing their pigments into this range. Theodore Vernardakis establishes this point in his enlightening discussion of pigment dispersion in the *Coatings Technology Handbook*.[2] This section contains several electron micrographs of pigments, along with particle size analysis showing materials with mean particle size around 100-200 nanometers. For the sake of discussion, we will assume that the nanoparticles desired are less than 200-300 nanometers.

There are now and have been for some time materials available that are essentially nanoparticles. However these nanoparticles, like carbon black or ultrafine titanium

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dioxide, are agglomerated just by the nature of the manufacturing process or storage. The goal is to disperse these particles to their primary particle size. We will address the required operating conditions for a bead mill to grind and disperse particles to less than 200 nanometers and the requirements for grinding large particles to a nanometer range.

PARTICLE SIZE CONTROL

The particle size achieved from a bead mill is a direct function of the media size used for the grinding process. The average particle size that can be achieved quickly in a bead mill is about 1/1000 the size of the grinding media. *Figure* 1 illustrates this point. In this experiment we processed limestone using two different media sizes: 0.4-0.6 mm zirconia-silica grinding media (SAZ) and 1.6–2.5 mm SAZ. We can see that rapid particle size reduction occurs and the curve plateaus at around 0.5 µm for the 0.5 nominal media and the curve starts to plateau around 1.5 to 2 µm for the 2 mm nominal media. Many other examples could be given, but this simple curve suffices to demonstrate the idea.

CURRENT INDUSTRIAL APPLICATIONS

The smallest bead size regularly used on a commercial basis is 200-300 µm. The applications of this media are primarily in the pigment manufacturing and ink industry for fine grinding and dispersion of pigments such as phthalocyanine blue and green and carbon black. The uses for these inks are in the ink jet market, textile inks, etc. As will be seen, there should be more interest in the coatings industry to quickly achieve maximum color development and transparency. Some other applications are pharmaceutical materials, ceramic materials for electronics applications, and dyes. Most of the work in this area is proprietary, but a lot of information can be obtained by searching patents. For example, U.S. patent 5,500,331 discusses the use of media less than 100 µm to grind various dyes.[3] In this example, various bead sizes are used to grind a dye to nanometer particle size. At least in this case, using beads smaller than 50 µm does not have as great an effect on the particle size reduction as the 50- and 75-µm beads. This indicates that at some point media size and feed particle size become important points. This is true for any bead milling application. Normally for efficient grinding and dispersion, the feed particle size should have a d_{90} (90% of the particles are less than) 1/10 the media size. For example, for 100-µm beads, the d_{90} should be about 10 microns (see *Table* 1).

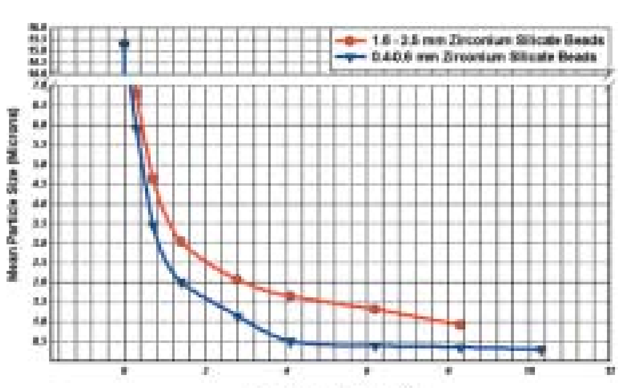


Figure 1—Media size test using Minizeta bead mil: 50% limestone slurry in water, 1% dispersant, 580 gram batched process, 3500 RPM, 200 ml media charge.

