Positive property enhancement of water-borne coatings using nanoparticle based performance additives

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Outline

1. The introduction: Buhler PARTEC

2. The challenge: Reduction of VOC in coatings

3. The technology: Novel use of agitator bead mills

4. The solution: Nanoparticle based performance additives

5. Conclusion
Milestones in nanotechnology at Buhler

1990 - Grinding and comminution of materials down to sub-micron and nanometer size (inks, ceramics) by business unit grinding and dispersion

2002 Start of the strategic collaboration with the INM Leibniz Institute for New Materials in Saarbrucken, Germany

2002 Start of a dedicated team at Buhler for market analysis and development of a suitable business model

2004 Launch of products Buhler-Tailored Nanobatch® and Buhler-Tailored Nanoprocess® based on patented converting technology

2005 Bundling of all activities in nanotechnology in new business unit PARTEC* and foundation of subsidiary Buhler PARTEC GmbH in Saarbrucken, Germany

* PARTEC = PARticle TEChnology
Question: How can the functionality of nanoparticles unfold in real world products?

Value chain

Nanoparticle-Producer

Buy my nanoparticles!

Nanoparticle-User

How to incorporate them in my product?

Names Degussa and Vernel used as illustrative examples only
Innovation: Mastering of converting interface between producers and users of nanoparticles

Value chain

Nanoparticle-Producer

Improvement: Surface modification of nanoparticles ensures ability to process the latter in real world product

Nanoparticle-User

Dispersion device

Surface modifier
Buhler PARTEC main fields of activity
Revenue breakdown by type of business

By material

- ZrO₂
- Al₂O₃
- TiO₂
- SiO₂
- ZnO

By application

- Various emergent applications
- Reinforcement (chemical/mechanical/UV)
- Easy-to-clean
Close to high tech developments ...
Development center Saarbrucken - 100kg scale
Production Site Uzwil with capacity 500 tons pa
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Water borne paints and coatings account for ¼ of the total global paints and coatings market

Technology segments for paints and coatings (global) in %

Global paints and coatings market (2007):
By volume: 28.8 mio t/a
By revenues: 83 BCHF
Environmentally friendly coatings are on the rise

Technology segments in paints and coatings over time* in %

* Western European Coatings Market
Source: 2005 estimate on internet by Gesellschaft Deutscher Chemiker

Reduction of solvent borne coatings not in line with original expectations
Pressure rising: European initiative for clean air (CAFE) will increase market share of water-borne coatings

* VOC: Volatile Organic Compounds (organische Lösungsmittel)

Source: Deutsches Lackinstitut GmbH
Can nanoparticles improve waterborne coatings?

- **Chemical properties**
  - Resistance against solvents e.g. MEK, IPA
  - MEK double rub resistance
  - IPA double rub resistance
  - Water permeation

- **Mechanical properties**
  - Adhesion (Crosscut, tape)
  - Abrasion resistance (Taber 100; 200 Cycles)

- **Optical properties**
  - Gloss (60°)

- **Processing parameters**
  - Drying time
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Ready to use nanodispersions to overcome obstacles

Surface modification of nanoparticles ensures compatibility to solvent or matrix material

**Functional group X:**
- $X = \text{alky, aryl...}$
- $X = \text{multiple bonds } z.B. \ C=\!C, \ C=C, \ C=\!N...$
- $X = -\text{NR}_2, \ -\text{COOH}, \ -\text{SH}, \ .....$

**Tailored properties:**
- hydrophobicity/hydrophilicity
- acidity/basicity
- $pH$ of the isoelectric point
- polymerizable groups, etc.
Dispersions of surface modified nanoparticles: Production by chemomechanical processing

Agglomerated nanoparticles, incompatible with matrix and processing

Agitator Bead Mill

De-agglomerated nanoparticles, surface modified and compatible with matrix and processing (tailor-made)
Performing SMSM through chemomechanical processing in an agitator bead mill

**Process setup**

1. ABM
   - C
   - P

2. ABM
   - S
   - C
   - P

3. ABM
   - C
   - E
   - P

4. ABM
   - S
   - C
   - E
   - P

**Devices**

- **Increasing Viscosity**
  - Bühler K60
  - Drais\textsuperscript{DM} Super Flow
  - Drais\textsuperscript{DM} SuperTex\textsuperscript{®}

ABM=Agitator Bead Mill, P=Pump, C=Container (S=Start, E=End)
The reaction kinetics with fast diffusion and coordinative bonding of SMSM are key.

