

# Converting of nanoparticles in industrial product formulations:

## Unfolding the innovation potential

S. Schaer, G. Arnosti, S. Pilotek, F. Tabellion and H. Naef

Buhler AG, Division Engineered Products, Uzwil 9240, Switzerland, samuel.schaer@buhlergroup.com

### ABSTRACT

Potential users of nanoparticles seek for particles in a ready-to-use form. The market currently offers practically only raw materials and standard nanoparticles not tailored to a specific application. A newly developed chemo-mechanical converting process for ready-to-use nanoparticles and formulation is presented. This technology is based on the combination of the mechanical comminution in agitator bead mills and the small molecule surface modification concept. Tailored nanoparticle formulations are developed in close cooperation with the client, scaled to the required amounts and subsequently are produced. Our business model is focused on tailor-made solutions for our client's product innovation allowing the flexible and in-time implementation as well as an easy access to nanotechnology at a low risk.

**Keywords:** nanoparticle dispersion, converting technology, surface modification, agitator bead mill, tailored processing

## 1 NANOPARTICLE MARKET

Market experts estimate the potential of nanoparticles to be overwhelming. For example the US-NSF (National Science Foundation) projected an expected market size for nanomaterials alone of USD 340 billion by 2010-2015. Product developers around the world agree on the large potential linked to the use of nanoparticles in products. Actual and future application areas of nanoparticles will include the sectors of coatings, inks, plastics, resins, sealants, adhesives, technical pastes, ceramics as well as consumer products, catalytic applications ranging from chemistry to electronics, pharmaceutical and cosmetic products. Furthermore the use of nanomaterials will not only enhance the performance of already existing products, but also lead to entire new products and production processes. From this point of view, it can be assumed that these materials will be ubiquitous in our near future.

However, sales in ceramic nanoparticles only totaled an estimated USD 150 million in the US for 2003. If one accepts the NSF figures, that market should be growing at incredibly high double-digit percentage rates, which it currently does not. This is even more astonishing, since in the last decade a tremendous amount of research was focused on the production of these fine particles. The

production technologies for various materials including  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , ITO etc. are well known and the necessary industrial production capacities are established.

But why are the sales and consequently the utilization of nanomaterials still on such low levels and far away from the predictions?

### 1.1 The Gap in the value chain

One of the main reasons for this is the fact that industrial converting techniques suitable for the user, meaning the manufacturer of the final products, are not available or not developed yet. This includes the whole processing route, starting from the particle handling, particle processing and converting up to the final material components and application. Nanopowders suffer from agglomeration due to the enormous particle-to-particle interaction and chemical forces, which cannot be resolved by traditional dispersion technology. Using a nanoparticle to unfold its inherent functionality in an application means incorporating or technically speaking converting it into a product on the nanoscale. This is where the difficulty starts: Nanopowders currently available on the market are not readily dispersible and therefore not ready-to-use.

In other words, today we see a massive gap in the value chain of nanomaterials.

On the one side of the value chain are more than 200 producers of nanoparticles selling raw materials, not customized to the customer's prerequisite. On the other side are thousands of potential users of nanoparticles representing various industry branches.

### 1.2 Standard vs. tailored product approach

Chemical companies as well as start-ups have introduced standard nanoproducts in the form of dispersions into the market. It is self-evident though, that such standard materials in most cases cannot fulfill the different requirements of the diverse industrial applications. Typically product developers of companies interested in using nanoparticles test these materials on a trial and error basis in their formulation. As those standard nanoparticle dispersions are not tailored to the end product formulation, dispersion and stability does not work out. In consequence the nanoparticles agglomerate. In addition, the nanoparticles are typically not functionalized for the end application. Thus developers are not obtaining the

improvement results they are looking for through the use of nanoparticles. Scratch-proof coatings end up not being scratch-proof enough or too expensive, nanocomposites do not show the desired enhancement of the mechanical properties, transparent UV protection using nanoparticles ends up not being transparent enough just to name a few.