Table 1—Particle Size Related to Bead Diameter

Bead Size	*Particle Size (nanometers)*
No media	92.4
5 µm	86.4
25 µm	90.2
50 µm	56.5
75 µm	63.7
450 µm	80.6

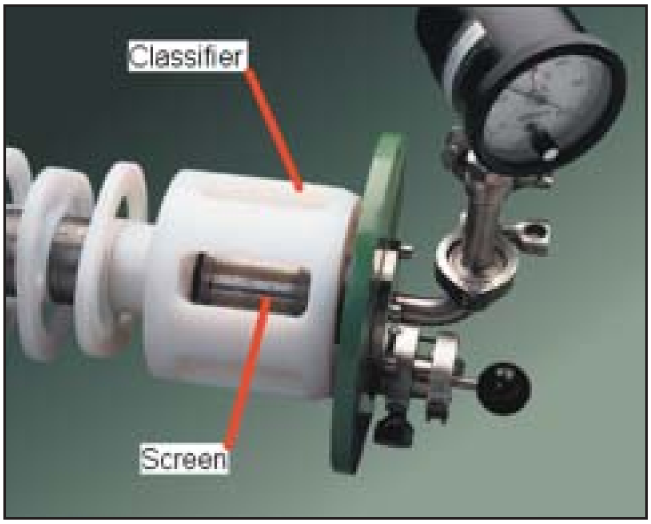
In these markets in North America, we know of at least 50 Netzsch bead mills operating with the 200-µm media in either steel or ceramic material. Certainly other manufacturers are supplying machines into this field or trying to at least on the lab scale. These machines range from lab equipment up to 300 horsepower machines. Worldwide, we can probably double this figure again. This is a significant amount of capacity for this small media and this type of process. And this application will continue to grow. But how does it work, and what does a bead mill manufacturer need to consider for more efficient design?

BEAD SEPARATION PARAMETERS

What is the most important aspect of using small media? Getting the beads out of the slurry. It is fine to say that using very small beads grinds or disperses a particle to a very fine particle size, but after the grinding process, how do you separate such a fine particle from the slurry? How do you do this on a continuous basis? In the case of the modern bead mill, this process is achieved by centrifugal separation of the beads from the slurry.

Figure 2 shows a horizontal disc mill with a classifying rotor for separating the beads from the slurry. The beads are retained to the left, separation occurs at the discharge end of the machine by centrifugal force. This

Figure 2—Horizontal disc mill with classifying rotor.



concept is covered in U.S. patent 4,620,673.[4] If we were to rely on the classic bead mill design of filtering the beads from a slurry using some type of screen inserted into the chamber or mounted in the end or wall of the chamber, the immediate problem that will occur is the screen or filter will block with layer upon layer of media until the entire surface is completely blocked. At this point the pressure in the vessel will increase to an unacceptable level and the mill will shut down on the over pressure safety device.

The principle of efficient bead separation is based on centrifuging the media out of the slurry. This allows continuous operation of the mill, not a batch process. Centrifugal force is calculated by multiplying the square of the peripheral velocity of the rotor by the mass of the object at hand and dividing by the radius of the rotor. However, we also have to consider the mass flow rate of the product through the mill, i.e., there is balance that must occur, separation force by the centrifuging of the rotor must be greater than the flow force of the product travelling through the mill. The factors that affect the bead separation curve are:

- Product viscosity
- Product mass flow
- Product density
- Bead density
- Bead size and bead charge
- Rotor peripheral speed and geometry
- Separation system geometry

In practice the smallest bead size that can currently be separated on lab scale equipment is 30 μm. The limitations on separating grinding media by centrifuge force are:

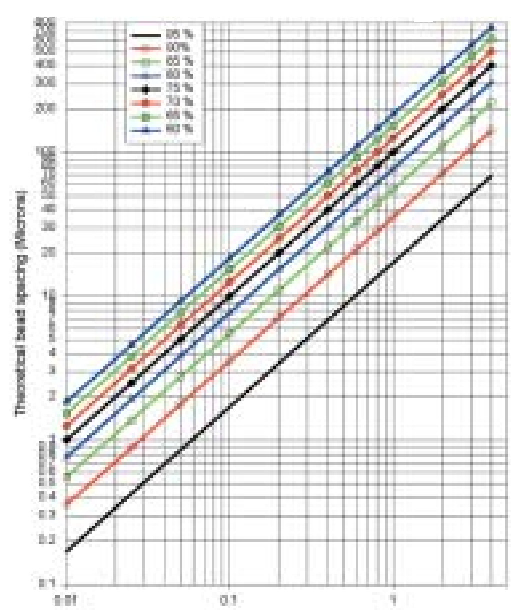
(1) PRODUCT VISCOSITY—If the material is very viscous two things happen to limit the separation. First, the power required to rotate the shaft is very high, or in other words, the power needed to agitate the media is high, limiting the speed of the mill, therefore limiting the separation system speed. The viscosity inside a bead mill is much higher than the apparent viscosity of the slurry being fed to the mill because of the addition of the grinding media as part of the slurry. Second, the high viscosity forces the media toward the discharge screen. The answer is simply to apply more power to the mill volume. However, this also requires some mechanical considerations; there is a limit to how much power can be applied to an existing shaft design.

