NANOPARTICLES: Mild Dispersion

BIG BUSINESS OF NANOTECHNOLOGY

Nanotechnology is a collective term for a wide range of applications dealing with structures and processes with product dimension of less than 100 nm (0.1 μm or 10^{-7} m). Specific applications include solid particles in suspensions, powders, dust, liquid drops in emulsions, fog, sprays or foam.

Nanoparticles are useful in a wide variety of industries. Smaller than viruses or bacteria, nanoparticles are able to enter cells unhampered, making them of great interest in the pharmaceutical industry for use as transporting agents. Nanoparticles have excellent optical properties, such as gloss transparency, color strength and jetness. They are extremely hard and scratchproof, which is valuable to the paint and coatings market. They also provide new properties for low-sintering-temperature ceramics, amorphous (translucent) metals, materials with high fracture strengths and toughness at low temperatures, or extreme plasticity at high temperatures.

With this variety of applications, nanotechnology business is booming. In 2007, the U.S. government is providing approximately $1.3 billion for nanotechnology research — almost triple the amount provided in 2001. The National Science Foundation expects the global market for nanotechnology products to approach $1 trillion by 2015. So with this growing market, equipment and processes for grinding and dispersion must meet and exceed user requirements. ❐

With this technique it is possible to maintain the chemical integrity and structure of submicron particles even through the grinding and dispersion processes

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As the nanoparticle market continues to swell, expertise is surfacing about nanoparticle grinding and dispersion processes. A grinding solution (wet grinding with agitator bead mills) achieves the production of nanoparticles with an average fineness of 40–100 nanometers (nm). However, dispersion doesn't always come as easily. Chemists and process engineers found that many dispersion processes can break down the primary particles, ruining the nanoparticles' surface condition, crystal structure and overall chemistry, thereby rendering them ineffective.

This article discusses grinding and dispersing of nanoparticles, as well as a new trend in wet grinding called mild dispersion that makes it possible to maintain the chemical integrity and structure of submicron particles, even through grinding and dispersion.

Grinding and dispersing

The grinding mechanism for almost any material is more complicated than it initially appears. The first variable to consider is the material and its form. For example, in the ink and paint industry, raw materials start out at the desired particle size in powder form. The powder needs to be deagglomerated and dispersed into liquid. Although this sequence of steps technically falls into the category of dispersion, it's often referred to as grinding.

The production of stable suspensions or dispersions of nanometer-size particles is accomplished via a comminuting process using a small media mill or an agitator bead mill. The principle of agitator bead mills is based on grinding suspended solid particles by impact and shearing forces between moving grinding beads. Certain horizontal grinding mills include an enclosed vessel that are filled with grinding media that are activated by an agitator shaft, creating shearing and impacting forces. The rotation of the agitator imparts energy to the surrounding media. These forces act on the solids suspended in a liquid as they are continuously pumped through the grinding chamber. The forces tear apart or crush the solids, resulting in overall reduction in particle size. The particles are simultaneously dispersed in the liquid.

Final particle fineness is primarily defined by two parameters: stress intensity and number of contact points. Stress intensity is a function of kinetic energy, which is transmitted to the grinding media by the agitator shaft. The stress intensity must be high enough to initiate the grinding process. The number of contact points determines how often the media interact within the grinding chamber. Nanoparticles require a high number of contact points in the grinding chamber, so smaller grinding media are used.

Fine bead mills are widely used as a low-cost, efficient way to grind and disperse nanoscale particles from 20 to 200 nm for laboratory and production applications. These fine bead mills are popular because they are simple, scalable and moderately low cost.

