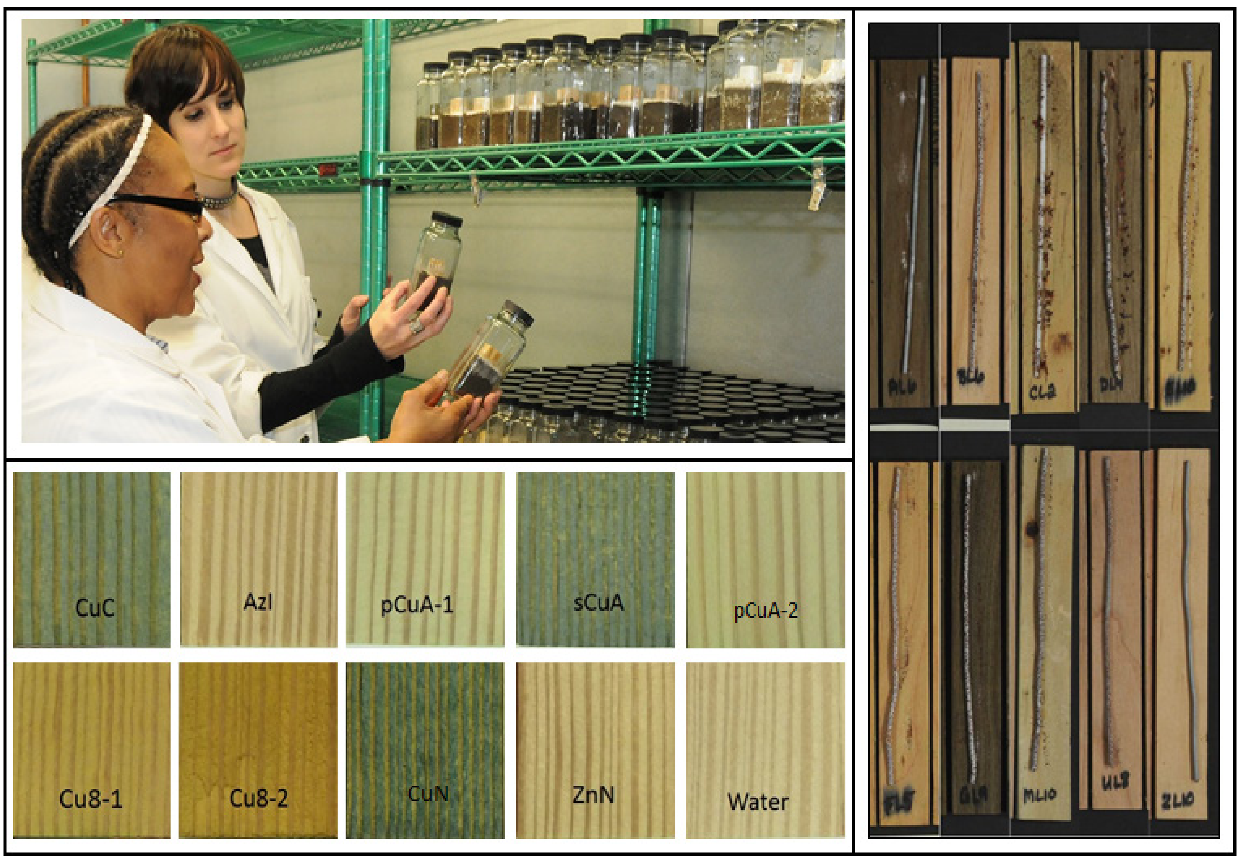
United States Department of Agriculture

Evaluation of Nonpressure Wood Preservatives for Military Applications

Stan T. Lebow
Samuel L. Zelinka
Rachel A. Arango
Bessie M. Woodward
Patricia K. Lebow
Katie M. Ohno
Nathaniel P. Chotlos



Forest Service

Forest Products Laboratory

Research Paper FPL–RP–693

October 2017

Abstract

Zinc naphthenate (ZnN) has been widely used for dip treatment of Department of Defense wood packing materials but is no longer available. Research was conducted to evaluate the preservative efficacy and corrosiveness of U.S. Environmental Protection Agency (EPA) registered alternatives to ZnN. Efficacy of "green" preservatives (defined here as not containing pesticides that require EPA registration) was also evaluated. Most of the EPA-registered preservatives evaluated provided decay and termite protection similar to or greater than that of ZnN. Four of the formulations provided protection equivalent to or greater than that of ZnN against termites and all decay fungi evaluated. The registered formulations tended to be more effective than ZnN in preventing termite feeding on Southern Pine, but some were less effective than ZnN in protecting yellow-poplar from termites. However, the "green" preservatives were not effective in preventing decay or termite attack. Corrosion testing revealed that all but one of the registered formulations were more corrosive than ZnN. The results of the laboratory fungal, termite, and corrosion testing were used to develop a protection index with recommended applications for the formulations evaluated.

Keywords: wood preservatives, nonpressure, dip, decay, termites, corrosion, Department of Defense, wood packing materials

October 2017

Lebow, Stan T.; Zelinka, Samual L.; Arango, Rachel A.; Woodward, Bessie M.; Lebow, Patricia K.; Ohno, Katie M. 2017. Evaluation of nonpressure wood preservatives for military applications. Research Paper FPL–RP–693. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 30 p.

A limited number of free copies of this publication are available to the public from the Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398. This publication is also available online at www.fpl.fs.fed.us. Laboratory publications are sent to hundreds of libraries in the United States and elsewhere.

The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin.

Contents

Evaluation of Nonpressure Wood Preservatives for Military Applications

Stan T. Lebow, Research Forest Products Technologist
Samuel L. Zelinka, Supervisory Research Engineer
Rachel A. Arango, Research Entomologist
Bessie M. Woodward, Microbiologist (retired)
Patricia K. Lebow, Research Mathematical Statistician
Katie M. Ohno, Biologist
USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin

Nathaniel P. Chotlos, Student
University of Wisconsin-Madison, Department of Forest and Wildlife Ecology, Madison, Wisconsin

Introduction

The U.S. Army uses wood for construction of containers (such as ammunition boxes) and shipping materials (such as pallets). These wood packaging materials (WPMs) are expected to have a useful life of up to 20 years, and although the majority of their service will be indoors, there may be extended periods of outdoor exposure. The wood may also be exposed in climates that present a severe risk for both insect and fungal attack. To protect the wood from biodegradation, current Department of Defense (DOD) specifications stipulate that the assembled wood products be dip-treated with a wood preservative (Fig. 1). A thorough evaluation of the efficacy of preservatives in protecting ammunition boxes was conducted by the USDA Forest Service, Forest Products Laboratory (FPL), and U.S. Army Armaments Research and Development personnel in the 1980s (DeGroot and Stroukoff 1986). That study indicated that water-based zinc naphthenate (ZnN), copper naphthenate (CuN), and copper-8-quinolinolate (Cu8) would be effective for treatment of ammunition boxes, and these three preservatives were incorporated into DOD specifications. Of these, the most commonly used preservative has been ZnN. However, ZnN no longer has U.S. Environmental Protection Agency (EPA) registration for use as a wood preservative and will not be available after existing stocks are depleted. Also, changes have occurred in the available formulations of CuN and Cu8, and new types of preservatives have become available since the study by DeGroot and Stroukoff (1986). To adapt to these changes and ensure future availability, U.S. Army Armament Research Development and Engineering Center (ARDEC) and FPL personnel conducted research to evaluate the efficacy of potential preservatives for use in protecting WPMs.

Figure 1. Nailed ammunition boxes are one example of durable wood packaging materials that are dip-treated with preservative.

Current Treatment Specifications

Preservative treatment of WPMs is covered in multiple specifications. Two commonly used military specifications are MIL-DTL-2427H (AR) (September 2007) for nailed wood boxes and MIL-DTL-46506E (August 2009) for wire-bound wood boxes. These specifications state that the boxes, or their finished wood parts, shall be completely immersed for a minimum of 1 min in the preservative solution. The preservative solutions listed are

- PQ56 reduced with water down to 1.8% Cu8 (this is an older version of Cu8 that is no longer being produced).
- An emulsion of wood preservative M-GARD W550 (ZnN) reduced with water down to 3% zinc as metal.
- An emulsion of M-GARD W510 (CuN) reduced with water to 2% copper as metal (this is an older version of CuN that is no longer being produced).
- A solution of Cunapsol 5 (CuN) reduced with water to 2% copper as metal (this is an older version of CuN that is no longer being produced).

The specification also requires that all interior and exterior surfaces (when finished wood parts are dipped) be completely inundated with preservative. Immediately following the dip treatment, the wood products are to be drained for at least 5 min and then air-dried for at least 24 h while allowing full air circulation around all surfaces. Accelerated drying in an oven or kiln is permitted providing oven or kiln temperatures do not exceed 71 °C. The treated boxes must be dried to a maximum moisture content of 18% prior to shipment. Verification of preservative treatment is accomplished by applying an indicator solution that produces a characteristic color if the applicable preservative is present.

A range of softwood and hardwood species are permitted under these specifications; all must be dried to a maximum moisture content of 19%. Typical boxes are constructed of solid wood or plywood panels with additional cleats added on the ends and lid to improve stiffness and connection strength. The thickness of these members is typically 13 to 18 mm, although greater thicknesses may also be used.

Nail, wire, or staple fasteners are permitted, and flat or wire steel strapping may also be applied. The specifications typically call for metal components to be protected with a zinc coating to lessen corrosion, although the thickness of the zinc coating is often not specified.

Characteristics of Formulations Currently in Military Specifications

Various forms of CuN, Cu8, and ZnN have been used as preservatives for decades, although these previous formulations may not be identical to those listed in current military specifications.

Water-Based Copper Naphthenate

CuN has been used as a wood preservative since the 1940s, although not as widely as creosote, chromated copper arsenate (CCA), or pentachlorophenol. It is an organometallic compound formed as a reaction product of copper salts and petroleum-derived naphthenic acids. In recent years, use of CuN has increased for pressure treatment of poles, glue-laminated beams, and railroad ties. CuN has been primarily used as an oil-based formulation, but a water-based formulation containing ethanolamine has also been standardized as Standard P34 by the American Wood Protection Association (AWPA) for pressure treatment (AWPA 2017). Standardized retentions range from 1.12 kg/m^3 for above-ground use to 1.76 kg/m^3 for ground-contact applications (retentions expressed as elemental copper). FPL compared the durability of stakes treated with oil- and water-based formulations of CuN and found that the oil-based formulations were more durable at lower concentrations. However, at the highest concentration evaluated (1.2% copper), both formulations were highly effective. DeGroot and Stroukoff (1988) also found that 2% copper formulations of oil- or water-based CuN were highly effective in protecting ammunition boxes from decay, even in jungle exposure in Panama.

Water-Based Copper-8-quinolinolate

Cu8 is an organometallic preservative comprised of 10% Cu8 and 10% nickel-2-ethylhexoate. It is characterized by its low mammalian toxicity and is permitted by the U.S. Food and Drug Administration for treatment of wood used in direct contact with foodstuffs. The treated wood has a greenish brown color and little or no odor. It can be dissolved in a range of hydrocarbon solvents and has often been used and evaluated as an oil-based treatment (Lebow and others 2014). However, it can be formulated for use in water, and the water-based form is used commercially for dip treatment and as a component of antisapstain preservatives.

Durability evaluations of water-based Cu8 have produced somewhat conflicting results. FPL researchers evaluated the durability of stakes treated with water-based Cu8 in both 19- by 19-mm and 38- by 89-mm stake sizes. The 19- by 19-mm stakes treated to retentions of 5.44, 15.04, 20.80, and 29.44 kg/m^3 survived an average of 3.3, 6.2, 7.3, and 8.6 years, respectively. This relatively poor durability contrasts with that of the larger stakes treated to 17.9 kg/m^3, which had only 40% failures after 17 years. Highley (1993) evaluated the ability of a 5% water-based Cu8 brush application to protect cross-brace specimens exposed above ground in Wisconsin and Mississippi. In this test, two treated pieces of wood, 19 by 76 by 153 mm long, were nailed together at their centers to form a cross-brace test unit. The design of the cross-brace unit was intended to allow trapping of rainwater between side-grain surfaces. However, this is not a standardized test method and is not especially severe because moisture is not trapped in the end-grain. Water-based Cu8 did not perform particularly well in this test, with decay observed within 7 years in pine specimens and within 2 years in maple specimens exposed in Mississippi (Table 1). In contrast, pine specimens brushed with 1% water-based copper or ZnN had no decay after 9 years and maple specimens resisted decay for 7 years. Mitchoff and Morrell (1988) evaluated the ability of water-based Cu8, ZnN, and other preservatives to protect red alder using AWPA Standard E10 soil-block tests (AWPA 2017). They found that water-based Cu8 was less effective than other preservatives tested in protecting red alder. However, DeGroot and Stroukoff (1986) found that at 1.2%, water-based Cu8 solution provided protection to ammunition boxes that was nearly equivalent to that of water-based ZnN or CuN. They also noted that a Cu8 emulsion did not protect as well, suggesting that the efficacy of Cu8 may be dependent on how the Cu8 is stabilized in the treatment solution. This formulation dependence may explain the range of results presented by previous researchers.

Table 1—Durability of brush-treated cross-brace units exposed above ground in southern Mississippi (data from Highley (1993))

Preservative (waterborne)	Solution conc. (%)	Years to visual decay by wood species[a]		
		Pine	Maple	Oak
Copper-8-	1	7	2	8
quinolinolate	5	7	2	8
Copper	1	9+	6	8
naphthenate	3	9+	7	9+
	8	9+	9+	9+
Zinc	1	9+	5	6
naphthenate	3	9+	5	6
	8	9+	6	7

[a]Some specimens did not develop visual decay during the test. Test durations were either 9, 10, or 11 years.

Zinc Naphthenate

ZnN is formed as a reaction product of zinc salts and derived naphthenic acids. Until recently, ZnN was used extensively as a component in over-the-counter wood preservative products. As with CuN, it can be formulated as either a solvent- or water-based preservative. Unlike CuN, ZnN imparts little color to the wood. Zinc is not as effective a fungicide as copper (Barnes and others 2004), and ZnN is not used as a stand-alone preservative for exposed structural members, nor is it standardized for pressure treatment. Barnes and others (2004) compared the durability of stakes treated with a range of retentions of water-based CuN or ZnN and found that approximately three times more zinc was needed to provide protection equivalent to copper. However, ZnN does have some preservative efficacy, especially in above-ground applications. A comparison of above-ground specimens exposed in Mississippi found that brush-on treatments of water-based ZnN were only slightly less effective than CuN after 9 years of exposure (Table 1) (Highly 1993). Dip treatments with a 3% (as zinc) formulation also protected pine and hemlock L-joints for 11 years in western Oregon (Morrell and others 1999). DeGroot and Stroukoff (1986) also reported that dips in a 3% (as zinc) formulation protected ammunition boxes nearly as well as CuN after 36 months of jungle exposure. Interestingly, there was no benefit from increasing dip time from 1 to 3 min. Water-based ZnN also provided good protection for ammunition boxes exposed in an open field in Panama, with 100% of the panels and cleats remaining serviceable after 36 months of exposure. An advantage of ZnN, relative to copper-containing water-based preservatives, is lower corrosiveness to metal fasteners. However, ZnN is currently not registered for pesticide use, and it does not appear likely that it will be registered in the near future.

Considerations for Alternative Preservatives

Preservatives have a range of properties that may make them more or less suitable for dip treatment of WPMs. Clearly, efficacy in preventing degradation by decay fungi and termites is critical, but factors such as regulatory status, allowable methods of application, handling characteristics, and simplicity of mixing and use must also be considered. Data on efficacy against decay fungi and termites are available for many types of preservative formulations, although the bulk of this information was developed with pressure-treated wood. Pressure-treated wood typically has deeper and more uniform penetration and retention than wood treated by nonpressure processes (although extended soaks can create similar treatment quality in some species). Dip- or brush-treated wood can have a higher surface concentration of preservative. However, its location near the wood surface makes the preservative more vulnerable to depletion, and even small drying checks expose untreated wood. As a result, the durability of pressure-treated wood is often substantially greater than that of wood treated by nonpressure means.

Conventional wood preservatives contain antimicrobial pesticides (such as copper) that require registration and labeling with EPA. Some preservatives developed for pressure treatment have not been labeled for dip treatment application and/or may be labeled for concentrations below that needed for dip treatment. In some cases, the properties of a preservative, such as odor or volatility, may make them less amenable for use in a dip treatment facility. Corrosiveness to metal fasteners may also be a concern because WPMs are typically dipped after assembly.

