

Nanoparticles in coatings

Tailoring properties to applications.

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In order to fully realise the potential advantages of nanoparticles in coatings, it is necessary to consider carefully the techniques of dispersion and stabilisation used. Surface modification is essential to retain the particles in a dispersed state, and this must be tailored to the coatings formulation. The chemomechanical processing of nanoparticles in an agitator bead mill is a versatile means of producing tailored nanoparticles in a highly dispersed state.

The market potential of nanoparticles is estimated by market researchers to be enormous [1], and coatings are among the first applications to be discovered by the nanoparticle industry. This is understandable in the light of the many potential advantages nanoparticles offer in coatings applications.

This interest derives from the property profiles of nanoparticles. First, nanoparticles possess the intrinsic properties of the material they are made of. Silica remains silica at small scales, titanium dioxide still has a high refractive index, and zinc oxide still absorbs UV light if its particles are nano-scale. These features can be retained within a coating. Probably the most notable property as the particle size is reduced is the change in light scattering: particles which are small enough may produce transparent coatings.

This situation is not simple, however. Nanoparticles do not induce transparency directly, but rather their light-scattering effects decrease with decreasing particle size. At the same time, light scattering is dependent on the difference in refractive index between particle and surrounding medium. A close match in refractive indices favours the creation of transparent mixtures.

Defining the dimensions of nanoparticles

There are several different approaches to defining the term "nano". Because of the interest that the subject has generated, "nano" has become a new term with which to advertise established products. At the other extreme, "nanotechnology" is used in science to describe effects which arise from the quantum structure of fine particles. A pragmatic approach is to use a size criterion to define the "nano"-regime. Here, the term "nanoparticles" refers to solid particles with a size between 1 and 100 nm.

The "dimensional properties" of nanoparticles that arise from their size are quite striking. As an example, consider the colour of inorganic fluorescent pigments, which changes gradually from red to green as the particle size becomes smaller [2].

Miniaturisation might be regarded as a dimensional feature in itself: if the film thickness of a coating is restricted by the size of fillers, the use of small particles permits the application of thinner coatings, and thus the application of coatings to more finely structured objects or simply the use of less paint material.

Powders of small particle size necessarily possess high specific surface areas. Therefore, the specific surface area itself could also be considered a dimensional property. High surface areas are attractive in various applications. In paints and coatings, "surface" translates into "interface" between particle and medium. A higher proportion of interfaces results in more interaction between matrix and particle and thus a toughening of the material.

Dispersion is the key to effectiveness

The typical property profile of nanoparticles is only observed if the particles are dispersed down to the nanoscale. For example, particles must be very well dispersed to achieve transparency in a nano-scale system, since agglomerated nanoparticles show the same optical properties as particles having the same size as the agglomerate. Processable nano-dispersions of particles are rare on the market, and this may be a major reason why nanoparticles have not yet achieved their predicted market volumes.

There are several methods of producing nanoparticles, through gas phase-, liquid phase- and solid state reactions [3-6]. Because of the general tendency to reduce surface energy, smaller particles tend to agglomerate more easily. The utilisation of nanoparticles in coatings therefore requires a process that provides simultaneous deagglomeration and chemical stabilisation of the particles.

Chemomechanical processing: a versatile dispersion technique

A new technique of nanoparticle processing in agitator bead mills, involving the concurrent use of chemical and mechanical effects and called chemomechanical processing, allows the production of nanodispersions from a wide range of materials and for a wide range of applications. Agitator bead mills offer a number of advantages in the processing of nanoparticles. These mills process suspensions with high energy under controlled conditions in a defined volume. The particles are processed in the liquid phase, which facilitates further processing into paints and reduces the risk of dust generation.

The method itself is well-established, and therefore a great deal of experience is available concerning its principles, operational and processing capabilities. The process is scaleable and thus industrially relevant. For nanoparticle processing, the milling chamber can be understood as a reaction vessel where chemical reactions can be conducted under well-defined mechanical conditions.

Experience has shown that for traditional wet grinding processes a particle size in the region of 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 may be interpreted in terms of specific surface area (Figure 1). The specific surface area increases rapidly with decreasing particle size in this size range. As the particles interact via their surfaces, inter-particle forces similarly increase, resulting in a strong tendency to build up agglomerates. For larger particles these may be called flocculates, in which the interstices between individual particles are filled with medium. This may not be true for nanoparticles, as their attractive forces may be so strong that real agglomerates are formed.