A small grinding medium is the key to nanoparticle dispersion with a bead mill. The final particle size is directly

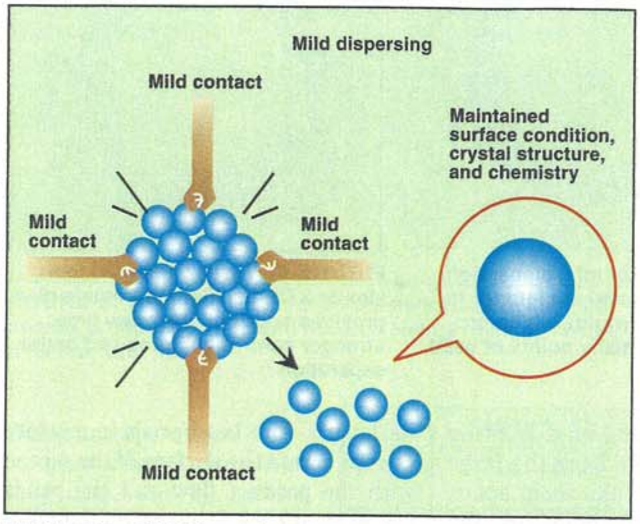

FIGURE 1. Mild dispersion uses a bead mill and multiple mild contacts, which is much less destructive to particles than one strong contact (see Figure 2, right)

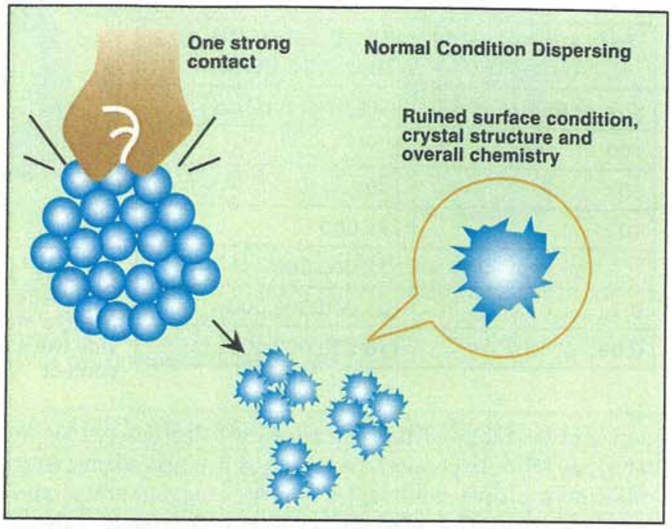

FIGURE 2. If high energy is applied to nanoparticles to achieve size reduction, loss of shape and surface characteristics are two examples of undesirable side effects

related to the size of the beads. In general, the mean particle size produced by the bead mill is about 1/1,000 of the diameter of the beads. Using this correlation, a dispersion with an average particle size of 100 nm would require 100 µm beads.

Dispersion dilemmas

The technology of bead mills with grinding media as small as 100 microns has been available for more than 10 years. In practice, however, obstacles with dispersion are often encountered.

Cohesive forces. In grinding, intermolecular forces increase as particles become smaller, thereby increasing the effects of cohesive forces (agglomerates, aggregates, or primary particles) in the product. Agglomerates are formed by point-focal or linear-cohesive primary particles, while aggregates form by laminar binding. Primary particles are crystalline or amorphous particles that are separated against each other. The goal is to disperse these particles to their primary particle size.

Nanoparticle characteristics. The tremendous surface area and surface energy provides the main beneficial effect of nanoparticles. In catalysts, for instance, the large surface areas result in more reactive area exposure. This is important in applications such as fluid-cracking catalysts for oil refining, wash coats applied to automotive catalytic converters, and ultraviolet-light absorption on glass coatings or skin coatings, including sunscreens.

More surface area in pigments allows more color effect using less pigment or color effects when combined with other materials such as aluminum flake, certain plastics or mica, which is used in automotive paints.

However, high-shear dispersion and ultrasonic dispersion used in conventional technologies are not always sufficient to disperse large-surface-area particles as discrete entities in a liquid. These mixing technologies do not have the needed energy to break apart materials, such as nano-TiO_2, that have high bonding forces. A bead mill, however, can apply the needed energy and shear force.

