Feasibility of Nanozinc Oxide as a Wood Preservative

Carol A. Clausen  
Vina W. Yang  
Rachel A. Arango  
Frederick Green III  
US Forest Service  
Forest Products Laboratory  
Madison, Wisconsin

ABSTRACT

Nanometals have the potential to affect the field of wood preservation through the development of new and improved biocides with unique properties. A preliminary study on nanometals suggested that 1% nanozinc oxide was leach resistant, caused moderate termite mortality, inhibition of termite feeding and inhibition of decay by Trametes versicolor. In this study, Southern yellow pine and yellow poplar vacuum-treated with 2.5% and 5.0% nanoZnO were evaluated for leaching, mold and decay inhibition, termite resistance, and visible signs of weathering. Virtually no leaching occurred at any treatment concentration of nanozinc oxide. All concentrations of nanoZnO showed inhibition of termite feeding, (i.e. low mass losses) and 31%-35% mortality. Only the highest concentration of nanoZnO resulted in moderate inhibition of mold growth (20-32% coverage). Decay inhibition was variable. NanoZnO did not inhibit brown-rot test fungi as well as soluble ZnSO$_4$. Weight loss for the white-rot fungus was inhibited by all concentrations of nanoZnO tested. Specimens treated with nanoZnO demonstrated UV protection after 8 weeks of weathering. Overall, nanoZnO has desirable wood protection properties, namely leach resistance, UV protection and termite resistance, but would not provide adequate protection against decay or mold as a stand alone treatment.

Key words: nanozinc, nanometals, decay, wood preservation, mold, termite, weathering

INTRODUCTION

Nanotechnology is defined as the development and application of materials, devices and systems using particles in the size range of 1 to 100 nanometers with fundamentally new properties and functions because of their structure (Siegel et al., 1999). Nanopreparations of metals, such as zinc, may possess unique characteristics that are totally different from the characteristics of the elemental metal. Nanopreparations of metals alter several characteristics such as size, charge, and dispersion properties that may improve their performance in wood protection applications (Clausen 2007). Nanometals created by pyrolysis demonstrate precisely controlled particle size in the 1 to 100 nanometer range which may improve penetrability of the chemical into wood relative to nanometals prepared by grinding. Preparation of nanometer-size metal particles essentially increases the effective surface area of the metal in an evenly dispersed layer. If the particle size is smaller than the diameter of the wood window pit (<10,000 nm) or the opening of the bordered pit (400 to 600 nm), complete penetration and uniform distribution would be expected (Freeman and McIntyre, 2008). Nanoparticles demonstrate high dispersion stability, but in concentrated form they are subject to Van der Waals forces. The addition of a surfactant increases dispersion stability thereby enabling liquid dispersion of higher concentrations of nanometals. In a study on microdistribution of a micronized copper wood preservative (10 to 700 nm), Matsunaga et al. (2007) saw numerous particle deposits of
copper in ray tracheids and pit lumens within the wood. These deposits created a different microdistribution pattern in wood treated with the micronized copper than was observed in wood treated with other copper-based preservatives. Fixation of micronized copper is believed to occur primarily through deposition in pit chambers and on tertiary cell wall layers rather than via chemical reaction (Freeman and McIntyre, 2008). Perhaps the unique properties of nanometals e.g. nanozinc, will provide more uniform distribution within the wood cell wall and may demonstrate reduced leachability due to increased reactivity with the woody substrate.

In a preliminary study on nanometal preparations, nanozinc oxide demonstrated some unique characteristics deemed worthy of further study. The objective of this study was to evaluate nanozinc oxide-treated wood for weathering characteristics, leach resistance and inhibition of fungi and termite attack in laboratory tests compared to soluble zinc sulphate.

**MATERIALS AND METHODS**

*Test chemicals*

A 50% solution of 30-nm nanozinc oxide particles (Nanophase Technologies Corp., Romeoville, IL) was diluted to 1.0%, 2.5%, and 5.0% aqueous solutions based on the metal oxide (ZnO). Zinc sulfate was obtained from Mallinckrodt Chemicals, Inc., St. Louis, MO, and diluted to obtain a 1% concentration on a zinc oxide basis.

