Nanoparticle

Grinding and Dispersing

A variety of advances in fine bead mill equipment have been developed to carry out the tasks associated with grinding at the nano level.

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The special properties often exhibited by nanoparticles have led to advancements such as extremely hard and scratch-proof coatings, low-sintering-temperature ceramics, materials with a high fracture strength and toughness at low temperatures, and amorphous metals, to name but a few. Of course, materials like carbon black and ultra-fine titanium dioxide, which are essentially nanoparticles, have been available for some time, having emerged before the widespread popularity of nanoparticles as both a concept and a term. Today, most pigments used in inks and coatings have a primary particle size from 20 to 200 nanometers (nm), and materials smaller than 100 nm are increasingly being used in advanced ceramic applications, meaning that many operators of bead mills are already grinding and dispersing in the nano range.

But just as the benefits of nanoparticles are being more widely appreciated, issues in their manufacture and dispersion have also emerged. Key among these is the problem of particle agglomeration, or the tendency of the particles to adhere in small clumps, which makes dispersion and the effective use of nanoparticles much more difficult and costly.

Whether the material is agglomerated due to the nature of the manufacturing process or from storage, the ultimate goal of manufacturers and users is to disperse all nanoparticles to their primary particle size. To this end, a variety of advances in fine bead mill equipment have been developed to carry out the tasks associated with grinding at the nano level, especially with regard to dispersion.

Dispersing Nanoparticles

The traditional plasma gas process promises superior particle uniformity but does not offer the ability to *disperse* particles in a solution at their primary size. A fine bead mill with grinding media on the order of 100 to 200 microns (μm) provides a simple, scaleable, efficient way to both grind and disperse nanoscale particles to the primary particle size, usually in just one or two passes. Unfortunately, conventional fine bead mills also have some drawbacks. For example, research

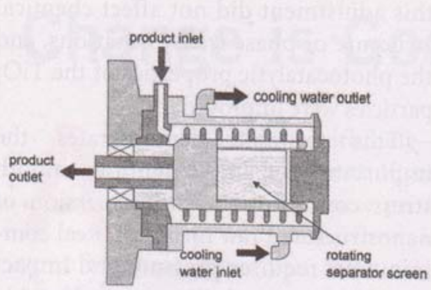

Figure 1. The design and operation of the new mill facilitate effective nanoparticle dispersion.

shows that when running passes through a media mill, a portion of the batch bypasses the grinding process, short-circuiting through the chamber. This phenomenon is inherent in all fine media mills, regardless of design.

The ideal mill would therefore feature "plug flow," where all the material passes through the machine at the same velocity, producing a uniform grind and residence time distribution. To achieve near plug flow, high throughput rates that result in a uniform velocity of particles through the mill are required.

It's important to remember that at high flow rates, horizontal or vertical bead mills are very sensitive to hydraulic packing of the media. A design is required that will increase the kinetic energy of the beads and thus reduce hydraulic packing associated with high-velocity flow. The open surface area of the discharge must be increased to allow the high-flow rate to occur without high chamber pressure, while at the same time accommodating for the risk of damaging nanoparticles through the use of excessive energy and rotational forces.

Overcoming Challenges

Nanoparticles must be first dispersed in a liquid to be used effectively. However, the tremendous surface area and surface energy that deliver the beneficial effects of nanomaterials also prevent their easy dispersion into liquids. In addition, conventional technologies for dispersing powders into liquids are not sufficient for dispersing these tiny particles as discrete entities.

The system was developed to achieve very narrow submicron particle size distributions through high-energy, high-flow, multiple-pass grinding.

Producing stable suspensions or dispersions of nanoparticles actually requires a comminution process, such as that provided by a small-media mill. On an industrial level, this grinding of coarser particles into the nanometer range or dispersing agglomerated nanosized primary particles is done with a bead mill, even though the high energy and bead speeds typically required can lead to material contamination or the destruction of the crystalline structure of the particle.

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It has been discovered that mills using very fine media beads, in the range of 70-125 μm, can economically grind materials into the nanometer range. It has also been discovered that unique mill designs using ultra-fine grinding beads of 30-50 μm in size offer an effective solution for dispersing these particles with significantly improved process efficiency.

One limitation in the process up to this point has been a lack of knowledge concerning scalable industrial equipment that uses these small beads. Additionally, this method is not widely accepted due to the difficulty of handling the small grinding beads (e.g., removing the beads from the suspension after dispersing the particles, or loading and discharging the small beads into the machine).