Fine bead mills. Fine bead mills present their own set of obstacles. For example, research shows that when a product run passes through a media mill, a portion of the batch bypasses the grinding process. This phenomenon is inherent in all fine-media mills regardless of design. The ideal mill would have "plug flow," where all the material passes through the machine at the same velocity, producing a uniform grind and a uniform dispersion.

High flowrates. The high flowrates needed to achieve near plug flow also make horizontal (or vertical) disc mills very sensitive to hydraulic packing of the media. A design that increases the kinetic energy of the beads and reduces the hydraulic packing associated with high-velocity flow eliminates this problem. The open surface area of the discharge must be increased to allow the high flowrate to occur without high chamber pressure. Also keep in mind that in fine-media-mill designs the use of excessive energy and rotational forces will damage the nanoparticles.

Traditional plasma-gas process. It is particularly challenging to achieve reliable, repeatable distribution of submicron particles. The traditional plasma-gas process promises advanced particle uniformity, but it does not offer the ability to disperse the particles in solution at their primary size. The plasma gas process produces a dry, agglomerated powder. When these agglomerates are mixed into a solution of solvents and resins, the particles require some mechanical means to break them apart. This may be possible using a high-shear mixer or some form of ultrasonic dispersion. If these methods are not adequate, however, processing through a stirred media mill is a viable alternative.

Successful production

Although superior dispersion of nanoparticles has eluded scientists for many years, mild dispersion is a new technique that eliminates contamina-

TABLE 1. RELATIONSHIP BETWEEN THE SIZE AND RELATIVE WEIGHT OF BEADS

Size of beads, mm	Weight of a bead
100	1
50	1/8
10	1/1,000
1	1/1,000,000
0.1	1/1,000,000,000
0.05	1/8,000,000,000

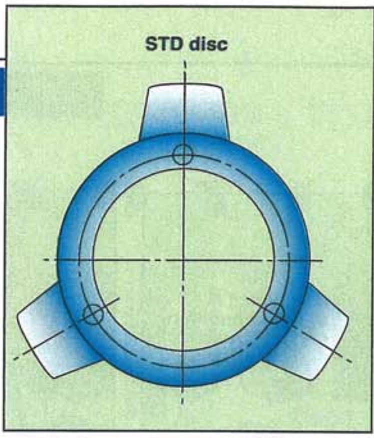

FIGURE 3. For mild dispersion, STD discs (above) are inferior to triangle discs (right), which provide twice as many points of bead contact

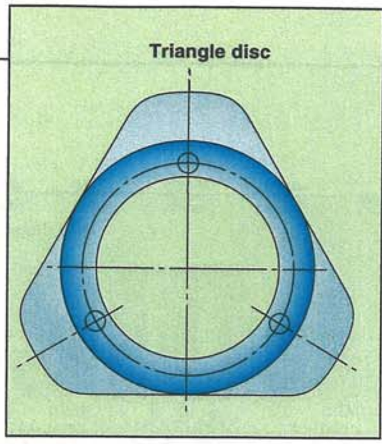

FIGURE 4. When compared to a similar STD disc (left), a triangle disc provides shorter dispersion time, stronger centrifugal force and better separation

tion and breakage of particle characteristics. Mild dispersion uses a bead mill and multiple mild contacts (Figure 1) instead of one strong contact (Figure 2), which can cause breaking and destruction.

Many factors affect the function of mild dispersion, but the main principle is bead size. The use of microbeads is an ideal way to achieve multiple mild contacts. In fact, ultrafine grinding beads, down to 50 µm, do not damage the nanoparticles. As bead diameter decreases, there are four primary results:

- The number of beads is increased dramatically
- Contact of the beads with the product is increased dramatically
- The weight of one bead is decreased dramatically (weight ∝ diameter^3)
- The energy of one bead is decreased dramatically (mean energy of one bead is equal to the specific energy input divided by the number of grinding beads)

The smaller the bead size, the more beads there are per unit volume. For example, if 1-mm dia. beads are loaded into a 1-liter (L) vessel, there are around 1.1 million beads; if 0.5-mm dia. beads are loaded into the 1-L tank, there are about 9.4 million beads; with 0.1-mm dia. beads, there are 1.2 billion beads; and with 0.05-mm dia. beads, there are 9.4 billion beads. So the probability of contacts between particles and beads increases by using smaller beads. The outcome is non-destructive dispersion. Table 1 demonstrates the correlation between size and weight of beads.

