Application-Optimized Processing of Nano-Dispersions with Micro Beads

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Abstract

The manufacturing of nano-dispersions requires either the deagglomeration, wetting and stabilization of nano-scaled powders or a top-down size reduction by comminution. Treatment with micro beads is in both cases an efficient means for an outstanding quality enhancement compared to the previous milling technology. A new bead mill concept specifically designed for the reliable use of micro beads down to 50 µm and below is introduced. Case studies on the identification of optimized operating conditions are discussed for a variety of applications requiring the full range of milling mechanisms from gentle dispersing to high energy grinding. Examples include products from functional inorganic nano-additives to organic pigment dispersions.

1. Introduction

Inks for conventional printing technologies like offset or gravure processes feature a comparatively high viscosity from several hundred to more than 10.000 mPas and maximum particle sizes of several microns down to the higher submicron range. After premixing and prewetting, the actual size reduction and development of quality properties is accomplished in agitated bead mills and/or downstream three-roll mills. In order to handle the above product viscosity and due to the target fineness, agitated bead mills are operated with bead diameters from 2 mm down to 0.5 mm or 0.3 mm as a minimum in case of exceptionally high-grade liquid gravure inks for packaging or foil printing.

Research and industrial implementation in almost any technical field utilizing fine particle systems, particularly dispersions, have revealed that innovative, previously unknown quality properties are designable, if the particle size distributions are shifted to the nanometer range.

Nano-particles can be produced by bottom-up methods like thermal, precipitation and mechano-chemical processes or by a top-down approach like comminution of crystalline or amorphous matter in a liquid carrier, see figure 1.

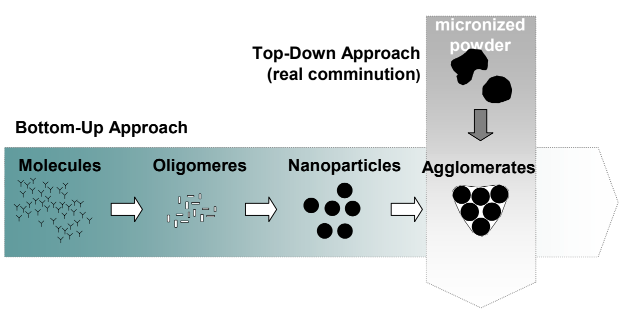

***Fig. 1**: Top-down and bottom-up manufacturing of nano-particles*

Due to the general physical principle of minimizing the free surface energy, particles tend to agglomerate the smaller the more intensely. Nano-particles, on the other hand, entirely lose their advantageous dimensional properties if they are distributed in the carrier as agglomerates. In order to develop functional nano-dispersions, agglomerates and aggregates have to be separated by appropriate mechanical mechanisms and subsequently or concurrently the state of separation has to be stabilized.

2. Concept of Small Molecule Surface Modification

The limitation of traditional dispersing and stabilization technology can be overcome for a wide variety of inorganic nano-materials by the patented concept of chemical surface modification with comparatively small molecules [1, 2], in the following referred to as **S**mall **M**olecule **S**urface **M**odification = SMSM, see figure 2.

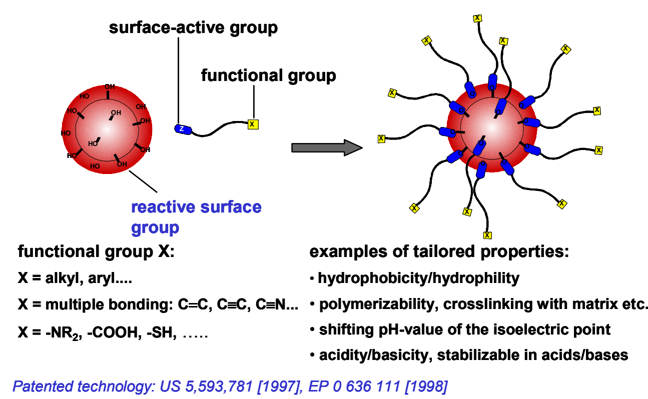

***Fig. 2**: Concept of **S**mall **M**olecule **S**urface **M**odification*

3. Agitated Bead Mill as SMSM Reactor

The industrial manufacturing of tailored nano-particles, i.e. functional colloids, is accomplished by a novel and proprietary process where suspended particles are milled under concurrent chemical reaction with a surface modifier [3]. The most efficient means for this process are specifically designed agitated bead mills under application-optimized operating conditions utilizing micro beads, see figure 3.

