The use of dispersed nanosized functional materials in Coating applications

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• Relationship between preparation and shape

• Why dispersion of nano particles is important.

• How Al$_2$O$_3$ and SiO$_2$ influence scratch resistance

• What types of coatings can benefit from nano.

• Improvement of UV protection in Paint and Plastic using nano
Unique Nanoparticles

- Nanoparticles from other methods may overlap, but do not share the same particle properties.
- Plasma-produced nanoparticles have unique properties.
Comparative Processes → Alumina

Plasma Vapor Alumina
- Spherical & discrete particles

Flame Synthesis Alumina

Precipitated Alumina
- Irregular, aggregated & agglomerated
How to
Disperse?
Stabilize?
Functionalize?

NANOPARTICLES
Wetting and Dispersing Process

1. Wetting
   - Displace air and wet particle

2. Dispersion
   - Energy input

3. Stabilization
   - Prevent re-flocculation
Wetting Additives
Dispersing Additives
W&D Additives vs. Covalent Surface Treatment
Impact of W&D–additive on deflocculation / stabilization

System: 2 Pack Acrylate / NCO

No W&D–additive

W&D–additive
Functionalized Nanoparticles

Nanoparticle Core
- mechanical, chemical electrical
  - Nanoparticle Shell
    - reactivity ↔ compatibility
  - Tailored Interface

Nanoparticle Shell
- Solubility
- Resin Compatibility

Nanoparticle Boundary Phase
- Solubility
- Reactivity
- Compatibility
Role of Boundary Phase

Expansion of boundary phase on Nanoparticles provides

- compatibility
- extends functionality (e.g. scratch resistance)
- lower loading requirements
Dispersing Nanomaterials
Example “Baytubes®”
Dispersing Carbon Nanotubes
Cooperation with Bayer Material Science

1% MWCNTs in PMA
Without dispersant

1% MWCNTs in PMA
With dispersant
Wetting & Dispersing – Key Factor in Stabilization

Microscopic images

Decreasing Agglomerate Size

Increasing Stability

Pictures were taken 2 months after dispersing

0,1% CNT in PMA
0,05% W&D

0,1% CNT in PMA
0,1% W&D

0,1% CNT in PMA
0,15% W&D
Dispersing Nanomaterials
Example ZnO
Dynometer Testing – 5% ZnO dispersions to estimate the time of settlement

Crystal density 5.6g/cc

- 5% 60 nm not treated
- 5% 60 nm
- 5% 40 nm
- 5% 20 nm
Hot box testing – 7 days at 140° F
Why Nano Dispersions Work for Scratch and Wear Resistance
Mechanisms of Scratch Resistance - Boundary Phase Properties

homogeneously distribution of NP in coating system
- good improvement of scratch resistance properties
- good long time stability
- good elasticity
Nanotechnology Advantage

1 wt% particles dispersed in a coating:

- 1 um diameter = 4 particles
- 20 nm diameter = 10,000 particles

Nanotechnology enables more particles per unit area, and significantly decreases particle-particle separation.
## Scratch Damage of Polymeric Materials

<table>
<thead>
<tr>
<th>Response (Pictorial)</th>
<th>Generic</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic</td>
<td></td>
<td>180°</td>
</tr>
<tr>
<td>Ironing</td>
<td></td>
<td>150°</td>
</tr>
<tr>
<td>Ductile Ploughing</td>
<td></td>
<td>120°</td>
</tr>
<tr>
<td>Ductile Machining + Cracking</td>
<td></td>
<td>90°</td>
</tr>
<tr>
<td>Brittle Machining</td>
<td></td>
<td>60°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0°</td>
</tr>
</tbody>
</table>
Scratch Profiles at 49 mN for Filler B system
NB-3610 / 20 nm Alumina / ST 2
Scratch Results – Images