Another factor affecting the grind is the interstitial space between beads and particles. As the bead size decreases, the space between the beads decreases, too, working as a filtering mechanism that holds back the large agglomerates and breaks them apart. A rough calculation indicates the stand-off distance between the beads would be 4.3 µm for 1 mm beads; 2.1 µm for 0.5 mm beads; 430 nm for 0.1 mm beads; and 215 nm for 0.05 mm beads. Mild dispersion provides a dynamic filtering mechanism holding back particles larger than the standoff distance, and it shears them apart to their primary size.

Other factors in mild dispersion. Equipment choice, such as disc type, is among the many factors that affect mild dispersion. The STD disc (Figure 3) provides many impacts and is good for grinding. Yet, the triangle disc (Figure 4) is best for mild dispersion because the points of bead contact double (point of bead contact = revolution × time × number of beads). There is a short dispersion time, stronger centrifugal force, and better separation. The triangle disc also accepts higher product flow and viscosity. With an STD disc and a tip speed of 4 m/s, for instance, the mean energy of one bead is 4.27×10^{-15} W. By contrast, with a triangle disc and a tip speed of 8 m/s the mean energy of one bead is 4.54×10^{-15} W.

Another important piece of the puzzle is a slotted rotor. A slotted rotor minimizes hydraulic packing, increases product flowrate, and reduces energy input by means of its low rotor speeds. Testing of dispersions using lower stirrer speeds than that required for unslotted rotors provided excellent performance without damaging the structure or integrity of nanosize particles. An agitator should be slotted approximately one-third of its length. The bead/product mixture sweeps across the surface of the screen with the product flow and the beads are thrown back into the high-energy grinding zone — a critical factor in the machine's operation.

The rotor works hand in hand with the screen to prevent increased pressure when increased flow resistance is caused by a blocked bead-separation system. Common systems like separation gap, screen plate or plug screen fail to prevent this problem, allowing the product's outlet temperature to increase to damaging levels. A screen that rotates with the rotor is ideal so products go out through the shaft via rotary union. The product flow goes from the inlet on the bearing side axially along the rotor to its rear edge in the separation area between the rotor and gap screen. Grinding beads that followed the return of flow on the rear edge of the rotor achieve a high centrifugal acceleration. They are returned back to the grinding chamber through the slots of the rotor. The product suspension flows out of the mill without any problems (Figure 5). This provides for excellent separation, even when using microbeads.

An important factor to consider when handling micron-sized media is that it can damage the seal face and rupture the seal rings. Meanwhile, it's essential to handle fine media with great care when processing small product batches that require frequent changes of the grinding media; emptying and filling the grinding chamber can be very time consuming. New agitator bead mills are designed similarly to laboratory mills, where the grinding chamber can be rotated vertically into different positions for easy emptying,

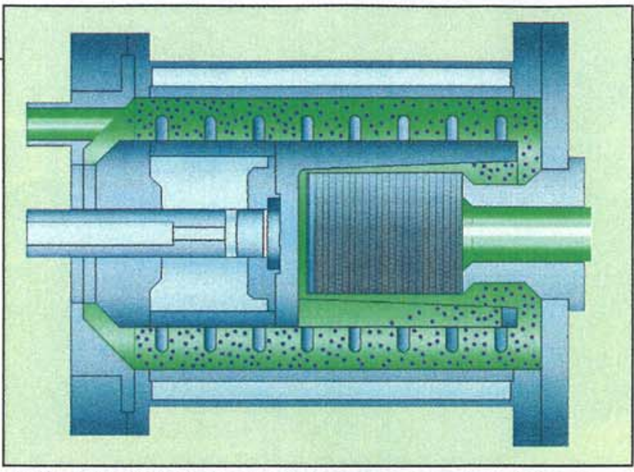

FIGURE 5. A slotted rotor minimizes hydraulic packing, increases product flowrate and reduces energy input by means of its low rotor speeds

FIGURE 6. These vials illustrate the value of low agitator speeds. The unmixed solution (left) is cloudy because of particle agglomeration. Meanwhile, the vial mixed at the highest speed is also cloudy because destruction of surface characteristics causing them to reagglomerate

filling and operation.

