Anti-UV waterborne nanocomposite coatings for exterior wood

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INTRODUCTION

World demand for Architectural Paints is forecast to rise 3.9% per year through 2011 to a total of 21.5 million metric tons, valued at 47$ billion (US).

Water-based paints will expand their share of the global market to 73%.

Source: The Freedonia Group, Inc.
# MOTIVATION

## Effects of UV on wooden substrates and wood coatings

<table>
<thead>
<tr>
<th>Wooden substrates</th>
<th>Wood coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin degradation</td>
<td>Embrittlement, cracking</td>
</tr>
<tr>
<td>Destruction of cell structure</td>
<td>Yellowing of resins</td>
</tr>
<tr>
<td>Discoloration</td>
<td>Loss of adhesion, delamination</td>
</tr>
<tr>
<td>Cracking</td>
<td>Discoloration</td>
</tr>
<tr>
<td>Increase of water retention</td>
<td>Loss of gloss, chalking</td>
</tr>
<tr>
<td>Decay attack</td>
<td>Environmental etching</td>
</tr>
</tbody>
</table>

## Photostabilization using nanosized UV absorbers

- **Zinc oxide** (broad absorption spectrum from UVA to UVC)
- **Titanium oxide** (absorption edge 350 nm)
- **Cerium oxide** (broad absorption spectrum from UVA to UVC)
AGGREGATION TENDENCY OF NANOPARTICLES

*high specific surface area* => *high surface energy*

Surface modification involves dispersants which stabilize the colloidal dispersion of nanoparticles.

**A. Steric stabilization** - this involves polymers added to the system adsorbing onto the particle surface and preventing the particle surfaces from coming into close contact.

**B. Electrostatic or charge stabilization** - this is the effect on particle interaction due to the distribution of charged species in the system.

**Factors affecting Zeta Potential:**
1. pH;
2. Conductivity (particles with zeta potentials > +30 mV or < -30 mV are considered stable);
3. Concentration of a formulation component.
MATERIALS

Exterior acrylic latex paint (SICO)

Nanoparticles of ZnO:
Hydrophilic version (Degussa, 20 nm)
Silanized version (Degussa-Evonik, 20 nm)

Nanoparticles of TiO$_2$:
Uncoated (Sigma, 20 nm)
Coated with Si and Al (Sachtleben, 10 nm)

Commercial water-based dispersions:
Predispersed nano-CeO$_2$, 10 nm (Byk Chemie)
Predispersed nano-ZnO, 20 nm (Byk Chemie)
Predispersed nano-ZnO, 40 nm (Byk Chemie)
Predispersed nano-ZnO, 60 nm (Byk Chemie)
Predispersed nano-ZnO, 20 nm (Degussa)

Dispersants:
Poly(acrylic acid) sodium salt PAA (M=2100 and 5000)
Poly(methacrylic acid) PMAA
Polyacrylamide PAM (M=17000)
Copolymer of acrylic acid and sulfonated monomers
Substrate

Black Spruce (Picea mariana):

✓ softwood used for the production of structural timber (frames, lining, roofs, scaffolding, forgery - floors, skirting, decking);
✓ easy to dry;
✓ good quality of machining;
✓ weak aptitude to impregnation with preservatives;
✓ low natural durability (decay attack).

<table>
<thead>
<tr>
<th>$D_b$, kg/m³</th>
<th>$D_0$, kg/m³</th>
<th>$\beta_r$, %</th>
<th>$\beta_t$, %</th>
<th>$\beta_v$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>406</td>
<td>445</td>
<td>3,8</td>
<td>7,5</td>
<td>11,1</td>
</tr>
</tbody>
</table>

Surface preparation prior to coating:

✓ conditioning at 8% humidity (2 weeks);
✓ final sanding was made with the sandpaper 150 (average particle diameter=92 μm)
EXPERIMENTAL

Acrylic resin (latex)
Additives
(wetting agent, pigment dispersant, defoamer, levelling, thickener, rheologic and plasticizer agent, filler, surfactants, biocide etc.)
Pigment (TiO₂, rutile, 250 nm)
Nanoparticles (ZnO, TiO₂, CeO₂)
(powder or aqueous dispersions)
Water & co-solvent

Nanoparticles Dispersant Water

High speed mixing
High-frequency sonication

Colloidal dispersion of nanoparticles

Nanoparticles Dispersant Water

Dispersion

Nanocomposite paint

Application & air drying

Nanocomposite coating

Cole-Parmer® 750-Watt Ultrasonic Processors with Temperature Controller
Weather-Ometer ATLAS Ci3000+

Water cooled Xenon lamp
- Inner and outer filter: Borosilicate
- Wavelength: 340 nm
- Irradiance: 0.35 W/m²
- Temperature on black panel: 63°C

Cycle A (400 hours): 100% UV exposure
Cycle B (400 hours): 108 minutes UV and 12 minutes UV and water spray.