Unfilled

NB-3610

NB-3650

Control

25 nm $\text{Al}_2\text{O}_3$

~ 2 % Nanoparticles
Scratch Resistance of Aqueous Acrylic AD Coating
High Gloss over time

Gloss 20° [%], ASTM D 2486 abrasion tester, 100 cycles 00 steel wool
Effect of Nano-particles in Aqueous AD Coatings

1.0% Loading of Nano Alumina
• improves scratch resistance (gloss retention)
• 20nm alumina imparts early resistance properties (24 hrs)
• 40 nm requires longer dry time 96 hours for same properties
Scratch Resistance of Aqueous Acrylic/Urethane AD Satin over time 25% PUD 75% Acrylic

Gloss 60 ° [%], ASTM D 2486 abrasion tester, 100 cycles 00 steel wool

<table>
<thead>
<tr>
<th>Condition</th>
<th>No Rubs</th>
<th>96 hr 100 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% 40nm Al2O3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% 60 nm Al2O3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% 60 nm Al2O3 + wax</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% 40nm Al2O3 + wax</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Best
Taber Abrasion
Abrasion Resistance of Aqueous Acrylic/Urethane AD Satin Finish

25% PUD 75% Acrylic

CS 10 Abrading wheel, 1000g load, 3X4 mil WFT coats

Graph showing weight loss at 100 cycles and 1000 cycles for different treatments:
- Control
- Wax
- 1% 40nm Al2O3
- 1% 60 nm Al2O3
- 1% 60 nm Al2O3 + wax
- 1% 40nm Al2O3 + wax
Effect of Nano-particles in Aqueous AD Coatings

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• improves scratch resistance (gloss retention)
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• Improves burnish resistance of matted coatings
• Nano-Alumina with wax for best burnish resistance
• Nano-Alumina with wax for best Taber Abrasion resistance
Adhesion and Scratch Resistance of Acrylic Water borne Coating to Fiberglass

Control

1% 60 nm Al₂O₃
Effect of Nano-particles in Aqueous AD Coatings

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- Improves burnish resistance of matted coatings
- Nano-Alumina with wax for best burnish resistance
- Nano-Alumina with wax for best Taber Abrasion resistance

- Improves stress relief resulting in better adhesion
AFM Control

Gloss 20 ° [%] Haze, modified abrasion scrub tester, ASTM D2486

No Rubs

1000 Rubs
AFM 1.2% (40nm) Nano Alumina

Gloss 20 ° [%]  Haze, modified abrasion scrub tester, ASTM D2486

No Rubs

1000 Rubs
AFM 1.2% Nano Alumina (25 nm)

Gloss 20 ° [%] Haze, modified abrasion scrub tester, ASTM D2486

No Rubs

1000 Rubs
500 rubs        Control

UV Clear
Effect of Nano-Particles on Scratch resistance

- Prevents gloss loss in high gloss systems
- Prevents burnishing in flatted and satin systems
- Smaller nano-particles provide greater scratch resistance
UV light damages surfaces

Surfaces exposed to direct sunlight usually suffer from the solar UV radiation that destroys organic compounds such as

- dyes and pigments
- binders
- polymers
- organic substances in wood
Types of UV-Absorbers for Coatings

Organic UV absorbers and HALS

- Absorbers
  - Hydroxyphenylbenzotriazoles
  - Hydroxybenzophenones
  - Hydroxyphenyl-S-triazines
  - Oxalic anilides
- HALS (Hindered Amine Light Stabilizers)

Inorganic UV absorbers

- **Zinc oxide**
- **Cerium oxide**
- Titanium dioxide
- Transparent iron oxide
The Ideal UV Absorber

Transmittance [%] vs. Wavelength [nm]

- UV
- Visible
## Nanoadditives for UV protection

<table>
<thead>
<tr>
<th>Property</th>
<th>ZnO*</th>
<th>CeO₂</th>
<th>TiO₂</th>
<th>Organic Absorbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarity</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>Chemical Stability</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>UV-Absorption Edge</td>
<td>≈ 375 nm</td>
<td>≈ 350 nm</td>
<td>≈ 375 nm</td>
<td>varies</td>
</tr>
<tr>
<td>Absorption Efficiency</td>
<td>o</td>
<td>o</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