Agitator speed also affects mild dispersion by controlling the stress intensity applied by the grinding media to the particles. Figure 6 illustrates the value of low agitator speeds. The first vial (going left to right), labeled 0 pass, has nano TiO_2 particles mixed into the solvent. The particles are in the range of transmitted or natural light due to agglomeration and so appear opaque in the solvent.

TABLE 2. EXAMPLES OF MILD DISPERSION OF NANOPARTICLES

Product	Application	Beads	Diameter, mm	Tip speed, m/s	Arrival size, nm	Product quality
Pigment	LCD	YTZ	0.1	6	D50 = 40 - 60	Excellent
Pigment	Ink jet	YTZ	0.1	6	D50 = 13	Excellent
TiO_2	Photo catalyst	YTZ	0.1	6	D50 = 44	Excellent
ITO	Electrode	YTZ	0.1	6	D50 = 44	Excellent
ZrO_2	Electrical parts	YTZ	0.05	4	D50 = 37	Excellent
Diamond	Polishing	YTZ	0.1	10	D50 = 19	Excellent
Nickel	MLCC	Quartz	0.1	3	D50 = 200	Excellent
SiO	Paper	Quartz	0.1	8	D50 = 40	Excellent

The middle vial shows the original TiO_2 slurry (TiO_2 nanoparticles just mixed into solvent) was processed on a bead mill at a high agitator speed with high energy input (13 m/s, peripheral speed on the mill agitator). Although a finer particle size than the original slurry is measured, it is not in the preferred nanoparticle range according to SEM (scanning electron microscope) analysis. The high energy input destroys the surface characteristics, or particle morphology, so that the particles re-agglomerate and don't function properly.

The third vial, 4 m/s, displays the original slurry after processing on a bead mill at a low agitator speed – the mild dispersion process. This simply deagglomerates the particles to the point where they are finer than the wavelength of natural light, making them appear transparent, without damaging them.

The interstitial space between grinding media varies at different bead charge levels. The amount of interstitial space directly affects the stress intensity applied to particles because the pressure or contact force increases with less space. For example, if a 2-mm bead is used at 60% bead charge, the calculated space is approximately 400 µm. Using 100-µm beads at a 95% bead charge, the space is about 1.5 µm. In this case, one must account for the effect of hydraulic pressure due to flow resistance created by the tighter spacing (or filtering effect) of the smaller grinding media and higher charge.

Advantages of mild dispersion

The most important advantage of mild dispersion is the ability to protect the product from damage, keeping its crystal structure, characteristics and surface conditions by using multiple mild contacts.

Also, the product undergoes this dispersion process in a short period of time, reducing the possibility of contamination from the grinding media, and improves the overall production rate of the dispersed slurry.

Mild dispersion is a contamination-free process. Low rotor speed and short processing time means less exposure to the grinding stress applied by the beads, resulting in a clean product. Using machines made of highly wear-resistant material, such as yttria stabilized zirconia (YTZ), polyurethane, silicon carbide or hardened steel, further improves wear-resistance, allowing processing of abrasive nanomaterials like diamonds, boron carbide, silicon carbide, titania, nano alumina, and silica. The low agitator speed also results in low energy consumption.

This process allows for precise control of process temperature, which may be necessary depending on the chemistry of the dispersion. For example, maintaining a low temperature might be required for a certain surfactant with a low cloud point. Other examples include temperature-sensitive waxes and dyes.

