Nanotechnology Additives

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Nanotechnology and Nano-based Additives

Nanotechnology deals with the fact that properties of materials can change drastically when the size falls below approximately 100 nanometers (1 nm = 10⁻⁹ m) in at least one dimension. Nano-scale materials have already found applications in paint and coatings.

Nanoparticles can improve the properties of coating systems in several ways, but at the moment, the focus is clearly on the improvement of UV-stability (ZnO, CeO₂) and scratch resistance. Alumina (Al₂O₃) and silica (SiO₂) particles have been found useful for this application.

**Scratch resistance**

It is well known, that hard particles, such as alumina and silica, will improve scratch and abrasion resistance when they are brought into a coating film. However, when large particles of several microns in diameter are used, serious drawbacks are encountered: gloss and transparency of the (clear) coatings are markedly reduced and flexibility is lost. Therefore, this approach oftentimes cannot be used in practice.

With nanoparticles, the situation is different. Nano-sized alumina and silica will also improve scratch resistance but these particles have a very minor influence on other coating properties. Specifically, gloss, transparency, flexibility remain unchanged. This combination of properties can only be achieved with nanoparticles (figure 1).

**UV Absorption**

Conventional organic UV absorbers are prone to degradation and do not provide long-term protection. Inorganic UV absorbers on the other hand, have excellent long-term efficiency and titanium dioxide as well as zinc oxide are used in various industries. Titanium dioxide requires special surface treatments to mask its inherent photoactivity. Zinc oxide as well as ceria exhibit no photoactivity, and their lower refractive index result in less impact on transparency. Nano-sized zinc oxide and ceria particles are therefore ideal UV absorbers (figure 2).

**Nanoparticle dispersion**

Most important is the perfect dispersion and stabilization of the nanoparticles in the coating. The advantage of the NANOBYK additives is, that they already come in form of a liquid additive where the nanoparticles are perfectly dispersed in a liquid carrier (water or organic solvents). The additives can be added to the coating system with moderate shear forces and in this way it is very easy to make use of nanotechnology in your coatings.

**Improved Scratch Resistance in a Coating with Nano-sized Alumina Particles.**

![Improved Scratch Resistance in a Coating with Nano-sized Alumina Particles.](image1)

**UV Protection of a Clear Wood Stain**

![UV Protection of a Clear Wood Stain](image2)
Nanoparticles are characterized by their
• Chemical composition,
• Size,
• Shape,
• Structure,
• Surface chemistry
and it should be noted, that different
methods of synthesis can lead to marked
differences in the structure and
properties of the nanoparticles. With
different manufacturing processes non-
porous particles are created with a mean
particle size between 5 and 100 nm.
The particles have a low aspect ratio,
high chemical purity and a controlled
surface chemistry. The surface character-
istics become extremely important when
the particles are introduced into a liquid
medium such as water, organic solvents,
or directly into aqueous or solvent-borne
coatings. The ease of dispersion,
dispersion stability (flocculation,
segregation) and rheology of the systems
depend heavily on the surface properties
of the particles.
Post treatment (coating) of the
nanoparticles either in the vapor or liquid
phase offer even more possibilities to
modify and control the surface properties.
Figure 5 shows the different
nanoproducts and their corresponding
processes.

Due to their non-porous structure and
controlled surface chemistry,
nanoparticles synthesized by the vapor
phase plasma process are easy to disperse
in liquid media, and the resulting
dispersions are highly stable, low
viscosity (even at higher concentrations)
and therefore easy to handle.
Chemically there is a wide variety of
nanoparticles that can be manufactured
using the described methods. For
coatings, the focus today is on alumina
and silica particles (Al₂O₃, SiO₂) to improve
scratch resistance, and ZnO as well as
CeO₂ particles for UV protection.
Alumina and ZnO particles are produced
by vapor phase synthesis and the silica
and ceria nanoparticles are chemically
synthesized colloidal particles.
All these materials are currently produced
in commercial quantities and additives
making use of such nanoparticles in
form of dispersions in water and organic
media are now brought to market under
the trade name NANOBYK.
UV protection of coatings
A coating must withstand various environmental conditions, and light, especially UV radiation (short wavelength, high energy) plays an important role in the deterioration of coating films. UV radiation experienced during exterior exposure is strong enough to break the covalent bonds of the polymeric backbone of coating systems. Free radicals formed by the UV degradation destroy the polymer matrix.