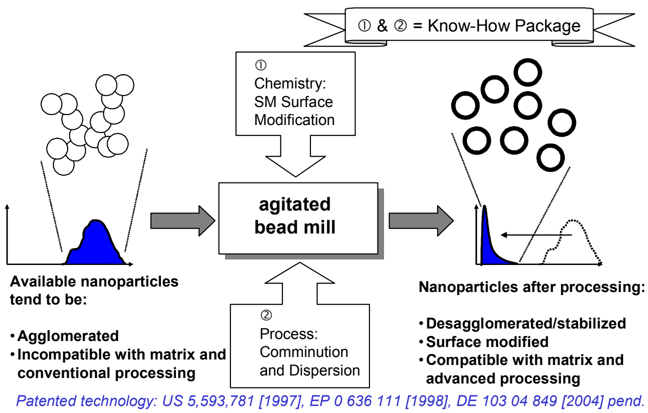

Fig. 3*: Chemo-mechanical processing in agitated bead mill*

4. Agitated Bead Mill for Nano-Processing in General

The side requirements for mechanical processing of nano-dispersions in various industries, for individual applications and including organic formulations like:

- Ink jet inks
- Color filters
- Scratch-resistant coatings
- Functional ceramics
- Metal pastes

may be quite different and almost contradictory. As introduced in the following, a most efficient and versatile means to fulfil the various requirements is the processing in a novel bead mill, specifically designed for micro beads and an unusually wide range of operating conditions.

4.1 Mill-Related Requirements

Typcial mill-related requirements for nano-processing are:

- Suitability for micro beads down to 50 µm and below
- High flow rate capability for narrow particle size distributions
- Defined relative motion (shear) of beads with adjustable intensity, because:
  a.) Comminution (scattering of crystals) requires high-energy collisions of beads
  b) Separation of agglomerates while preserving the surface morphology requires gentle dispersing
- Even distribution of beads across the mill

4.2 Novel Bead Mill Concept Optimized for the Use of Micro Beads

In figure 4 a simplified schematic of a proprietary novel mill design [4], type MicroMedia® is given, specifically developed and optimized for the efficient use of micro beads. The energy is introduced by rotor pegs in a unique double-helical arrangement (compare figure 5). This set-up results in centrifuging the beads in the active outer milling annulus (green layer in fig. 4). The product is treated while flowing axially through the highly turbulent layer of centrifuged beads. The screen on top of the inner stator is efficiently kept clear from beads. Consequently it merely functions as a protection device in stand-by in case the mill is being operated beyond the range of optimum parameters.

