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Efficacy of alternatives to zinc naphthenate for dip treatment of wood packaging materials

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ABSTRACT

Research is being conducted to evaluate potential preservatives to replace zinc naphthenate (ZnN) for use in dip-treatment of wooden packaging materials. In this study, laboratory tests evaluated the efficacy of preservatives in protecting Southern pine and yellow poplar against decay fungi and termites. Nine preservatives were evaluated at one or two concentrations, and in some cases with two dip times. The results of this study indicate that higher concentrations of most of the preservatives evaluated will provide protection similar to or greater than that of ZnN. Four of the formulations provided protection equivalent to or greater than that of ZnN across all of the test organisms. Lower concentrations of some of the copper-based preservatives were less effective than ZnN in preventing colonization of Southern pine by the copper tolerant fungus *Postia placenta*, but most formulations were more effective than ZnN in protecting yellow poplar against white-rot fungi. The test 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. Efficacy was found to increase with preservative concentration in several cases, but did not increase with a longer dip time.

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1. Introduction

With the exception of a few naturally durable wood species, wood products used outdoors are treated with preservatives to prevent degradation by decay fungi and termites. Although the majority of preservative-treated wood is pressure-treated, some products are protected with only dip treatments. The U.S. Army specifies that certain wood packaging materials (WPMs), or their fabricated parts, be completely immersed for a minimum of one minute in a preservative solution. These dip treatments create a shallow layer of preservative on the wood surface, but do not protect the wood's interior. The treated WPMs are expected to have a useful life of up to 20 years, and although they will be in protected locations for much of their service, there may be extended periods of outdoor exposure. The WPMs may also be exposed in locations that present a severe risk for both insect and fungal attack.

An evaluation conducted in the 1980's (De Groot and Stroukoff, 1986) indicated that water-based zinc naphthenate (ZnN), copper naphthenate, and copper-8-quinolinolate would be effective for dip treatment of WPM's, and these three preservatives were subsequently incorporated into Department of Defense specifications. Of these, the most commonly used preservative has been ZnN. However, ZnN no longer has a US. Environmental Protection Agency (EPA) registration for use as a wood preservative, and will not be available once existing stocks are depleted. Changes have also occurred in the available formulations of copper naphthenate and copper-8-quinolinolate, and new types of preservatives have become available since the De Groot and Stroukoff study (1986).

Researchers from the USDA Forest Service, Forest Products Laboratory (FPL) and U.S. Army Armaments Research, Development and Engineering Center are undertaking a series of studies to evaluate potential preservatives for use in protecting WPM's. These evaluations include both efficacy and potential corrosiveness to metal fasteners (Zelinka and Lebow, 2015). The approach used in these studies is to compare the performance of alternative preservatives to waterborne ZnN, which is thought to have provided adequate protection of WPMs over the past two decades. In the study reported here, laboratory tests were used to evaluate the efficacy of current copper-8-quinolinolate and copper naphthenate formulations, as well as several alternative preservatives. Field and laboratory evaluations with plywood have recently been initiated, but are not reported here.

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2. Materials and methods

2.1. Formulations evaluated

Preservatives have a range of properties that may make them more or less suitable for dip treatment of WPM's. Clearly efficacy in preventing degradation by decay fungi and termites is critical, but other factors must also be considered. These additional factors include EPA registration and allowable methods of application, as well as handling characteristics and simplicity of mixing and use. Based on these criteria, several formulations were selected for evaluation (Table 1). All but one of the formulations evaluated contained copper as a key active ingredient. In two of these formulations mechanically ground particulate copper was dispersed or suspended in the formulation. 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 under 1000 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 utilizing copper solubilized in ethanolamine, was also evaluated. Only waterborne formulations were evaluated to allow compatibility with existing treatment facilities and use practices. Note that the active concentrations evaluated are relatively high compared to those used for other applications of the same preservatives. This reflects the concentrations shown to be effective for ZnN, copper-8-quinolinolate and copper naphthenate in earlier testing (De Groot and Stroukoff, 1986).