Three methods of stabilisation

Suspensions of particles in liquids may be stabilised by electrostatic, steric or electrosteric means. Electrostatic stabilisation is easily achieved by adjusting the pH value of the suspension. The principle of steric stabilisation refers to geometric arrangements for holding particles apart, whereas electrosteric stabilisation describes a combination of both methods.

Polymeric or oligomeric compounds are often employed as classical dispersants. These molecules provide several sites to attach to the particle surface, such that the physisorption of each site provides in total enough energy to attach the dispersant molecule to the particle. When polymeric dispersants are used, electrosteric stabilisation can be

induced by polyelectrolytes such as sodium polyacrylates.

Nanoparticles need nanodispersants

The molecular weight of the dispersant is chosen to overcome the attractive forces between the particles. While this also holds true for nanoparticles, the relationship between the molecular size of the dispersant and the size of the particles in question also needs to be considered. In nanoparticle processing, the molecular size of the dispersant needs to be reduced for several reasons.

As an initial geometric consideration, large molecules can hide nanoparticles inside their large volume. At the same time, the solids content in terms of percentage by volume is rather limited. In consequence, if the dispersant constitutes a major part of the functional nanoadditive, the freedom of formulation is reduced. Critically, the many binding sites of a polymeric dispersant may also lead to the formation of a new type of agglomerate when the sites bind not to the same but to adjacent nanoparticles.

In contrast, small molecules provide a sufficient barrier for holding nanoparticles apart. In addition, molecular surface modifiers allow the particles' surface to be specifically tailored, which is indispensable for manufacturing processable nanoparticle dispersions.

The chemistry of nanoparticles may be compared to that of molecular compounds, which is a consequence of one of the scientifically interesting features of the nano dimension, i.e. that the description of nanoscale matter may be approached from the macroscopic or from the molecular direction. Nanoparticles can thus be considered as large chemical compounds and therefore as reaction partners for specific molecular surface modifiers. This concept allows a broad range of reactants to be utilised, enabling the particle surface to be tailored to specific applications.

Compatibility: a key issue

Bifunctional molecules are employed as surface modifiers for nanoparticles. One group is reactive towards the surface of the particles to form a stable link between particle and surface modifier, whereas the other group can be chosen arbitrarily. For the stabilisation of nanoscale suspensions the surface modifier needs to be compatible with the solvent, i.e. the relevant part of the surface modifier needs to be soluble. Where the mechanical properties of coatings are to be improved by nanoparticles, the situation is more complex. Mechanical impact such as scratches leads to propagation of stress inside the coating material. At the interface between separate phases inside the material, the stress increases since it cannot be transferred. If the stress exceeds a material-dependent threshold, the coating fractures. As a result, the simple addition of particles does not necessarily yield mechanically improved materials. By contrast, if a surface modifier chemically connects the coating polymer and particles, stress can be transferred to the particles and thus be dissipated.

The chemical binding of surface modifiers can be observed analytically, for example through the shift of the carboxyl resonance of a carboxylic acid in the FTIR spectrum (Figure 2) [7].

High levels of particle-medium interface are important to improve mechanical properties. Consequently, particles with a high specific surface area, that is to say nanoparticles, are useful even if transparency is not the main goal.

Choice of starting materials affects particle size

The crucial point of chemomechanical processing of nanoparticles is the combination of mechanical and chemical processes. Chemical processing of agglomerated powders in general does not lead to stable

nano-suspensions, nor does grinding alone achieve the required results, as explained above. The comminution of particles may be regarded as a reaction in itself and thus the grinding chamber is a vessel where the reactions of fracturing and surface modification take place.

The processing of zirconia has been investigated quite thoroughly. Of course, one parameter is that the outcome of the process is dependent on the starting materials. Using precipitated nanoscale zirconia (with primary particle size < 10 nm) a suspension could be prepared in which 90% of the particles were smaller than 30 nm (d_{90} , measured in terms of volume distribution). Figure 3 shows a TEM micrograph of the particles before and after chemomechanical processing. This result was achieved using a carboxylic acid and production-scale parameters. However, using zirconia synthesised via a flame pyrolysis process (with a primary particle size of ca. 30 nm), a suspension with d_{90} of ca. 100 nm was obtained. Zirconia might be interesting as a nanoadditive in coatings because of its high hardness as well as its high refractive index.