(2) PRODUCT FLOW RATE—If the flow velocity is higher than the separation velocity, the beads are taken to the screen.

(3) PRODUCT DENSITY—If a high slurry density is processed, this also has a counter effect to the centrifugal force of the separator.

(4) **Bead Size and Density**—Centrifugal force is a function of the mass multiplied by the square of the velocity. For example, if we use a 1-mm bead that has a density of 2.6 grams per cubic centimeter like glass media and a constant rotor speed we can more than double the separation force by using an yttrium stabilized zirconium oxide (YTZP) grinding media that has a density of 6 or quadruple the separation force by using a tungsten carbide (WC) media with a density of 14. This is why we recommend using high-density beads in high viscosity slurries. We need the mass of the bead to increase the centrifuging force to overcome the drag force

Figure 3—Bead spacing calculated based on 60-95% bead charge.



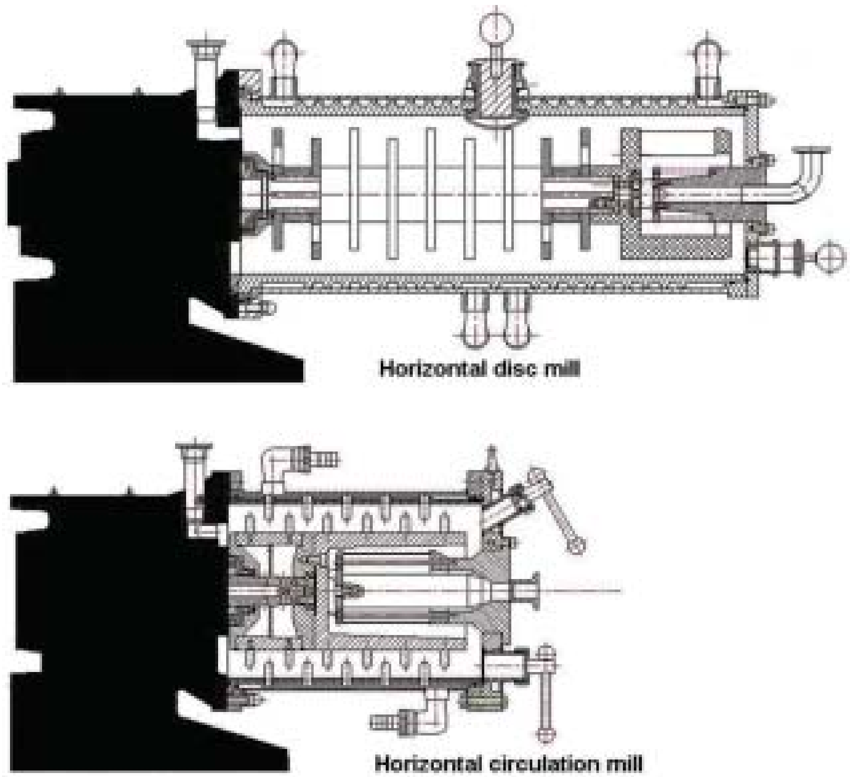
of the product flow. Now if we decrease the bead size the mass of the bead decreases as well by a factor of 8. So if we are using a 0.6-mm glass bead, calculations show this bead weighs around 2.3 milligrams. If we decide that 0.4-mm beads are going to grind better, we might want to consider using steel beads, because 0.4-mm steel weighs about 2 milligrams.