A newly developed bead mill design and improved grinding media separation system* enables the use of beads with diameters down to 50 μm. The new design prevents damage to nanoparticles through the use of a revolving screen that facilitates adequate product throughput at slow, low-energy motor speeds while pro-

*The ZetaMill® RS, developed by Netzsch Fine Particle Technologies, Exton, Pa.

Table 1. Test results of the new mill in various applications.

Product	Application	Grinding Media Material	Media Diameter (mm)	Stirrer Tip Speed (m/s)	Obtained Particle Size x_{50} (nm)
Pigment	LCD	$ZRO_2(Y_2O_3)$	0.1	6	40-60
Pigment	Ink jet	$ZRO_2(Y_2O_3)$	0.1	6	13
TiO_2	Photo catalyst	$ZRO_2(Y_2O_3)$	0.1	6	44
ITO	Display	$ZRO_2(Y_2O_3)$	0.1	6	44
ZrO_2	Electronics	$ZRO_2(Y_2O_3)$	0.05	4	37
Ni	MLCC	Glass	0.1	3	200
SiO_2	Paper	Glass	0.1	8	40
Diamond	Polishing	$ZRO_2(Y_2O_3)$	0.1	10	19

viding practical methods for handling fine grinding media (see Figure 1, p. 19).

The design and operation of the new mill facilitate effective nanoparticle dispersion. The traditional method for preventing damage to nanoparticles is to run the mill at a slow rotor speed; however, this reduces separation efficiency, in effect limiting the use of that equipment for dispersion. The new mill design also addresses the practical handling of the ultra-fine grinding media.

The media separator screen and mechanical seal are crucial components in the new stirred media mill design. One danger of this design is the chance for media to damage the face seal by causing a rupture in the seal rings. Easy handling of the media is essential when dealing with small product batches requiring frequent changes of the grinding media bulk. The new stirred media mill system eliminates this risk through a rotating grinding chamber that can be adjusted vertically into different positions for easy emptying, filling and operation.

Improved Dispersions

Testing has revealed that dispersions using low stirrer speeds provide excellent performance without damaging the structure or integrity of nanosized particles. Nanostructured TiO_2 particles for use in photocatalytic coatings were dispersed in the new mill. Y_2O_3-stabilized ZrO_2 grinding media was used at a diameter of 100 µm and tested at different stirrer speeds, and the grinding media was retained in the grinding chamber by a centrifugal separator system.

Tests with a stirrer tip speed of 13 m/s were carried out, and although the desired dispersion effect was reached, there was a significant reduction of the photocatalytic effect and increasingly amorphous properties of the material system. Further tests with X-ray structure analysis proved that,

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because of the high energy stress inside the mill, the mesh structure of the TiO_2 experienced considerable change. Additional peaks in the diffraction pattern are an indication of phase transformations on the surface. This result illustrates that smoother dispersion conditions are required to process nanoparticles without structural deterioration.

Subsequent tests with a tip speed of 4 m/s demonstrated that essentially better dispersion results can be obtained at lower specific energy inputs without additional dispersion time. Furthermore, this adjustment did not affect chemical structure or phase transformations, and the photocatalytic properties of the TiO_2 particles were improved.

This example demonstrates the importance of implementing smooth stress conditions in the dispersion of nanostructured raw materials. Real comminution requires pressure and impact stress that may lead to considerably worse dispersion as a result of the required time and energy input. It can also cause mechanochemical reactions and structural changes, which often have a negative effect on the product properties. The new mill avoids these pitfalls through implementing numerous grinding media-to-grinding media contacts at low stress energies.

Table 1 shows different sample applications where the use of very fine grinding media in the newly developed mill has been tested under smooth operating conditions. Excellent dispersion results were obtained without any changes in the product properties.

A New Milling Option

Using the dispersion of nanostructured TiO_2 as an example, the differences between processes with intended real comminution and dispersion processes (which destroy agglomerates without changing the material's structure) are evident. The importance of implementing smooth conditions during the dispersion of nanostructured raw materials is exemplified through the condition of the TiO_2 at 13 m/s vs. the more desirable conditions at 4 m/s.

This new technology, which has achieved excellent results in a number of different applications, overcomes the usual pitfalls of other bead mill systems without sacrificing the benefits of the media mill. ⊕

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