Applications of mild dispersion

Nanosize particles. Mild dispersion is useful for particles that are already nanosize, including certain materials in photomicrographs of carbon black, nano zirconia, nano titania, nano ceria. If high energy is applied to these particles, real-size reduction occurs, as well as loss of spherical shape and/or surface characteristics. Mild dispersion's low energy grinding effect, by contrast, simply deagglomerates the

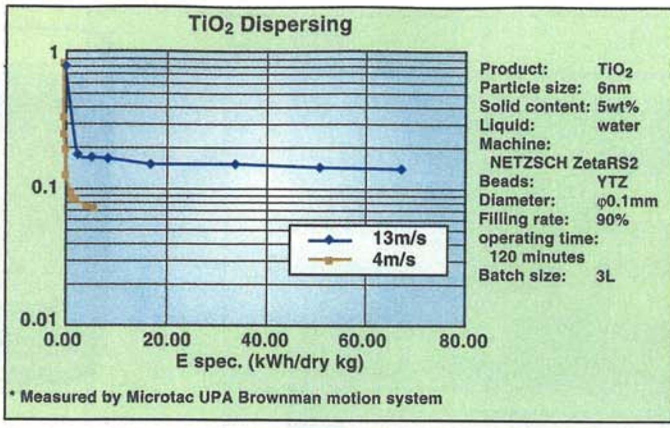

FIGURE 7. This graph illustrates the mild dispersion technique used for TiO_2 as a photo catalyst

particles, allowing them to stabilize in the dispersion medium.

General dye applications. In the ink-jet market, the inks are usually dyes or pigments. The dyes are dispersed in the water/ resin solution and filtered, dispersing the pigments. Ink-jet manufacturers found that grinding the pigment, also known as real-size reduction of the primary particles, facilitates more efficient jetting because the inks don't clog the printer nozzles. However, many of these pigments are supplied with a surface treatment to the primary particle. So if the primary particles are ground, this surface treatment is disrupted, resulting in particles with untreated surfaces that can reagglomerate or lose their light-fast properties.

This grinding of the pigments from the 50–150-nm range into the 10–80-nm range is nano-grinding and may require special additives and processing procedures to prevent reagglomeration. With the combinatino of grinding at high-energy input for the real-size reduction of the pigment, then processing at a mild condition, a stabilization effect occurs.

Nickel for multi-layers ceramic capacitor (MLCC). Smaller and smaller capacitors used in micro electronics, such as cell phones and audio players, require fine-particle materials in their production. Nickel powder for the circuits in these products has now reached the nanosize. The primary particle size is 0.2 µm with a round shape. The particles must first be deagglomerated and then dispersed. A strong dispersion condition would break the round shape, therefore mild dispersion is necessary. Through testing, researchers found the optimal process employs φ0.1-mm glass beads with a tip speed of 3 m/s. This condition gives enough power to disperse, but not so much power as to break the shape.

TiO_2 dispersion for photo catalyst. Nanosized TiO_2 has extraordinary catalytic properties. One possible use for this material is the reduction of carbon monoxide from combustion of petroleum products. For example, coating automotive radiators and highway barriers with this type of material could help reduce air pollution. When dispersing TiO_2 for photo catalyst it is fairly easy to reach the nano size, but mild dispersion is the only method to maintain the desired photo-catalytic properties. Traditional dispersion conditions break the crystal structure of the TiO_2 and change it to an amorphous crystal structure or a hydrated form. Figure 7 illustrates the processing specifics used in this mild dispersion process.

Table 2 shows various other examples of mild dispersion of nanoparticles.

Conclusions

As the nanotechnology market continues on a growth path, it is important for grinding and dispersion technology to exceed the needs of the market. Mild dispersion, a step in that direction, provides chemists and process engineers the ability to disperse nanoparticles without damage to the crystal structure. ■

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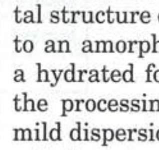

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