*Treatment*

Test specimens were prepared from sapwood portions of southern yellow pine (SYP) for termite, mold and brown-rot decay tests. For the white-rot decay tests, yellow poplar sapwood specimens were used. All specimens were pre-weighed and conditioned at 20°C and 65% relative humidity (RH) for 2 weeks prior to treatment. Specimen size varied for leaching, termite, mould, and decay tests according to American Wood Protection Association (AWPA) and American Standard for Testing and Material (ASTM) standard methods. Specimens were vacuum-treated (45-min vacuum at 550-mm Hg) with aqueous solutions of nanozinc oxide. Zinc sulphate was prepared to contain an equivalent amount Zn for comparison with the 1% nanozinc. Untreated specimens served as controls. Treated specimens were weighed, dried at 40°C for 3 days, and re-conditioned at 27°C and 70% RH for two weeks. Some treated specimens were ground to pass a 30-mesh screen and analyzed for zinc with inductively coupled plasma (ICP) emission spectroscopy (AWPA 2008a) to determine chemical retention (Table 1).

<table>
<thead>
<tr>
<th>Treatment (%)</th>
<th>Retention (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.61</td>
</tr>
<tr>
<td>2.5</td>
<td>3.78</td>
</tr>
<tr>
<td>5.0</td>
<td>12.96</td>
</tr>
</tbody>
</table>

*Chemical leaching*

Leaching procedures were similar to AWPA E11-06 standard method (AWPA 2008b). After conditioning, five specimens were placed into individual 500-mL beakers, submerged in 100 mL of deionized (DI) water, and subjected to a vacuum to impregnate the specimens with the leaching solution. The sample bottles were then subjected to mild agitation for a total of 14 days, and leachates were collected after 6 h, and 1, 2, 4, 6, 8, 10, 12, and 14 days. Leachates were analyzed for zinc with ICP and expressed as ppm zinc for the average leach rate of the 5 blocks per treatment concentration.

*Termite tests*

A no-choice termite resistance test with Reticulitermes flavipes Kollar (Eastern subterranean termites) was performed using five unleached test specimens (25 × 25 × 5 mm) for 1.0, 2.5, and 5.0% nanozinc. Termites were collected from Janesville, WI. One specimen was placed in the bottom of an acrylic
cylindrical container (90 mm diameter and 60 mm tall) with 1 g of R. flavipes and moist sand. The containers were maintained at 27° C and 85% RH for 4 weeks based on AWPA El-06 standard method (AWPA 2008c). Tests were periodically checked for moisture and mortality. At the end of the incubation, wood specimens were oven dried, reconditioned at 27° C and 70% RH, and reweighed to calculate mass losses. The termite mortality rate was estimated by counting the remaining live termites. Following incubation, wood specimens were visually rated on a scale of 0-10 with 10 being sound and zero equaling failure. Zinc sulphate-treated specimens were not included in this trial, but have been reported previously (Kartal et al. 2009).

**Mold and sapstain tests**

Unleached specimens (7 mm × 20 mm × 7 cm long) were evaluated for resistance to mold fungi according to American Society for Testing and Material D4445-91 (ASTM 1998). Three mold fungi, Aspergillus niger 2.242, Penicillium chrysogenum PH02, and Trichoderma viride ATCC 20476 were grown and maintained on 2% malt agar (Difco, Detroit, MI) at 27° C, and 80% RH. One sapstain fungus, Aureobasidium pullulans, was grown and maintained on 2% potato dextrose agar (Difco, Detroit, MI). Aspergillus niger, Penicillium chrysogenum, and Aureobasidium pullulans were isolated and identified at Forest Products Laboratory, Madison, WI. Individual spore suspensions of the three test fungi were prepared by washing the surface of 2-week-old Petri plate cultures with 10–15 mL of sterile deionized (DI) water. Washings were transferred to individual spray bottles and diluted with DI water to yield approximately 3 × 10^7 spores/mL. The spray bottle was adjusted to deliver 1 mL inoculum per spray. Treated and untreated wood specimens (5 specimens per treatment group) were sprayed with 1 mL spore inoculum and incubated at 27° C and 80% RH for 4 weeks. Following incubation, specimens were visually rated on a scale of 0–5 with 0 indicating the specimen was completely free of mould growth and 5 indicating the specimen was completely covered with mould growth. Specimens treated with 1% nanoZnO or zinc sulphate were not included in this trial, but have been previously reported (Kartal et al. 2009).

**Decay tests**

Five SYP specimens per treatment group were exposed to Postia placenta (Fr.) M. Lars. Et Lomb. (MAD 698), Antrodia sp. (formerly Meruliporia incrassata TFFH-294) and Gloeophyllum trabeum (Pers.: Fries) Murr. (MAD 617), in a soil-block test following the guidelines of AWPA standard E10-01 (AWPA 2008d). Five yellow poplar specimens per treatment group were similarly exposed to Trametes versicolor (L. ex Fr.) Pilat (MAD 697) and incubated at 27° C and 80% RH for 12 weeks. Following incubation, fungal mycelium was brushed from the specimens, specimens were oven dried, reconditioned, and reweighed. Percentage mass loss was calculated. Specimens treated with 1% nanoZnO or ZnSO₄ and exposed to Antrodia sp. were previously reported (Kartal et al. 2009).