(5) BEAD CHARGE AND POROSITY—This is an important consideration when we think about some of the other operational aspects of a bead mill. *Figure* 3 shows the calculated interstitial space between the grinding media at various charge levels. For example, if a 2-mm bead is used at 60% bead charge, the calculated space is around 400 μm. If we use 100 μm beads at a 95% bead charge the space is about 1.5 μm. What we have to consider for bead separation and flow is the effect of the hydraulic pressure due to resistance to flow created by the tighter spacing or filtering effect of the smaller grinding media and higher charge.

(6) AGITATOR SPEED—A fast rotor speed, or peripheral speed, increases the centrifugal force, but there are limitations to how fast the rotor can turn. These considerations are the installed power, wear, and the mechanical seal. These are all areas that can be addressed through engineering modifications, but these changes have engineering costs.

(7) DIMENSIONS OF THE SEPARATION SYSTEM—This includes the distance between the screen and rotor and the length of the screen. The design of the screen is critical; normal screen designs do not have the open surface area necessary to allow flow through the mill without creating a high velocity through the screen slots. High velocities at the screen slot usually result in poor bead separation and eventually screen blocking. The slots have to be precise in this application, otherwise they are blocked.

Figure 4—Comparison of horizontal disc mill (upper) and high energy pin mill (lower).



SELECTING A BEAD MILL FOR SMALL MEDIA

Considering the above points, how do we select the right mill design? There are essentially two types of bead mill that can use small media: a disc mill and a high-energy pin mill. Our view is that the better machine for using small media is the high-energy pin mill.

Horizontal disc mills, which have been the predominant type of mill used in industry in the past few years, have a limitation in this application due to the large volume of media required in the mill. The large volume of media requires tremendous power at high rotor speeds. This is a function of the viscosity of the bead/slurry dispersion in the mill. The high contamination and cost associated with a large media volume have to be considered. If the product has to pass through a large media volume, this increases the likelihood of contamination. To charge a 20-liter mill with 125 micron YTZP beads would cost around $43,000, about the same price as the mill.

Figure 4 shows a comparison between a horizontal disc mill and a high-energy pin mill. If we imagine the flow pattern through the disc mill, we can see that the long length or high length to diameter ratio would result in high resistance to flow. Disc mills typically have a length to diameter ratio of around 3:1.

The high volume of media required also results in a high filtration effect, and therefore, a high drag force to the separation system.

Figure 5—Comparison of disc mill to high energy pin mill. CPC blue conversion.

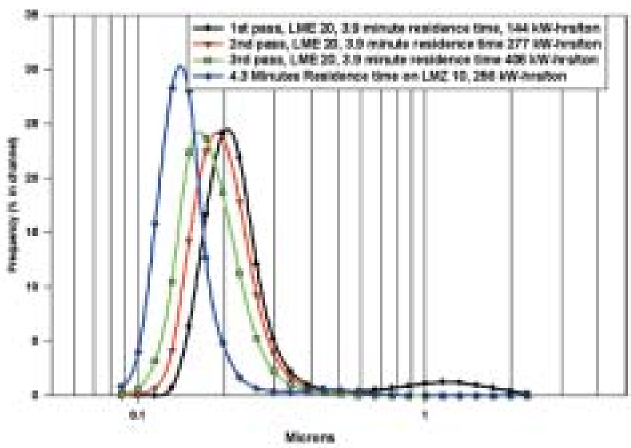
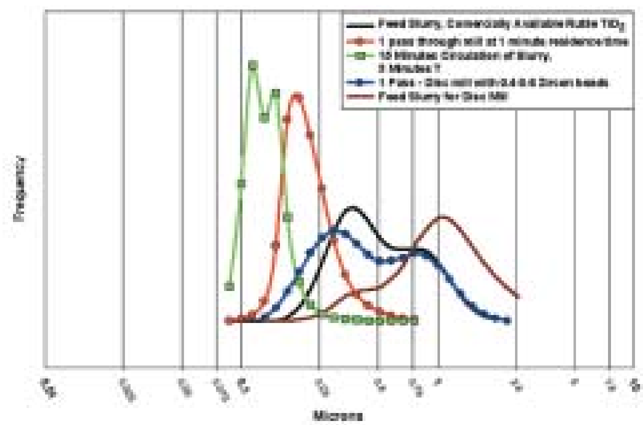


Figure 6—Titanium dioxide grinding: 40% solids/2% dispersant, 100-µm tungsten carbide spheres.