2.2. Wood species

Although a wide range of softwood or hardwood species could potentially be utilized in WPM's, this study was limited to two species. Southern pine (a species group of the southeastern United States, primarily *Pinus taeda*) was selected because of its widespread use and low natural durability. Yellow poplar (*Liriodendron tulipifera*) was selected as a representative hardwood because of its widespread use and distribution in the eastern United States, and because it was previously evaluated by De Groot and Stroukoff (1986).

Table 1
Preservatives and concentrations evaluated in laboratory fungal and termite testing.

Preservative designation	Description and ratio of actives in formulation	Concentrations evaluated	Dip times (minutes)
AzI	Azole[a] (95%), imidacloprid (5%)	1.05% total actives	1 and 3
CuC	Copper-carboxylic acid (100%)	1 and 2% as copper	1
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 and 1.8%[b] as Cu8-quin	1 and 3 for 1.2%, 1 min for 1.8%
Cu8-2	Copper-8-quinolinolate (100%)	1.2 and 1.8%[b] as Cu8-quin	1
CuN	Copper naphthenate (100%)	1 and 2%[b] as copper	1
ZnN	Zinc naphthenate (100%)	2.9%[b] as zinc	1

[a] Tebuconazole or equal parts tebuconazole and propiconazole.
[b] Concentrations required in current military specifications for similar formulations. ZnN is specified at 3% zinc.

2.3. Dipping and leaching procedure

A similar dipping procedure was used for both fungal and termite testing. A single layer of specimens was separated with plastic mesh to allow preservative access to all surfaces, and submerged in a container of preservative. The container was agitated with an orbital shaker to maintain homogeneity of the treatment formulations and enhance preservative movement around the specimens. A one minute dip time, which is specified as the minimum immersion period in military specifications, was utilized in most cases. However, a three minute dip was also used for two formulations to allow evaluation of the effect of dip time on efficacy (Table 1). After dipping specimens were allowed to drip for 5 min before obtaining a second weight to determine uptake (Table 2). They were then allowed to air-dry for one week under ambient laboratory conditions prior to leaching. Leaching was conducted with simulated rainfall, rather than immersion, to better correspond to anticipated in-service exposure conditions. The specimens were sprayed with deionized water at a rate of 10 mm/h over a period of 5 days. An alternating schedule of 1 h rainfall/5 h rest was used until a total of 20 h, or 200 mm of rainfall, had occurred.

2.4. Fungal tests- soil-block decay

The method used in this study followed American Wood Protection Association Standard E10, Standard Method of Testing Wood Preservatives by Soil-block Cultures (AWPA, 2013). Four decay fungi were chosen for this study. Two brown-rot fungi (*Gloeophyllum trabeum and Postia placenta)* were used to evaluate southern pine specimens, while two white-rot fungi (*Trametes versicolor* and *Irpex lacteus*) were used to evaluate the yellow poplar specimens. These fungi are among those commonly isolated from wood in service, and are frequently used in evaluation of wood preservative formulations. Soil bottles with inoculated feeder strips were prepared in accordance with AWPA Standard E10. Soil block specimens (19 mm) were weighed and then immersed for either one or three minutes into the diluted preservative solutions as

Table 2
Uptake of preservative solution (g) after dipping of fungal and termite specimens (dip treatment times are 1 min unless otherwise noted).

Preservative and % Actives	Fungal specimens				Termite specimens			
	Southern pine		Yellow poplar		Southern pine		Yellow poplar	
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
Water	1.7	0.24	0.7	0.08	1.47	0.13	0.51	0.05
AzI, 1.05%	1.39	0.18	1.02	0.19	1.71	0.11	0.58	0.06
AzI, 1.05%, 3 min dip	1.47	0.41	1.13	0.23	1.6	0.14	0.56	0.07
CuC, 1%	0.82	0.12	0.9	0.15	1.32	0.39	0.46	0.12
CuC, 2%	0.91	0.2	0.93	0.09	1.79	0.23	0.55	0.05
PCuA-1, 1%	0.91	0.15	0.87	0.15	1.62	0.23	0.39	0.09
PCuA-1, 2%	0.95	0.13	0.99	0.18	1.32	0.35	0.45	0.06
PCuA-2, 1%	1.23	0.18	0.79	0.16	1.45	0.22	0.44	0.09
PCuA-2, 2%	1.27	0.1	0.55	0.06	1.25	0.18	0.44	0.04
SCu-A, 1%	1.06	0.22	0.91	0.16	1.33	0.36	0.48	0.07
SCu-A, 2%	1.17	0.3	0.78	0.26	1.75	0.19	0.52	0.08
Cu8-1, 1.2%	1.06	0.24	0.95	0.08	1.45	0.24	0.43	0.04
Cu8-1, 1.8%	0.98	0.19	0.94	0.09	1.5	0.23	0.42	0.06
Cu8-1, 1.2%, 3 min dip	1.57	0.22	1.12	0.16	1.52	0.14	0.45	0.06
Cu8-2, 1.2%	0.98	0.1	1.05	0.2	1.72	0.3	0.46	0.06
Cu8-2, 1.8%	0.89	0.13	0.95	0.1	1.4	0.26	0.45	0.08
CuN, 1%	1.07	0.2	1.08	0.18	1.7	0.3	0.58	0.11
CuN, 2%	1.2	0.2	1.1	0.12	1.46	0.36	0.7	0.04
ZnN, 2.9%	1.09	0.18	0.92	0.12	1.48	0.25	0.5	0.08