Silica: a transparently popular additive

Silica particles are of considerable interest in coatings. This is partly because of the price of silica, but also due to the favourable match between the refractive index of silica and that of many organic polymers. If a colloidal suspension is used as the starting material, the comminution part of the process may be omitted. Figure 4 shows a particle size distribution for colloidal silica particles. Nevertheless, to obtain processable nanoparticles, their surface needs to be tailored to be usable as nanoadditive in organic matrices. The effect of surface modification of silica on compatibilisation with paints has been investigated.

As a first step, the transparency of compositions containing 5% silica nanoparticles by weight in a paint formulation was investigated (Table 1). The transparency may be evaluated using the transmission coefficient γ , which combines the effects of both particle size and differences in refractive indices. Small values of γ indicate high transparency, while values of $\gamma > 100$ indicate opaque materials. Using a suitable surface modification, excellent states of dispersion were achievable.

Theoretically, using 100 nm silica particles highly transparent mixtures with $\gamma < 10$ in epoxy resins, and still transparent mixtures with $\gamma > 10$ in polyols are obtainable, but opaque mixtures with $\gamma > 100$ are obtained in butyl acetate. Using 20 nm silica particles, transparent compositions are in theory achievable with either medium. We used epoxy- and alkyl- silanes to produce suitable surface modification of colloidal silica particles. This produced particles in a highly dispersed state in the respective paint components as shown by the low values of γ in Table 1.

In a sample polyurethane paint, the particles were introduced into the hydroxyl component, the hardener was added and coatings were prepared. The results emphasise the importance of surface modification. Whereas both modifications led to transparent coatings using the basic system, the addition of a levelling additive resulted in incompatibility when the particles had an epoxy group surface modification. In contrast, when using a suitable alkyl silane modification, transparent coatings could be obtained even with the levelling agent (Table 2). This shows that the tailoring of surface modification has to take into account the complete paint formulation rather than single components, as nanoparticles are highly sensitive to their environment.

Controlled particle size makes UV protection invisible

Zinc oxide may be taken as an example of a UV-protective agent. Zinc oxide produced by solid state synthesis in particular has a very narrow particle size distribution, especially when compared with that synthesised by other routes. The size of the particles was 25 nm as confirmed by BET, XRD, and TEM analysis (Figure 5). The combination of the small particle size and narrow particle size distribution leads to a sharp band edge profile in the UV-VIS spectrum (Figure 6).

This feature makes it extremely interesting for applications as a UV-protective agent in coatings such as wood coatings. The transparency is high in the visible range yet low at UV wavelengths. The inorganic particles were modified to be compatible with a highly non-polar solvent ("Shellsol 100"). This allow a highly dispersed state to be achieved in this solvent.

Key considerations for success with nanoparticles

In conclusion, modification of the surface of nanoparticles is essential if the application demands particles in a nano-dispersed state. The particles need to be tailored to the application, principally to the paint composition, as nanoparticle systems are quite sensitive to changes in the formulation. The chemistry of nanoparticles is comparable to that of molecular substances and thus established chemical concepts can be applied. Using agglomerated nanoparticles as starting materials, the chemomechanical processing of nanoparticles in an agitator bead mill is a versatile means of producing tailored nanoparticles in a highly dispersed state.

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Results at a glance

- Modification of the surface of nanoparticles is essential if the application requires particles to remain in a nano-dispersed state.
- Nanoparticle systems are very sensitive to changes in formulation and thus the surface modification must be tailored to the application.
- High levels of performance and transparency can be

obtained when using appropriately modified nano-particles.

- The chemistry of nanoparticles can be considered as comparable to that of molecular substances.
- Chemomechanical processing of nanoparticles in an agitator bead mill is a versatile means of producing tailored nanoparticles in a highly dispersed state.

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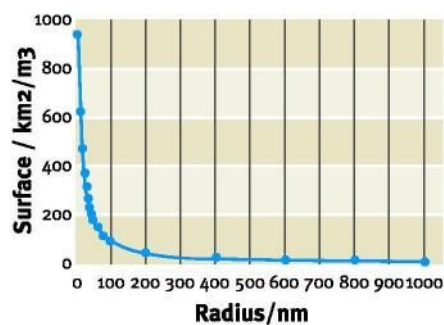