Nonconventional wood preservatives were also considered in this study. As part of a broader effort to evaluate green packaging materials, the U.S. Army is seeking information on green wood preservatives that might be used for protection of WPMs. In this case, "green" is defined as preservatives that do not contain pesticides requiring EPA registration. The basis for this classification is somewhat unclear because the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) defines a pesticide as "any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest" and because any such substance must be registered unless it was otherwise specifically exempted. However, there are a number of commercial products that appear to claim wood preservative efficacy but do not contain EPA-registered pesticides. Because these products are not EPA-registered, they do not necessarily identify or quantify their ingredients. Thus, it can be difficult to understand their mechanism of action or gauge their potential efficacy. Examples include products derived from wood extracts (for example, cedar oil) and minerals (for example, silicates) and those that claim to act by physically blocking movement of water or deterioration organisms into the wood (for example, water repellents or sealants).

The potential use of extractives from naturally durable wood species as wood preservatives has been studied since at least the early 1940s (Rennerfelt 1948), and research continues today (Kirker and others 2013a). Although this research shows that extracts such as cedar oil do have antifungal properties in agar plate testing (Du and others 2009), their efficacy in protecting wood of nondurable wood species is less clear. Two studies have indicated that wood treated with cedar oil extracts has only slight improvement in decay resistance but may have substantially increased resistance to termite attack (Eller and others 2010, Kirker and others 2013b). Earlier research at FPL (unpublished) found that cedar extracts at concentrations up to 2% provided no benefit in preventing attack by two types of decay fungi. However, research with essential oil extracts from a range of plant species indicated that essential oils can be efficacious against decay fungi if used at high concentrations (Yang and Clausen 2007). Generally, it appears possible that extractives from naturally durable species may be capable of protecting nondurable woods, but the expense of concentrations required may limit practical implementation.

Various forms of silicates have drawn considerable interest as pesticide-free wood treatments. Research efforts on organosilicons summarized in papers by Mai and Miltz (2004a, 2004b) and Weigenand and others (2009) indicated that although certain formulations provide some decay resistance, silicon was generally insufficient without substantial loadings, modification with amino groups, or the addition of a fungicide such as boron. Other common minerals have also been proposed for wood protection. For example, formulations of iron and aluminum have been evaluated at FPL. Those evaluations indicated that these metals have relatively little efficacy against decay fungi or termites when wood is placed into contact with the ground. They do, however, impart some increase in durability for wood exposed above ground.

Moisture barriers and coatings have also been considered as potential mechanisms of wood protection. On larger material, water-proof coatings have generally not been as effective as wood preservatives because the coating is typically breached either through coating decomposition or from cracks that develop as wood shrinks and swells (Feist 1988). However, they can provide some level of protection for wood above ground as long as the coating is intact. One study found that painting alone provided some protection for Douglas-fir specimens exposed above ground but was less effective for pine specimens (Highley and Scheffer 1998). Coatings would be expected to be most effective on wood species and products with minimal shrinkage and low water permeability (such as Douglas-fir) and on wood products with smaller dimensions that undergo less shrink and swell with time. With sufficient penetration, water-repellent treatments can also be effective. Pressure treatment with paraffin wax to a loading of 416 kg/m^3 increased the average life of stakes exposed in Mississippi from 2.3 (untreated) to 18.4 years (Woodward and others 2011).

Based on these considerations, nine EPA-registered preservative formulations and six green preservative formulations were evaluated for resistance to fungal decay and feeding by subterranean termites. EPA-registered preservatives were also used in corrosion testing. With the exception of one green preservative, only water-based formulations were evaluated to allow compatibility with existing treatment facilities and use practices.

Materials and Methods

EPA-Registered Formulations Evaluated

All but one of the evaluated alternative formulations contained copper as a key active ingredient (Table 2).

Table 2—Preservatives and concentrations evaluated (only the higher concentrations were evaluated in corrosion testing)

Preservative	Description	Key active ingredient (% actives)	Dip time (min)
CuC	Copper-carboxylic acid (100%)	1% and 2% as copper	1
AzI	Azole[a] (95%), imidacloprid (5%)	0.5%[b] or 1.05% total actives	1 and 3
pCuA-1	Particulate copper (96%), azole[a] (4%)	1% and 2% as copper	1
pCuA-2	Particulate copper (96%), azole[a] (4%)	1% and 2% as copper	1
sCuA	Soluble copper (96%), azole[a] (4%)	1% and 2% as copper	1
Cu8-1	Copper-8-quinolinolate (100%)	1.2% as Cu8-quin	1 and 3
		1.8%[c] as Cu8-quin	1
Cu8-2	Copper-8-quinolinolate (100%)	1.2% and 1.8%[c] as Cu8-quin	1
CuN	Copper naphthenate (100%)	1% and 2%[c] as copper	1
ZnN	Zinc naphthenate (100%)	2.9%[c] as zinc	1

[a]Tebuconazole or equal parts tebuconazole and propiconazole.
[b]0.5% AzI concentration evaluated in green preservative study and limited to the 1-min dip time.
[c]Concentrations required in current military specifications for similar formulations. ZnN is specified at 3% zinc.

Copper has been used in wood preservatives for centuries and remains a common component in current formulations. It is effective against most types of decay fungi as well as major insect pests. However, certain types of decay fungi have been found to be copper-tolerant and can sporadically cause rapid damage and even structural failure of copper-treated wood. Thus, commercial copper-based preservatives typically include a co-biocide (for example, triazoles, naphthenic acids, quinolinolate) to provide additional protection. In two of the test formulations, mechanically ground particulate copper was dispersed or suspended in the formulation (particulate copper azole (pCuA-1 and pCuA-2)). This type of formulation, often referred to as micronized copper, is commonly used for pressure treatment of lumber in the United States. Copper particle sizes generally range between 1 and 25,000 nm, with the majority less than 1,000 nm. Polymeric dispersants are used to improve the uniformity and stability of the treatment solution (Freeman and McIntyre 2008). A formulation with a similar composition of active ingredients but with copper solubilized in ethanolamine (sCuA) was also evaluated. All three formulations also included one or both of the triazoles, tebuconazole, and/or propiconazole, which are agricultural fungicides that have been incorporated into some wood preservative formulations. An additional copper formulation contained copper solubilized in ethanolamine as well as a carboxylic acid (CuC). The one formulation evaluated that did not contain copper instead contained a combination of azoles and imidacloprid (AzI). The active concentrations of the formulations evaluated were relatively high compared with those used for other applications of the same preservatives. This reflects the concentrations shown to be effective for ZnN, Cu8, and CuN in earlier testing (DeGroot and Stroukoff 1986).

Green Preservatives Evaluated

Green preservatives were selected based on a combination of availability and possible mode of action. For the purposes of this study, the products will be described based on their characteristics or proposed method of action rather than by use of commercial trade names. With the exception of the cedar oil extract, only water-based products were considered to correspond to current use practices for WPM dip treatment.

Cedar Oil–Organosilicon

Cedar oil–organosilicon (Cedar) is a solvent-based product that is marketed as a wood preservative and stabilizer. It functions through a combination of eastern redcedar oil and organosilicon polymerization. Efficacy is claimed against cellulose-consuming insects and fungal decay organisms. The method of action is proposed by the manufacturer to be encapsulation of antimicrobial and termiticidal ingredients (presumably the cedar oil) within the cell wall structure by silicon molecules. The manufacturer provides instructions for application by dipping, hot and cold bath immersion, or spraying. During discussions, the manufacturer recommended that the product be applied using two dips with a short drying period between dips. We duplicated this process for an additional set of specimens in this trial.

Silica Gel Wood Stabilizer

Silica gel wood stabilizer (LiqSil) is a water-based product that claims to function as a silica gel that hardens with time into a glass-like consistency. Given this description, it is likely that this product contains sodium silicates. The product claims to be a wood stabilizer–hardener that keeps the moisture content below that needed for attack by decay fungi. The product does not appear to make claims of efficacy against termites or other insects. Recommended application is two brush coats with a drying interval of at least 6 to 12 h between coats. This study evaluated the two brush coats application as well as a 1-min dip treatment.

Natural Minerals 1

The manufacturer of this natural mineral (Mineral-1) emphasizes its use as a stain but also claims that the product protects against mold, rot, and fungi. No claims are made regarding termites. Little information is provided about its ingredients or method of action other than a statement that it is composed of natural substances from minerals. However, in one area of the website, it does note that a key component is silica that solidifies to form a glass-like moisture barrier. Thus, it is likely that the product contains sodium silicate. It is sold as a packet of granules, which are then mixed with water for application by brush, sprayer, or roller. The information provided by the manufacturer indicates that only one application is needed. This product was applied by dipping in this study.

Natural Minerals 2

The manufacturers of this natural mineral (Mineral-2) claim that it is effective against moss, mold, wet rot, dry rot, and fungi. A mechanism of protection is not provided by the manufacturer other than to state it is based on natural materials and penetrates into wood fibers, altering the wood structure at a molecular level. As with Mineral-1, the product is sold as a packet of granules, which is then mixed with water for application. Given the similarity in description to Mineral-1, it is likely that this product also contains sodium silicate. Manufacturer guidelines state that it can be applied by dipping and that only one application is required.

Polymer Seal

The polymer seal (Polymer) provides efficacy by forming a waterproof seal on the exterior of the wood. It contains an undisclosed proprietary polymer (99% concentration) that is a white emulsion, dispersible in water. However, it is applied full strength, without dilution. Although marketed primarily as a water-proofer and sealer for fencing, siding, posts, and furniture, it also claims to protect against decay, rot, and pests. The recommended method of application is by sprayer, but in this study, it was applied only by dipping.

Nonpreservative Deck Water Repellent

Some of the products evaluated in this study claim efficacy in part because they create a barrier to water intrusion on the wood surface. The laboratory fungal and termite tests used in this study use small test specimens with a relatively high surface area to volume ratio. Thus, specimens are completely encapsulated with the test formulations during dip treatment. This raised the question of whether these standard methods are a sufficiently rigorous test of the water-repellent surface treatments. To address this concern, we evaluated an example of a water-based commercial water-repellent deck treatment (Deck WR) that does not make any claims of efficacy against decay fungi and termites. The product is manufactured and marketed by one of the leading suppliers of deck finishes. It is intended to be applied by brush or roller but was applied by dip treatment in this study.

Zinc Naphthenate

The same water-based ZnN (3% Zn) formulation used in the evaluation of EPA-registered preservatives was included as a positive control in the green preservative evaluation.

Azoles–Imidacloprid

This formulation was included in the evaluation of EPA-registered preservatives and appeared to be highly effective (Lebow and others 2015). It was included here as a positive control but was diluted to a lower (0.5%) concentration.

Soil-Block Decay Tests

The soil-block (also referred to as soil bottle) method is the most common laboratory test used to evaluate the efficacy of wood preservatives against wood decay fungi. This test exposes preservative-treated blocks (and untreated controls) to specific, known decay fungi under conditions favorable for their growth (Fig. 2). The effectiveness of the

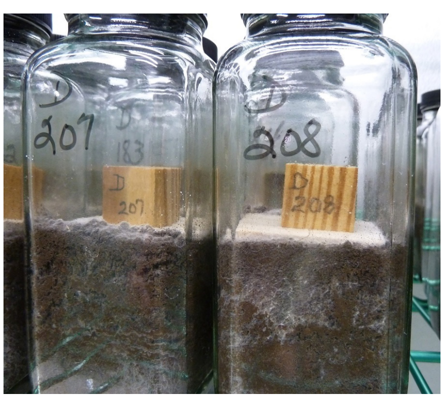


Figure 2. Soil-block test configuration.

preservative is based on the amount of weight loss in the test block compared with untreated controls. The method used in this study was AWPA Standard E10 (AWPA 2017).

Selection of Wood and Fungal Species

Two wood species (one softwood and one hardwood) were evaluated in this study. Southern Pine (*Pinus* spp.) was selected because it is a widely used softwood with a large, nondurable sapwood zone. Yellow-poplar (*Liriodendron tulipifera*) was selected because it is a common, nondurable hardwood that grows across a large geographical area. It was also selected because it was used in the earlier ammunition box study by DeGroot and Stroukoff (1986). Soil bottles with feeder strips were inoculated with one of five decay fungi selected for use in this study in accordance with AWPA Standard E10 (AWPA 2017). Brown-rot fungi (*Gloeophyllum trabeum* (Pers. ex Fr.) Murr.; Mad617 and *Postia placenta* (Fr.) M. Lars. & Lomb.; Mad698) were used to evaluate the Southern Pine specimens, and white-rot fungi (*Trametes versicolor* (L. ex Fr.) Pilat; Mad697 and *Irpex lacteus* (Fries)(Schw.); Mad517) were used to evaluate the yellow-poplar specimens. The soft-rot fungus *Chaetomium globosum* (Kunze et Fr.) was evaluated against both Southern Pine and yellow-poplar specimens but only for testing of EPA-registered preservatives. The soft-rot method was modified with use of a filter paper feeder strip and burial of the test block in moist, sterile vermiculite. These fungal species were selected because they are among those most commonly isolated from wood in service and are frequently used in evaluation of wood preservative formulations.

Preservative Treatment Application

EPA-Registered Preservatives

Blocks for soil-block tests (19 mm^3) were cut from the sapwood of Southern Pine and yellow-poplar lumber, weighed, sorted by density, and then immersed for either 1 or 3 min into the diluted preservative solutions (Table 3). Groups of 18 blocks were dipped for each species. Fifteen of the blocks were used for fungal testing, and the other three were reserved. The blocks were reweighed to determine uptake of preservative solution (Table 3) and then allowed to air-dry for 1 week prior to leaching.

Green Preservatives

Soil-block specimens (19 mm^3) for green preservatives were treated in the same manner as described for EPA-registered preservatives, with a few exceptions. Some of the products evaluated claimed that only one application was needed, whereas others indicated that two applications would improve performance. Given that two applications might increase application cost and complexity for WPMs and in the interest of direct comparison, we evaluated all products with a single, 1-min dip, which is current commercial practice. This allowed comparison with earlier tests of EPA-

Table 3—Uptake of preservative in soil blocks after dip treatment (EPA-registered formulations)

Preservative	Concentration	Dip time (minutes)	Southern Pine weight gain (g) Average	Southern Pine weight gain (g) Std. dev.	Yellow-poplar weight gain (g) Average	Yellow-poplar weight gain (g) Std. dev.
Water	none	1	1.71	0.27	0.74	0.14
CuC	1% as Cu	1	0.86	0.16	0.87	0.16
	2% as Cu	1	0.89	0.19	0.89	0.12
AzI	1.05% total	1	1.46	0.23	0.96	0.20
	1.05% total	3	1.50	0.42	1.11	0.25
pCuA-1	1% as Cu	1	0.89	0.17	0.77	0.19
	2% as Cu	1	0.95	0.16	0.92	0.24
sCuA	1% as Cu	1	1.13	0.23	0.86	0.16
	2% as Cu	1	1.27	0.39	0.84	0.30
pCuA-2	1% as Cu	1	1.22	0.19	0.72	0.18
	2% as Cu	1	1.25	0.13	0.60	0.15
Cu8-1	1.2% as Cu-8	1	1.08	0.30	1.07	0.22
	1.2% as Cu-8	3	1.60	0.32	1.11	0.18
	1.8% as Cu-8	1	0.94	0.23	0.94	0.14
Cu8-2	1.2% as Cu-8	1	0.98	0.11	1.06	0.24
	1.8% as Cu-8	1	0.91	0.13	0.96	0.12
CuN	1% as Cu	1	1.08	0.18	1.21	0.42
	2% as Cu	1	1.18	0.22	1.09	0.15
ZnN	2.9% as Zn	1	1.10	0.20	0.90	0.13

registered wood preservative formulations. However, two of the products (Cedar and LiqSil) were also evaluated in a manner more closely matching manufacturer's instructions (Table 4). All specimens were then air-dried for 1 week prior to leaching.

Leaching

Leaching was conducted on all specimens using simulated rainfall, rather than immersion, to better correspond to anticipated in-service exposure conditions (Fig. 3). Specimens were placed on wire racks in a rainfall simulator in which they were sprayed with rainfall at a rate of 10 mm/h. An alternating schedule of 1 h rainfall and 5 h rest was used until a total of 20 h, or 200 mm, of rainfall occurred (5 days). After leaching, the blocks were reconditioned to a constant weight in an environmental chamber maintained at 27 °C and 30% relative humidity (RH).