To improve the light-fastness of coating systems, it is essential to protect the paint film from UV radiation with UV stabilizers. Basically, there are two methods for stabilization:

- Absorption of the UV radiation before free radicals that damage the polymer structure (filter effect) are formed; compounds that adsorb UV radiation, called UV absorbers are used.
- Trapping the initially formed free radicals before they can further destroy the polymeric matrix; free radical scavengers, or hindered amine light stabilizers (HALS) are used.

In practice, combinations of both additives types are typically used together.

UV absorbers
Conventional UV absorbers are organic molecules with various chemical structures. They have the drawback that they do not exhibit long-term stability in coatings. Inorganic compounds such as titanium dioxide, ceria and zinc oxide also absorb radiation in the UV region and they have the additional advantage of greater long-term protection (figure 6). Their disadvantage is, that – because they are solid particles – they can reduce the transparency of the coating film. This effect can be minimized by reducing their particle size to nanometers; the smaller the particle size, the greater the transparency (figure 7). In addition to particle size, refractive index will also impact transparency. The smaller the difference between the refractive index of the polymer matrix (typically around 1.5) and the solid particles, the greater the transparency. Therefore, zinc oxide with a refractive index of 2.0, outperforms titanium dioxide with a refractive index of 2.7 (figure 8).

Comparison of Organic and Inorganic UV Absorbers

<table>
<thead>
<tr>
<th>Property</th>
<th>ZnO</th>
<th>CeO₂</th>
<th>TiO₂</th>
<th>Organic Absorbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparency</td>
<td>o</td>
<td>+</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>Long-term Stability</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>No Migration</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>No Photoactivity</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>UV-Absorption Edge</td>
<td>&lt; 370 nm</td>
<td>&lt; 350 nm</td>
<td>&lt; 370 nm</td>
<td>varies</td>
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</tbody>
</table>

Influence of Particle Size on Film Transparency

<table>
<thead>
<tr>
<th>Haze</th>
<th>ZnO 40 nm</th>
<th>ZnO 60 nm</th>
<th>Control</th>
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</thead>
<tbody>
<tr>
<td>228</td>
<td>113</td>
<td>92</td>
<td>192</td>
</tr>
</tbody>
</table>

Influence of Refractive Index of Particles on Film Transparency

<table>
<thead>
<tr>
<th>Haze</th>
<th>ZnO, refractive index 2.0</th>
<th>TiO₂, refractive index 2.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>262</td>
<td>92</td>
<td>97</td>
</tr>
</tbody>
</table>

Nano-sized Zinc Oxide and Cerium Dioxide for UV Absorption
One of the main applications of nanoparticles in coating materials is their incorporation to improve scratch and abrasion resistance. This application is interesting for automotive clearcoats, wood and furniture coatings and industrial coatings.

Using NANOBYK additives containing nano-sized alumina particles is an easy way to improve scratch resistance. This concept of additives containing dispersed and stabilized nanoparticles was evaluated in different aqueous and solvent-free UV clearcoat systems as well as solvent-borne baking formulations.

Scratch resistance was evaluated using a dry scrub abrasion tester and measuring the gloss after testing. The appearance of the surface without and with nanoparticles in the clearcoat was previously shown in figure 1 while figure 9 shows typical gloss values. Various test methods for evaluating scratch resistance are available and they are often application specific. Test results depend to a large extend on the method and equipment employed.

Results show that the combination of nanoparticles and conventional silicone surface additives (organically modified polysiloxanes) can enhance the performance of the nano additives. This effect is shown in figure 10. This synergistic effect between nanoparticles and silicone-based surface additives is not yet entirely understood. It is evident that the specific combination of nanoparticles and silicone additives gives the best scratch resistance, the extent of this effect depending on the chemical nature of the matrix and on the additive structure and composition.