Figure 1: Variation of specific surface area with particle size

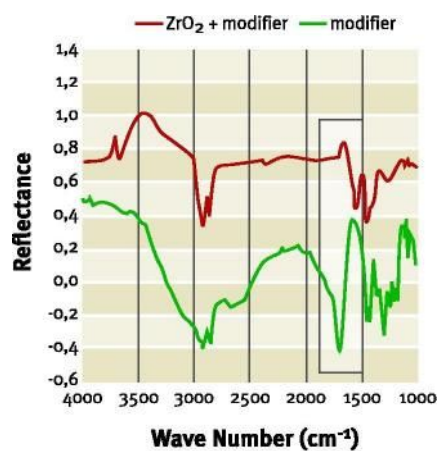
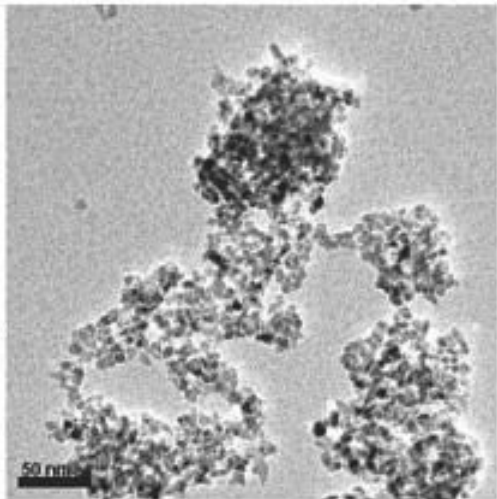


Figure 2: FTIR spectra of surface modifier (green line) and surface modifier when bound to zirconia particles (red line)

**agglomerated ZrO_2
before processing**



**ZrO_2
after processing**

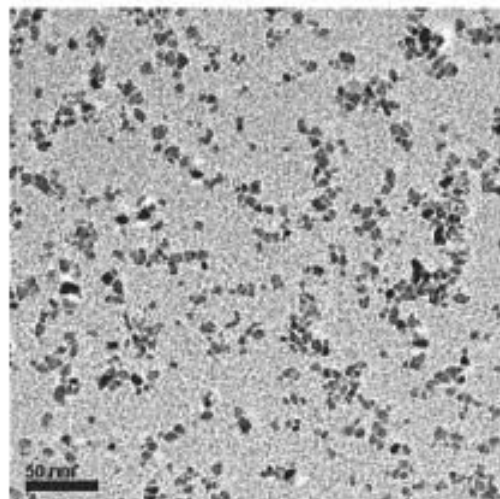


Figure 3: TEM micrograph of zirconia particles before (left) and after (right) chemomechanical processing. Bar length corresponds to 50 nm

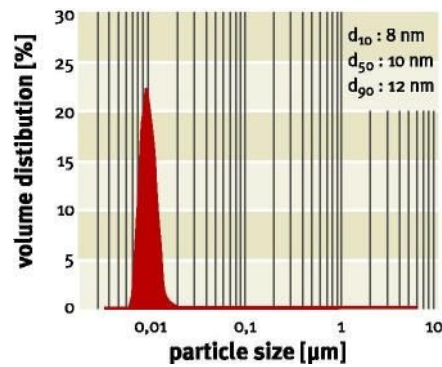


Figure 4: Particle size distribution of colloidal silica, showing 90% of particles with diameter less than 12 nm