Decay Testing

Blocks were placed, singly, into the previously inoculated soil bottles and maintained in an incubation chamber (27 °C and 80% RH) for 8 weeks and 12 weeks for EPA-registered preservatives and green preservatives, respectively. After fungal exposure, the blocks were brushed to remove fungal mycelium and reconditioned to constant weight in a room maintained at 27 °C and 30% RH. The blocks were then reweighed to determine percentage weight loss.

Table 4—Summary of formulations and application methods for green preservatives

Formulation (short name)	Concentration	Application method
Cedar–organosilicon (Cedar)	As is	1-min dip
Cedar–organosilicon (Cedar)	As is	30-s dip, 3-min dry, 30-s dip
Silica gel wood stabilizer (LiqSil)	As is	1-min dip
Silica gel wood stabilizer (LiqSil)	As is	Brush coat, 24-h dry, brush coat
Natural minerals (Mineral-1)	As is	1-min dip
Natural materials (Mineral-2)	As is	1-min dip
Polymer seal (Polymer)	As is	1-min dip
Deck water-repellent (Deck WR)	As is	1-min dip
Azoles/imidacloprid (AzI)	0.5% actives	1-min dip
Zinc naphthenate (ZnN)	3% zinc	1-min dip
Water	As is	1-min dip

Figure 3. Device used to subject specimens to leaching with simulated rainfall.

Laboratory Termite Tests

Wood Test Specimens

Southern Pine and yellow-poplar wood samples were cut into 25- (radial) by 25- (tangential) by 6- (longitudinal) mm blocks. Specimens with 5 to 8 growth rings were then selected for treatment.

Preservative Treatment Application

EPA-Registered Preservatives

Wood samples were placed in staining trays, separated by plastic mesh for dip treatments (Fig. 4). Trays were then submerged into glass staining dishes containing the preservative for either 1 or 3 min on a shaker depending on the treatment. Blocks were then removed from the trays, blotted gently to remove excess liquid, and weighed to determine uptake of the preservative. Samples were left to dry in a hood for 1 week and then conditioned to a uniform moisture content in a 27 °C, 30% RH incubator prior to leaching.

Figure 4. Termite specimen preparation for dip treatment.

Green Preservatives

Test specimens were weighed and then immersed for 1 min into the test solution or treated as described in Table 4. Following drying and leaching, blocks were conditioned to constant weight in a room maintained at 27 °C and 30% RH prior to leaching.

Leaching

As in decay tests, all specimens for termite testing were leached on wire racks in a rainfall simulator in which they were sprayed with rainfall at a rate of 10 mm/h. An alternating schedule of 1 h rainfall and 5 h rest was used until a total of 20 h, or 200 mm, of rainfall occurred (5 days).

No-Choice Termite Tests

The methods used in this study were patterned according to ASTM D 3345-08 (ASTM 2008). The no-choice testing arenas consisted of small, plastic dishes containing 50 g sterile, filtered sand and 9 mL deionized water, with test specimens placed on top of the sand. One gram of eastern subterranean termites, *Reticulitermes flavipes* (Kollar), collected from Janesville, Wisconsin, was then added to each container. Testing arenas were maintained in an incubator at 27 °C and 80% RH for the 4-week testing period. After the test, blocks were removed, brushed free of debris, dried in a hood, and reconditioned to a uniform moisture content before final weights were obtained. Termites from each container were separated into dishes for mortality to be determined.

Statistical Analysis of Decay and Termite Tests

EPA-Registered Preservatives

To compare the preservative treatment groups for each organism–wood species combination, percentage weight losses from the soil-block decay tests and the termite tests were each analyzed using heteroscedastic linear models in SAS V9.4 (SAS Institute, Inc., Cary, NC). Families of comparisons were constructed to compare percentage weight losses between treatments and the positive control (ZnN), as well as to test for possible changes caused by treatment concentration or dip treatment time. Other comparisons, such as comparing treatment groups to the negative control (water) were also included but not reported. Simulation-based multiple comparison adjustments were used as described in Westfall and others (2011).

Green Preservatives

The weight losses from the laboratory decay and termite tests were compared with the water-treated negative control and the results obtained with ZnN and 0.5% AzI (positive controls). One-way analyses of variances with treatment as the factor (at 11 levels) were carried out on percentage weight loss in SAS V9.4. These analyses were conducted separately for each wood species–test organism combination. Multiple pairwise comparisons were adjusted based on the Tukey–Kramer method in SAS, with adjusted p-values <0.05 considered significant.

Above-Ground Field Exposure (In Progress)

Laboratory fungal decay and termite tests have the advantage of producing relatively rapid results under controlled conditions. However, they do not include factors such as weathering, wetting–drying cycles, and possible effects of secondary organisms such as bacteria. To create more realistic exposure conditions, specimens treated with EPA-registered preservatives and one green preservative (Cedar) are also being tested in outdoor exposure.

Testing methods followed AWPA Standard E18 (AWPA 2017). In this method, groups of concrete blocks are placed flat on the ground with the distance from the top of the block to the ground at approximately 100 mm. Specimens are placed on top of the cinder blocks, and then the assembly is covered with a shade cloth frame. The shade cloth allows wetting but slows drying of the specimens, creating an environment more conducive to both decay and termite attack. Specimens will be inspected annually and given a numerical rating for extent of decay and termite attack. This test will be conducted for 5 years, at which time the specimens will be returned to FPL, conditioned to constant moisture content, and weighed to allow calculation of percentage weight loss.

Test blocks were treated in groups of five replicates (one set for each wood species) in stainless steel pans, with blocks weighted down with stainless steel weights and covered with 2,000 g of treatment solution. Dip times were 1 or 3 min, with the exception of the Cedar specimens. Those specimens were dipped for 30 s, followed by a 3-min rest period, and then dipped for an additional 30 s. After dipping, the specimens were allowed to drip for 5 min and then weighed to determine solution uptake (Table 5). They were then dried under ambient laboratory conditions for 14 days before being placed in a room maintained at 70 °C and 50% RH to equilibrate. Additional sets of 13 untreated specimens of each species were also prepared. These specimens were placed on top of three sets of six concrete blocks; the specimens were assigned to the blocks in such a way that each treatment group was represented in each set of six blocks. The specimens will be evaluated annually and given ratings for the extent of fungal decay and termite attack, which will be published in a subsequent report.

Corrosion Tests (EPA-Registered Preservatives Only)

In the manufacturing process, galvanized wires are attached to several sheets of plywood and the assembly is dipped in the preservative treatment for 1 min before being removed from the bath. The plywood assemblies are then stored flat in stacks until they are ready to be shipped. Because of how the boxes are stacked, air flow is restricted to boxes in the middle of the stack. It has been observed that boxes dipped in Cu8 and CuN will occasionally arrive with red rust when delivered to the army from the manufacturer, indicating that the galvanized coating has been corroded entirely.

The goal of the laboratory testing was to determine which preservative systems are the least likely to cause corrosion issues in the packaging crates. The test methodology was designed to simulate the production process of the wire-bound crates (Zelinka and Lebow 2015). To simulate the production process, wires were attached to thin strips of plywood, which were then dipped in the preservative treatment for 1 or 3 min and then stored in polyethylene bags for either 2 or 8 weeks. The sealed polyethylene bags were used to simulate the slow drying with little air flow encountered for the stacked boxes. This represents, in some ways, a worst case scenario because there was no air flow and little potential for the wood to dry. Preliminary testing compared exposures in a room with 90% RH to the polyethylene bag exposure. In the preliminary testing, less corrosion was observed in the 90% RH room. However, it was hard to differentiate the performance of the wires exposed to different preservative systems. The polyethylene bag method was chosen because little corrosion was observed on the wires exposed to treatments that were known to be noncorrosive yet still able to produce measureable corrosion in other preservative systems, which allowed differentiation of the preservative systems.

Both the wires and the wood strips used in the testing came from untreated packaging crates that were disassembled. The wires were removed from the crates and cut into segments that were approximately 150 mm long (the actual size of each segment was measured and recorded). Additional segments of wire were examined using scanning electron microscopy to examine the galvanization (a characteristic micrograph is shown in Fig. 5). In most places, the thickness of the galvanized coating was between 10 and 20 μm.

Prior to the exposure test, the wires were cleaned in an ultrasonic bath with a soap solution, rinsed with distilled water, and finally rinsed with acetone. After the cleaning procedure, the wires were weighed and then attached with a plastic fastening ring to a small (25- by 178-mm) strip of wood cut from the packaging crate. These assemblies of wood and wire were then dipped into the preservative treatment solutions, removed, and stored in a polyethylene bag for either 2 or 8 weeks.

Following the exposure, the extent of the corrosion was examined both qualitatively with a visual examination and quantitatively by gravimetric analysis. Photographs of the

Table 5—Uptake of preservative in field exposure specimens after dip treatment

Preservative	Concentration	Dip time (min)	Southern Pine weight gain (g) Average	Southern Pine weight gain (g) Std. dev.	Yellow-poplar weight gain (g) Average	Yellow-poplar weight gain (g) Std. dev.
CuC	1% as Cu	1	4.07	0.30	3.34	0.56
	2% as Cu	1	4.65	0.40	3.40	0.35
AzI	1.05% total	1	6.10	0.49	3.56	0.74
	1.05% total	3	8.64	2.49	4.34	0.78
pCuA-1	1% as Cu	1	4.20	0.15	2.95	0.55
	2% as Cu	1	4.62	0.76	3.05	0.46
sCuA	1% as Cu	1	5.50	0.78	4.15	0.72
	2% as Cu	1	5.18	0.47	4.17	1.18
pCuA-2	1% as Cu	1	5.32	0.87	3.01	0.81
	2% as Cu	1	4.72	0.67	2.43	0.54
Cu8-1	1.2% as Cu-8	1	5.69	1.24	3.90	0.76
	1.2% as Cu-8	3	6.09	0.95	3.35	0.37
	1.8% as Cu-8	1	5.11	0.88	3.21	0.30
Cu8-2	1.2% as Cu-8	1	4.65	0.61	3.86	0.61
	1.8% as Cu-8	1	5.18	0.83	3.20	0.82
CuN	1% as Cu	1	5.01	1.02	4.80	1.08
	2% as Cu	1	4.55	0.67	4.52	1.47
ZnN	2.9% as Zn	1	6.26	0.92	3.34	0.36
Cedar	As is	0.5, 0.5[a]	5.23	0.49	1.87	0.14

[a]Based on manufacturer recommendations, these specimens were dipped for 30 s, allowed to rest for 3 min, and then dipped for another 30 s.

wires were taken immediately after removal from the polyethylene bags. Afterward, the plastic fastening rings were removed and the wires were flipped over and photographed again. This second photograph showed both the extent of corrosion when the wire was in direct contact with the wood and also the amount of corrosion products deposited on the wood surface. Gravimetric analysis was performed by first removing the corrosion products of metal in contact with wood using the method of Zelinka and Rammer (2009). The wires were placed in an ultrasonic cleaner for 60 min in a bath comprised of 1:1 water/EvapoRust solution (Orison Marketing, Abilene, Texas). The wires were then wiped dry and weighed.

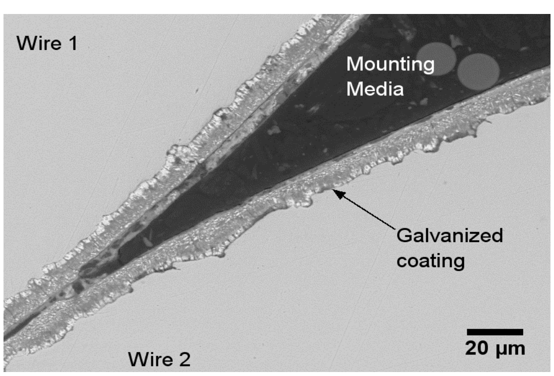


Figure 5. Scanning electron micrograph of the wires tested. Two different wire segments are shown.

The preservatives evaluated, their compositions and concentrations, and the time the wood and wires were dipped in the treatment solution are shown in Table 6. All but two treating solutions (AzI, ZnN) contained 2% or less of copper and various types and amounts of organic biocides. Previous research has shown that the amount of copper in preservative treatments strongly affects the corrosiveness of the treated wood and that the effect of the organic biocides is small compared with other differences in preservatives such as pH and copper concentration (Kear and others 2009, Zelinka 2014, Zelinka and Stone 2011). Two preservatives did not contain copper: ZnN, which had less than 3% concentration of zinc, and AzI, which

Table 6—Preservatives and concentrations evaluated in corrosion testing

Preservative	Concentrations evaluated	Dip times (min)
CuC	2% as Cu	1
AzI	1.05% total actives	3
Cu8-1	1.8% as Cu-8-quinolinolate	3
Cu8-2	1.8% as Cu-8-quinolinolate	1
CuN	2% as Cu	1
pCuA-2	2% as Cu	1
Water	—	1
ZnN	2.9% as Zn	1

contained only organic biocides. In addition to these nine preservative treatments, a water control group (U) was tested. In this group, the wood–wire assemblies were dipped in a bath of deionized water for 1 min and sealed in polyethylene bags.

Results and Discussion, EPA-Registered Preservatives

Fungal Soil-Block Tests

Southern Pine

The most effective preservatives were Cu8-2 and AzI, which allowed little if any decay (Fig. 6). The higher solution concentration (1.8%) of Cu8-1 also provided excellent protection of Southern Pine. However, substantial weight loss did occur with some of the other preservative–concentration–fungus combinations. CuC appeared to be the least effective at protecting Southern Pine, although the lower concentrations of pCuA-1, sCuA, and CuN were also heavily attacked by the fungus *P. placenta*. The soft-rot fungus *C. globosum* caused little weight loss, even in the controls, and thus provided limited information on preservative efficacy. A statistical analysis was conducted to compare the performance of test preservatives to those currently allowed under military specifications (ZnN, Cu8-1, Cu8-2, and CuN). Table 7 summarizes the results of that statistical analysis. Each column shows which preservative–concentration combinations suffered significantly more weight loss (performed more poorly) than each of the reference preservatives. CuC (both concentrations) and CuN (1% concentration) often allowed significantly more weight loss than the reference preservatives for one or more of the fungi evaluated. The 1% concentrations of pCuA-1 and sCuA also allowed significantly more weight loss than the reference preservatives when challenged with the fungus *P. placenta*. AzI and pCuA-2 did not allow significantly more weight loss than any of the reference preservatives–fungi evaluated.

In the case of pCuA-2, one or more blocks exposed to *P. placenta* did have substantial weight loss at each solution concentration, whereas the other blocks were not degraded (Table 8). This variability between replicates may have prevented a finding of statistically significant difference between the performance of pCuA-2 and that of any of the reference preservatives. Similar variability was observed within blocks treated with 2% pCuA-1 and 2% CuN. This high degree of variability within replicates is unusual but may be a function of the dip-treatment process (typically soil blocks are vacuum–pressure impregnated).

Yellow-Poplar

Most of the test preservatives were highly effective in protecting yellow-poplar from fungal attack (Fig. 7). The exception was the lower (1%) concentration of CuC, which did allow substantial decay by the fungus *I. lacteus*. Interestingly, the preservatives that were least effective in protecting yellow-poplar were Cu8-1 and ZnN, both of which are already allowed under military specifications.

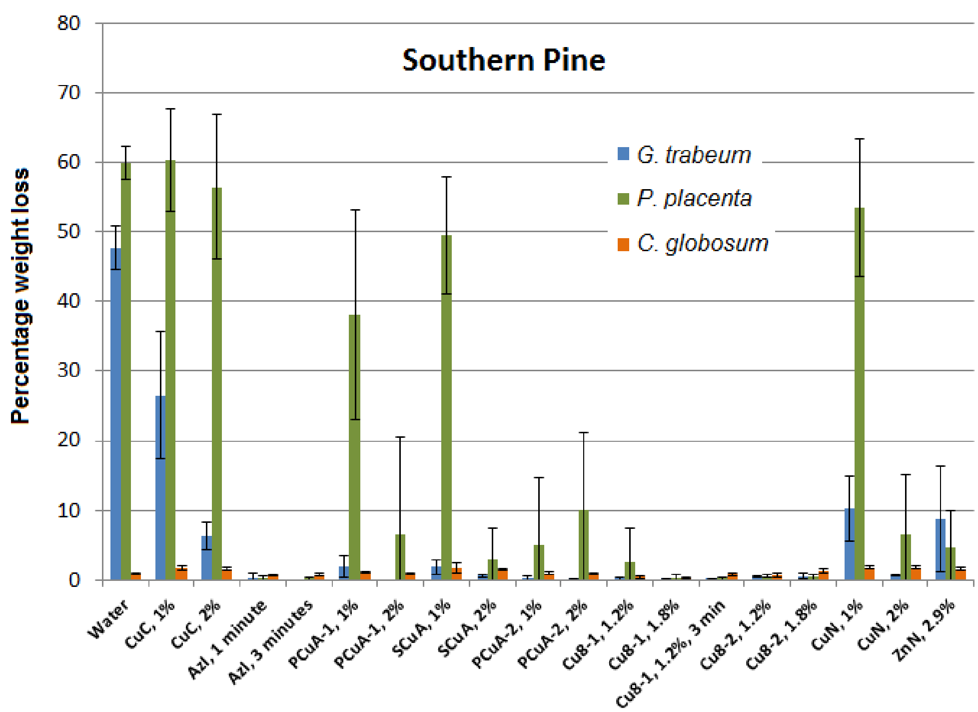


Figure 6. Average weight losses in Southern Pine cubes treated with the preservatives shown. Error bars show plus or minus one standard deviation from the mean.

