Ultrasonic Milling and Dispersing Technology for Nano-Particles

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1. Ultrasonic Milling and Dispersing in the Nano Technology Sector
The dispersing and deagglomeration of solids into liquids is an important application of ultrasonic devices. If powders are wetted, the individual particles build agglomerates and are held together by attraction forces of various physical and chemical nature, including van der Waals forces and liquid surface tension. This effect is stronger for higher viscosity liquids, such as polymers or resins. The attraction forces must be overcome on order to deagglomerate and disperse the particles into liquid media. An even dispersion and deagglomeration is important to use the full potential of the particles. Especially nano particles offer extraordinary characteristics, which can only be exploited in highly even dispersed state.
The application of mechanical stress – e.g. generated by ultrasonic cavitation - breaks the particle agglomerates apart. Also, liquid is pressed between the particles. Different technologies are commonly used for the dispersing of powders into liquids. This includes high pressure homogenizers, agitator bead mills, impinging jet mills and rotor-stator-mixers. High intensity ultrasonication is an interesting alternative to these technologies and particularly for the particle treatment in the nano-size range the only effectual method to achieve the required results.

2. Ultrasonic Cavitation
By high-power/ low-frequency ultrasound high amplitudes can be generated. Thereby, high-power/ low-frequency ultrasound can be used for the processing of liquids such as mixing, emulsifying, dispersing and deagglomeration, or milling. When sonicating liquids at high intensities, the sound waves that propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles, with rates depending on the frequency. During the low-pressure cycle, high-intensity ultrasonic waves create small vacuum bubbles or voids in the liquid. When the bubbles attain a volume at which they can no longer absorb energy, they collapse violently during a high pressure cycle. This phenomenon is termed cavitation. Cavitation, that is "the formation, growth, and implosive collapse of bubbles in a liquid. Cavitational collapse produces intense local heating (~5000 K), high pressures (~1000 atm), and enormous heating and cooling rates (>109 K/sec)" and liquid jet streams (~400 km/h)”. (Suslick 1998)
There are different means to create cavitation, such as by high-pressure nozzles, rotor-stator mixers, or ultrasonic processors. In all those systems the input energy is transformed into friction, turbulences, waves and cavitation. The fraction of the input energy that is transformed into cavitation depends on several factors describing the movement of the cavitation generating equipment in the liquid. The intensity of acceleration is one of the most important factors influencing the efficient transformation of energy into cavitation.
Higher acceleration creates higher pressure differences. This in turn increases the probability of the creation of vacuum bubbles instead of the creation of waves propagating through the liquid. Thus, the higher the acceleration the higher is the fraction of the energy that is transformed into cavitation. In case of an ultrasonic transducer, the amplitude of oscillation describes the intensity of acceleration. Higher amplitudes result in a more effective creation of cavitation. In addition to the intensity, the liquid should be accelerated in a way to create minimal losses in terms of turbulences, friction and wave generation. For this, the optimal way is a unilateral direction of movement. This makes ultrasound an effective means for the dispersing and deagglomeration but also for the milling and fine grinding of micron-size and sub micron-size particles. (Hielscher 2005)

In addition to its outstanding power conversion, ultrasonication offers the great advantage of full control over the most important parameters: Amplitude, Pressure, Temperature, Viscosity, and Concentration. This offers the possibility to adjust all these parameters with the objective to find the ideal processing parameters for each specific material. This results in higher effectiveness as well as in optimized efficiency.

3. Parameters
Ultrasonic liquid processing is described by a number of parameters. Most important are amplitude, pressure, temperature, viscosity, and concentration. The process result, such as particle size, for a given parameter configuration is a function of the energy per processed volume. The function changes with alterations in individual parameters. Furthermore, the actual power output per surface area of the sonotrode of an ultrasonic unit depends on the parameters. The power output per surface area of the sonotrode is the surface intensity (I). The surface intensity depends on the amplitude (A), pressure (p), the reactor volume (VR), the temperature (T), viscosity (η) and others.

\[ I[W/\text{mm}^2] = (A[\mu\text{m}], p[\text{bar}], VR[\text{ml}], T[^\circ\text{C}], \eta[\text{cP}],...) \] .