To bridge the gap in the value chain, Buhler is pursuing a different approach to overcome the massive disadvantages of standard products. This approach is based on tailor made nanoparticle formulations specifically customized for the users needs and requirements. Nanoparticle formulations are developed in close cooperation with the client, scaled to the required amounts and subsequently produced. The business model allows the flexible and in-time implementation and enables access to nanotechnology at a low risk. The underlying technology, the business model including the products and services will be discussed in the following.

## 2 TECHNOLOGY

### 2.1 Chemomechanical processing approach

Conventional industrial powder converting tasks involve processes including three-roller-mills, mixers, dissolvers, extruders and agitator bead mills. Whereas this technology is sufficient for micron- and sub-micron-sized particles, a new approach is mandatory for the processing of nanoparticles.

We propose a technique for converting nanoparticles in agitator bead mills comprising the simultaneous utilization of chemical and mechanical competences called chemomechanical processing.

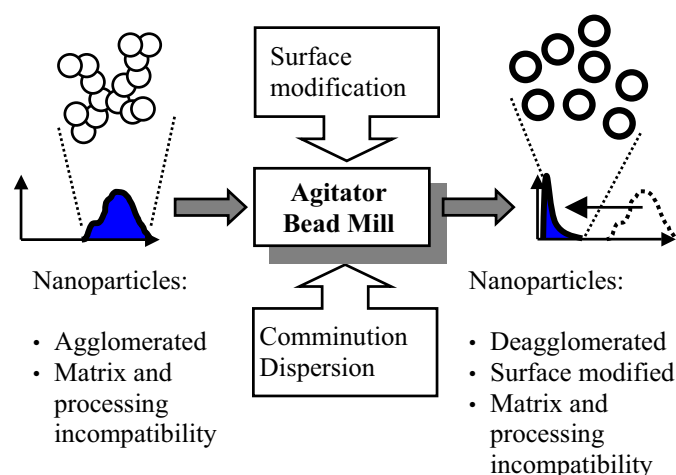


Figure 1: Chemomechanical processing

This technique is based on the combination of a) the mechanical comminution of agglomerated nanopowders in agitator bead mills and b) the rules of colloidal chemistry utilizing surface modification in order to tailor the particle

surface chemistry. Using this technology agglomerated nanoparticles, which are incompatible for the further processing techniques will be converted into tailor made deagglomerated and functionalized dispersions ready for the later processing (fig.1). Furthermore this technology has the potential for the production of nanoparticles and nanodispersions by real comminution of larger particles. This applies also for application areas, where to-date no production technology exists.

### 2.2 Agitator bead mill reactor

Agitator bead mills provide a number of advantages in the processing of nanoparticles. Agitator bead mills are devices to process suspensions with high energy at controlled conditions. Solid state nanoparticles are processed in the liquid phase, which facilitates their easy further processing into the end products. The method itself is established, known and used for a long time. Therefore, a lot of experience is available about principles, constructive possibilities as well as about the processing details. Grinding in agitator bead mill is a scaleable process and thus industrially relevant. The large variety of available constructive details provides many possibilities for optimising processes, e.g. different grinding chamber geometries, grinding media separation, and cladding materials. For nanoparticle processing the milling chamber has to be understood as a reactor where complex chemical reactions can be conducted under well-defined mechanical conditions in the wet phase. Agitator bead mills are advantageous in this respect, as they provide a defined volume and a readily controllable energy input. Because of the large tendency of nanoparticles to form conglomerates, the challenge of separating the particles to obtain a highly dispersed state is comparable to a real comminution rather than a dispersion process. Therefore, the mill will be operated usually in the recirculation mode, as this set-up allows for a higher energy input than passage-wise operation. (fig.2).