Color: L*, a*, b*
(ASTM E2366)
every 48 hours

Gloss, 60°
(ASTM D523)
48 hours or more

Colorimeter
BYK-GARDNER

Micro-TRI-glossmeter
BYK-GARDNER

Adhesion strength by pull-off method
(ASTM D4541)
before and after the weathering

Accelerated weathering (ASTM G155, ASTM D6695, ISO 11341)
RESULTS

Cycle A

Color changes

CIE L*a*b* system

- △ L*
- △ a*

- 1% nano-ZnO (pH=10.5)
- 2% nano-ZnO predispersed in PAA
- 0% nano
- 5% nano-ZnO (pH=10.5)
- 5% nano-ZnO predispersed in PAA
- 7% nano-ZnO (pH=10.5)
- 2% nano-ZnO (pH=10.5)

80 µm

Time, h

Time, h
Color changes

**Cycle A**

1% nano-ZnO (pH=10.5)  
2% nano-ZnO predispersed in PAA  
0% nano  
5% nano-ZnO (pH=10.5)  
5% nano-ZnO predispersed in PAA  
7% nano-ZnO (pH=10.5)  
2% nano-ZnO (pH=10.5)

\[ \Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \]
2% predispersed nano-ZnO (40 nm)  
1% nano-TiO₂  
2% nano-TiO₂  
0% nano  
0.4% predispersed nano-ZnO (40 nm) + 0.54 nano-CeO₂ (10 nm)  
1% predispersed nano-ZnO in PMAA  
2% predispersed nano-ZnO (60 nm)  

**Cycle B**

- 2% predispersed nano-ZnO (40 nm)  
- 1% nano-TiO₂  
- 2% nano-TiO₂  
- 0% nano  
- 0.4% predispersed nano-ZnO (40 nm) + 0.54 nano-CeO₂ (10 nm)  
- 1% predispersed nano-ZnO in PMAA  
- 2% predispersed nano-ZnO (60 nm)  

**Color changes**

- ΔL*  
- ΔE*  
- Δb*  

**Graphs:**

- Time, h  
  - 0 100 200 300 400  
  - ΔL*  
  - ΔE*  
  - Δb*  

**Cycle B**

70 µm
Gloss changes

**Cycle A**
- 1% nano-ZnO (pH=10.5)
- 2% nano-ZnO predispersed in PAA
- 0% nano
- 5% nano-ZnO (pH=10.5)
- 5% nano-ZnO predispersed in PAA
- 7% nano-ZnO (pH=10.5)
- 2% nano-ZnO (pH=10.5)

**Cycle B**
- 1% nano-ZnO predispersed in PAA (2100)
- 5% nano-ZnO predispersed in PAA (2100)
- 2% nano-ZnO predispersed in PAA (2100)
- 0% nano
- 1% nano-ZnO predispersed in PAA (5000)
- 1% predispersed nano-ZnO (40 nm)
Color and gloss changes

<table>
<thead>
<tr>
<th></th>
<th>0% nano</th>
<th>1% silanized ZnO</th>
<th>2% silanized ZnO</th>
<th>2% predisp. ZnO*</th>
<th>2% predisp. ZnO**</th>
<th>2% predisp. ZnO***</th>
<th>1% coated TiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial gloss, 60°</strong></td>
<td>4,49</td>
<td>5,89</td>
<td>5,75</td>
<td>4,43</td>
<td>4,83</td>
<td>4,04</td>
<td>5,55</td>
</tr>
<tr>
<td><strong>Final gloss, 60°</strong></td>
<td>4,10</td>
<td>4,64</td>
<td>4,37</td>
<td>4,76</td>
<td>4,85</td>
<td>3,75</td>
<td>4,37</td>
</tr>
</tbody>
</table>

* predispersed nano-ZnO (20 nm) in polyacrylamide (PAM, M=17000);
** predispersed nano-ZnO (20 nm) in copolymer of acrylic acid and sulfonated monomers;
*** water-based commercial dispersion of nano-ZnO (20 nm).
Adhesion measurement by the pull-off method

Positest Adhesion Tester

**Adhesion strength =**

max. tensile strength

\[ H = \frac{F}{A} \]