**Weathering**

Treated and untreated SYP specimens (7.6 × 10.2 × 1.3 cm) were weathered outdoors in Madison, WI for 12 wks and visually evaluated for UV damage (i.e. splitting, checking, graying) and water repellency.

**RESULTS**

**Chemical leaching**

Figure 1 shows the leach rate of three concentrations of nanoZnO and 1% ZnSO₄. Virtually no leaching of nanoZnO occurred at any treatment concentration while zinc sulfate, previously reported by Kartal et al. (2009), readily leached. Pyrolytic nanometal preparations result in changes in charge properties and the resulting nanometal dispersions are subject to Van der Waals forces (Clausen 2007). Such changes in properties may account for the low leaching of nanometals.
Figure 1. Leach rates of zinc from nanoZnO (1% ♦, 2.5% ■, and 5% ▲) and ZnSO₄ (×) from SYP-treated blocks.

**Termite tests**

All nanozinc solutions tested (1.0, 2.5, and 5.0%) inhibited termite feeding (<10% mass loss), and caused moderate levels of mortality (31% to 35%) (Table 2). In contrast, 1% ZnSO₄ only caused 5% mortality (Kartal et al. 2009). Average visual ratings were 9 for all concentrations of nanoZnO.

**Table 2: Mass loss, mortality and visual rating of SYP treated with nanoZnO in termite tests with *R. flavipes*.

<table>
<thead>
<tr>
<th>Concentration of ZnO (%)</th>
<th>Average Mass loss (%)</th>
<th>Estimated mortality (%)</th>
<th>Visual rating (Ave)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.0</td>
<td>8.5</td>
<td>31</td>
<td>9</td>
</tr>
<tr>
<td>2.5</td>
<td>1.1</td>
<td>32.5</td>
<td>9</td>
</tr>
<tr>
<td>5.0</td>
<td>1.0</td>
<td>34.5</td>
<td>9</td>
</tr>
</tbody>
</table>

**Mold and sapstain tests**

A dose response was seen between the 2.5% nanoZnO treatment (ratings ranging from 2.2 to 4.2) and the 5.0% treatment (ratings ranging from 1.0 to 1.6). At the highest concentration, nanoZnO provided moderate mold and sapstain inhibition; the ratings translate into 20% to 32% coverage.
Figure 2: Average rating (% growth on a scale of 0 to 5) of molds and sapstain fungi on nanoZnO-treated SYP.

Decay

NanoZnO-treated blocks did not significantly inhibit zinc-tolerant *Postia placenta* at 2.5 or 5.0% or *Antrodia* sp. at 1.0% (Figure 3). At 5.0% treatment concentration, nanoZnO caused 74% lower mass losses in *G. trabeum* than the untreated control. The white-rot fungus, *Trametes versicolor*, was inhibited at all treatment concentrations (9-16% mass loss). Soluble ZnSO$_4$ significantly inhibited all test fungi compared to the untreated controls, however ZnSO$_4$ was not challenged with zinc-tolerant *P. placenta*.

Figure 3: Mass loss of ASTM soil-block test on nanoZnO and ZnSO$_4$-treated SYP (brown-rot fungi) and yellow poplar (white-rot fungus).
Weathering

Zinc oxide, a highly effective UV blocker in sunscreen products, may serve a similar function to protect wood from weathering. After 12 weeks of natural weathering, SYP samples treated with nanozinc oxide remained bright while untreated controls are beginning to gray (results on shown). NanoZnO appears to provide UV protection at all treatment concentrations. Long shallow checks were present in specimens treated with 1% and 2.5% nanoZnO, but are absent in the untreated controls. The checks appear to be filled with ZnO and the specimens had not grayed significantly during the short exposure time. Controls are beginning to gray, but the short duration of the test does not reveal significant differences. No checks or graying were noted in specimens treated with 5.0% nanoZnO. After 6 wks, water beaded on the surfaces of specimens treated with 5% ZnO, but repellency was no longer observed after 8 wks. A milky white surface coating was observed in specimens treated with the 2.5% and 5.0% formulations. The weathering test will continue until significant graying occurs in controls.

CONCLUSIONS

Three concentrations of nanoZnO were leach resistant and provided UV protection and termite resistance, but did not provide adequate protection against brown-rot decay, mold or sapstain fungi.

REFERENCES