shown in Table 2. Following leaching the blocks were conditioned to constant weight in a room maintained at 27 °C and 30% relative humidity. The five replicate blocks were then placed, singly, into the previously inoculated soil bottles which were maintained in an incubator for the duration of the test. After 8 weeks of fungal exposure blocks were brushed to remove fungal mycelium, reconditioned to constant weight, and re-weighed to determine percent weight loss.

2.5. Termite tests

The method used in this study followed the no-choice test patterned after ASTM D 3345-08 (Standard Test Method for Laboratory Evaluation of Wood and other Cellulosic Materials for Resistance to Termites). Test specimens (25 by 25 by 6 mm) were weighed and then immersed for either one or three minutes into the diluted preservative solutions as shown in Table 2. Following drying and leaching, blocks were conditioned to constant weight in a room maintained at 27 °C and 30% relative humidity. The 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 and reconditioned to equilibrium moisture content before final weights were obtained. Termites from each container were separated into dishes and weighed to determine mortality.

2.6. Statistical analysis

To compare the preservative treatment groups for each fungus-wood species combination, percent weight losses from the soil-block decay tests and the termite tests were each analyzed using heteroscedastic linear models in SAS® V9.4. Families of comparisons were constructed to compare percent weight losses between treatments and the positive control (ZnN), as well as, to test for possible changes due to 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 et al. (2011).

3. Results

3.1. Fungal soil block tests

3.1.1. Southern pine

The most effective preservatives for Southern pine samples were Cu8-2 and AzI, which allowed little if any decay (Table 3). None of the test formulations allowed statistically greater weight loss than ZnN when blocks were exposed to *G. trabeum*, although the average weight loss for blocks treated with 1% CuC was approximately 3 times greater than for blocks treated with ZnN. The higher solution concentration (1.8%) of Cu8-1 also provided excellent protection of Southern pine against both *P. placenta* and *G. trabeum*. The 2% (as copper) concentrations of SCuA, PCuA-1, PCuA-2 and CuN were also generally effective, but showed some vulnerability to colonization by *P. placenta*. CuC appeared ineffective in protecting southern pine against *P. placenta*, and lower concentrations of PCuA-1, SCuA and CuN were also heavily attacked by this fungus. *Postia placenta* is known to have some degree of copper tolerance (Clausen and Green, 2003; Green and Clausen, 2005), and can potentially colonize wood in which copper is the only biocide. When compared to ZnN at the 90% confidence level, blocks treated with CuC (both concentrations), 1% SCuA, 1% PCuA-1 and 1% CuN showed significantly more weight loss from *P. placenta* (Table 3). In the case of PCuA-2, one or more blocks exposed to *P. placenta* did have substantial weight loss at each solution concentration, while the other blocks were not degraded (Table 4). This variability between replicates may have prevented a finding of

Table 3
Percent weight loss for Southern pine specimens exposed to one of two brown-rot fungi and yellow poplar specimens exposed to one of two white-rot fungi (dip treatment times are 1 min unless otherwise noted).