Table 7—List of formulations that provided less fungal protection to Southern Pine than the reference preservatives at either the 90% or 95% confidence levels

	Decay fungus and confidence level			
Reference preservative	*G. trabeum* 90%	*G. trabeum* 95%	*P. placenta* 90%	*P. placenta* 95%
ZnN, 2.9% Zn	None	None	CuC, 1% CuC, 2% CuN, 1% sCuA, 1% pCuA-1, 1%	CuC, 1% CuC, 2% CuN, 1% sCuA, 1%
Cu8-2, 1.8%	CuC, 1% CuC, 2% CuN, 1%	CuC, 1%	CuC, 1% CuC, 2% CuN, 1% sCuA, 1% pCuA-1, 1%	CuC, 1% CuC, 2% CuN, 1% sCuA, 1% pCuA-1, 1%
Cu8-1, 1.8%	CuC, 1% CuC, 2% CuN, 1%	CuC, 1%	CuC 1% CuC 2% CuN 1% sCuA, 1% pCuA-1, 1%	CuC, 1% CuC, 2% CuN, 1% sCuA, 1% pCuA-1, 1%
CuN, 2% Cu	CuC,1% CuC, 2% CuN, 1%	None	CuC, 1% CuC, 2% CuN, 1% pCuA-1, 1%	CuC 1% CuC 2% CuN 1%

Statistical analysis indicated that Cu8-1 and ZnN were also the only preservatives to allow significantly greater weight loss than any of the reference preservatives (in this case, the reference preservatives were limited to 1.8% Cu8-2 and 2% CuN) (Table 9). However, 1% pCuA-2 had marginally greater weight loss than 2% CuN in yellow-poplar exposed to *T. versicolor*. Statistical analyses sometimes produce results that we might find counterintuitive. CuC exposed to *I. lacteus* had greater weight loss than 1% pCuA-2 exposed to *T. versicolor*, but the CuC result was not statistically significant because of the greater variability associated with those comparisons. As with Southern Pine, soft-rot *C. globosum* resulted in such little weight loss in the controls that it provided little information on preservative efficacy.

Table 8—Individual soil-block percentage weight losses for Southern Pine blocks decayed by *Postia placenta*

			Replicate number					
Preservative	Concentration	Dip time (min)	1	2	3	4	5	Mean
Water	none	1	59.16	61.13	59.01	57.03	63.29	59.92
CuC	1% as Cu	1	65.35	66.28	58.66	48.05	63.03	60.27
	2% as Cu	1	63.07	63.26	39.20	62.92	53.84	56.46
AzI	1.05% total	1	-0.21	0.00	-0.23	0.67	0.72	0.19
	1.05% total	3	-0.23	0.03	0.08	0.41	-0.08	0.04
pCuA-1	1% as Cu	1	42.69	54.61	22.84	21.78	48.62	38.11
	2% as Cu	1	0.31	0.31	0.52	0.00	31.62	6.55
sCuA	1% as Cu	1	53.08	55.73	57.71	42.14	38.77	49.49
	2% as Cu	1	1.05	1.57	0.46	10.86	0.76	2.94
pCuA-2	1% as Cu	1	0.59	22.13	0.51	1.39	1.11	5.15
	2% as Cu	1	0.26	0.08	13.73	8.65	27.09	9.96
Cu8-1	1.2% as Cu-8	1	11.29	0.10	0.18	0.31	0.71	2.52
	1.2% as Cu-8	3	0.54	0.03	0.13	0.10	0.10	0.18
	1.8% as Cu-8	1	0.25	0.35	0.61	0.94	-0.10	0.35
Cu8-2	1.2% as Cu-8	1	0.43	0.40	0.33	0.89	0.53	0.52
	1.8% as Cu-8	1	0.25	0.35	0.61	0.94	-0.10	0.41
CuN	1% as Cu	1	55.01	60.49	38.11	50.28	63.24	53.43
	2% as Cu	1	0.34	14.11	17.50	0.87	0.18	6.60
ZnN	2.9% as Zn	1	1.02	0.49	0.46	8.89	11.95	4.56

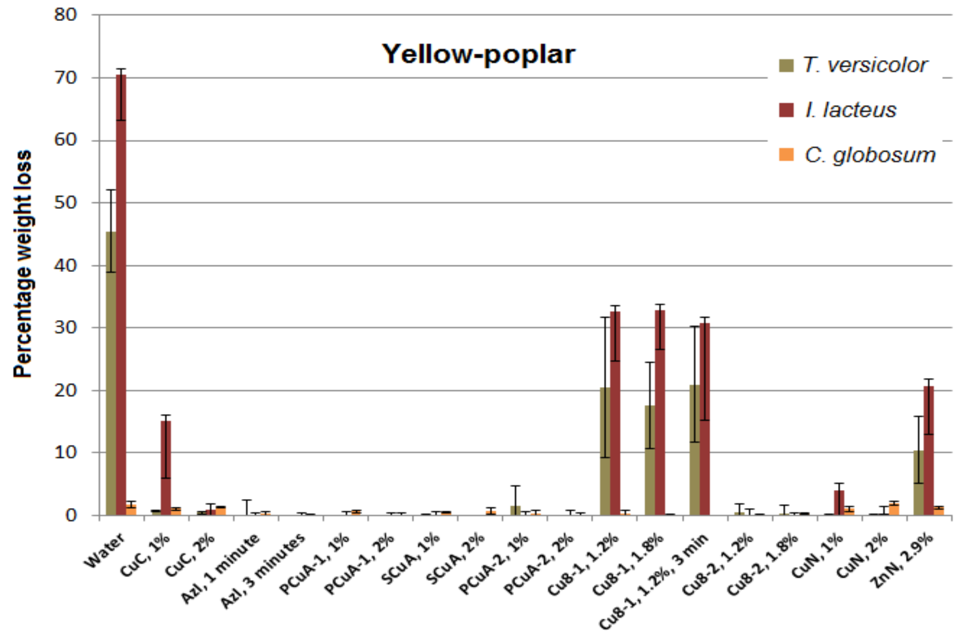


Figure 7. Average weight losses in yellow-poplar cubes treated with the preservatives shown. Error bars show plus or minus one standard deviation from the mean.

Effect of Solution Concentration

A statistical analysis was conducted to determine if solution concentration significantly affected weight loss. The analysis indicated that the performance of the 2% CuC was significantly better than that of the 1% solution when Southern Pine wood was exposed to *G. trabeum* or when yellow-poplar was exposed to *I. lacteus*. The higher concentrations of pCuA-1 and sCuA also provided significantly greater protection when Southern Pine was exposed to *G. trabeum* or *P. placenta*. In contrast, pCuA-2, Cu8-1, and Cu8-2 did not provide significantly greater protection at the higher solution concentration.

Effect of Dip Time

AzI (1.05%) and Cu8-1 (1.2%) were evaluated using both 1- and 3-min dip times. The longer dip time did not result in a statistically significant increase in protection in either case. Because AzI was highly effective with the 1-min dip in all cases, a significant improvement with the longer dip time could not be determined.

Additional Evaluation of Copper Tolerance

The extent of copper tolerance observed for *P. placenta* in this study was somewhat surprising given the efficacy of several of the preservatives when used for pressure treatment of wood placed in contact with the ground. Although the specimens used in this study were dip-treated rather than pressure-treated, the solution concentration used was relatively high. To further evaluate the effect of treatment process (dip versus pressure), additional sets of Southern Pine blocks were either dipped for 3 min or vacuum-impregnated with 1% concentrations of copper-based preservatives. The vacuum treatment involved 30 min

Table 9—List of formulations that provided less fungal protection to yellow-poplar than the reference preservatives at either the 90% or 95% confidence level

	Decay fungus and confidence level			
Reference preservative	*T. versicolor* 90%	*T. versicolor* 95%	*I. lacteus* 90%	*I. lacteus* 95%
ZnN, 2.9% Zn	None	None	None	None
Cu8-2, 1.8%	Cu8-1, 1.2%	None	Cu8-1, 1.2%	Cu8-1, 1.2%
	Cu8-1, 1.8%		Cu8-1, 1.8%	Cu8-1, 1.8%
	ZnN 3%		ZnN, 3%	ZnN, 3%
Cu8-1, 1.8%	None	None	None	None
CuN, 2% Cu	pCuA-2	None	Cu8-1, 1.2%	Cu8-1, 1.2%
			Cu8-1, 1.8%	Cu8-1, 1.8%
			ZnN, 3%	ZnN, 3%

immersion at –94 kPa (gauge) followed by 30 min immersion at atmospheric pressure. Based on weight gain following treatment, the dip- and vacuum-treated specimens absorbed an average of 1.2 and 4.5 g of treatment solution, respectively. The treated specimens were air-dried and subsequently leached prior to being exposed to *P. placenta* in soil-block testing as described earlier.

As shown in Figure 8, vacuum impregnation yielded a dramatic decrease in weight loss caused by the fungus *P. placenta*. The interesting exception was CuN, in which the dip treatment also provided good protection. This finding is notable because the 1% CuN dip-treated blocks were highly susceptible to attack by *P. placenta* when dipped for only 1 min (Table 8). It is possible that the additional 2 min of dip time provided sufficient naphthenic acid to deter the test fungus. An increase in efficacy was not observed with longer dip time for Cu8-1 in earlier testing, and it is possible that the effect of dip time on efficacy is formulation-dependent. In general, this supplemental testing indicates that dip-treated (that is, surface-treated) specimens may be more vulnerable to degradation by copper-tolerant fungi than pressure-treated specimens. Recent research also suggests that copper tolerance is a function of fungus adaptability to a copper-rich environment (Jenkins and others 2014). In theory, the copper ions are more readily chelated by natural byproducts of *P. placenta*, such as oxalate, in surface-treated specimens. It is also possible that surface-treated copper ions could be easier for the fungus to bypass compared with pressure-treated copper. Research also showed that test specimens surface-treated with 1.2% copper citrate and exposed to copper-sensitive *G. trabeum* only marginally inhibited decay, whereas specimens pressure-treated with 1.2% copper citrate completely inhibited decay (Jenkins and others 2014).

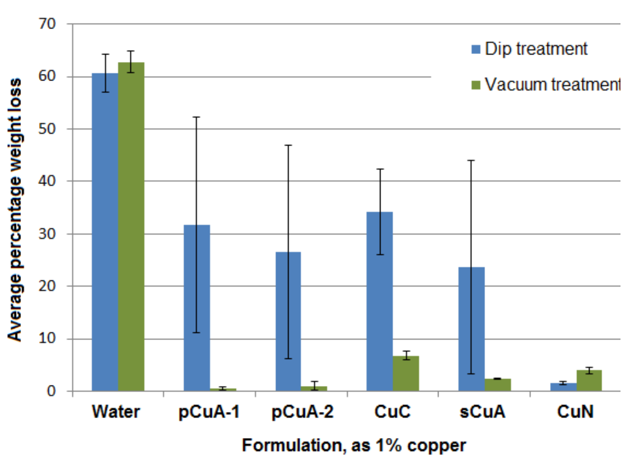


Figure 8. Average percentage weight loss for 1% (as Cu) formulations applied by either dip or vacuum treatment and exposed to *Postia placenta*. Error bars represent one standard deviation from the mean.

Laboratory Termite Tests

Mean percentage weight loss for each test group and termite mortality classification results are shown in Table 10. Termite mortality is estimated as follows, slight (0–33%), moderate (34–66%), heavy (67–99%), or complete (100%). Despite leaching, the majority of preservative dip treatments showed resistance to termite feeding either through repellency and/or direct toxicity of the preservative to the termites. The six most promising treatments in terms of weight loss to wood specimens were 1.05% AzI, 2% CuC, 2% sCuA, 2% pCuA-2, 1.8% Cu8-2, 1% or 2% CuN, and 2.9% ZnN. Treatments that showed higher amounts of termite feeding were 1.2% and 1.8% Cu8-1, suggesting that they may not perform as well as other treatments in a field situation with termite exposure.

A statistical analysis was conducted to determine which experimental treatments, if any, allowed more weight loss than preservatives currently allowed under military specifications (Table 11). None of the experimental treatments allowed greater weight loss than ZnN in Southern Pine blocks, with the exception of the Cu8-1 formulation. In yellow-poplar, ZnN provided significantly greater protection than the lowest concentration of several preservatives evaluated (Table 11) as well as all formulations of Cu8-1. Cu8-2 (1.8%) had significantly less weight loss than ZnN and all Cu8-1 formulations in Southern Pine but did not offer significantly greater protection (95% confidence level) than any of the other formulations in yellow-poplar. 1.8% Cu8-1 suffered the greatest weight loss of any formulation in Southern Pine and nearly the greatest weight loss in yellow-poplar and did not provide significantly greater protection than any other preservative. A substantial number of significant differences were observed when other formulations were compared with the reference preservative 2% CuN. This is because 2% CuN suffered virtually no weight loss and had little variation between replicates. The only formulations that did not allow significantly more weight loss than 2% CuN were AzI and 2% sCuA.

Dip times of 1 min compared with 3 min did not seem to make a difference in overall results. In terms of weight loss, however, there was a difference between wood species. In the controls, weight loss of Southern Pine blocks was slightly higher than yellow-poplar blocks. However, in a number of the treated groups, yellow-poplar showed higher amounts of feeding than Southern Pine. Interestingly, termite mortality tended to be more moderate in yellow-poplar, despite the higher levels of feeding. Future studies should determine if it is possible that certain preservative treatments were more readily leached from yellow-poplar than from Southern Pine.

Table 10—Percentage weight loss of test specimens and termite mortality classification (dip treatment times are 1 min unless otherwise noted)

Preservative formulation	Percentage weight loss, Southern Pine	Termite mortality classification	Percentage weight loss, yellow-poplar	Termite mortality classification
1% CuC	1.61	Heavy	8.23	Moderate
2% CuC	0.00	Heavy	2.43	Heavy
1.05% AzI	0.00	Complete	0.00	Complete
1.05% AzI (3-min dip)	0.00	Complete	0.00	Complete
1% pCuA-1	1.96	Heavy	11.52	Moderate
2% pCuA-1	0.00	Heavy	6.61	Moderate
1% sCuA	0.24	Heavy	6.64	Moderate
2% sCuA	0.00	Heavy	1.77	Heavy
1% pCuA-2	0.44	Heavy	10.1	Moderate
2% pCuA-2	0.43	Heavy	3.84	Moderate
1.8% Cu8-1	4.32	Moderate	12.35	Moderate
1.2% Cu8-1	8.63	Moderate	11.83	Moderate
1.2% Cu8-1 (3-min dip)	14.87	Moderate	11.33	Moderate
1.2% Cu8-2	0.28	Heavy	9.13	Moderate
1.8% Cu8-2	0.57	Heavy	5.74	Moderate
1% CuN	0.55	Heavy	0.74	Heavy
2% CuN	0.00	Heavy	0.00	Heavy
2.9% ZnN	1.59	Heavy	2.34	Heavy
Untreated wood	19.59	Slight	17.33	Moderate

Table 11—Preservatives with significantly (95% confidence) greater termite weight loss than reference preservatives currently specified

Reference preservative	Southern Pine	Yellow-poplar
ZnN, 2.9% Zn	Cu8-1, 1.2% Cu8-1, 1.2%, 3-min dip Cu8-1, 1.8%	CuC, 1% pCuA-2, 1% Cu8-2, 1.2% Cu8-1, 1.2% Cu8-1, 1.2%, 3-min dip Cu8-1, 1.8% sCuA, 1% pCuA-1, 1%
Cu8-2, 1.8%	Cu8-1, 1.2% Cu8-1, 1.2%, 3-min dip Cu8-1, 1.8% ZnN, 3%	None (Cu8-1 had greater weight loss at the 90% confidence level)
Cu8-1, 1.8%	None	None
CuN, 2% Cu	Cu8-1, 1.2% Cu8-1, 1.2%, 3-min dip Cu8-1, 1.8% ZnN, 3%	CuC, 1% CuC, 2% pCuA-2, 1% pCuA-2, 2% Cu8-2, 1.2% Cu8-1, 1.2% Cu8-1, 1.2%, 3-min dip Cu8-1, 1.8% sCuA, 1% pCuA-1, 1% pCuA-1, 2% ZnN, 3%

In terms of termite mortality with treatment, the most toxic treatment was AzI at 1.05% for both Southern Pine and yellow-poplar blocks. Within days of exposure to the treated blocks, mobility of the termites became arrested; even typical foraging behaviors were not observed. These groups began showing mortality between 1 and 2 weeks after the start of the test and had 100% mortality by the end of the 4 weeks. The active component in the AzI treatment is likely to be imidacloprid because the insecticidal properties of this compound are already well characterized for termites (Thorne and Breisch 2001). Imidacloprid is a neonicotinoid compound that affects the insect nervous system by targeting nicotinic acetylcholine receptors (Meijer and others 2014).