The impact of the generated cavitation depends on the surface intensity. In the same way, the process result correlates. The total power output of an ultrasonic unit is the product of surface intensity (I) and surface area (S):

\[ P[W] = I[W/\text{mm}^2] \times S[\text{mm}^2] \]

3.1. Amplitude
The amplitude of oscillation describes the way (e.g. 50 µm) the sonotrode surface travels in a given time (e.g. 1/20,000s at 20kHz). The larger the amplitude, the higher is the rate at which the pressure lowers and increases at each stroke. In addition to that, the volume displacement of each stroke increases resulting in a larger cavitation volume (bubble size and/or number). When applied to dispersions, higher amplitudes show a higher destructiveness to solid particles. Table 1 shows general values for some ultrasonic processes.
### 3.2. Pressure

The boiling point of a liquid depends on the pressure. The higher the pressure the higher is the boiling point, and reverse. Elevated pressure allows cavitation at temperatures close to or above the boiling point. It also increases the intensity of the implosion, which is related to the difference between the static pressure and the vapor pressure inside the bubble (cf. Vercet et al. 1999). Since the ultrasonic power and intensity changes quickly with changes in pressure, a constant-pressure pump is preferable. When supplying liquid to a flow-cell the pump should be capable of handling the specific liquid flow at suitable pressures. Diaphragm or membrane pumps; flexible-tube, hose or squeeze pumps; peristaltic pumps; or piston or plunger pump will create alternating pressure fluctuations. Centrifugal pumps, gear pumps, spiral pumps, and progressive cavity pumps that supply the liquid to be sonicated at a continuously stable pressure are preferred. (Hielscher 2005)

### 3.3. Temperature

By sonicating a liquid, power is transmitted into the medium. As ultrasonically generated oscillation causes turbulences and friction, the sonicated liquid – in accordance with the law of thermodynamics - will heat up. Elevated temperatures of the processed medium can be destructive to the material and decrease the effectiveness of ultrasonic cavitation. Innovative ultrasonic flow cells are equipped with a cooling jacket (see picture). By that, the exact control over material’s temperature during ultrasonic processing is given. For the beaker sonication of smaller volumes an ice bath for heat dissipation is recommended.

<table>
<thead>
<tr>
<th>Process</th>
<th>Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersing/Deagglomeration</td>
<td>10 to 30 micron</td>
</tr>
<tr>
<td>Emulsifying</td>
<td>20 to 60 micron</td>
</tr>
<tr>
<td>Primary Particle Reduction</td>
<td>40 to 120 micron</td>
</tr>
</tbody>
</table>

Table 1 - General Recommendations for Amplitudes
3.4. **Viscosity and Concentration**

Ultrasonic milling and dispersing are liquid processes. The particles have to be in a suspension, e.g. in water, oil, solvents or resins. By the use of ultrasonic flow-through systems, it becomes possible to sonicate very viscous, pasty material.

High-power ultrasonic processor can be run at fairly high solids concentrations. A high concentration provides the effectiveness of ultrasonic processing, as ultrasonic milling effect is caused by inter-particle collision. Investigations have shown that the breakage rate of silica is independent of the solid concentration up to 50% by weight. The processing of master batches with highly concentrated material’s ratio is a common production procedure using ultrasonication.

3.5. **Power and Intensity vs. Energy**

Surface intensity and total power do only describe the intensity of processing. The sonicated sample volume and the time of exposure at a certain intensity have to be considered to describe a sonication process in order to make it scalable and reproducible. For a given parameter configuration the process result, e.g. particle size or chemical conversion, will depend on the energy per volume ($E/V$).

\[
\text{Result} = f\left(\frac{E}{V}\right)
\]

Where the energy ($E$) is the product of the power output ($P$) and the time of exposure ($t$).

\[
E[Ws] = P[W]*t[s]
\]

Changes in the parameter configuration will change the result function. This in turn will vary the amount of energy ($E$) required for a given sample value ($V$) to obtain a specific result value. For this reason it is not enough to deploy a certain power of ultrasound to a process...
to get a result. A more sophisticated approach is required to identify the power required and the parameter configuration at which the power should be put into the process material. (Hielscher 2005)

4. Demonstration of Ultrasonic Milling and Dispersing Effects by means of Specific Material Examples
In the ink, paint and coating industries the dispersing, deagglomeration, and wet-milling of pigment powders and nano particles is a basic application with fundamental consequence for the product quality. For pigments, the characteristic of changing the color of reflected or transmitted light as the result of wavelength-absorption, makes organic and inorganic pigments the important raw material in the production of inks, printing colors, varnishes, coatings etc. The majority of pigments is metallic and bases on titanium, iron oxide, zinc, copper, cadmium, cobalt, mercury, ultramarine, lead, chromium, and clay earth. Carbon is another important material of ink and paint pigments.

