Innovative Use of Ultrasound in the Manufacture of Paints and Coatings

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ABSTRACT

For the color, paint and coating industry, these nanomaterials are of particular interest, as by the addition of nano-sized particles may be prepared paints, varnishes and coatings with special decorative and functional properties. Color and gloss characteristics are numbered among the decorative aspects; conductivity, microbial inactivation or antistatic properties are numbered to the functional aspects. By addition of nanoparticles, also the protective functions of paints and coatings, such as scratch resistance and UV stability can be improved. In the production of novel color and coating formulations, special nano-sized metal oxides, such as TiO₂ and ZnO or alumina, ceria, silica, and nano-sized pigments, have been proven to be extremely promising components.

Conventional devices such as high shear or shear mixer, high-pressure homogenizers or colloid and disk mills do not deliver sufficient power to separate nanomaterial into its individual particles. Particularly for substances in the range of a few nanometers to a few micrometers, the use of high power ultrasound have proven to be a highly efficient and effective means to destroy the agglomerates, aggregates and even primary particles. During the preparation of highly concentrated batches, through the liquid jets, generated by ultrasonic cavitation, interparticle collision is caused. These particles collide with each other at speeds of up to 400 mph. Due to the high intensity interparticular collision, the van der Waals forces in agglomerates and even in the primary particles becomes broken.

Keywords: high performance ultrasound, nano particles, milling, dispersion, deagglomeration

1 NANOMATERIALS IN COATINGS

Nanomaterials are defined by its size of less than 100nm. Since a fairly long time they are part of the innovative materials for industry and research. Therefore, they are in the focus of research and development. In formulations of paints, coatings, inks and coatings increases the use of nanomaterials rapidly. Nanomaterials can be differentiated into three categories: metal oxides, nanoclays and carbon nanotubes.

The metal oxide nanoparticles include nano-sized zinc oxide, titanium oxide, iron oxide, zirconium oxide and cerium oxide, as well as mixed metal compounds, such as indium tin oxide, zirconium and titanium. For the color, paint and coating industry, these nanomaterials are of particular interest, as by the addition of nano-sized particles may be prepared paints, varnishes and coatings with special decorative and functional properties. Color and gloss characteristics are numbered among the decorative aspects; conductivity, microbial inactivation or antistatic properties are numbered to the functional aspects. By addition of nanoparticles, also the protective functions of paints and coatings, such as scratch resistance and UV stability can be improved. In the production of novel color and coating formulations, special nano-sized metal oxides, such as TiO₂ and ZnO or alumina, ceria, silica, and nano-sized pigments, have been proven to be extremely promising components.

Materials in the nano-sized range are very interesting as additives in formulations since they are changing its material properties: When changing the size of these materials, also the material properties are changing, such as the color, the interaction with other substances and the chemical reactivity. This change in material properties results from a change in the electronic properties. By particle size reduction the total surface of the material is increased. Thereby, a higher percentage of atoms can interact with other substances, e.g. with the matrix of epoxy resins. Accordingly, an increased surface activity is given. However, if particles agglomerate or aggregate, the surfaces are blocked and the interaction with other substances is prevented or reduced. Only with well-dispersed and individually dispersed particles exploit the potential of nanomaterials can be fully exploited [4]. The better the particles are dispersed, the higher the amount of active nanomaterial, which causes the desired effects in the final product. Consequently, the consumption of necessary nanomaterial is reduced. Since most nanomaterials are very cost-intensive, the required amount is a major economic factor in the marketing of product formulations.

The conventional production of nanomaterials happens in dry processing. For preparation of formulations, the nanoparticles have to be introduced into a liquid medium. As soon as nanoparticles are wet, they tend mostly to strong agglomeration, so that the surface activity and the specific properties become reduced or even lost. In particular, carbon nanotubes (CNTs) offer high cohesion, which makes it difficult to produce a good dispersion from the nanoparticles and a liquid medium, such as water, oil, ethanol, polymer or epoxy resins.

2 DISPERSION OF THE AGGLOMER-ATES OF NANO-PARTICLES

Conventional devices such as high shear or shear mixer, high-pressure homogenizers or colloid and disk mills do not deliver
sufficient power to separate nanomaterial into its individual particles. Particularly for substances in the range of a few nanometers to a few micrometers, the use of high power ultrasound have been proven as a highly efficient and effective means to destroy the agglomerates, aggregates and even primary particles. During the preparation of highly concentrated batches, through the liquid jets, generated by ultrasonic cavitation, interparticle collision is caused. These particles collide with each other at speeds of up to 400 mph. Due to the high intensity interparticular collision, the van der Waals forces in agglomerates and even in the primary particles becomes broken.

3 THE EFFECT OF ULTRASOUND
As highly intensive ultrasound waves are inserted into fluids, ultrasound cavitation is generated. By the sound waves, alternating high-pressure phases (compression) and low-pressure phases (rarefaction) are created. During the low-pressure phases vacuum bubbles are generated by the ultrasonic waves, which grow and, once they absorb no more energy, implode in a high-pressure phase. During such an implosion, in the so-called hot spots very high temperatures (4500°C) and very high pressures (approx. 2000 bar) are achieved [5]. Also high-speed liquid jets of up to 1000km/h are achieved in the liquid. This phenomenon is called cavitation (Fig. 1).