The size of the separation system is designed for using larger media, 0.6 mm and above. The open surface area available and the diameter of the rotor are not optimized for very small beads. Basically what happens is that the flow velocity through the mill compacts the beads to the separation system, resulting in a slow process (20 or 30 min) of accumulating beads onto the screen. The mill then shuts down. The way to overcome this problem is to run slow flow rate. However this is a waste of efficiency and increases the contamination rate of the product with media.

The high-energy mill shown in *Figure* 4 has a lower length to diameter ratio, typically about 1.5:1, a larger diameter rotor, and larger separation system. The grinding zone is more defined by the use of the larger diameter rotor and the installation of shaft pegs or pins for media agitation. Approximately $^{2}/_{3}$ of the shaft length is used for bead separation. The product flow enters from the bearing housing end, flows through the grinding zone around the end of the shaft, and enters the screen area. The slots cut into the shaft centrifuge the beads out of the slurry. This separation flow of the grinding media results in a higher compression of the beads in the grinding zone. This means the packing of the media is much higher, and uniform through the grinding zone, than can be achieved in a disc agitator design. In a disc agitator design, the compression of the media in each grinding zone is a function of the rotor speed and the area near the edge of a disc.

An important consideration between these two machines is the fact that they both have the same installed horsepower, i.e., a 20-liter disc mill has 25 or 30 hp, while a 10-liter pin mill also has 25 or 30 hp. The higher energy input available on the pin mill means that we have the capability of running the machine at higher tip speeds required in the discussion on bead separation above. Also in the pin mill the higher tip speed increases the centrifugal compression of the media, decreasing the gaps between the beads, increasing the filtration effect, and therefore, resulting in tighter, finer particle size distribution.

Figure 5 illustrates the increase in grinding efficiency and bead compression. This is grinding phthalo blue pigment for ink. In this case we are processing the same slurry, using 250-µm steel grinding media in a disc mill and a pin mill. Three passes through the disc mill at a total residence time of 11.7 min, a specific energy consumption (E_{spec}) of 406 kilowatt-hours per ton does not produce as fine a particle size as circulation grinding on a pin mill at 4.3 min of residence time, 256 kW-hr/ton E_{spec}.

Because of the larger size of the separation system, we can have much higher flow rates through the pin mill versus the disc mill. This results in higher grinding efficiency, higher energy efficiency. We will not go into the benefits of high flow multiple pass grinding here; the theory and benefits of fast flow rates and multiple passes are well documented. Suffice it to say that high flow rates result in close to plug flow through the mill and therefore uniform particle size reduction.

Screen open surface area is another area for examination. For example, A 20-liter mill using a 100-µm screen has about 12 cm^2 screen open surface area, about the same open surface area as $1^{1}/_{2}$ in. pipe. But the 10-liter pin mill has about 30 cm^2 open surface area, or about the same area as a $2^{1}/_{2}$ in. pipe. Remember this is spread over a large number of 100-µm slots. The velocity through these slots is very high, so to reduce the velocity we need more slots—thus the requirement for a larger open surface area screen. The problem encountered with using even smaller media is the further reduction in open surface area, i.e., even higher velocity though the slots. A 100-µm wedgewire screen has an open surface area of about 7%; reducing to a 50-µm wedgewire screen basically reduces the open surface area to about 3.5%. Also the best tolerance the wedgewire screen manufacturer can provide is about 25 µm, so we have large slots up to 75 µm to 25 µm. We have found a source for screens that have greater open surface area for 100- and 60-µm slots, up to about 10-14%. The slots are precisely made to 60 and 100 µm. This has been one of the key solutions to this process. These screens are commercially available and have been for many years.