Obviously a type of core-shell-structure is formed that controls the compatibility between the nanoparticles, resin matrix, and at the same time optimizes stabilization in the coating system.

Therefore the general recommendation is: NANOBYK additives that contain unmodified nanoparticles should always be used in combination with polysiloxane-based surface additives to enhance their efficiency.
Surface-modified Nanoparticles
As previously shown, the effect of nanoparticles on scratch resistance can be enhanced, when they are combined with modified polysiloxanes. The next step is to use silicone-modified nanoparticles, where the polysiloxane is chemically linked to the particle’s surface. Figure 11 shows the typical result of such surface-modified nanoparticles in an automotive refinish clearcoat (2-pack acrylic/isocyanate).

The “control” sample, in practice, often uses an additive blend of 0.1% silicone additive and 1% acrylate leveling additive. The sample with nanoparticles contains only these particles as additives, no additional silicone or acrylate additives.

Additionally, these nano-additives have no negative influence on viscosity, potlife (in case of 2-pack systems), flow and leveling of the liquid coating as well as gloss, haze, adhesion, flexibility, recoatability and water resistance of the final coating.

Alumina vs. silica particles
Alumina and silica nanoparticles can both be used for the improving scratch resistance. Oftentimes alumina particles are preferred for its higher hardness (Mohs hardness of alumina: 9, silica: 7). Because silica particles are softer, considerably higher dosages are required to achieve the same level of scratch resistance. However, silica particles have a distinct advantage: they have less influence on the transparency of clearcoats.

The haziness that is created by solid particles in a clearcoat depends on their size and the refractive index of the particles. Nanoparticles between 20 and 40 nm are already small enough so that they only have a minor effect on haze. However, there remains a difference between alumina and silica particles because of their different refractive indices. Important here, is the difference of the refractive indices between the particles and the resin of the coating system. The greater the refractive indices difference, the greater the haze.

Alumina has a refractive index of 1.72 and silica of 1.55, while most resins are in the range of 1.5. This explains why silica nanoparticles have less influence on the haze of clear coatings. So alumina particles are better for scratch resistance, while silica particles give less haze in highly transparent coatings. This statement is true for unmodified nanoparticles; the situation changes when nanoparticles with silicone surface-modifications are considered. The silicone-modification improves the performance of the nanoparticles considerably and brings silica particles into the same range of efficiency as the unmodified alumina particles.

This is demonstrated in figure 11: a small amount of surface-treated silica nanoparticles giving excellent scratch resistance. Silicone-modified silica nanoparticles are ideally suited for applications where extremely transparent coatings are required (such as automotive refinish systems or other industrial applications) as well as excellent scratch resistance.

These surface modified NANOBYK additives normally need no additional silicone or acrylate surface additives in the formulation.

Improved Scratch Resistance with Silicone-modified Silica Nanoparticles

Mohs Hardness and Refractive Indices of Alumina and Silica Particles

<table>
<thead>
<tr>
<th>Particle</th>
<th>Mohs Hardness</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>9</td>
<td>1.72</td>
</tr>
<tr>
<td>Silica</td>
<td>7</td>
<td>1.55</td>
</tr>
</tbody>
</table>
Products and Applications

BYK Additives
Additives are used during the production of coatings, printing inks and plastics to optimize the production process and to improve the quality of the final product.

Product Range Additives
• Additives to improve surface slip, leveling and substrate wetting
• Adhesion Promoters
• Defoamers and air release agents
• Foam stabilizers
• Processing additives
• Rheological additives
• UV-absorbers
• Viscosity depressants
• Waxes
• Wetting and dispersing additives for pigments and extenders

Application Areas
• Ambient curing resins (FRP)
• Architectural coatings
• Automotive OEM
• Automotive refinishes
• Can coatings
• Coil coatings
• Color masterbatches
• Industrial coatings
• Leather coatings
• Marine paints
• Molding compounds
• Paper coatings
• Pigment concentrates
• Polyurethane foams
• Powder coatings
• Printing inks
• Protective coatings
• PVC plastisols
• Thermoplastics
• Wood and furniture coatings