Preservative and % Actives	Southern pine				Yellow poplar			
	G. trabeum		*P. placenta*		*T. versicolor*		*I. lacteus*	
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
Water	47.7^{G}	3.2	59.9^{G}	2.4	45.4^{G}	6.6	70.4^{G}	7.2
AzI, 1.05%	0.4	0.6	0.2	0.5	-2.7^{L*}	5.2	-0.5^{L}	0.4
AzI, 1.05%, 3 min dip	−0.2	0.1	0.0	0.2	-0.3^{L*}	0.2	-0.6^{L}	0.2
CuC, 1%	26.5	9.2	60.3^{G}	7.4	0.7^{L*}	0.2	15.1	9.2
CuC, 2%	6.3	2.0	56.5^{G}	10.4	0.4^{L*}	0.3	1.0^{L}	1.5
PCuA-1, 1%	1.9	1.6	38.1^{G*}	15.0	-0.3^{L*}	0.1	-0.4^{L}	0.5
PCuA-1, 2%	−0.1	0.1	6.6	14.0	-0.4^{L*}	0.1	-0.5^{L}	0.1
PCuA-2, 1%	0.0	0.5	5.1	9.5	1.6	3.2	-0.3^{L}	0.3
PCuA-2, 2%	0.1	0.1	10.0	11.2	-0.3^{L*}	0.1	-0.2^{L}	0.4
SCu-A, 1%	1.9	1.0	49.5^{G}	8.5	0.0^{L*}	0.1	-0.4^{L}	0.2
SCu-A, 2%	0.6	0.2	2.9	4.4	-0.3^{L*}	0.3	-1.8^{L}	3.5
Cu8-1, 1.2%	0.2	0.2	2.5	4.9	20.5	11.3	32.6	7.8
Cu8-1, 1.8%	0.0	0.2	0.4	0.4	17.6	6.9	32.8	6.3
Cu8-1, 1.2%, 3 min dip	0.1	0.1	0.2	0.2	21.0	9.3	30.7	15.6
Cu8-2, 1.2%	0.5	0.1	0.5	0.2	0.6^{L*}	1.2	-0.1^{L}	0.5
Cu8-2, 1.8%	0.5	0.4	0.4	0.4	0.4^{L*}	1.2	-0.6^{L}	0.7
CuN, 1%	10.2	4.7	53.4^{G}	9.9	0.1^{L*}	0.2	4.1^{L*}	5.7
CuN, 2%	0.6	0.1	6.6	8.5	0.2^{L*}	0.1	0.4^{L}	0.2
ZnN, 2.9%	8.8	7.6	4.6	5.5	10.5	5.3	20.7	7.8

^{G} Significantly greater weight loss than zinc naphthenate specimens, 95% confidence level.
^{G*}Significantly greater weight loss than zinc naphthenate specimens, 90% confidence level.
^{L} Significantly less weight loss than zinc naphthenate specimens, 95% confidence level.
^{L*}Significantly less weight loss than zinc naphthenate specimens, 90% confidence level.

Table 4
Weight losses (%) for individual Southern pine specimens exposed to *P. placenta* (dip treatment times are 1 min unless otherwise noted).

Preservative and % Actives	Replicates					Mean
	1	2	3	4	5	
Water	59.2	61.1	59.0	57.0	63.3	59.9
AzI, 1.05%	−0.2	0.0	−0.2	0.7	0.7	0.2
AzI, 1.05%, 3 min dip	−0.2	0.0	0.1	0.4	−0.1	0.0
CuC, 1%	65.4	66.5	58.7	48.2	63.0	60.3
CuC, 2%	63.1	63.3	39.2	62.9	53.8	56.5
PCuA-1, 1%	42.7	54.6	22.8	21.8	48.6	38.1
PCuA-1, 2%	0.3	0.3	0.5	0.0	31.6	6.6
PCuA-2, 1%	0.6	22.1	0.5	1.4	1.1	5.1
PCuA-2, 2%	0.3	0.1	13.7	8.7	27.1	10.0
SCu-A, 1%	53.1	55.7	57.7	42.1	38.8	49.5
SCu-A, 2%	1.1	1.6	0.5	10.9	0.8	2.9
Cu8-1, 1.2%	11.3	0.1	0.2	0.3	0.7	2.5
Cu8-1, 1.8%	0.1	0.1	0.1	0.4	1.0	0.4
Cu8-1, 1.2%, 3 min dip	0.5	0.0	0.1	0.1	0.1	0.2
Cu8-2, 1.2%	0.4	0.4	0.3	0.9	0.5	0.5
Cu8-2, 1.8%	0.3	0.6	0.6	0.9	−0.1	0.4
CuN, 1%	55.0	60.5	38.1	50.3	63.2	53.4
CuN, 2%	0.3	14.1	17.5	0.9	0.2	6.6
ZnN, 2.9%	1.0	0.5	0.5	8.9	12.0	4.6