Nanoscaled ZnO: TEM

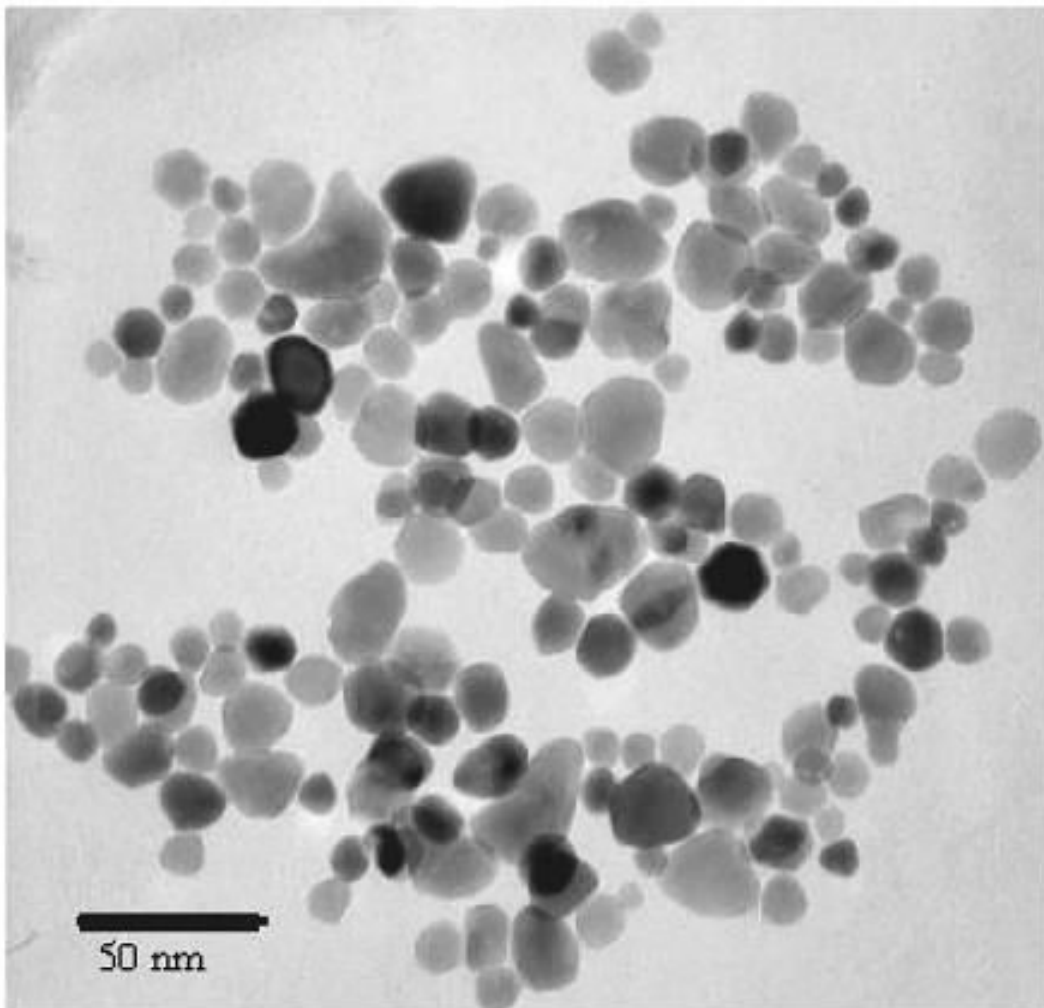


Figure 5: TEM micrograph of nanoscale Zn. Bar length corresponds to 50 nm. By courtesy of APT

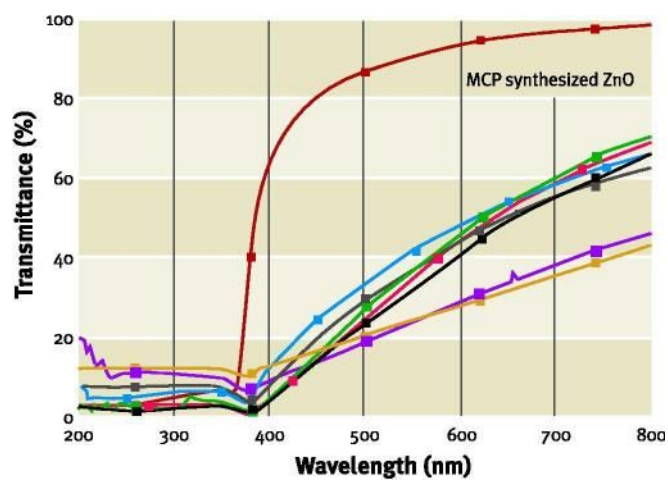


Figure 6: Absorption spectra of nanoscale zinc oxide synthesised by different methods. MCP = mecha-nochemical synthesis (solid state reaction); by courtesy of APT

Table 1: Practical and theoretical values of the transmission coefficient γ for compositions of modified silica in paint components

Transparency (Transmission-coefficient) of SiO ₂ -formulation	D ₉₀ /nm	γ Epoxy resin	γ Polyol resin	γ Butylacetate
n_D^{20} of organic component		~ 1,50	~ 1,48	~ 1,39
Modification A	< 20	0,5	0,8	2,0
Modification B	< 20	0,2	0,6	3,1
Theory	20	0,01	0,1	2,3
Theory	100	1,5	14	290

Table 2: Haze of nanocomposite coatings containing 5% modified silica and comparative values for coatings without silica

Formulation	Without silica	Epoxy silane	Alkyl silane
2-K polyurethane	$\leq 0.3\%$	$\leq 0.3\%$	$\leq 0.3\%$
Above + levelling additive	$\leq 0.3\%$	3.0%	$\leq 0.3\%$