**Cycle A**

- **Before weathering**
- **After weathering**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adhesion strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0% nano</td>
</tr>
<tr>
<td>B</td>
<td>2% predispersed nano-ZnO (60 nm)</td>
</tr>
<tr>
<td>C</td>
<td>5% predispersed nano-ZnO (20 nm)</td>
</tr>
<tr>
<td>D</td>
<td>2% predispersed nano-ZnO (20 nm)</td>
</tr>
<tr>
<td>E</td>
<td>1% nano-ZnO predispersed in linseed oil emulsion</td>
</tr>
<tr>
<td>F</td>
<td>1% nano-ZnO predispersed in PMAA</td>
</tr>
</tbody>
</table>

Actuator

Cross-Sectional View of Actuator

Dolly
Pull-off tests

**Cycle B**

Adhesion strength, MPa

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A'</td>
<td>0% nano</td>
</tr>
<tr>
<td>B'</td>
<td>2% predispersed nano-ZnO (60 nm)</td>
</tr>
<tr>
<td>G</td>
<td>2% predispersed nano-ZnO (40 nm)</td>
</tr>
<tr>
<td>H</td>
<td>1% nano-TiO₂</td>
</tr>
<tr>
<td>I</td>
<td>2% nano-TiO₂</td>
</tr>
<tr>
<td>K</td>
<td>0.4% predispersed nano-ZnO (40 nm) + 0.54% predispersed nano-CeO₂ (10 nm)</td>
</tr>
<tr>
<td>L</td>
<td>1% nano-ZnO predispersed in PAA (5000)</td>
</tr>
<tr>
<td>M</td>
<td>2% nano-ZnO predispersed in PAA (2100)</td>
</tr>
<tr>
<td>N</td>
<td>5% nano-ZnO predispersed in PAA (2100)</td>
</tr>
</tbody>
</table>

Before weathering

After weathering

0% nano

2% predispersed nano-ZnO (60 nm)
Images of Scanning Electron Microscopy

JEOL 840A (Tokyo, Japan) microscope equipped with EDX (energy dispersive X-ray analysis)

- 2% nano-ZnO (pH=9)
- 3% nano-ZnO (pH=10.5)
- 1% nano-ZnO predispersed in aqueous sol. of PMAA
- 1% nano-ZnO predispersed in aqueous sol. of PAA
- 1% nano-ZnO predispersed in linseed oil emulsion
- 2% predisperssed nano-ZnO (40 nm)
OUTDOOR EXPOSURE (118 days)

<table>
<thead>
<tr>
<th>Without coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% nano (acrylic latex paint) (A)</td>
</tr>
<tr>
<td>5% nano-TiO₂ (20 nm) (B)</td>
</tr>
<tr>
<td>2% nano-TiO₂ (20 nm)</td>
</tr>
<tr>
<td>5% predispersed nano-ZnO (40 nm)</td>
</tr>
<tr>
<td>2% predispersed nano-ZnO (40 nm)</td>
</tr>
<tr>
<td>2% nano-ZnO (20 nm) predispersed in aqueous sol. of PAA (C)</td>
</tr>
<tr>
<td>5% nano-ZnO (20 nm)</td>
</tr>
<tr>
<td>2% nano-ZnO (20 nm)</td>
</tr>
</tbody>
</table>

**Color changes ΔE***
Nanoparticles size distribution by DLS

Principle of Dynamic Light Scattering

Aquous dispersion of 20% nano-ZnO (20 nm) with PAA (M=5000)

Aquous dispersion of 20% nano-ZnO (20 nm) with a polyacrylamide

Commercial aqueous dispersion 40% nano-ZnO (40 nm)
CONCLUSIONS

- Nanocomposites coatings prepared with ZnO nanoparticles hydrophilic and silanized version (in powder form and predispersed) showed higher protection against UV radiations (accelerated weathering and outdoor exposure) and antibacterial properties (outdoor exposure) compared with the acrylic latex paint;
- Nanocomposites coatings prepared with uncoated TiO₂ nanoparticles showed anti-UV and self-cleaning properties in outdoor exposure;
- Nanocomposites coatings prepared with coated TiO₂ nanoparticles showed anti-UV properties in accelerated weathering;
- High durability against UV radiations demand an efficient nanoparticles dispersion (without aggregation or flocculation);
- The dispersant must not accelerate the polymer matrix degradation by yellowing ($\Delta b^*$).
- The nanoparticles protect the coatings against photodegradation caused by UV radiations, therefore adhesion strength values were slightly improved after the accelerated weathering.
ACKNOWLEDGEMENTS

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FQRNT
SICO