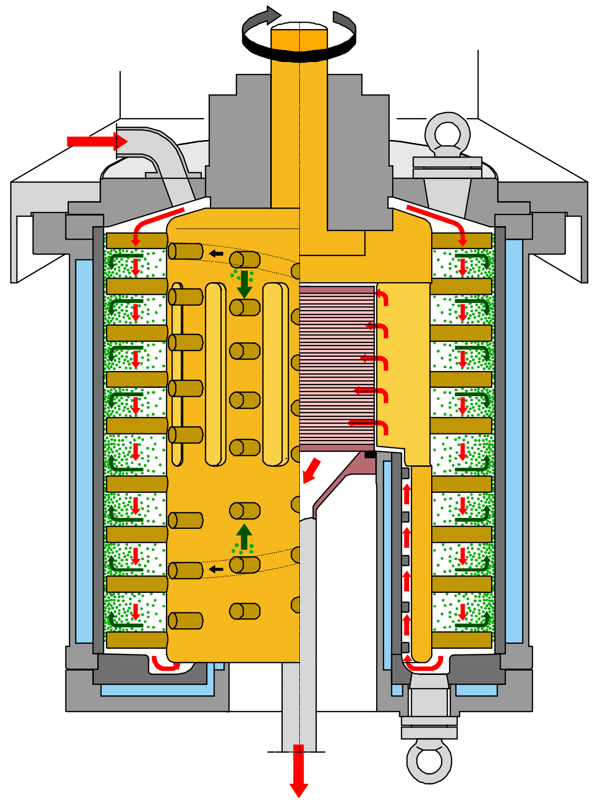

Fig. 4*: Simplified schematic of novel mill concept MicroMedia®*

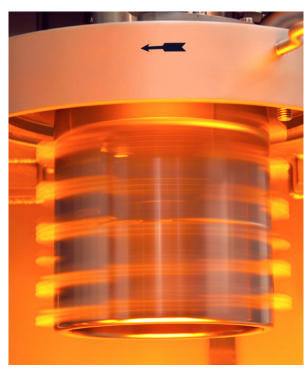

Fig. 5*: Specific bead motion initiated by double helical peg arrangement*

Fig. 6*: Nano-grinding in pilot-size mill MicroMedia® P1 (from ceramics)*

Exceptionally high flow rates are possible in combination with beads as small as from 300 µm to 50 µm and below and for a product viscosity well exceeding several hundred mPas. The MicroMedia® concept allows for linear scale-up to large production size mills.

5. Industrial Examples of Nano-Processing

5.1 SMSM-Reactive Grinding – Influence of Diameter of Micro Beads

Figure 7 represents a case study on the influence of the diameter of micro beads on energy requirement and achievable fineness for SMSM reactive grinding of ZrO_2 utilizing an optimized SM surface modifier.

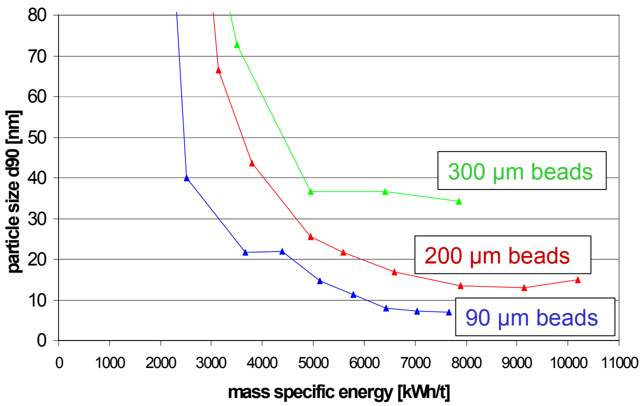

Fig. 7: *SMSM grinding of synthesized ZrO_2, d_{90} against mass specific energy E_m, effect of bead diameter*

Milling with 300 µm beads results in a d_{90} of 35 nm after introducing 8 kWh/kg into the system. Continuation of the process does not result in any appreciable further size reduction. Employing 200 µm beads allows for a substantially quicker reaction process and a minimum d_{90} value of 13 nm. The utilization of 90 µm beads results in a fully translucent dispersion (d_{90} < 40 nm) with less than half the specific energy compared to processing with 300 µm beads. An astonishing equilibrium fineness of some 7 nm is achievable with 90 µm beads treatment after introducing 7 kWh/kg. The product is totally dispersed to the primary particle size distribution and fully stabilized in the carrier. The application-optimized Small Molecule Surface Modifier allows for an unusually high value of solids concentration of c_m = 40%.