Combining Laboratory Fungal and Termite Results

Interpretation of the laboratory fungal and termite tests is somewhat complex because the results vary between fungal and termite exposure, as well as with wood species and type of fungus. Only one formulation, AzI, exhibited consistently high efficacy against all organisms and for both wood species. To simplify comparison between formulations, Figure 9 shows the combined total average weight loss allowed by each formulation across both wood species and all organisms. About half the formulations evaluated yielded less than 20% total average weight loss. Included within this group were AzI, both concentrations of Cu8-2 (1.2% and 1.8%), as well as the 2% concentrations of sCuA, pCuA-1, pCuA-2, and CuN. The 1% pCuA-2 concentration was also within this group, although it allowed greater weight loss than its counterparts. Then there was a group of formulations that allowed at least 50% total average weight loss, including two of the reference preservatives, ZnN and 1.8% Cu8-1. The higher (2%) concentration of CuC was also within this group because it was found to be effective against most organisms but was severely degraded by the fungus *Postia placenta* in Southern Pine. The greatest total weight loss occurred with 1% CuC, which was severely degraded by three types of fungi and somewhat degraded by termites in yellow-poplar.

It is apparent from Figures 6 and 8 that the fungus *P. placenta* was a major cause of weight loss in Southern Pine specimens treated with several of the copper-based formulations. *P. placenta* is known to have some degree of copper tolerance and can sometimes damage wood in which copper is the only biocide. There are other wood decay fungi that also have this ability, and thus copper-based preservatives typically also contain cobiocides (that is, naphthenic acid in CuN, quinolinolate in Cu8, and azoles in copper azole formulations) to help prevent attack by copper-tolerant fungi. These cobiocides appeared to be fairly effective at higher concentrations, although some degradation still occurred in several preservatives. As previously noted, the CuC formulation was particularly vulnerable to this fungus, even at the higher 2% concentration.

The practical consequences of a preservative being vulnerable to copper-tolerant fungi warrants further discussion. There is some evidence that the risk of degradation by copper-tolerant fungi is primarily a concern for wood placed in direct contact with soil. This is because wood placed in contact with the ground is exposed to the

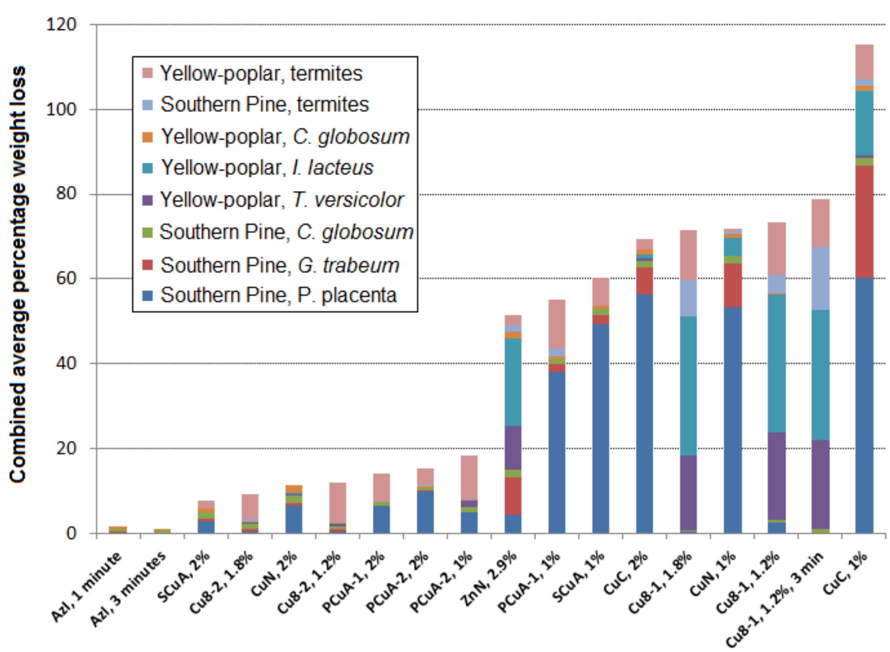


Figure 9. Average percentage weight loss for each formulation combined across all organisms (fungi and termites) and both wood species.

fully developed fungal strands (mycelium) that exist in the soil. This mycelium is able to produce chemicals that help to detoxify the copper. Conversely, wood used above ground is primarily infected by air-borne fungal spores. These fungal spores appear to be less resistant to copper than the fully developed mycelial strands present in soil (Choi and others 2002). In many situations, the wooden material used in army shipping and storage containers is not placed in direct contact with the ground, and thus, decay is initiated by fungal spores. Copper tolerance may be less of a concern in these situations.

Corrosion Testing Results

Figure 10 shows the percentage weight loss after 2 weeks for each of the nine preservatives. The wires dipped in ZnN had the lowest amount of corrosion and thus the lowest percentage weight loss. Surprisingly, wires exposed to seven of the preservatives exhibited a lower mean percentage weight loss than the water group. The most corrosion was exhibited in wires that had been treated with pCuA-1. To determine differences among the groups, the means were compared using a Tukey honest significant difference test. There were no significant differences between ZnN and CuC. The mean percentage weight losses from CuN, pCuA-2, and sCuA could not be differentiated but were higher than the group with ZnN and CuC. pCuA-1 had the most corrosion and was statistically different from the next lowest group.

Figure 11 shows the percentage weight loss after 8 weeks for each of the nine preservatives. Apparently, this exposure time was more realistic because the relative rankings of preservatives for which corrosiveness has been measured in previous experiments were consistent with previous testing (Zelinka and Stone 2011). In samples exposed for 8 weeks, treatments CuC and ZnN clearly exhibited the least amount of corrosion and were at least five times less corrosive than the remaining treatments. Of the remaining preservatives, AzI was significantly lower than Cu8-2, Cu8-1, and CuN, but the difference between AzI and the water control was not statistically significant. The soluble copper system had the most corrosion, and the difference between the soluble copper system and the next most corrosive system, pCuA-2, was statistically significant.

Figure 12 shows the ratio of the percentage weight loss after 8 weeks to the percentage weight loss after 2 weeks. If the corrosion rate was constant during this time period, the expected ratio would be four. A ratio less than four indicates the corrosion rate was decreasing after 2 weeks. A ratio of 1 suggests that all corrosion happened in the first 2 weeks. Three preservative systems (pCuA-2, sCuA, and CuN) exhibited a ratio of 4, suggesting that the corrosion rate was constant throughout the test. These preservatives would be expected to have even more corrosion in longer exposure times because the rate was not decelerating. Two preservative systems, ZnN and CuC, had a ratio of 1, suggesting that the corrosion had stopped after 2 weeks and little if any further corrosion would be expected.

Figure 13 shows photographs of one wire from each group after the 2-week exposure. The wire that was dipped in ZnN is in the bottom right corner and shows no signs of corrosion. The other wires had white corrosion products consistent with the corrosion of zinc, although the degree of corrosion varied among the wires. The wires from AzI, which had no copper in the treatment solution, exhibited some minor splotches of red rust, indicating that the

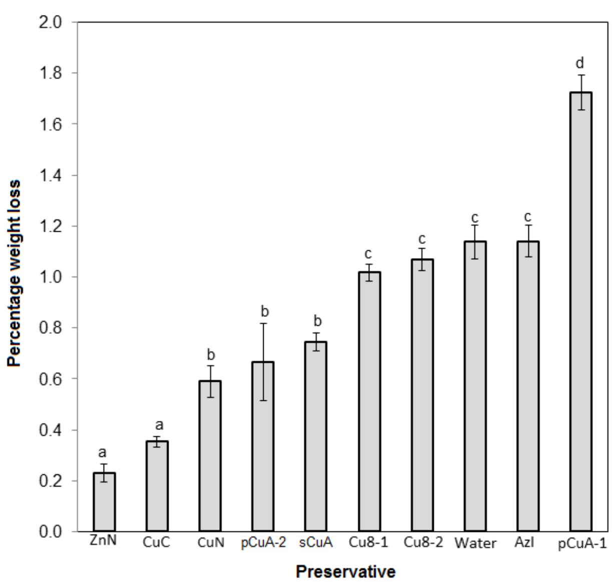


Figure 10. Percentage weight loss of wires after the 2-week exposure. Error bars represent the standard error. The letters above the bars are results of the Tukey's honest significant difference test; groups with the same letter have means that are not statistically different.

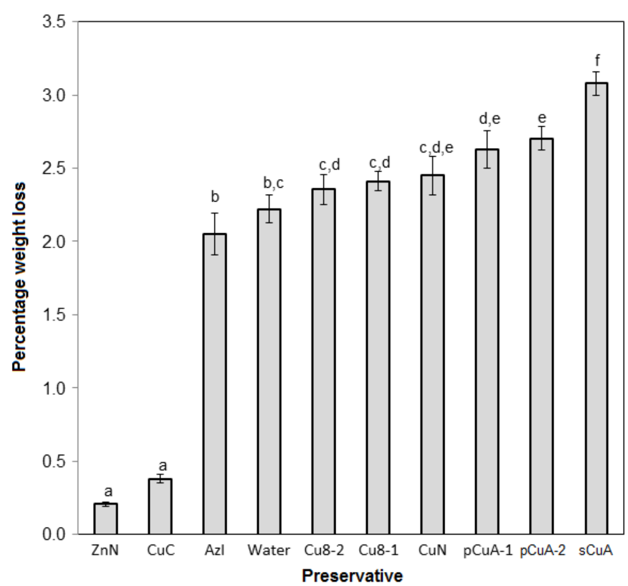


Figure 11. Percentage weight loss of wires after the 8-week exposure. Error bars represent the standard error. The letters above the bars are results of the Tukey's honest significant difference test; groups with the same letter have means that are not statistically different.

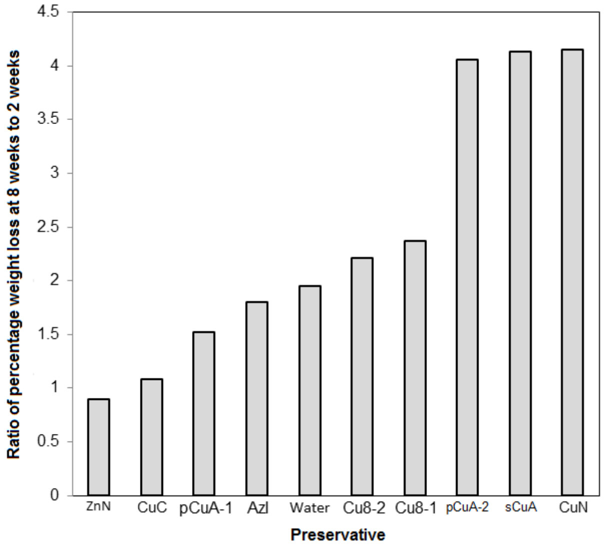


Figure 12. Ratio of percentage weight loss after 8 weeks to percentage weight loss after 2 weeks (a ratio of 4 indicates no deceleration in corrosion).

galvanized coating layer had corroded and the underlying steel wire was corroding. In addition to AzI, significant amounts of corrosion products were also visible on wires from pCuA-1, sCuA, Cu8-2, and the water-treated group.

Figure 14 shows the same wires as Figure 13 after they were rotated 180 degrees, exposing the metal that had been in direct contact with the wood. In some cases, the corrosion products became attached to the wood, and examining the wood that was in contact with the metal gave additional insights into the severity of corrosion. The back sides of the wire revealed that wires exposed to sCuA and Cu8-2 also had red rust that was not visible from the top view. Half of the treatments (CuC, pCuA-1, sCuA, Cu8-2, and CuN) resulted in white or red corrosion deposited on the wood.

Table 12 summarizes the visual inspection of the corrosion products by placing the different treatments into groups according to the amount of corrosion exhibited.

Figure 15 shows the top view of the wires after 8 weeks of exposure. All but two wires (CuC and ZnN) exhibited red rust. For the remaining groups, the red rust appeared as small, red dots on top of a layer of white corrosion products, and these red dots were evenly distributed throughout the wire. Because of this distribution of rust, it was difficult to visually rank the different treatments exhibiting red rust based on the amount of wire covered with red rust.

Figure 16 shows the same wires as Figure 15 after they were rotated 180 degrees to expose the metal that had been in direct contact with the wood surface. For six of the eight wires exhibiting red rust, corrosion products were deposited on the wood and differences between treatments could be observed. The amount of corrosion products deposited in the wood can be used to separate the treatments. These observations are summarized in Table 13, which groups the

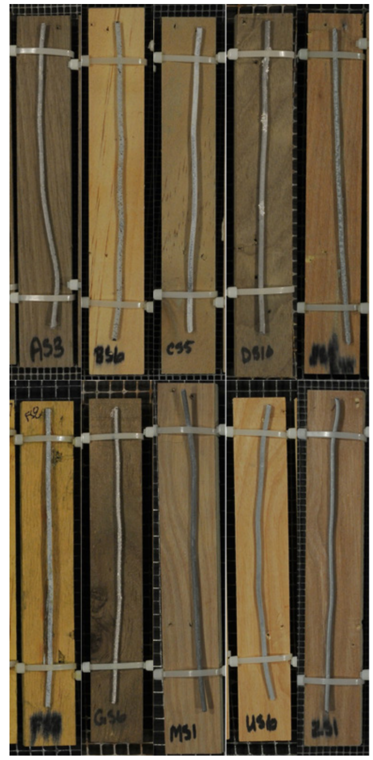


Figure 13. Tops of wires after the 2-week exposure. Dip formulations from left to right. Top row: CuC, AzI, pCuA-1, sCuA, Cu8-1. Bottom row: Cu8-2, CuN, pCuA-2, water, ZnN.

Figure 14. Bottoms of wires after the 2-week exposure. Dip formulations from left to right. Top row: CuC, AzI, pCuA-1, sCuA, Cu8-1. Bottom row: Cu8-2, CuN, pCuA-2, water, ZnN.

Figure 15. Tops of wires after the 8-week exposure. Dip formulations from left to right. Top row: CuC, AzI, pCuA-1, sCuA, Cu8-1. Bottom row: Cu8-2, CuN, pCuA-2, water, ZnN.

Figure 16. Bottoms of wires after the 8-week exposure. Dip formulations from left to right. Top row: CuC, AzI, pCuA-1, sCuA, Cu8-1. Bottom row: Cu8-2, CuN, pCuA-2, water, ZnN.

Table 12—Summary of the corrosion visual inspection after the 2-week exposure

Condition	Preservative
No visible corrosion	ZnN
White rust, slight	CuC, Cu8-1, CuN, pCuA-2
White rust, moderate to heavy	AzI, pCuA-1, water
White and red rust on surface, heavy deposits on wood	Cu8-2, sCuA

different treatments according to their corrosiveness.

Corrosion Testing Discussion

The exposure condition was chosen to be a challenging representation of what may occur in the production of the wire-bound packaging crates. In the production process, the crates are typically stacked on top of each other, dipped, and then stored until they are shipped. This process is difficult to replicate in the laboratory because there are, in actuality, a wide range of potential conditions the boxes could face post-treatment, depending on the ambient environment and how tightly they are stacked. The polyethylene bag method was chosen because it represents a worst case scenario (that is, no air flow), and the goal of the test was to differentiate the formulations evaluated. However, this environment may have been overly challenging, because even the untreated controls (dipped in a water bath) exhibited red rust and significant corrosion in the 8-week test. Despite this, preservative treatments could be grouped into several categories according to their corrosiveness.