As pigments are hard and insoluble, higher efforts during the processing are required. High-performance pigments provide an intense color-strength, good gloss, transparency, light fastness, weather fastness, resistance against heat, moisture, as well as chemical resistance, stability during processing and transfer efficiency.

Most pigments are very cost-intensive – consequently, the endeavor of the ink manufacturing industry is focused on production of high-quality ink with the most color strength from the least possible amount of pigment. A faster dispersion and an increase of the production capacity help reducing the costs. The grade of the uniformity of particles and the evenness of the dispersion are essential to achieve higher ink gloss, more intensive color strength and a better overall appearance. (cf. Pekarovicova et al. 2009)

Due to these facts, reliable high-power equipment for pigment processing is needed. Ultrasonic milling and dispersing processors tested in different studies for their efficiency and reliability in regards to their performance of pigment treatments. For the ink manufacture, pigments have to be finely grounded and dispersed into a liquid medium. The requirements, that have to be fulfilled by pigment dispersions, include a particle size less than 150nm, colloidal stability, the compatibility of various ink components, and purity. Ultrasonic milling and dispersing is a well-known and proven technology to achieve small particles with particle sizes in the range from 500µm down to approx. 10nm.

4.1. Titanium Dioxide

To use the full potential of specific particles, their size is one of the main quality features. Some characteristics will only appear, if the particle size is reduced to nano scale. Titanium dioxide is the most frequently used white pigment due to outstanding characteristics, such as brightness and its very high refractive index. It is a common pigment added to paints, coatings, food, cosmetics, etc.
For the particle size reduction of TiO2, the use of ultrasonics is an effective method as shown in table 3. The red curve shows the particle size distribution before sonication, the green curve shows the TiO2 particles after sonication with the intensity of 250Ws/ml and the yellow curve after sonication with the intensity of 500Ws/ml. It is obvious that the ultrasonic processing causes a shifting of the curve to the left side. Further, the curves becomes drastically narrower and the right tailing as visible at the red curve (before sonication) disappears.

Table 3 – Ultrasonic Milling of TiO2
(red: before ultrasonication; green: ultrasound 250Ws/ml; yellow: ultrasound 500Ws/ml)
4.2. Ultrasonic Milling of Pigments for Inks

The images below show the result of ultrasonic dispersion of carbon black pigment in UV ink. The particle size reduction and the even dispersion grade are conspicuous.

![before ultrasonication](image1.png) ![after ultrasonication](image2.png)

Picture 2 - Carbon Black Pigments, ultrasonically dispersed in UV ink (resolution 100x)

The table below shows the distribution curve of carbon black. The red narrow curve shows the even distribution of the carbon black particles after ultrasonic treatment. The green curve shows the particle size distribution without ultrasound. The significant right tailing of the curve is obvious.

![Particle Size Distribution](image3.png)

Table 4 – Particle Size Distribution of Carbon Black before (green curve) and after (red curve) ultrasonication

As the particle size is determinant for color strength, surface finish, and influences the delivery method, finally the dispersion is decisive for the ink quality. The stability of the ink, its long-term performance and rheology are results of dispersion technique, too.

The microscope pictures below show the milling effect of ultrasound, using oil-based magenta pigment.
The powerful application of ultrasonics for pigment milling and dispersion is a well-known and proven fact. A comparison between ultrasonic mills and various other standard mills shows the advantages of high-power ultrasonic equipment.