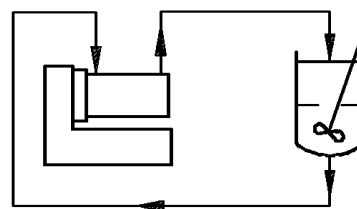


Figure 2: Flow sheet of passage-wise operation of agitator bead mills

Experience has shown, that for traditional wet grinding processes a particle size of ca. 100-200 nm seems to constitute a major barrier in comminution. In many cases, increasing the energy input does not lead to finer particles. This has to be interpreted in terms of specific surface area

and Van der Waals forces, which increases rapidly by reducing the particle size and approaching the barrier of 200 nm. If no precaution for the stabilization is carried out, a balance between deagglomeration and agglomeration leads to a stagnation of the comminution process and the resulting particle size distribution.

### 2.3 Chemical surface modification

In principle suspensions can be stabilized by making use of electrostatic, steric and electrosteric stabilization techniques. The purpose of these techniques is to prevent the re-agglomeration, meaning the formation of large agglomerates and the subsequently occurring destabilization of the suspension.

The simplest way to stabilize nanoparticles is to make use of the electric repulsion by generating an electrical charge at the particle surface due to a pH value change.

Unfortunately, the usability of this approach in product formulations is heavily restricted and permits its broad utilization. The second principle of steric stabilization refers to geometric arguments of holding particles apart, whereas electrosteric stabilization describes a combination of both means. Such sterical/electrosteric stabilizers are mostly polymeric or oligomeric compounds with high molecular weight. These large molecules provide several bonding sites to occupy the surface groups of the nanoparticles. The utilization of such large molecules for the stabilization of nanoparticles, especially particles in the size range between 10-100 nm, suffers from different drawbacks. As a first geometric argument, large molecules are able to hide nanoparticles inside of their large volume. This phenomenon might be relevant for certain applications, where particle-medium interaction is important, e.g. scratch resistance. At the same time, the solid content in terms of volume % is rather limited. Albeit for functional nanoadditives small degrees of filling are preferred, the freedom of formulation is reduced, if the dispersant constitutes a major part in the functional nanoadditive. Importantly, with nanoparticles, the many binding sites of a polymeric dispersant may lead to the generation of a new type of agglomerates, when the sites do not bind to the same but to adjacent particles. In dependence of the molecular size of the dispersant, these conglomerates may even encompass several particles. The resulting conglomerates will not show the wanted properties of nanodispersions.

Based on these considerations the herein presented chemomechanical processing technology utilizes the so called small molecule surface modification concept. This concept relies on the chemical bond principles known from solution chemistry and employs them for the anchoring of the surface modifiers (small molecules) on the nanoparticle surface. The basic principle of the surface modification, using organic acids as an example, is shown in figure 3.

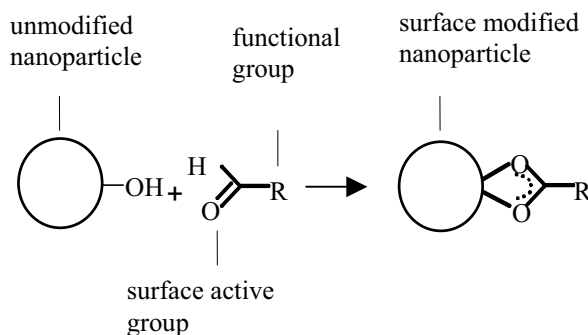


Figure. 3: Basic principle of a surface modification

As surface modifiers for nanoparticles bifunctional molecules are employed. One of the groups is reactive towards the surface of the particles to form a stable connection between particle and surface modifier, whereas the other group is to be chosen in terms of the later application or the required functionality. For the stabilization of nanoscaled suspensions the surface modifier needs to be compatible with the solvent, i.e. the respective part of the surface modifier needs to be soluble. Those small molecules still provide sufficient barrier for holding nanoparticles apart, but reduce the organic content to a minimum. Moreover, molecular surface modifiers are paradigm for nanoparticles, as they allow the specific tailoring of the particles' surface by introducing a functionality. This in turn is indispensable for manufacturing processable nanoparticle dispersions, as nanoparticles are highly responsive to their environment.

## 3 BUSINESS MODEL, PRODUCTS AND SERVICES

Buhler is a global technology, know-how and project partner for efficient production systems, engineering solutions and related services. As the world market leader in grinding & dispersion equipment we consequently own massive know-how in comminution down to the nano range and are powerfully present in the vital markets. From this point of view, it was a natural evolution to move into the nanoparticle technology market making the chemomechanical processing technology utilizable for the benefit of our customers. For this reason, three years ago Buhler has formed a strategic alliance with the INM (Institute for New Materials), which is a world wide leading institute for nanotechnology with more than ten years experience in this area. This alliance comprises the compulsory competence, know how and IP in mechanical comminution and surface modification. In combination with Buhler's competences in engineering and logistic as well as its strong market position all the vital components for a successful market implementation are given.

The Buhler nanotechnology business model is particular focused on tailor-made solutions for our clients product

innovation by closing the gap in the value chain of nanomaterials. This will be accomplished by an overall processing solution for the production of customized nanoparticle formulation as well as customized toll production.

From the company perspective the mission of nanotechnology is clear: a) to foster and stimulate the existing machinery business, b) to open up larger market shares in the area of process sales and c) to create new business in the area of products (Fig 4.). This strategic direction towards a more process and product oriented business will subsequently create recurring revenues compared to the traditional machinery business.

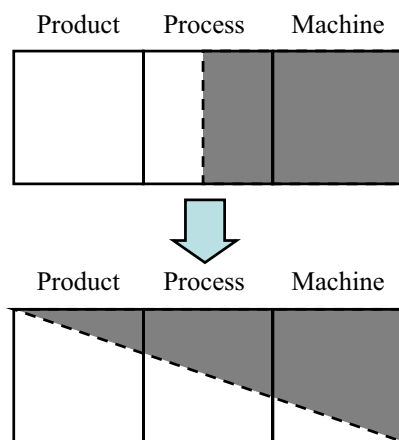


Figure 4: Mission of Nanotechnology

Beside the existing markets, where Buhler is already strong, our material independent technology allows to target various additional markets ranging from currently hot areas in the coating and lacquer industry, the electronic or cosmetic industry to markets where the use of nanoparticles is on a low level or even nanoparticles are not introduced yet.

From the customer's perspective Buhler's strategy offers easy excess to nanoparticle technology, especially to a tailored one. Furthermore this approach permits the customers to protrude into hitherto unanticipated markets, or to distinguish themselves from their competitors. Because customized solutions are specifically developed for the ennoblement of the customer's product, the time to market will be short. In contrast to classical contract research, carried out by institutes, the development and adaptation necessary to achieve a tailored solution will be carried out by Buhler, on our own expense, tremendously reducing the risk and capital expenditure for the customer. Additionally, the required development goes far beyond the horizon of the capability of classical contract research covering all steps from the laboratory, to the pilot plant till to the final industrial scale.

Foreseeing the diverse customers requirements, especially regarding the production place, Buhler has launched the product Buhler-Tailored Nanoprocess® and the service

Buhler-Tailored Nanobatch®. Both offers are focused on the production of the tailored nanoparticle formulations. In the case of the Nanoprocess, the customer will be put into the position to carry out the production at its own facility, whereas in the case of a Nanobatch® Buhler is the toll producer and supplies the ready to use formulation. Apart from a small symbolic retention free paid by the customer Buhler is covering the whole expenses for the development. The retention free is later refunded by a discount on the purchase of materials from Buhler.

## 4 CONCLUSION

Buhler offers, for the first time, with its product Buhler-Tailored Nanoprocess® and the service Buhler-Tailored Nanobatch® an easy access to tailored nanoparticle formulations and production processes. It can be anticipated that such tailored solutions will close the currently existing gap in the value chain of nanomaterials and sustainably shape the landscape of this new emerging technology by unfolding the potential of the inherent particle functionality in real-life applications.