![Ultrasonic cavitation](https://www.hielscher.com)

The enormous generated forces turn ultrasound into a powerful technology of mixing and grinding for many applications in research, development and production: This high-energy liquid jets break up droplets and agglomerates and let collide the particles with each other, so they are reduced. When mixing of powders into liquids, e.g. in the manufacture of paints, varnishes, coatings, as well as cosmetics, medicines and food, agglomerates are broken up and the particles are dispersed into the liquid medium evenly. This application is also practicable in media with high viscosity, such as in epoxy resins.

In wet milling and micro grinding processes hard particles, such as ceramic, alumina trihydrate or metal oxides, are broken due to interparticle collision caused by ultrasonic cavitation, hence it is possible to produce very fine, even highly concentrated slurries. Especially in processing nanomaterials, the high shear forces of ultrasound have shown as a considerable advantage, as nanoparticles in liquids tend to strong agglomeration.

4 FUNCTIONALIZATION OF PARTICLE SURFACES
In order to turn nanomaterials into suitable fillers in high performance coatings, a functionalization of the particle surface is necessary. To functionalize the entire surface of each particle, an effective dispersion method is needed [4]. If the particles are dispersed, they are usually surrounded by a boundary layer of molecules that are attracted to the particles. The production of new functional groups on the particle surface, the boundary layer must be broken or replaced. The liquid jets, which are generated by the cavitational forces, can reach speeds of up to 1000km/h. The resulting pressure supports the abolition of the bounding forces and transports functional molecules onto the particle surface. In sonochemistry, this effect is used to enhance the performance of dispersed catalysts.

5 PAINT AND COATING QUALITY – DEPENDING ON DEAGGLOMERATION AND DISPERSAION
Titanium dioxide and silica are among the most frequently used additives in paint and coating formulations. The special properties of the materials should improve the product formulation. For such quality enhancements of coatings, particle size and particle distribution are decisive. Ultrasound is a suitable method because of the outstanding cavitational forces outstanding results in de-agglomeration and dispersion of particles can be achieved. Below, the advantages of ultrasonic deagglomeration and dispersing of TiO2 and silica are demonstrated.

5.1 TiO2 Decorative Effects for Optics and UV Resistance
Titanium dioxide is a chemically very inert, light-resistant and inexpensive material. TiO2 is mainly known as white pigment (so-called titanium white) and is valued for its brightening effects, and its dirt-repellent properties. Therefore, TiO2 is often frequented as an additive for coating formulations. TiO2
particles are used in the coatings industry because of its strong color, high opacity, and to improve the light resistance and dirt resistance of a formulation.

![Image of TiO2 particle size reduction](https://www.hielscher.com)

Figure 2: Particle size reduction of TiO2 in water before and after dispersing by a 1 kW ultrasonic processor (© www.hielscher.com)

However, in order to achieve the desired effects the TiO2 particles must be finely grinded and dispersed very evenly into the formulation. Due to the enormous cavitation forces, which are generated by ultrasound, the ultrasonic technology is the appropriate technique to reduce the particle size of TiO2 effectively. Table 1 shows the reduction curves of TiO2 before sonication (red curve) and after sonication (green curve).

### 5.2 Scratch Resistance by Silica

There exists a wide variety of hydrophilic and hydrophobic types of silica, which are mostly used with very small particle diameters, in order to achieve the maximum effect. After wetting, silica is hard to disperse. During the dispersing process, a large number of micro bubbles attain into the product formulation. In most applications, this affects quality and property of formulations negatively.

![Image of silica particle size distribution](https://www.hielscher.com)

Figure 3: Particle size distribution of silica fume before and after sonication with an 1 kW ultrasonic processor (© www.hielscher.com)

If silica is used in coatings and paints to increase the scratch resistance, especially a uniform dispersion is important. The silica particles must be small enough so that they do not interfere with the visible light. Only by a high quality of dispersion, cloudiness can be avoided and transparency can be achieved. Therefore, for most coatings nano-sized silica that is less than 40 nm, is needed as it only can fulfill these requirements. The high tendency of silica particles to agglomerate with each other makes it difficult to assure that every single silica particle can react with the surrounding medium. The reaction of the individual particles with the medium is important for many applications in order to achieve the desired results.

Compared with other high shear mixing technologies, ultrasound-assisted processing shows a more effective method for dispersing of silica. Figure 3 shows a typical result that is achieved by ultrasonic dispersion silica fumes in water. Particle size reduction starts (green curve) at an agglomerated particle size of greater than 200 microns (D50), most particles are reduced to less than 200 nanometers. The significant tailing of the curve to the right results from the material composition (agglomerates and larger primaries). While agglomerates can be reduced quickly and easily, it takes longer processing to grind down larger primary particle.

Pohl and Schubert compared the process efficiency of ultrasonic dispersion of silica with other high shear mixing technologies, such with an Ultra-Turrax. Pohl [2] investigated the particle size reduction of Aerosil 90 (2% wt) in water by means of rotor-stator and ultrasonic system. He compared an Ultra-Turrax (rotor-stator system) at various settings with those of a 1 kW ultrasonic processor in flow mode. The Figure 4 shows the results. Pohl sums in his studies up that ultrasound with a consistent specific energy EV is more effective than the rotor-stator system. Accordingly to the applied ultrasonic frequency in the range of 20 kHz up to 30 kHz, there can no greater effect on the dispersion process be measured.

![Image of particle size reduction comparison](https://www.hielscher.com)

Figure 4: Particle size reduction: comparison of a rotor stator mixer and high performance ultrasound - relation of energy and particle size of Aerosil90 [2]

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