In all exposure conditions, the wires exposed to the ZnN treatment exhibited little, if any, corrosion. Furthermore, they had five times less corrosion than wires that were strapped to wood and dipped in water, suggesting that ZnN was acting as a strong corrosion inhibitor. This behavior should not be surprising, because the treatment is made up of soluble zinc ions and the wires are coated with solid zinc. Unlike the preservatives with cupric ions, where it is thermodynamically favorable for the cupric ions to be reduced and the zinc to oxidize, the zinc ions in solution should not cause a displacement reaction. If anything, excess zinc ions in solution may solidify on the wire surface, increasing the thickness of zinc coating. This compatibility between the zinc ions in solution and the galvanized wires is the reason for the low amount of corrosion exhibited by the wires dipped in the ZnN solution.

CuC also exhibited an extremely low amount of corrosion relative to the other groups. Surprisingly, CuC contained cupric ions yet performed better than the untreated control group in which the wires were dipped in water. Because one of the likely corrosion mechanisms involves the reduction of cupric ions, one would expect this preservative to be more corrosive than the untreated group with just water. Beyond cupric ions, Zelinka and Stone (2011) have shown that preservative treatments can modify the pH of the wood, and as the pH is lowered, more corrosion is expected. CuC is

Table 13—Summary of the corrosion visual inspection after the 8-week exposure

Condition	Preservative
No visible corrosion	ZnN
Only white rust visible	CuC
Red rust on surface, no deposits on wood	Water
Red rust on surface, slight deposits on wood	AzI, Cu8-2, CuN, pCuA-2
Red rust on surface, heavy deposits on wood	pCuA-1, sCuA, Cu8-1

alkaline (pH = 10.2), and this may be one reason why it was less corrosive. However, two other preservatives, CuN and sCuA, have a pH above 9 and still exhibited more than five times the corrosion as CuC. In short, from a chemical perspective, it is unclear why CuC had such a low corrosion rate. It is possible that this preservative contains a proprietary corrosion inhibitor or some other additive that resulted in the low observed corrosion rates.

The differences in corrosion among the remaining eight treatments were small, but they had a much higher corrosion rate than either ZnN or CuC. AzI had a significantly lower amount of corrosion than the other remaining preservatives but was still much more corrosive than ZnN or CuC. The soluble copper azole solution (sCuA) had the greatest amount of corrosion, which was expected.

In addition to ranking the amount of corrosion after the 8-week test, the ratio of the corrosion rate between the 2- and 8-week tests can be used to identify preservatives for which corrosion rate was not decreasing with time. The ratio of the percentage weight loss between the 8- and 2-week tests was equal to the ratio of exposure time (4) for pCuA-2, sCuA, and CuN. This ratio indicates that the corrosion rate did not change during the exposure time and suggests that the amount of corrosion could continue to increase at the same rate for longer exposures. Because the corrosion rate is not slowing down with time, these preservatives may have a higher likelihood of causing corrosion problems if the crates are exposed to prolonged wetting.

The results of these tests can be used to compare the relative amounts of corrosion that would be expected to occur in the production of the boxes. The amount of corrosion that the packaging materials exhibit not only depends on the preservative treatment but is a strong function of the wood moisture content (Zelinka and others 2014). Manufacturing processes that allow the packaging materials to dry more quickly after treatment may help prevent corrosion problems.

Summary of Corrosion Testing

Nine different preservative treatments and an untreated control were evaluated for their corrosiveness toward wire-bound packaging crates. Wires were attached to strips of wood, dipped in the preservative treatment, and then stored in a polyethylene bag for either 2 or 8 weeks to simulate the time between treatment and shipment. After 8 weeks, seven of the nine preservatives and the untreated control caused red rust to form on the galvanized wires.

The only two wires that did not exhibit red rust were those treated with ZnN, which was previously the most commonly used preservative, and CuC. The active biocides in CuC were similar to other preservatives tested, and it is unclear why this preservative exhibited such a low amount of corrosion.

The percentage weight loss of three of the preservatives (pCuA-2, sCuA, and CuN) increased linearly with time, indicating the corrosion rate was constant through the 8-week test. These preservatives may have a higher likelihood of corrosion problems because the corrosion rate was not decelerating with time.

The goal of this research was to find alternatives to ZnN that do not pose a corrosion concern. The testing clearly indicated that CuC was the least corrosive alternative. The remaining preservatives all exhibited red rust in the 8-week test and more than five times the corrosion that was observed in the ZnN solution.

Verifying Treatment and Solution Concentration

Verifying preservative treatment is an important part of conformance inspections, and treaters need a method of verifying the concentration of the treatment solution. Existing military specifications describe methods for verifying the presence of ZnN, Cu8, or CuN preservative on wooden materials. These methods rely on the use of colorimetric indicator solutions that react to the presence of active ingredients in the preservative (Table 14). The indicator currently used for CuN could also be used for the other soluble and particulate copper formulations evaluated in this study. The dark color imparted by the CuN and CuC formulations is also an indicator of treatment (Fig. 17) and should make any untreated areas readily apparent. Verifying preservative treatment is most challenging for the AzI formulation, which is a clear formulation that does not impart an obvious color change to the treated wood. Also, AzI does not contain copper or zinc, which have available colorimetric indicator solutions listed under military specification. In the pressure-treatment industry, detection of colorless treatments is addressed by adding a more easily detected chemical, such as boron or copper, to the formulation. In this case, the addition of low concentrations of boron in the form of boric acid or sodium borate (for example, borax, disodium octaborate tetrahydrate) is recommended because of the availability and water solubility of borates.

Table 14—Indicators available for verifying treatment of dipped wood packaging materials

Preservative	Type of indicator	Ingredients used in indicator
Cu8-1, Cu8-2	1-(2-pyridylazo)-2-napthol (PAN)	PAN, methanol
AzI	Curcumin–salicylic acid (requires addition of at least 0.033% elemental boron to treatment solution)	Curcumin, ethanol, salicylic acid, hydrochloric acid
CuC, pCuA-1, sCuA, pCuA-2, CuN	Chrome azurol-S	Chrome azurol-S, sodium acetate, water
ZnN	Dithizone	Dithizone (diphenylthiocarbazone), methyl ethyl ketone or chloroform

However, verifying the concentration of the treatment solution is more complex than verifying the presence of a preservative on a wood surface. In the pressure-treatment industry, x ray fluorescence analyzers are used for routine analysis of copper in treating solutions, but these devices are relatively costly compared with the colorimetric indicator kits. It may be more practical to have treatment solution concentrations periodically analyzed by the preservative manufacturer using one of the test methods standardized by AWPA (Table 15). There are also private and university laboratories that can assay liquid samples for copper on a fee basis.

Results and Discussion, Green Preservatives

Decay Testing

Overall, the green preservative formulations tested were largely ineffective in protecting Southern Pine against attack from brown-rot fungi, allowing weight losses similar to those observed for specimens treated only with water (Fig. 18a). The lack of efficacy was also visually apparent, especially for Southern Pine specimens exposed to *P. placenta* (Fig. 19). A similar pattern was observed for yellow-poplar exposed to white-rot fungi (Fig. 18b). One of the treatments, Deck WR, did appear to lessen weight loss caused by the fungus *I. lacteus*, despite not making any claims regarding antifungal activity. Application method, which was examined in two of the treatments (Cedar and LiqSil), appeared to have little to no effect on preservative efficacy. In the nongreen preservatives selected for comparison, results showed that 0.5% AzI was the most effective formulation against both white- and brown-rot fungi, followed by the 3% ZnN formulation. Interestingly, performance of ZnN against *P. placenta* was highly variable, with two replicates having no weight loss and three replicates having substantial weight loss.

Termite Testing

As was observed for decay testing, the green preservatives selected for termite testing were not effective in protecting Southern Pine specimens from attack. Yellow-poplar specimens were less attacked overall, which is probably the

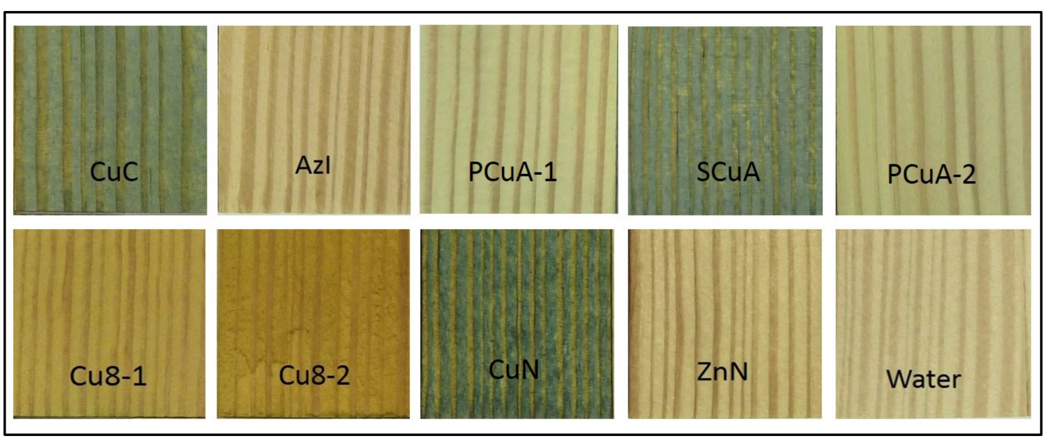


Figure 17. Color change imparted to Southern Pine sapwood after immersion in treatment formulations. Water treatment (bottom right) included for comparison.

Table 15—Analysis methods for verifying solution concentration standardized by the American Wood Protection Association (AWPA 2017)

Active ingredients and preservatives	AWPA standard
Azoles (AzI, pCuA-1, sCuA, pCuA-2)	A28, A31, or A48
Boron (AzI indicator additive)	A21
Copper (CuC, pCuA-1, sCuA, pCuA-2, CuN)	A21
Imidacloprid (AzI)	A43 or A48
Napthenic acid (CuN, ZnN)	A41
Zinc (ZnN)	A21

result of wood species preference rather than difference in treatment. Two green treatments (Polymer and Deck WR) did show some termite resistance in Southern Pine specimens in terms of weight loss but still allowed substantial feeding on the blocks (Fig. 20). As noted for decay, the Deck WR product also did not claim any termite resistance properties but still appeared to provide somewhat greater termite protection than the other green formulations, which did claim to have preservative properties.

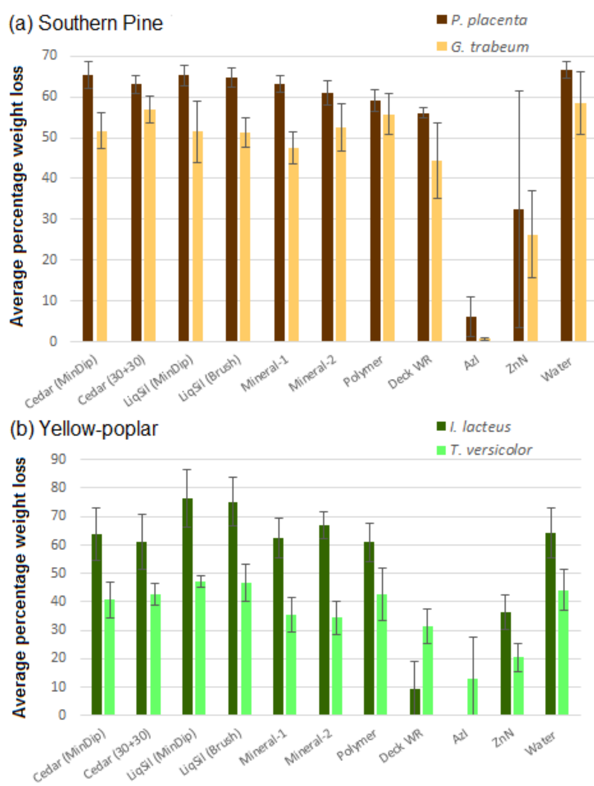


Figure 18. Average percentage weight losses for treated (a) Southern Pine and (b) yellow-poplar specimens exposed to brown- or white-rot fungi. Error bars show plus or minus one standard error.

Statistical Analysis

The distribution of percentage weight losses associated with decay and termite attack are shown in Figures 21 and 22, respectively. In some cases, the variability in weight losses within treatment groups varied substantially (see ZnN specimens exposed to *P. placenta*, for example).

One-way analyses of variance with treatment as the factor (at 11 levels) were carried out on percentage weight loss. These analyses were conducted separately for each wood species–test organism combination. Multiple pairwise comparisons were adjusted based on the Tukey-Kramer method in SAS, with adjusted p-values <0.05 considered significant. Responses for some of the treatment groups (Southern Pine–*Postia* and yellow-poplar–*Trametes*) exhibited heterogeneity, and nonconstant variance models were used to improve model fits in those cases. The nonconstant variance models resulted in some nonconstant group difference standard errors. Therefore, mean separations in those cases may not be fully represented by simple letter connections, and SAS's conservative representation is used with footnotes giving exceptions (Tables 16 and 17) (Westfall and others 2011).

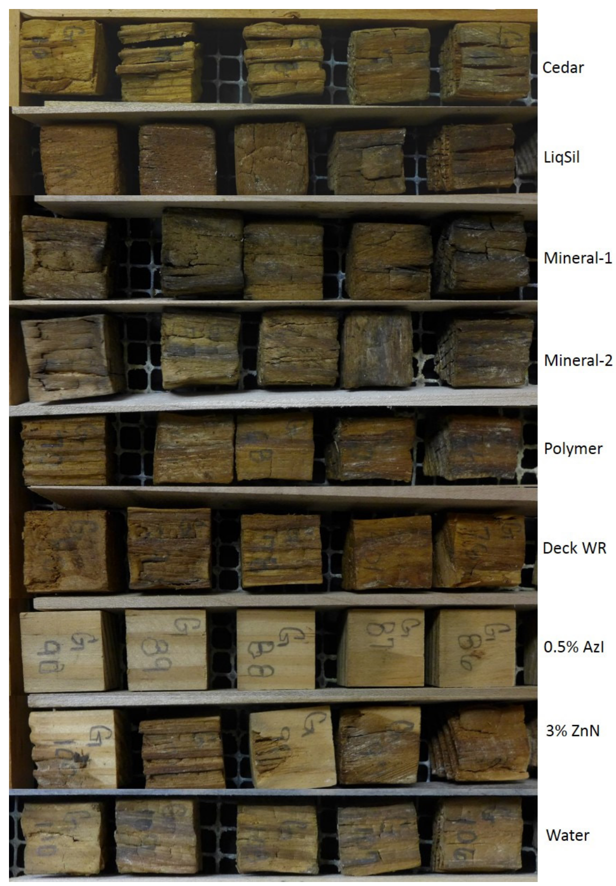


Figure 19. Appearance of Southern Pine specimens treated by 1-min dip and exposed to the brown-rot fungus *P. placenta*. Each row shows the five replicate specimens in that treatment group.

For Southern Pine specimens exposed to brown-rot fungi, weight losses from specimens treated with the various green preservatives tested were rarely different from the water controls (Table 16). The exceptions were the Polymer and Deck WR treatments exposed to *P. placenta* (see also footnote, Table 16). All the green treatments allowed significantly greater weight loss than the 3% ZnN and 0.5% AzI reference treatments, with the exception of ZnN blocks exposed to *P. placenta*. This latter finding, however, is probably the result of the relatively high and quite variable weight losses observed with ZnN blocks within this test group (Fig. 21).

For yellow-poplar specimens exposed to white-rot fungi, the green preservatives generally did not provide significantly greater protection than water (Table 17). The exception was Deck WR, which did have significantly lower weight losses than water controls in specimens exposed to *I. lacteus*. Both 0.5% AzI and 3% ZnN provided significantly greater protection than the green preservatives for *I. lacteus*, even though ZnN sustained substantial weight loss. Comparisons among the treatments exposed to the fungus *T. versicolor*, however, were more complicated; none of the green preservatives were significantly different from 0.5% AzI, despite the much lower average weight loss with AzI. This result again reflects how increased variability among replicates can obscure treatment differences (Fig. 21). ZnN did provide significantly greater protection than most of the green preservatives with the exceptions of Deck WR and Mineral-2 (see Table 17 footnote for additional significant differences).