statistically significant difference between the performance of PCuA-2 and ZnN. Similar variability was also observed in blocks treated with 2% PCuA-1 and 2% CuN after exposure to *P. placenta*.

The extent of variability between replicates exposed to *P. placenta* was greater than that typically observed for pressure-treated specimens, and suggests that dip-treated (i.e. surface treated) specimens may be more vulnerable to degradation by copper-tolerant fungi than pressure-treated specimens. On-going laboratory testing has shown that increasing copper concentrations has a tendency to increase variability between replicates. Recent research also suggests that copper-tolerance is a function of fungus adaptability to a copper rich environment (Jenkins et al., 2014). In theory, the copper ions are more readily chelated by natural by-products 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 in comparison to pressure-treated copper. Recent research showed that test specimens surface-treated with 1.2% copper citrate and exposed to copper-sensitive, *G. trabeum*, only marginally inhibited decay while specimens pressure-treated with 1.2% copper citrate completely inhibited decay (Jenkins et al., 2014). Copper-based preservatives, therefore, typically also contain co-biocides (i.e. naphthenic acid or azoles) to help prevent attack by copper-tolerant fungi. In this study, these co-biocides appeared to be fairly effective at higher concentrations, although some degradation still occurred in several preservatives. However, CuC was particularly vulnerable to *P. placenta*, even at the higher 2% concentration. This susceptibility indicates that the carboxylic acid used in CuC may not be as effective as the naphthenic acid in copper naphthenate in preventing attack by copper-tolerant fungi.

3.1.2. Yellow poplar

Most of the test formulations were highly effective in protecting yellow poplar from fungal attack (Table 3). 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, preservatives which are already allowed under military specifications. None of the test formulations allowed significantly greater weight loss than ZnN, and many provided significantly better protection (Table 3).

3.1.3. Effect of solution concentration

A statistical analysis was conducted to determine if solution concentration significantly affected weight loss. The analysis indicates that performance of 2% CuC was significantly better than that of the 1% solution in Southern pine wood exposed to *G. trabeum* or yellow poplar 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.

3.1.4. Effect of dip time

AzI (1.05%) and Cu8-1 (1.2%) were evaluated using both 1 min and 3 min dip times. Although the longer dip time yielded greater uptake of Cu8-1 in pine (Table 2), it did not result in a statistically significant increase in protection for either pine or poplar. For AzI, the longer dip time produced little increase in uptake and no an increase in protection. However, because AzI was highly effective with the one-minute dip in all cases, a significant improvement with the longer dip time was not possible.

3.2. Laboratory termite tests

Mean percentage weight loss for each test group and termite mortality classification results are shown in Table 5. Termite mortality was classified as follows, slight (0–33%), moderate (34–66%), heavy (67–99%) or complete (100%).

3.2.1. Southern pine

Most treatments were fairly effective in protecting Southern pine, although 1.2% and 1.8% Cu8-1 did allow notable termite feeding. Slight feeding was observed with the lower concentrations of CuC and PCuA-1, but when compared at the 90% confidence level, all formulations except Cu8-1 protected at least as well as ZnN. Several formulations provided statistically greater protection of Southern pine than did ZnN (Table 5). In regards to treatment toxicity, exposure to dip treated Southern pine resulted in heavy termite mortality for the majority of treatments, with complete mortality in AzI treated groups.