5.2 Processing of Metal Powder Dispersion for Electronic Application

A typical application from the electronics industry is the deagglomeration, dispersing and coating of conductive metal particles with a primary size range from 100-200 nm. As a side requirement, the surface morphology of the particles must not be changed or damaged in order not to inversely influence the electric properties.

REM analysis revealed that dispersing in a conventional mill with 0.3 mm beads and a mill tip speed of 7.0 m/s was not successful. Even though the power density in the mill was only 0.3 kW/l, an undesired flattening of some particles was noticeable.

Filling the mill MicroMedia® with 100 µm beads and reducing the tip speed to 5.0 m/s it was possible to recirculate with 200 kg/h through a mill chamber of 1.2 l, now with a power density of only 0.1 kW/l. The resulting product was perfectly dispersed and showed no indication of structure deformation.

5.3 Grinding of a Functional Ceramic Powder Dispersion (Nano-Additive)

In numerous industrial applications there is a need to provide the opposite compared to the previous example of soft milling, i.e. an intense energy grinding process, yet taking advantage of the huge number of contact points when employing micro beads.

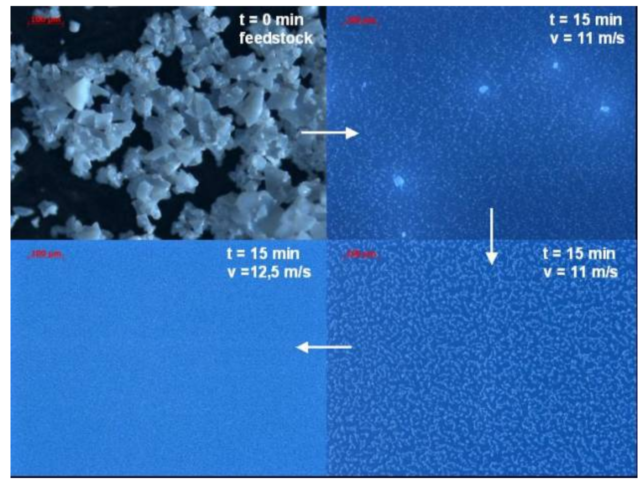

Fig .8.1/2/3/4 (clockwise*): Nano-grinding of a functional ceramic dispersion*

The nano-grinding and dispersing of a functional ceramic additive, see figure 8, requires an efficient separation of strongly aggregated crystalline matter. Fig. 8.1 indicates lumps up to 100 µm. Processing with 100 µm beads at a tip speed of 11 m/s during a period of 15 minutes in high flow rate recirculation results in a residue of only a few oversized particles (fig. 8.2). Further processing for another 15 minutes creates a homogeneous appearance as per fig. 8.3. All clusters were destroyed, but the basic fineness remains untouched, compared to fig. 8.2. Increasing the tip speed to 12.5 m/s clearly reveals that further size reduction requires exceeding a certain threshold of load intensity (fig. 8.4). The optimum tip speed was eventually identified to be 15.0 m/s with a power density in the mill in the order of 4 kW/l.

Note that in this typcial case of "high energy grinding" the power density in the identical mill is 40 times higher compared to the optimized condition of the "soft dispersing" example as described in 5.2.

5.4 Optimized Nano-Processing of an Organic Color Dispersion

The following case study is an example of the quality enhancement of a high grade color dispersion incorporating a lightfast organic pigment. The previous production method was already utilizing 100 µm beads, but in a more conventional bead mill. The question was to what extent an improvement of quality characteristics and productivity was possible by processing in a mill design which is optimized for the use of micro beads (MicroMedia®).

Figure 9 is a plot of the particle size d_{50} in nm against the milling time in minutes. With a tip speed of 14.7 m/s and a milling time of just 13 minutes the quality target of 50 nm is exceeded. Continuing milling for longer than 50 minutes results in reagglomeration after passing the minimum of d_{50} = 44 nm. In case of a tip speed of 12.8 m/s the size reduction is somewhat slower, the target window is reached from 23 through 135 minutes. For a tip speed of 11.0 m/s the target fineness is achieved after 65 minutes. Reagglomeration is not noticeable during the treatment up to 180 minutes.

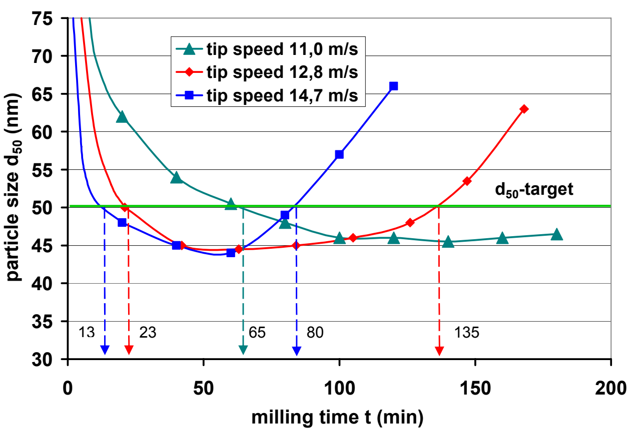

Fig .9: Particle size d_{50} versus milling time t (recirculation) for 3 rotor speeds

In figure 10 the results of the identical set of experiments is plotted, but now as d_{50} (nm) against the mass specific energy E_m (kWh/t) during recirculation milling. It is noteworthy that the mass specific energy is an excellent parameter for normalization: the results coincide with different tip speeds. The required fineness is exceeded after 300 kWh/t. Beyond 1700 kWh/t the d_{50} value is increasing prohibitively due to reagglomeration.

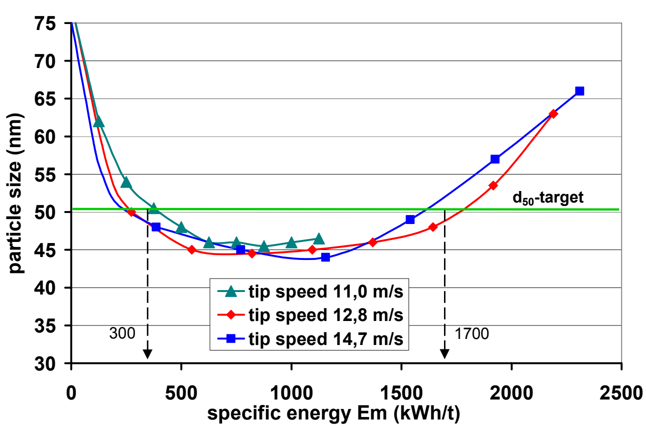

Fig. 10: Particle size d_{50} versus mass specific energy E_m for 3 rotor speeds

Figure 11 shows the mill base viscosity as a function of the mass specific energy. The standard viscosity of $\eta_{mb,max}$ = 30 mPas should not be exceeded. Regardless of the tip speed, about E_m = 1350 kWh/t can be introduced before the viscosity becomes prohibitively high. Beyond that value the increase of viscosity is much more pronounced with higher tip speed.

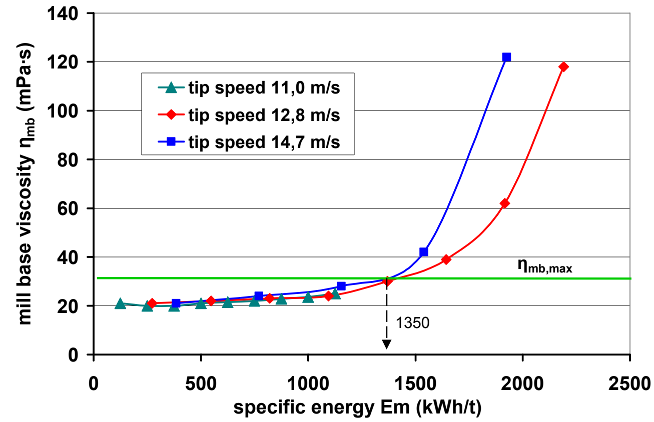

Fig. 11: Mill base viscosity against mass specific energy E_m for 3 rotor speeds

For the application under discussion the most important quality property is transparency. Per definition the achievable standard with the previous technology has been 100 % as given in figure 12.