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This brochure replaces all previous issues – printed in Germany.
NANOBYK Additives

Improved Scratch Resistance
UV Protection
# Surface Additives for Improved Scratch Resistance

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Non-volatile matter (%)</th>
<th>Nanoparticle content (%)</th>
<th>Liquid carrier</th>
<th>Particle size D50 (nm)</th>
<th>Recommended for</th>
<th>Applications</th>
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</thead>
<tbody>
<tr>
<td><strong>NANOBYK-3600</strong></td>
<td>Alumina</td>
<td>55</td>
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<td>Water</td>
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<tr>
<td><strong>NANOBYK-3601</strong></td>
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<td>30</td>
<td>TPGDA*</td>
<td>40</td>
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<tr>
<td><strong>NANOBYK-3602</strong></td>
<td>Alumina</td>
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<td>Methoxypropylacetate</td>
<td>20</td>
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<tr>
<td><strong>NANOBYK-3650</strong></td>
<td>Silica, surface modified with polysiloxane (linear, non-polar)</td>
<td>31</td>
<td>25</td>
<td>Methoxypropylacetate/Methoxypropanol 6/1</td>
<td>20</td>
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<td><strong>NANOBYK-3651</strong></td>
<td>Silica, surface modified with polysiloxane (branched, polar)</td>
<td>34</td>
<td>20</td>
<td>Methoxypropylacetate/Methoxypropanol 6/1</td>
<td>20</td>
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<tr>
<td><strong>NANOBYK-3652</strong></td>
<td>Silica, surface modified with polysiloxane (linear, medium polar)</td>
<td>31</td>
<td>25</td>
<td>Methoxypropylacetate/Methoxypropanol 6/1</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

* TPGDA = tripropylene glycol diacrylate  
** HDDA = hexanediol diacrylate

Our complete range of additives for coatings can be found in the Product Guide L-G 1.  
Further Product Guides for special topics:  
Additives for Radiation Curing Systems (L-G 5)  
Additives for Aqueous Coatings (L-G 6)
# Inorganic UV Absorbers

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Non-volatile matter (%)</th>
<th>Nanoparticle content (%)</th>
<th>Liquid carrier</th>
<th>Particle size D50 (nm)</th>
<th>Recommended for</th>
<th>Applications</th>
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<tr>
<td>NANOBYK-3810</td>
<td>Cerium oxide 23</td>
<td>18</td>
<td>Water</td>
<td>10</td>
<td></td>
<td>Architectural coatings (wood care)</td>
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<td>NANOBYK-3812</td>
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<td>Aromatic-free white spirits</td>
<td>10</td>
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<td>NANOBYK-3820</td>
<td>Zinc oxide 45</td>
<td>40</td>
<td>Water</td>
<td>20</td>
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<td>Wood and furniture coatings, wood stains</td>
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<td>NANOBYK-3821</td>
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<td>Methoxy-propylacetate</td>
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<td>Solvent-borne wood, furniture and industrial coatings</td>
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<td>Water</td>
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<td>Wood and furniture coatings, wood stains</td>
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<tr>
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<td>Zinc oxide 44</td>
<td>40</td>
<td>Methoxy-propylacetate</td>
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<td>Solvent-borne wood, furniture and industrial coatings</td>
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<tr>
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<td>Aromatic-free white spirits</td>
<td>40</td>
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<td>Architectural coatings (wood care)</td>
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<tr>
<td>NANOBYK-3860</td>
<td>Zinc oxide 55</td>
<td>50</td>
<td>Water</td>
<td>60</td>
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<td>Architectural coatings (wood care)</td>
</tr>
</tbody>
</table>

Typical usage level: 2-6% additive (as supplied) based upon resin solids. Optimal dosage of UV absorbers depends on coating thickness. Thin films require higher dosages whereas for thicker films lower dosages are sufficient. All UV absorbers can be used in combination with radical scavengers (HALS).

## Have a Look at our NANOBYK Website

![NANOBYK Website](www.NANOBYK.com)
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