Recirculation mode grinding
Mechanical comminution/deagglomeration and in situ functionalization
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Oxylink nanoparticles increase chemical resistance by chemical interaction with polymeric latex

Film formation without and with Oxylink nanoparticles

Stable dispersion:
• droplets of resin in water
• droplets carry reactive groups

Application and drying:
• water evaporates
• resin droplets stack
• physical drying (no chemical bonding)

Coalescence:
• resin droplets merge
• continuous film forms

resin droplet: polymer chain

• Oxylink nanoparticles are stabilized in coating formulation

H₂N

COOH

CH=CH₂

Oxylink nanoparticle

• nanoparticles connect reactive groups
• higher network density results in increased chemical resistance
Oxylink™: ZnO nanoparticle based performance additive

Characteristics of dispersion

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content</td>
<td>40 wt.%*</td>
</tr>
<tr>
<td>Density</td>
<td>1.5 g/ml*</td>
</tr>
<tr>
<td>Viscosity</td>
<td>4 mPas*</td>
</tr>
<tr>
<td>pH</td>
<td>8.5*</td>
</tr>
</tbody>
</table>

*: typical values, no specifications
Oxylink™: ZnO nanoparticle based performance additive

The dispersion challenge

1. Disperse water soluble particles in water with surface active surfactants
2. Make sure dispersion remains stable when mixed with coating formulation
3. Ensure amphiphilic behavior of nanoparticles during film formation to go from water in the acrylic phase
4. Ensure cross linking effect during drying

Controlled surface chemistry is the magic ingredient
MEK double rub stability improved for acrylic resins*

- Pure acrylic dispersion + coalescence agent
- Significant improvement due to nano additive

* End point detection: coating destroyed

according to ASTM D 5402
Not only „single point“ effect

- MEK double rub improvement for different other coating materials
- Both acrylates and PU-acrylate hybrid material can be improved
- Oxylink™ concentration: 0.9 wt.% (solids/solids)
Nano particles can also improve humidity resistance

Acrylic coatings exposed to saturated water vapor atmosphere
→ wax dispersion containing coating remains white after drying
→ Oxylink™ containing coating changes back to clear after drying

Coatings are placed face-down over water-filled petri dishes at 40 °C for 48 h

Wax additive (left sample) and Oxylink™ (right sample) after drying
## Fully formulated waterborne acrylic wood coatings

### EXTERIOR TRANSLUCENT HIGH BUILD STAIN BASED ON PRIMAL AC-337 ER (HBST)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primal AC-337 ER *¹ (45.5%)</td>
<td>655.1</td>
</tr>
<tr>
<td>TegoFoamex *² 825</td>
<td>2</td>
</tr>
<tr>
<td>Water</td>
<td>100.8</td>
</tr>
<tr>
<td>Texanol *³</td>
<td>23.1</td>
</tr>
<tr>
<td>Aqueous ammonia (28%)</td>
<td>2.7</td>
</tr>
<tr>
<td>Water</td>
<td>201.6</td>
</tr>
<tr>
<td><strong>OXYLINK</strong>™ *⁴</td>
<td>6.95</td>
</tr>
<tr>
<td>Acrysol RM-12W *¹(19%)</td>
<td>6.75</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
</tr>
</tbody>
</table>

*¹ Rohm & Haas, USA  
*² Evonik Tego Chemie GmbH, Germany  
*³ Eastman Chemicals ltd, UK  
*⁴ Bühler PARTEC, Germany  

### EXTERIOR TRANSPARENT WOOD GLAZING BASED ON WORLEECRYL 7461 (WG)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Worleecryl 7461*⁵</td>
<td>762</td>
</tr>
<tr>
<td>water</td>
<td>166</td>
</tr>
<tr>
<td>Dow Corning Add. 65</td>
<td>02</td>
</tr>
<tr>
<td>water: Ethylen glycol 1:1</td>
<td>42</td>
</tr>
<tr>
<td>Acrysol RM 5000 *¹</td>
<td>3</td>
</tr>
<tr>
<td>Dow Corning Add. 57*⁶</td>
<td>5</td>
</tr>
<tr>
<td><strong>OXYLINK</strong>™*⁴</td>
<td>11</td>
</tr>
<tr>
<td>water</td>
<td>9</td>
</tr>
</tbody>
</table>

*¹ Rohm & Haas, USA  
*⁵ Worlée-Chemie GmbH, Germany  
*⁶ Dow Corning, USA
Overall usage properties significantly improved (part 1)

EXTERIOR TRANSLUCENT HIGH BUILD STAIN BASED ON PRIMAL AC-337 ER (HBST)

- Drying time (drying stage 4)
- Gloss (60°)
- Gloss retention solvent rub, IPA
- Gloss retention solvent rub, MEK
- IPA double rub resistance
- MEK double rub resistance
- Water permeation
- Adhesion (Crosscut, tape)
- Taber 200 Cycles

Graph showing comparison of properties with and without Oxylink.
Overall usage properties significantly improved (part 2)

EXTERIOR TRANSPARENT WOOD GLAZING BASED ON WORLEECRYL 7461 (WG)
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Conclusion

- Can nano particles improve waterborne coatings?

  - Yes, they can!

- Oxylink™ can significantly improve the chemical resistance of waterborne coatings

- Oxylink™ can significantly reduce the drying time of waterborne coatings

- No negative impact on other usage properties found so far
CENARIOS – Managing nano-specific risks

- “CENARIOS” = Certifiable Nanospecific Risk Management and Monitoring System

- 3 Modules:
  1. Hazard Assessment/ Risk evaluation
  2. Monitoring trends in science, regulation and technology
  3. Issues-Management and Communication

- Implemented at Buhler in Sept. 2007
- Certified by German certification authority TÜV