Scale up parameters are always very important. The advantage that we have in selecting a high energy pin mill for this application is that as the machines are scaled up the important parameters like constant energy input to mill volume is linear, the geometry of the agitator rotor and separation system are constant. A further point for reflection is that as the mills become larger, the rotor tip speed available is faster. This is due to certain mechanical limitations on small machines, but what we can say is that the larger machines are capable of running faster tip speeds than the lab mills. Fundamentally, it is clear why this must occur—the tip speed scale up consideration historically used may not provide the required speed to utilize the full power available on the production mill. Looking at various factors such as centrifugal force for separation and equivalent kinetic energy may provide a more accurate method to determine the correct tip speed for operating the production size mill.

To summarize the mill selection points we need the following features:

(1) Low mill volume with high energy input
—Low volume of media required
—High energy for high rotor speed

(2) Large separation system
—High centrifugal force
—Greater screen open surface area for reduction in flow through velocity

(3) Low length to diameter ratio
—Reduction in hydraulic compression
—Lower drag force on media

These features are currently available in high-energy pin mill design. So the question becomes, does this process work?

EXAMPLES OF BEAD MILLING WITH SMALL MEDIA

Figure 6 shows titanium dioxide dispersion. In this example the difference between 0.5-mm zircon beads and 0.1-mm tungsten carbide (WC) beads is shown. A coarser feed slurry is passed through the discs mill, and some particle size reduction occurs which is apparently good enough because this is used as the final product for manufacturing TiO_2. We then take this slurry and pass it once through a pin mill with 100-µm WC spheres. We can see dramatic difference in the particle size reduction compared to the larger beads in a disc mill, down to a mean size around 0.2 µm, which is about the desired range for TiO_2. When we processed longer by circulating, we saw further reduction, down to around 0.15 µm. This test was run to evaluate claims in patent 5,407,464[5] in which it is claimed that using WC beads will grind TiO_2 and various other mineral and organic powders to 100% less than 100 nanometers very rapidly. In comparison to the test described in the patent, the bead milling is much higher energy and more efficient. Although still not below 100 nanometers, there is significant particle size reduction. The process is much more efficient than using larger beads.

Figure 7 illustrates a test to grind a biocide to a nanometer size. We can see again in a typical grinding

Figure 7—Biocide grinding with 150-250 µm zircon media and 90 mm glass beads.

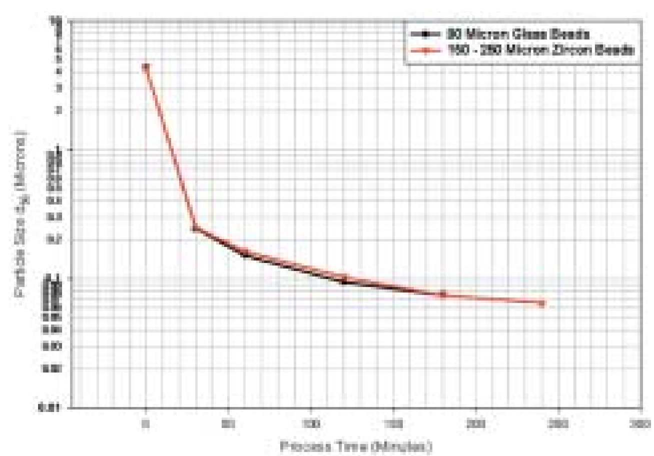


Figure 8—Pigment grinding with 0.3 mm and 0.125 mm YTZP beads.