*: ZnO was listed in Europe as Biocide until 2005
Nanoadditives for UV protection
Comparison of ZnO, Ceria and Titania

![Graph showing the comparison of ZnO, Ceria, and Titania in terms of UV protection. The graph displays the transmission percentage against wave length in nanometers. The x-axis represents wave length in nm, ranging from 200 to 900. The y-axis represents transmission percentage, ranging from 0 to 100. The graph includes curves for different film thicknesses: 60 nm ZnO, 40 nm ZnO, 20 nm ZnO, 10 nm Ceria, and 15 nm Titania. Each curve is color-coded for easy differentiation. The graph highlights the efficiency of various nanoadditives in absorbing UV light at different wavelengths.]
Uniform distribution of the proper particle size ZnO ensures maximum substrate and coating protection.

The smaller and finer the ZnO particle distribution the greater the protection!
Optimum Stabilization of Nanoparticles is necessary to see benefits of Nanotechnology
The smaller the particles the lower the haze!

Transparency of NANOBYK-3800 series
Influence of particle sizes

The smaller the particles the lower the haze!
Transparency of NANOBYK-3800 series
Influence of particle concentration

The lower the particle concentration the lower the haze!

Concentration of ZnO particles

HAZE [a.u.]

20 nm ZnO
20 µm film
Nanoscale ZnO for UV protection
Thin Film (30 µm) Coating – 2000 h QUV-A Testing
Furniture & Parquet Coating

A: Control
B: 0,5% Organic Absorber
D: 0,5% 40 nm ZnO
F: 0,5% 15 nm TiO₂
H/L: Competitive ZnO Samples

C: 1,0% Organic Absorber
E: 1,0% 40 nm ZnO
G: 1,0% 15 nm TiO₂
Results in Water Borne Coatings
Thin Film Glazing (Bayhydrol 2342 Aqueous Aliphatic)
750h QUV-B Dry Testing

Control  2.5% 40nm ZnO  2.5% 20nm ZnO
Latest’s Results from Water Based Coatings
Thick Film (120 µm) Coating – 1000 hrs QUV-A Dry Testing
Furniture & Parquet Coating
Nanoadditives for UV protection
Aqueous-based Acrylic PUD Formula – Natural Exposure: 15 months – 10 nm Ceria*

Douglas fir (1% on active matter)

Ceria
Conventional organic UV absorber
Organic UV absorber + Hals
Reference

*: Patent Protected Technology
Nanoadditives for UV protection
Aqueous-based Acrylic PUD Formula – 1600 h Xenon Test – 10 nm Ceria*

Red Cedar (1% on active matter)

Ceria
Conventional organic UV absorber
Conventional mineral UV absorber
Reference

*: Patent Protected Technology
Transparency and functionality is the key driver for nanotechnology in paint application

- Synthesis, Material, Particle size, and Boundary Phase determine nanomaterials performance benefits
- Low refractive index and high efficiency are key in nanotechnology for paint application.

Nanoparticles improve

- Scratch resistance of high gloss high transparent coatings to low gloss transparent coatings
  - UV Coatings: 0,3 – 2,0% Nanoparticles
  - 2K Coatings: 1,0 – 2,0% Nanoparticles
  - Air-Drying solvent based coatings: 0,3 – 2,0% Nanoparticles
  - Air-Drying water based coatings: 0,3 – 3,0% Nanoparticles
  - Forced-Dried solvent based coatings: 1,0 – 4,0% Nanoparticles

UV-Protection in transparent and pigmented coatings 1,0 – 6,0% NP
NANOBYK–3650: Handling Ease
“This could be the discovery of the century. Depending, of course, on how far down it goes.”