3.2.2. Yellow poplar

For a number of the treated groups, yellow poplar showed higher amounts of feeding than the equivalent treatment in Southern pine specimens. In addition, termite mortality tended to be more moderate in yellow poplar. This result was somewhat unexpected as feeding typically tends to be greater in softwoods compared to hardwoods. However, in this case the uptake of preservative was substantially less in yellow poplar than Southern pine specimens (Table 2). In the water-treated controls weight loss of Southern pine was slightly greater than that of yellow poplar. Although ZnN performed similarly in both wood species, the lower (and in some cases higher) concentrations of the copper-based test formulations were less effective than ZnN in protecting yellow poplar. The exception to this trend was CuN, which was effective at both 1 and 2% concentrations. When compared at the 90% confidence level, both AzI and 2% CuN provided greater protection than

Table 5
Percent weight loss and mortality classification of termite specimens (dip treatment times are 1 min unless otherwise noted).

Preservative and % Actives	Southern pine			Yellow poplar		
	Mean	Stdev	Mortality	Mean	Stdev	Mortality
Water	19.6^{G}	0.2	Slight	17.3^{G}	1.7	Moderate
AzI, 1.05%	−0.4^{L}	0.2	Complete	−0.4^{L}	0.1	Complete
AzI, 1.05%, 3 min dip	−0.7^{L}	0.1	Complete	−0.3^{L}	0.1	Complete
CuC, 1%	1.6	0.9	Heavy	8.2^{G}	0.8	Moderate
CuC, 2%	−0.6^{L}	0.1	Heavy	2.4	0.5	Heavy
PCuA-1, 1%	2.0	1.6	Heavy	11.5^{G}	2.6	Moderate
PCuA-1, 2%	0.0^{L}	0.3	Heavy	6.6^{G*}	1.9	Moderate
PCuA-2, 1%	0.4	1.2	Heavy	10.1^{G}	0.9	Moderate
PCuA-2, 2%	0.4	0.6	Heavy	3.8^{G*}	0.6	Moderate
SCu-A, 1%	0.2	0.8	Heavy	6.6^{G}	1.2	Moderate
SCu-A, 2%	−0.8^{L}	0.1	Heavy	1.8	0.9	Heavy
Cu8-1, 1.2%	8.6^{G}	2.1	Moderate	11.8^{G}	2.6	Moderate
Cu8-1, 1.8%	4.3^{G}	0.7	Moderate	12.4^{G}	2.6	Moderate
Cu8-1, 1.2%, 3 min dip	14.9^{G}	1.5	Moderate	11.3^{G}	2.4	Moderate
Cu8-2, 1.2%	0.3^{L}	0.2	Heavy	9.1^{G}	2.0	Moderate
Cu8-2, 1.8%	0.6^{L}	0.4	Heavy	5.7	3.4	Moderate
CuN, 1%	0.6^{L}	0.4	Heavy	0.7	0.8	Heavy
CuN, 2%	0.0^{L}	0.2	Heavy	−0.3^{L}	0.4	Heavy
ZnN, 2.9%	1.6	0.4	Heavy	2.3	0.8	Heavy

^{G} Significantly greater weight loss than zinc naphthenate specimens, 95% confidence level.
^{G*}Significantly greater weight loss than zinc naphthenate specimens, 90% confidence level.
^{L} Significantly less weight loss than zinc naphthenate specimens, 95% confidence level.
^{L*}Significantly less weight loss than zinc naphthenate specimens, 90% confidence level.

ZnN. As was observed in Southern pine, AzI caused complete termite mortality. 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 one and two weeks after the start of the test, with 100% mortality by the end of the four weeks. The active component in the AzI treatment is imidacloprid, a neonicotinoid compound that affects the insect nervous system by targeting nicotinic acetylcholine receptors (Meijer et al., 2014).

3.2.3. Effect of solution concentration

A statistical analysis was conducted to determine if solution concentration significantly affected weight loss from termite feeding. For Southern pine, termite feeding was relatively low for both high and low solution concentrations of most formulations. However, significantly less weight loss was observed for higher concentrations of CuC, Cu8-1, and PCuA-1. The effect of solution concentration was more notable in yellow poplar, where all formulations except Cu8-1 and AzI exhibited significantly less weight loss at higher solution concentrations. The greater concentration effect observed in yellow poplar may reflect the lower preservative uptake in this species.

3.2.4. Effect of dip time

Increasing the dip time from 1 to 3 min did not result in an increase in uptake or an increase in termite protection for any of the preservative/wood species evaluated. In the case of Cu8-1, weight loss in pine was actually greater with the longer dip time. As no weight loss occurred for the one minute dip time with AzI, no improvement was possible with a longer dip time.