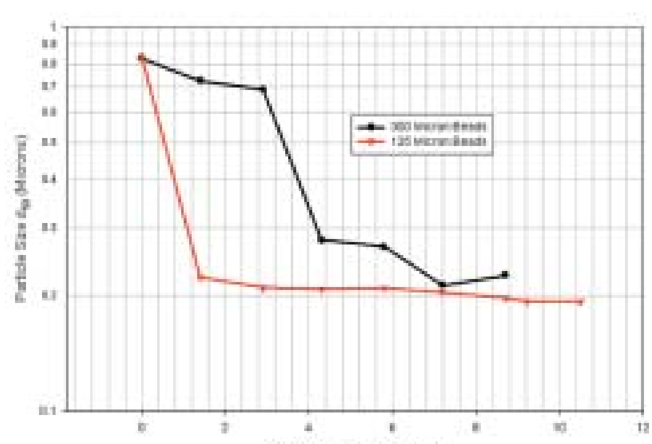
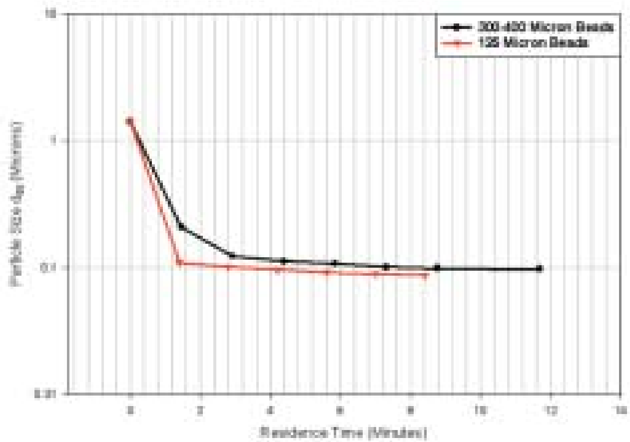


Figure 9—Alumina grinding with 0.3-0.4 mm zircon media and 0.125 mm YTZP beads.



curve rapid reduction to a 75 nanometer d_{50}, about 1/2000 the size of the grinding media, 0.15-0.25 mm SAZ in this case. Ninety micron glass beads appear to have slightly greater efficiency, producing at 65-nanometer d_{50}.

Figure 8 shows dispersion of a fairly hard grinding synthetic organic pigment. (We cannot discuss the pigment type or application in this case.) Product specifications were roughly 35% solids, viscosity was around 500 centipoise, with 6% dispersant on pigment solids. Flow-through rate on the bead mill was about a one-minute residence time. Particle size reduction is again very rapid down to the primary particle size of the pigment, but no significant reduction occurs at this point, i.e., we are not grinding the primary pigment particle, at least according to our particle size analysis. This could be a positive or negative point depending on the goal of the particle size distribution.

Figure 9 shows dispersion of alumina using 300-400-µm zircon beads and 125-µm YTZP beads. The mill was operated at tip speed of about 11 meters per second. Flow rate was 0.6 liter per minute. We can see in this case that grinding the alumina to a 100-nanometer particle size occurs rapidly, and the ultimate particle size was 87 nanometers (d_{50}).

We could show more data to the same effect, but the conclusion is that the particle size reduction is a function of the material properties. If the material is soft and easily friable, then particle size reduction to sub 100-nanometer size is possible. If it is a harder material, further particle size reduction may not occur. Each application becomes very product specific. Laboratory testing is required to determine whether the material can be processed.

CONCLUSION

Grinding with very small media is possible, and process parameters have been developed for using less than 200 µm grinding media. We have demonstrated that it is possible to operate a bead mill with 100-micron beads at least on a lab scale.

At this point the best available media is zircon and YTZP beads. Tungsten carbide beads are experimental, and using this media on certain materials of construction can cause severe wear. Zircon media is relatively inexpensive compared to YTZP, but the contamination rate is higher. Typically products that are to be produced in this size range are high value materials, and contamination is a concern.

The practicality of the process must be considered. Is the saving in time from using 200-micron beads, which are currently used in a significantly increasing number of processes, worth the order of magnitude of cost and potential difficulty versus the time saving? For example, if we demonstrate that we can make the product on a 10-liter mill in one-fourth the time, but with a potentially more difficult process condition and higher cost for media versus using a 60-liter mill to make the same production, is this the most practical choice?

ACKNOWLEDGMENT

I would like to thank my colleagues Gerhard Kolb and George Scherer of Netzsch Feinmahltechnik GmbH, Selb, Bavaria, Germany, for their invaluable information on the focus of bead separation. CT

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