<table>
<thead>
<tr>
<th>Production method</th>
<th>Ink type</th>
<th>Particle size (µm)</th>
<th>Advantage/disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three-roll mill</td>
<td>Paste</td>
<td>0.2–0.7</td>
<td>Paste ink processing/time consuming</td>
</tr>
<tr>
<td>Ball mill</td>
<td>Fluid</td>
<td>0.1 up</td>
<td>Large volumes/noisy</td>
</tr>
<tr>
<td>Media mill</td>
<td>Fluid</td>
<td>0.1–0.5</td>
<td>Well established/particle bypass</td>
</tr>
<tr>
<td>Small media mill/media centrifugal separation</td>
<td>Fluid</td>
<td>0.05 up</td>
<td>Uniform pigment particle for LCDs/expensive</td>
</tr>
<tr>
<td>Ultrasonic mill</td>
<td>Fluid</td>
<td>0.05 up</td>
<td>High conc. solids, nanotubes processing/none</td>
</tr>
</tbody>
</table>

Source: IntertechPira

Table 5 - Dispersing techniques and their advantages/ disadvantages (Pekarovicova et al. 2009)

5. Industrial Implementation of Ultrasound

Ultrasonic processing of particles allows processing all particles evenly. Hielscher’s industrial ultrasonic processors are commonly used for inline-sonication. Therefore, the suspension is pumped into the ultrasonic reactor vessel. There it is exposed to ultrasonic cavitation at a controlled intensity. The exposure time is a result of the reactor volume and the material feed rate. Inline sonication eliminates by-passing because all particles pass the reactor chamber following a defined path. As all particles are exposed to identical sonication parameters for the same time during each cycle, ultrasonication typically shifts the
distribution curve rather than widening it. Generally, "right tailing" cannot be observed at sonicated samples. The option of repeated ultrasonic processing by a loop setup (see graphic below) allows to find the perfect sonication for every pigment and every ink formulation. Such treated pigment particles result in better ink quality and show higher stability, an increased self life (also at elevated temperatures), freeze-thaw stability, reduced flocculation stable rheology and lower viscosity at higher particle loading.

High power equipment uses more electricity. Considering rising energy prices, this affects the costs of processing. For this reason, it is important, that the equipment does not lose much energy in the conversion of electricity into mechanical output. Regarding energy consumption, ultrasound is to name as very energy efficient. Hielser’s ultrasonic devices convince by outstanding performance and high efficiency. Hielser ultrasonic processors have and outstanding efficiency of >85%. This reduces your electricity costs and gives you more processing performance. Kusters et al. (1994) sum up in their study that ultrasonic fragmentation is equally efficient as conventional grinding.

In another study, Pohl et al. compared the processing efficiency of ultrasonic dispersion of silica with other high-shear mixing methods, such as with an IKA Ultra-Turrax (rotor-stator-system). Pohl et al. compared the particle size reduction of Aerosil 90 (2%wt) in water using an Ultra-Turrax (rotor-stator-system) at various settings with that of a Hielser UIP1000hd ultrasonic device in continuous mode. The table below shows the results.

Table 6 – Comparison of particle size reduction of Aerosil90 (2%wt) by an Ultra-Turrax and by a Hielser ultrasonic device (Pohl 2004)

The study of Pohl et al. concludes that "at constant specific energy E\textsubscript{V} ultrasound is more effective than the rotor-stator-system" and that "the applied ultrasound frequency in the range from 20 kHz up to 30 kHz has no major effect on the dispersion process."

![Graph showing particle size reduction vs specific energy](image)
The breakup of the agglomerate structures in aqueous and non-aqueous suspensions allows utilizing the full potential of nanosize materials. Investigations at various dispersions of nanoparticulate agglomerates with a variable solid content have demonstrated the considerable advantage of ultrasound when compared with other technologies, such as rotor stator mixers (e.g. ultra turrax), piston homogenizers, or wet milling methods, e.g. bead mills or colloid mills. Hielscher ultrasonic systems can be run at fairly high solids concentrations. For example for silica the breakage rate was found to be independent of the solid concentration up to 50% by weight. Ultrasound can be applied for the dispersing of high concentration master-batches – processing low and high viscosity liquids.

6. Conclusion

Dispersing and wet-milling by ultrasonic cavitation is a proven technique to achieve evenly distributed dispersions at nano range as well as particle size reduction down to micron- and nano-size. The full control over the most important parameters – amplitude, pressure, temperature, viscosity, concentration – allows to find the right process adjustment regarding particle characteristics and aimed size. By ultrasonic industrial processors in the power range between 500 watts up to 16 kilowatts per device it becomes possible to develop specific process setups to fulfill specific requirements. By the wide device range, all steps of development – from first testing to process optimization and final production – are covered. The advantages shown above turn ultrasonic dispersing and milling into a potential technology for industrial processing in various sectors, such as for the production of paints and coatings, ink and inkjet, cement and concrete, or cosmetics.
References: