Effectively Grinding And Dispersing Nanoparticles Using A Fine Bead Mill

By: Dr. Stefan Mende - Research and Development; Mr. Gerhard Kolb - Vice President, Sales; Mr. Udo Enderle - Manager, Engineering Department at NETZSCH-Feinmahltechnik GmbH

New and Not-So-New Nanoparticles

The special properties often exhibited by nanoparticles have made possible 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 ultrafine titanium dioxide, which are essentially nanoparticles, have been available for some time – emerging before the widespread popularity of nanoparticles as both a concept and a term.

Indeed, when one considers that particle sizes classified as “nanoparticle” range from 10 - 700 nanometers, it’s clear that most components processed on a bead mill fall into the area of nanotechnology. Most pigments used in inks and coatings, for instance, have a primary particle size from 20 to 200 nanometers, meaning that many operators of bead mills are already grinding and dispersing in the nano range.

However, there exist real difficulties in the effective design, development and delivery of nanoparticles, most particularly in the area of dispersion. Just as the benefits of nanoparticles are being more and more widely appreciated, issues in their manufacture and dispersion have also emerged. Key among these is the problem or particle agglomeration, or the tendency of the particles to adhere in small clumps, making dispersion and effective use of the nanoparticles much more difficult and costly.

Agglomerated due to the nature of the manufacturing process or storage the ultimate goal of manufacturers and users is to disperse all nanoparticles to their primary particle size. To this end, Netzsch Fine Particle Technologies has developed a variety of advances in fine bead mill equipment to carry out the tasks associated with grinding at the nano level – especially with regard to the dispersion function.

Using Fine Bead Mills to Disperse Nanoparticles

Nanoparticles must be first dispersed in a liquid to be used effectively, and over the past few years, the use of fine bead mills for grinding and dispersion of these particles has become more and more prevalent.

Fine bead mills, widely used in both laboratory and production applications, deliver an efficient method for the grinding and dispersion of nanoscale particles from 20 to 200 nanometers. Popular because of their simplicity and scalability, fine bead mills also offer lower costs when compared with alternative technologies such as plasma gas process techniques.

Often used in conjunction with these plasma gas process techniques, fine bead mills provide an especially efficient way to disperse the output to primary particle size - usually in just one or two passes.

So what are the operating conditions required for a bead mill to grind and disperse nanoparticles effectively and efficiently?

Achieving Repeatable Nanoparticle Dispersions

Researchers, manufacturers, and others need to be able to achieve reliable, repeatable distributions of submicron particles. 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 microns (µm) to 200 µm is the simplest, most scalable, most cost-efficient way to make and disperse nanoparticles, though this too presents obstacles. For example, research 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, therefore, would have “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.

Bear in mind though, that at high flow rates horizontal or vertical bead mills are very sensitive to hydraulic packing of 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.

New Media Mill Design for Dispersing Nanoparticles

Dispersing nanoparticles into liquids can be a challenging undertaking. The tremendous surface area and surface energy which delivers the beneficial effects of nanomaterials also prevents their easy dispersion into liquids.

On top of that, conventional technologies for dispersing powders into liquids are not sufficient for dispersing these tiny particles as discrete entities.

The production of stable suspensions or dispersions of nano particles actually requires a comminution process, such as a small-media mill provides. On an industrial level, this grinding of coarser particles into the nanometer range or dispersing agglomerated nano-sized 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.

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 30-50 µm in size offer an effective solution for dispersing these particles with significantly improved process efficiency.

The limitation in the process up to this point has been the lack of knowledge concerning scalable industrial equipment that use these small beads, or rather that this method is not widely accepted due to the difficulty in 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 by Netzsch Fine Particle Technologies makes possible the use of beads with diameters down to 50 μm. The new design prevents damage to nanoparticles through the use of a novel revolving screen that facilitates adequate product throughput at slow, low energy motor speeds while providing practical methods for handling fine grinding media.

The design aspects and operating modes of the new mill facilitate effective nanoparticle dispersion. The method for preventing damage to nanoparticles is to run a 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.

Improved Dispersions Using Ultra-fine 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 do damage to 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 Zeta RS stirred media mill system (See Illustration 1) from Netzsch Fine Particle Technologies eliminates this risk through a rotating grinding chamber that can be adjusted vertically into different positions for easy emptying, filling and operation.

Dispersion Advantages Under "Smooth" Conditions

Testing revealed that dispersions using low stirrer speeds provide excellent performance without damaging the structure or integrity of nano size particles. Nano-structured TiO_2 particles for use in photocatalytic coatings were dispersed in Zeta RS mill. Y_2O_3-stabilized ZrO_2 grinding media was used at a diameter of 100μm 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 v_t of 13 m/s were carried out, and it was found that although the desired dispersion effect could be 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 because of the high energy stress inside of 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 shows that smoother dispersion conditions are required to process nano particles without structural deterioration.

Subsequent tests with a tip speed of 4 m/s demonstrate 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 could be improved.

This example demonstrates the importance of implementing smooth stress conditions in the dispersion of nano-structured raw materials. Real comminution requires pressure and impact stress that may lead to considerably worse dispersion results in dependency of the required dispersion time and energy input. Real comminution can also cause mechanochemical reactions and structural changes, which more often than not have a negative effect on the product properties. The new Zeta RS avoids these pitfalls through implementing as many grinding-media to grinding-media contacts at low stress energies as possible.

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

Product	**Application**	**Grinding Media Material**	**Media diameter**	**Stirrer tip speed**	**Obtained particle size x_{50}**
Pigment	LCD	$ZRO_2(Y_2O_3)$	0.1 mm	6 m/s	40-60 nm
Pigment	InkJet	$ZRO_2(Y_2O_3)$	0.1 mm	6 m/s	13 nm
TiO_2	Photo catalyst	$ZRO_2(Y_2O_3)$	0.1 mm	6 m/s	44 nm
ITO	Display	$ZRO_2(Y_2O_3)$	0.1 mm	6 m/s	44 nm
ZrO_2	Electronics	$ZRO_2(Y_2O_3)$	0.05 mm	4 m/s	37 nm
Nickel	MLCC	Glass	0.1 mm	3 m/s	200 nm
SiO_2	Paper	Glass	0.1 mm	8 m/s	40 nm
Diamond	Polishing	$ZRO_2(Y_2O_3)$	0.1 mm	10 m/s	19 nm

Summary

Using the dispersion of nano-structured TiO_2 as an example, the differences between processes with intended real comminution and dispersion processes (which destroy agglomerates without changing materials structure) can be seen. The importance of the implementation of smooth conditions during the dispersion of nano-structured raw materials is exemplified through the condition of the TiO_2 at 13/ms versus the much more desirable conditions under the smooth conditions at 4 m/s.

The stirred media mill system ZETA® RS is presented as a further development of Netzsch Fine Particle Technologies mills with regard to the grinding media separator, the mechanical seals, and handling, particularly concerning the comminution in the nano range and the dispersion processes.

Moreover, a review of applications where excellent results have been obtained with this new technology is discussed, as well as ways that this new media grinding technology overcomes the usual pitfalls of other bead mill systems without sacrificing the benefits of the media mill.