The only example of a green preservative treatment providing significantly greater termite protection than the water control was Polymer applied to Southern Pine specimens (Table 18). The 0.5% AzI treatment was significantly more effective than all the green preservatives in both wood species, whereas ZnN was significantly more effective than all the green preservatives in Southern Pine treated blocks. For yellow-poplar, ZnN was also significantly more effective than all the green treatments, with the exceptions of Deck WR and Cedar (1-min dip).

Overall, the relative lack of efficacy observed in the green preservatives selected for this study indicates that they will not provide biological protection across the wide range of exposure conditions that might be encountered by WPMs. In addition, manufacturers of these green preservatives are not required to identify or quantify active ingredients used in the formulations, which was the case with most of the products evaluated in this study. This latter characteristic could make it difficult to develop specifications for using green preservatives and/or to conduct inspections to determine if WPMs are being adequately treated.

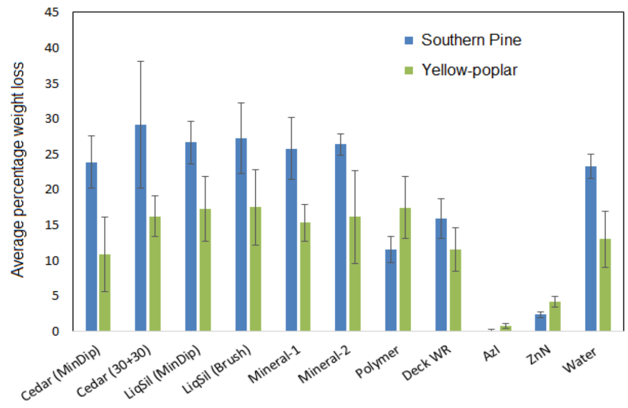


Figure 20. Average percentage weight losses for treated Southern Pine (blue) or yellow-poplar (green) specimens exposed to subterranean termites. Error bars show plus or minus one standard error.

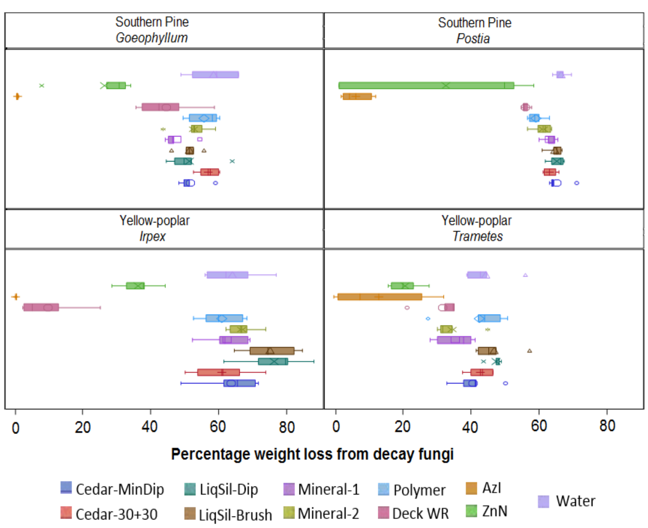


Figure 21. Distribution of percentage weight loss observed for each treatment–wood species–decay fungus combination.

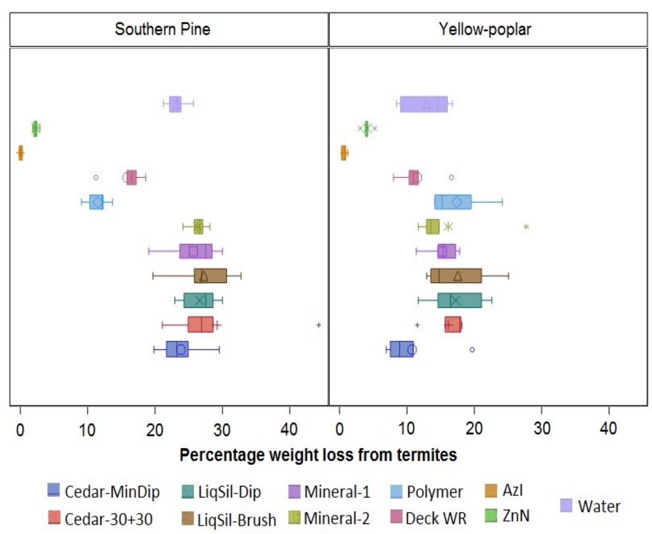


Figure 22. Distribution of percentage weight loss for each treatment–wood species combination after termite testing.

Table 16—Tukey mean comparisons for Southern Pine specimens exposed to two brown-rot fungi (Within a column, means that do not share the same letter are significantly different (adjusted *p*-value of <0.05))

	Gloeophyllum trabeum		*Postia placenta*[a]	
Treatment	LS mean estimate (SE)	Tukey mean comparison	LS mean estimate (SE)	Tukey mean comparison
AzI	0.71(2.8028)	A	6.07(2.1723)	A
Deck WR	44.45(2.8028)	C	56.06(0.5618)	B
Mineral-2	52.49(2.8028)	CD	61.11(1.3194)	B
Mineral-1	47.53(2.8028)	CD	63.12(0.9486)	B
Polymer	55.81(2.8028)	CD	59.16(1.1832)	B
Cedar 30+30	56.98(2.8028)	CD	63.11(0.9735)	B
Cedar MinDip	51.71(2.8028)	CD	65.27(1.4653)	B
LiqSil Brush	51.29(2.8028)	CD	64.71(1.0717)	B
LiqSil MinDip	51.47(2.8028)	CD	65.31(1.0979)	B
Water	58.49(2.8028)	D	66.59(0.9312)	B
ZnN	26.36(2.8028)	B	32.57(12.9668)	AB

[a]Modeled with heterogeneous variance for each treatment group (based on results from Levene's HOV test). This Tukey column does not reflect all significant comparisons. Because of lower variances for some groups, the following additional pairs are significantly different for *Postia*: (water–polymer), (water–Deck WR), (LiqSil MinDip–Deck WR), (Cedar MinDip–Deck WR), (LiqSil Brush–Deck WR), (Mineral-1–Deck WR), (Cedar 30+30–Deck WR).

Table 17—Tukey mean comparisons for yellow-poplar specimens exposed to two white-rot fungi (Within a column, means that do not share the same letter are significantly different (adjusted *p*-value of <0.05))

	Irpex lacteus		*Trametes versicolor*[a]	
Treatment	LS mean estimate (SE)	Tukey mean comparison	LS mean estimate (SE)	Tukey mean comparison
0.5% AzI	0.22(3.5000)	A	12.85(6.6341)	A
Deck WR	9.51(3.5000)	A	31.60(2.7008)	AB
Mineral-2	66.88(3.5000)	C	34.37(2.6974)	AB
Mineral-1	62.40(3.5000)	C	35.43(2.7038)	AB
Polymer	60.91(3.5000)	C	42.54(4.1107)	ABC
Cedar 30+30	61.09(3.5000)	C	42.66(1.7616)	BC
Cedar MinDip	63.73(3.5000)	C	40.69(2.8659)	ABC
LiqSil Brush	75.14(3.5000)	C	46.70(2.8358)	BC
LiqSil MinDip	76.35(3.5000)	C	47.34(0.9196)	C
Water	64.11(3.5000)	C	44.21(3.1392)	BC
ZnN	36.38(3.5000)	B	20.49(2.2066)	A

[a]Modeled with heterogeneous variance for each treatment group (based on results from Levene's HOV test). This Tukey column does not reflect all significant comparisons. Because of lower variances for some groups, the following additional pairs are significantly different for *Trametes*: (Polymer–ZnN), (CedarMinDip–ZnN), (Mineral-1–ZnN).

The results of this study do not preclude the possibility that future green preservatives could provide adequate protection of WPMs, because it is possible to increase the durability of wood products without the use of EPA-registered pesticides. For example, as noted in the Introduction, pressure treatment with high loadings of paraffin did substantially increase the durability of test stakes exposed in Mississippi. Cedar extracts have also been reported to have some efficacy against termites and decay, although that was not observed in this study, perhaps because the actives concentration was too low.

During the initial testing of EPA-registered preservatives, AzI was evaluated at a single (1.05%) actives concentration and was assumed to be highly effective against all

Table 18—Tukey mean comparisons for Southern Pine and yellow-poplar specimens exposed to termites (Within a column, means that do not share the same letter are significantly different (adjusted *p*-value of <0.05))

	Southern Pine		Yellow-poplar	
Treatment	LS mean estimate (SE)	Tukey mean comparison	LS mean estimate (SE)	Tukey mean comparison
AzI	0.09(1.7198)	A	0.75(1.8025)	A
Deck WR	15.92(1.7198)	BC	11.54(1.8025)	BC
Mineral-2	26.37(1.7198)	D	16.14(1.8025)	C
Mineral-1	25.78(1.7198)	D	15.33(1.8025)	C
Polymer	11.54(1.7198)	B	17.45(1.8025)	C
Cedar 30+30	29.19(1.7198)	D	16.24(1.8025)	C
Cedar MinDip	23.87(1.7198)	CD	10.87(1.8025)	BC
LiqSil Brush	27.22(1.7198)	D	17.51(1.8025)	C
LiqSil MinDip	26.67(1.7198)	D	17.31(1.8025)	C
Water	23.28(1.7198)	CD	13.02(1.8025)	C
ZnN	2.38(1.7198)	A	4.17(1.8025)	AB

organisms tested. This result suggested that a lower actives concentration might be adequate. During a subsequent study to determine the effect of laser marking on decay and termite resistance, a 0.5% concentration was evaluated (Arango and others 2016). Although the 0.5% AzI concentration did appear to be effective in the laser-marking research, several aspects of that test method differed considerably from the standard method used to evaluate the 1.05% AzI concentration. Thus, 0.5% AzI was evaluated as a positive control in the green preservative testing, using methods similar to those used in evaluating the 1.05% concentration. Results showed the 0.5% AzI to be highly effective in preventing decay in Southern Pine specimens exposed to the brown-rot fungus *G. trabeum* and in yellow-poplar specimens exposed to the white-rot fungus *I. lacteus*. It was also highly effective against termites in both wood species. However, it did allow slight weight loss by *P. placenta* in Southern Pine specimens and somewhat greater weight loss by *T. versicolor* in yellow-poplar. In contrast, the 1.05% concentration evaluated in the initial study allowed no measureable weight loss by any of the test fungi or termites in either wood species. Thus, although the 0.5% AzI concentration was effective, the effectiveness of even lower concentrations is not well supported by the data.

Summary and Recommended Applications

None of the green preservatives evaluated under the conditions of this study appeared suitable for protection of WPMs. However, several of the EPA-registered test formulations provided protection from fungal attack that was at least equivalent to that provided by current formulations. AzI was effective at both 0.5% and 1.05% concentrations, and pCuA-1 (2.0% Cu), sCuA (2% Cu), and pCuA-2 (1% and 2% Cu) were also shown to be effective alternatives. Although the 2% CuC formulation was highly vulnerable to copper-tolerant *P. placenta*, this formulation was effective against the other fungi evaluated. Variability observed between blocks exposed to *P. placenta* influenced interpretation of efficacy for some other copper formulations as well, but the actual risk of copper tolerance for WPMs in field settings remains unknown. In termite testing, only two test formulations (AzI and 2% sCuA) did not have significantly greater weight loss than the reference preservative CuN. However, higher concentrations of several other test formulations did protect at least as well as the ZnN and Cu8 reference preservatives.

Corrosion testing revealed that all of the test formulations, except CuC, were substantially more corrosive than ZnN. The copper concentration in CuC was similar to other preservatives tested, and it is unclear why this preservative exhibited such a low amount of corrosion. The percentage weight loss of pCuA-2, sCuA, and CuN increased linearly with time, indicating the corrosion rate was constant through the 8-week test. This suggests that these preservatives may actually have an increased likelihood of causing corrosion because the corrosion rate was not decelerating with time.

The results from the laboratory fungal, termite, and corrosion testing in this study were used to develop a relative protection index for the test formulations, as well as recommended applications and criteria for evaluating future formulations (Appendix). The severity of laboratory fungal and termite tests may vary depending on vigor of the test organisms. To help account for this biologic variability, the weight losses observed with preservative-treated specimens were divided by those of their respective untreated controls. The suitability of preservative formulations for WPM applications was then based on the resulting treated/untreated weight loss ratios and on the weight losses observed in corrosion testing. As part of this process, it was recognized that desirable preservative characteristics may vary depending on the type of WPM. Corrosion is particularly a concern for wire-bound boxes, whereas decay and insect resistance is of greatest concern for WPMs that are likely to be placed in contact with the ground. U.S. Army personnel created three classifications of WPM–preservative combinations to allow greater flexibility in matching the characteristics of the preservative to the expected exposure condition of the WPM. The suitability criteria for these three classifications are

Type I — preservatives for all WPMs must meet these conditions:

> Weight loss caused by corrosion test must be less than 3%.
>
> Sum of the six ratios calculated from decay and termite tests cannot exceed 1.0.
>
> No ratio for any single decay or termite test can exceed 0.4.

Type II — preservatives for wire-bound boxes only must meet these conditions:

> Weight loss caused by corrosion test must be less than 0.75%.
>
> Sum of the six ratios calculated from decay and termite tests cannot exceed 1.25.
>
> No more than one ratio for an individual decay or termite test can exceed 0.2.

Type III — preservatives for all WPMs except wire-bound boxes must meet these conditions:

> Weight loss caused by corrosion test may exceed 3%.
>
> Sum of the six ratios calculated from decay and termite tests cannot exceed 1.0.
>
> No ratio for any single decay or termite test can exceed 0.4.

Not suitable — preservatives that do not meet the criteria for Type I, II, or III are not suitable for treatment of WPMs.

Table 19 shows the results of applying these criteria to the formulations evaluated in this study.

AzI and six of the more concentrated copper formulations were classified as Type I (suitable for all WPMs). Despite a single high weight loss ratio with the fungus *P. placenta*, 2% CuC was judged to be suitable for wire-bound boxes because of its desirable corrosion properties. In contrast, the 2% sCuA formulation was judged unsuitable for wire-bound boxes because of its corrosiveness but suitable for other applications because of its efficacy against decay and termite attack. Future candidate preservatives may potentially be evaluated using the methods and criteria described in the Appendix. Based on the results of this study, U.S. Army personnel developed a drawing (similar to a specification) that covers dip preservative treatment of all wood products used for a wide range of applications (U.S. Army 2017a). A separate source control drawing lists approved sources of supply and details the tests and criteria that must be used to qualify future preservatives (U.S. Army 2017b).

Table 19—Weight loss ratios and wood packaging materials (WPMs) suitability assignments[a] (factors key to the WPM assignment are underlined and in bold)

		Biologic weight loss ratios, treated/untreated								
		Fungal				Termite				
Preservative formulation	Corrosion category[b]	*G. trabeum*	*P. placenta*	*T. versicolor*	*I. lacteus*	Southern Pine	Yellow-poplar	Sum of ratios	WPM type	Basis for suitability assignment
CuC, 1%	<0.75%	**<u>0.56</u>**	**<u>1.01</u>**	0.02	0.21	0.08	**<u>0.47</u>**	**<u>2.35</u>**	None	High biologic ratios
CuC, 2%	**<u><0.75%</u>**	0.13	**<u>0.94</u>**	0.01	0.01	0.00	0.14	1.24	II only	Low corrosion, high fungal ratio
AzI, 0.5%	0.75–3.0%	0.01	0.09	0.29	0.00	0.00	0.06	0.46	I	
AzI 1.05%	0.75–3.0%	0.01	0.00	–0.06	–0.01	0.00	0.00	–0.06	I	
pCuA-1, 1%	0.75–3.0%	0.04	**<u>0.64</u>**	–0.01	–0.01	0.10	**<u>0.66</u>**	**<u>1.43</u>**	None	High biologic ratios
pCuA-1, 2%	0.75–3.0%	0.00	0.11	–0.01	–0.01	0.00	0.38	0.47	I	
sCuA, 1%	**<u>>3.0%</u>**	0.04	**<u>0.83</u>**	0.00	–0.01	0.01	0.38	**<u>1.25</u>**	None	High fungal ratio, corrosion
sCuA, 2%	**<u>>3.0%</u>**	0.01	0.05	–0.01	–0.03	0.00	0.10	0.13	III only	Corrosion, low biologic ratios
pCuA-2, 1%	**<u>0.75–3.0%</u>**	0.00	0.09	0.04	0.00	0.02	**<u>0.58</u>**	0.72	None	High termite ratio, corrosion
pCuA-2, 2%	0.75–3.0%	0.00	0.17	–0.01	0.00	0.02	0.22	0.40	I	
Cu8-1, 1.2%	0.75–3.0%	0.00	0.04	**<u>0.45</u>**	**<u>0.46</u>**	0.22	**<u>0.71</u>**	**<u>1.89</u>**	None	High biologic ratios
Cu8-1, 1.8%	0.75–3.0%	0.00	0.01	0.39	**<u>0.47</u>**	**<u>0.44</u>**	**<u>0.68</u>**	**<u>1.98</u>**	None	High biologic ratios
Cu8-2, 1.2%	**<u>0.75–3.0%</u>**	0.01	0.01	0.01	0.00	0.01	**<u>0.53</u>**	0.57	None	High termite ratio, corrosion
Cu8-2, 1.8%	0.75–3.0%	0.01	0.01	0.01	–0.01	0.03	0.33	0.38	I	
CuN, 1%	**<u>0.75–3.0%</u>**	0.21	**<u>0.89</u>**	0.00	0.06	0.03	0.04	**<u>1.24</u>**	None	High fungal ratio, corrosion
CuN, 2%	0.75–3.0%	0.01	0.11	0.00	0.01	0.00	0.00	0.13	I	
ZnN, 3%	<0.75%	0.18	0.08	0.23	0.29	0.08	0.14	1.00	I	

[a]Suitability assignments are based on information available at the time of this report and may not reflect the current use practices. These recommendations are not and should not be used in lieu of military specifications.