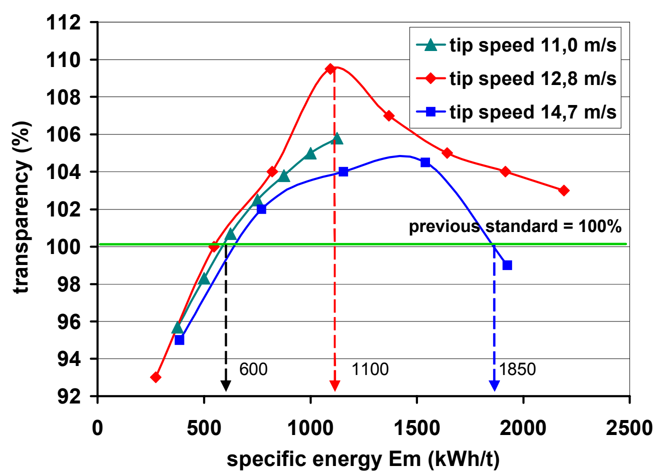

Fig. 12: Transparency in percent against mass specific energy E_m for 3 tip speeds

Processing in the novel mill MicroMedia® with an energy input exceeding 600 kWh/t results in a quality improvement of transparency surpassing the previous standard significantly. With a tip speed of 12.8 m/s an increase of transparency by 9 % is possible after introducing 1100 kWh/t. With the higher rotor speed of 14.7 m/s a maximum increase of 5 % transparency requires a mass specific energy input of about 1500 kWh/t. After this treatment the mill base viscosity exceeded the permissible value $\eta_{mb,max}$ (see fig. 11), whereas the d_{50} value would still be on target.

A tip speed of 11.0 m/s results in a transparency of + 5.5 % after 1100 kWh/t not yet having hit the maximum. But due to the lesser power input the milling time is about 50 % longer to introduce the same amount of energy into the batch compared to the tip speed of 12.8 m/s.

Processing with 12.8 m/s represents the relative optimum in light of achievable quality and productivity. With lower tip speed the productivity is reduced severely, quality properties develop slower and at a lower level. A tip speed as high as 14.7 m/s appears to be too aggressive, resulting in premature reagglomeration.

The main reason for the quality improvement compared to the previous state of the art is the huge flow rate capability in combination with micro beads of 100 µm and below with an optimized load intensity in the mill. Furthermore, this example impressively demonstrates how quality properties may largely develop independently. In order to define optimized processing conditions the various target features have to be evaluated individually.

6. Conclusion and Outlook

Treatment with micro beads is an effective means to develop an outstanding quality profile for a variety of applications. The mill concept MicroMedia®, optimized for handling micro beads, is a versatile tool to provide for a wide range of processing conditions from soft dispersing to high energy size reduction. This opens up new possibilities as well in the non-impact printing industry for a systematic research work to create nano-dispersions of enhanced quality standard without being hindered by limitations of the previous state of the art. The new technology is fully transferable to large-scale manufacturing.

7. References

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Biography

Norbert Stehr holds a Bacholors Degree in Mechanical Engineering and a Masters Degree in Process Technology . His Ph.D.-thesis is on comminution and transport phenomena in agitated bead mills, completed 1982 at the University of Braunschweig, Germany, Dept. of Particle Technology. After having worked with the University of Utah as postdoctoral research fellow on modelling of wet milling processing he joined Draiswerke GmbH, Germany in 1984 where he was in charge of various positions from R&D to general manager of the Wet Milling Division. After the integration of the latter into the business unit Grinding and Dispersing of Buhler AG, Switzerland he started his current position as Director of Innovation in 2004. He is author of numerous technical papers and patents.