[b]Corrosion category is based on the highest concentration evaluated for a formulation.

Acknowledgments

The authors acknowledge funding from the U.S. Army Armament Research Development and Engineering Center (ARDEC) and the invaluable assistance provided by Patrick DeWald, Mark Rehmstedt, and Jason Langel of ARDEC.

Literature Cited

Arango, R.; Woodward, B.; Lebow, S. 2016. Evaluating the effects of post dip-treatment laser marking on resistance to feeding by subterranean termites. In: Proceedings. Doc. No. IRG/WP 16-10854. Stockholm, Sweden: International Research Group on Wood Protection. 12 p.

ASTM. 2008. D3345-08. Standard test method for laboratory evaluation of wood and other cellulosic materials for resistance to termites. West Conshohocken, PA: ASTM International. www.astm.org.

AWPA. 2017. Book of standards. Birmingham, AL: American Wood Protection Association. 624 p.

- A21: Standard Method for Analysis of Wood and Wood Treating Solutions by Inductively Coupled Plasma Emission Spectrometry
- A28: Standard Method for Determination of Propiconazole and Tebuconazole in Waterborne Formulations and in Treating Solutions by HPLC.
- A31: Standard Methods for the Analysis of Solutions and Wood for Azoles by Gas Chromatography (GC)
- A41: Standard Method for Determination of Naphthenic Acid in Copper Naphthenate in Wood and Treating Solutions by Gas Chromatography (GC)
- A43: Standard Method for Analysis of Imidacloprid in Wood and Waterborne Formulations
- A48: Standard Method for Analysis of Propiconazole, Tebuconazole and Imidacloprid in Solutions and Treated Wood Products by High Performance Liquid Chromatography
- E1: Laboratory Methods for Evaluating the Termite Resistance of Wood-Based Materials: Choice and No-Choice Tests
- E10: Laboratory Method for Evaluating the Decay Resistance of Wood-Based Materials Against Pure Basidiomycete Cultures: Soil/Block Test
- E18: Standard Field Test for Evaluation of Wood Preservatives to be Used Above Ground (UC3B); Ground Proximity Decay Test
- P34: Standard for Copper Naphthenate, Waterborne (CuN-W)

Barnes, H.M.; Amburgey, T.L.; Sanders, M.G. 2004. Performance of zinc-based preservative systems in ground contact. Wood Design Focus. 14: 13-17.

Choi, S.M.; Ruddick, J.N.R.; Morris, P.I. 2002. The copper tolerance of mycelium vs spores for two brown rot fungi. In: Proceedings, Stockholm, Sweden: International Research Group on Wood Protection, Doc. No. IRG/WP 02-10422: 4 p.

De Groot, R.C.; Stroukoff, M. 1986. Efficacy of alternative preservatives used in dip treatments for wood boxes. Res. Pap. FPL–RP–481. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.

Du, T.; Shupe, T.F.; Hse, C.Y. 2009. Antifungal activities of three supercritical fluid extracted cedar oils. In: Proceedings. Doc. No. IRG/WP 09-30501. Stockholm, Sweden: International Research Group on Wood Preservation.

Eller, F.J.; Clausen, C.A.; Green, F.; Taylor, S.L. 2010. Critical fluid extraction of *Juniperus virginiana* L. and bioactivity of extracts against subterranean termites and wood-rot fungi. Industrial Crops and Products. 32: 481-485.

Feist, W.C. 1988. Chapter 11. Outdoor weathering and wood protection. In: Rowell, R.M.; Barbour, R.J., eds. Archaeological wood: properties, chemistry, and preservation. Advances in Chemistry Series 225. Proceedings of 196th meeting of the American Chemical Society; 1988 September 25-28; Los Angeles. Washington, DC: American Chemical Society: 263-298.

Freeman, M.A.; McIntyre, C.R. 2008. A comprehensive review of copper-based wood preservatives with a focus on new micronized or dispersed copper systems. Forest Products Journal. 58: 6-27.

Highley, T.L. 1993. Above-ground performance of surface-treated hardwoods and softwoods. Wood Protection. 2(2): 61-66.

Highley, T.L.; Scheffer, T.C. 1998. Long-term appraisal of on-site preservative treatments for preventing decay in exterior woodwork. Material und Organismen. 32: 29-40.

Jenkins, K.M.; Clausen, C.A.; Green, F. 2014. The effects of copper proximity on oxalate production in Fibroporia radiculosa. In: Proceedings. Doc. No. IRG/WP/14-10823. Stockholm, Sweden: International Research Group on Wood Protection. 12 p.

Kear, G.; Wu, H.-Z.; Jones, M.S. 2009. Weight loss studies of fastener materials corrosion in contact with timbers treated with copper azole and alkaline copper quaternary compounds. Corrosion Science. 51: 252-262.

Kirker, G.T.; Blodgett, A.B.; Arango, R.A.; Lebow, P.K.; Clausen, C.A. 2013b. The role of extractives in naturally durable wood species. International Biodeterioration & Biodegradation. 82: 53-58.

Kirker, G.T.; Blodgett, A.B.; Lebow, S.; Clausen, C.A. 2013a. Transferable durability: enhancing decay resistance of non-durable species with extractives from durable wood species. In: Proceedings annual meeting of the international research group on wood protection. Doc. No. IRG/WP 13-10808. Stockholm, Sweden: International Research Group on Wood Protection. 12 p.

Lebow, S.; Arango, R.; Woodward, B.; Lebow, P.; Ohno, K. 2015. Efficacy of alternatives to zinc naphthenate for dip treatment of wood packaging materials. International Biodeterioration & Biodegradation. 104: 371-376.

Lebow, S.T.; Ross, R.J.; Zelinka, S.L. 2014. Evaluation of wood species and preservatives for use in Wisconsin highway sign posts. Gen. Tech. Rep. FPL–GTR–231. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 45 p.

Mai, C.; Militz, H. 2004a. Modification of wood with silicon compounds. Inorganic silicon compounds and sol-gel systems: a review. Wood Science Technology. 37: 339-348.

Mai, C.; Militz, H. 2004b. Modification of wood with silicon compounds. Treatment systems based on organic silicon compounds — a review. Wood Science and Technology. 37: 453-461.

Meijer, M.; Dingemans, M.M.L; Van Den Berg, M.; Westerink, R.H.S. 2014. Inhibition of voltage-gated calcium channels as common mode of action for (mixtures of) distinct classes of insecticides. Toxicology Science.141: 103-111.

Mitchoff, M.E.; Morrell, J.J. 1988. Laboratory decay resistance of preservative-treated red alder. Wood and Fiber Science. 20(3): 370-377.

Morrell, J.J.; Miller, D.J.; Lebow, S.T. 1999. Above ground performance of preservative-treated western wood species. In: Proceedings of the ninety-fourth annual meeting of the American Wood-Preservers' Association, Scottsdale, Arizona, May 17-19 1998. 94: 249-256.

Rennerfelt, E. 1948. Investigations of thujaplicin, a fungicidal substance in the heartwood of Thuja- plicata D DON. Physiologia Plantarum. 1(3): 245-254.

Thorne, B.L.; Breisch, N.L. 2001. Effects of sublethal exposure to imidacloprid on subsequent behavior or subterranean termite Reticulitermes virginicus (Isoptera: Rhinotermitidae). Journal of Economic Entomology. 94: 492-498.

U.S. Army. 2017a. Drawing 13064136. Wood packing material, preservative treated. U.S. Army Armament Research, Development and Engineering Center (ARDEC) Drawing. Picatinny Arsenal, NJ: U.S. Army RDECOM-ARDEC. 26 p.

U.S. Army. 2017b. Drawing 13060578. Preservative, Wood. U.S. Army Armament Research, Development and Engineering Center (ARDEC) Drawing. Picatinny Arsenal, NJ: U.S. Army RDECOM-ARDEC. 3 p.

Weigenand, O.; Humar, M.; Daniel, G.; Militz, H.; Mai, C. 2009. Decay resistance of wood treated with amino-silicone compounds. Holzforschung. 62: 112-118.

Westfall, P.H.; Tobias, R.D.; Wolfinger, R.D. 2011. Multiple comparisons and multiple tests using SAS®, Second Edition. Cary, NC: SAS Institute, Inc. 625 p.

Woodward, B.M.; Hatfield, C.A.; Lebow, S.T. 2011. Comparison of wood preservatives in stake tests: 2011 progress report. Res. Note FPL–RN–02. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 120 p.

Yang, V.W.; Clausen, C.A. 2007. Antifungal effect of essential oils on southern yellow pine. International Biodeterioration and Biodegradation. 59: 302-306.

Zelinka, S.L. 2014. Chapter 23. Corrosion of metals in wood products. In: Aliofkhazraei, M., ed. Developments in corrosion protection. InTech, Rijeka, 2014, pp. 568-592.

Zelinka, S.L.; Derome, D.; Glass, S.V. 2014. The effect of moisture content on the corrosion of fasteners embedded in wood subjected to alkaline copper quaternary treatment. Corrosion Science. 83: 67-74.

Zelinka, S.L.; Lebow, S. 2015. Corrosion of wires on wooden wire-bound packaging crates. In: NACE International Corrosion Conference and Expo 2015 Paper No. 5617, 2015; Houston, TX: National Association of Corrosion Engineers. 15 p.

Zelinka, S.L.; Rammer, D.R. 2009. Corrosion rates of fasteners in treated wood exposed to 100% relative humidity. ASCE Journal of Materials in Civil Engineering. 21: 758-763.

Zelinka, S.L.; Stone, D.S. 2011. Corrosion of metals in wood: comparing the results of a rapid test method with long-term exposure tests across six wood treatments. Corrosion Science. 53: 1708-1714.

Appendix—Protection Index: Methods and Criteria for Evaluating Candidate Preservatives

1. Corrosion testing

A. Materials
1. Both wire and wood samples used in the testing shall come from untreated packing crates that are disassembled.
2. The wire shall be cut into 150-mm-long segments.
3. The wood box shall be cut into strips that are 25 mm wide by 175 mm long.

B. Predip wire cleaning procedure
1. The wires shall be cleaned in an ultrasonic cleaner with a soap solution for 5 min followed by a rinse under flowing deionized water. The wires shall then be placed in an ultrasonic cleaner for 5 min in deionized water.
2. The wires shall then be weighed to the nearest 0.1 mg.
3. After weighing, the fasteners shall be attached to the wood strip with a nonmetallic cable tie.

C. Dip procedure
1. The wood–wire assembly shall be dipped for 60 s in the treatment solution. The excess treatment shall be blotted from the wood, and the wood shall be sealed in a polyethylene bag.
2. At least 10 replicates should be run.
3. In addition to the treatment solution, 10 additional samples shall be dipped into deionized water, blotted dry, and sealed in a polyethylene bag. These are the water control samples.

D. Exposure
1. The wood–wire assemblies shall remain sealed in a polyethylene bag for 8 weeks. The bags shall be placed in a high humidity environment (>90% RH) that is maintained at 27 °C.

E. Postexposure procedure
1. The wire shall be separated from the wood by destroying the plastic cable tie.
2. The corrosion products of the wire shall be removed.
    a. The wire shall be placed in an ultrasonic cleaner in a solution of 50 vol% water and 50 vol% EvapoRust (Orison Marketing, Abilene, Texas) for 60 min.
    b. After being removed from the bath, the wires shall be wiped with a paper towel and allowed to air-dry.
3. The wires shall be weighed to the nearest 0.1 mg.

F. The percentage weight loss shall be calculated as

$$\text{Percentage weight loss} = 100\left(\frac{m_{\text{initial}} - m_{\text{final}}}{m_{\text{initial}}}\right)$$

2. Laboratory decay resistance testing

Testing shall be conducted in accordance with the most recent version of AWPA Standard E10 (AWPA 2017) with the following additional specifications:

A. The wood species used shall be the sapwood of Southern Pine and yellow-poplar.

B. Preservative shall be applied by immersing the specimen(s) in the treatment solution for 1 min at atmospheric pressure. If necessary, the treatment vessel shall be agitated to ensure homogenous concentration of active ingredient within the vessel.

C. The weathering (leaching) method after preservative treatment will deviate from the standard method in that

(i) specimens shall not be vacuum-impregnated with leaching water, and

(ii) the total duration of leaching shall be 7 days (168 h) with water changes after 6, 24, 48, and 96 h.

D. Specimen dimensions shall be 19 by 19 by 19 mm.

E. Only one specimen shall be placed into each bottle.

F. The fungi used for each wood species shall be

(i) *Gloeophyllum trabeum* (isolate Madison 617) and *Postia placenta* (isolate Madison 698) for Southern Pine and

(ii) *Trametes versicolor* (isolate Madison 697) and *Irpex lacteus* (isolate Madison 517) for yellow-poplar.

G. The following ratio shall be calculated for each fungus–wood species combination (four total ratios):

Average weight loss of preservative-treated specimens/Average weight loss of untreated specimens

3. Laboratory termite resistance testing

Testing shall be conducted in accordance with the most recent version of AWPA Standard E1 (AWPA 2017) with the following additional specifications:

A. The single-choice (no-choice) procedure shall be used.

B. The wood species used shall be the sapwood of Southern Pine and yellow-poplar.

C. Preservative shall be applied by immersing the specimen(s) in the treatment solution for 1 min at atmospheric pressure. If necessary, the treatment vessel shall be agitated to ensure homogenous concentration of active ingredient within the vessel.

D. The weathering (leaching) method after preservative treatment will deviate from the standard method in that

(i) specimens shall not be vacuum-impregnated with leaching water, and

(ii) the total duration of leaching shall be 7 days (168 h) with water changes after 6, 24, 48, and 96 h.

E. The following ratio shall be calculated for each wood species (two total ratios):

Average weight loss of preservative-treated specimens/Average weight loss of untreated specimens

4. Suitability determination

Suitability for WPMs shall be assigned based on the weight loss from corrosion testing (Note 1) and from the weight loss ratios calculated from decay and termite testing (Notes 2 and 3):

-Type I (all WPMs) must meet these conditions:

A. Weight loss caused by corrosion test must be below 3%.

B. Sum of the six ratios calculated from decay and termite tests cannot exceed 1.0.

C. No ratio for any single decay or termite test can exceed 0.4.

-Type II (wire-bounds only) must meet these conditions:

A. Weight loss caused by corrosion test must be below 0.75%.

B. Sum of the six ratios calculated from decay and termite tests cannot exceed 1.25.

C. One and only one ratio for an individual decay or termite test can exceed 0.2.

-Type III (all WPMs except wire-bound boxes) must meet these conditions:

D. Weight loss caused by corrosion test may be 3% or more.

E. Sum of the six ratios calculated from decay and termite tests cannot exceed 1.0.

F. No ratio for any single decay or termite test can exceed 0.4.

-Not suitable: Preservatives that do not meet the criteria for Type I, II, or III are not suitable for treatment of WPMs.

5. Validation of test conditions

G. Average corrosion weight losses in water-treated controls shall be between 2% and 3%.

H. Average fungal weight losses in water-treated controls shall equal or exceed 40% for each fungus–wood species combination.

I. Average termite weight losses in untreated control specimens shall equal or exceed 20% for each wood species evaluated.