4. Discussion

Four of the formulations evaluated (AzI, 2% SCuA, 1.8% Cu8-2 and 2% CuN) provided protection equivalent to or greater than that of ZnN across all of the test organisms. Most of the formulations evaluated were at least as effective as ZnN in preventing degradation by the test fungi other than *P. placenta*. This finding is not surprising as copper is generally thought to be a more effective fungicide than zinc at equivalent concentrations. Barnes et al. (2004) compared the durability of stakes treated with a range of retentions of waterborne copper or ZnN and found that approximately three times more zinc was needed to provide protection equivalent to copper. However, ZnN does have substantial efficacy, especially in above-ground applications. A comparison of above-ground specimens exposed in Mississippi found that brush-on treatments of waterborne ZnN were only slightly less effective than copper naphthenate after nine years of exposure (Highley, 1993). Dip treatments with ZnN (3% as zinc) also protected pine and hemlock L-joints for approximately eight years, after which decay began to occur in the pine specimens (Morrell et al., 1998). De Groot and Stroukoff (1986) also reported that dips in a 3% formulation protected ammunition boxes nearly as well copper naphthenate after 36 months of jungle exposure, and provided good protection for ammunition boxes exposed in an open field in Panama.

The weight losses for copper-treated specimens exposed to *P. placenta* indicate that copper tolerance may be more of a concern for dip-treatments than pressure treatments. Azole compounds are generally effective co-biocides with copper, and pressure-treatment formulations similar to those evaluated in this study are used for ground contact applications. The consequence of a WPM's vulnerability to copper-tolerant fungi, however, remains unclear. There is some evidence that copper tolerance is primarily a concern for wood placed in direct contact with soil (Choi et al., 2002). This may be because wood placed in contact with the ground may be exposed to the fully developed fungal mycelium existing in soil, while wood used above the 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 et al., 2002). With the exception of wood pallets, the majority of WPM's are not expected to be stored in direct ground contact, and thus colonization by copper-tolerant fungi may be less of a concern. However, the risk of copper tolerant fungi cannot be completely discounted because some circumstances, such as contact with decaying untreated wood, could provide a path of exposure to actively growing mycelium.

Somewhat surprisingly, most of the copper-based formulations allowed greater termite feeding in yellow poplar than did ZnN. This effect may be at least partly attributable to the differences in preservative uptake between the two wood species. However, greater feeding was observed in yellow poplar even for the higher concentrations of PCuA-1, PCuA-2, and Cu8-1. The notable exception was copper naphthenate, which was more effective than ZnN. Previous laboratory tests using nano-metals indicated that particulate copper may be less effective than particulate zinc in preventing termite feeding (Kartal et al., 2009; Green and Arango, 2007), but the results of Kartal et al. (2009) also indicated that soluble copper sulfate was at least as effective as soluble zinc sulfate. In this study, termite feeding on yellow poplar occurred with both soluble and particulate copper formulations, suggesting that wood species and the presence/absence of naphthenic acid played a role in the observed effects.

In many cases increasing the copper concentration from 1% to 2% did appear to provide a benefit in preservative efficacy. The concentration effect was less clear for the Cu8 formulations, although the higher concentrations did tend to provide greater protection against termite feeding. In contrast, increasing the dip time from one to three minutes did not provide an increase in durability for the Cu8-1 formulation. AzI was highly effective at the sole concentration evaluated, thus, a lower concentration is now being examined in on-going experiments with plywood.

5. Conclusions

The results of this study indicate that the higher concentrations of most of the preservatives evaluated, when applied by dip-treatment, will provide protection similar to or greater than that of ZnN. Four of the formulations (AzI, 2% sCu-A, 1.8% Cu8-2 and 2% CuN) provided protection equivalent to or greater than that of ZnN across all of the test organisms. For other formulations, performance relative to ZnN varied by organism. Several of the copper formulations, when applied at the lower 1% concentration, were more vulnerable to colonization by copper tolerant *P. placenta* than was ZnN. One of the preservatives evaluated (CuC) provided no protection against *P. placenta* at either the 1% or 2% concentrations. Copper tolerance is typically associated with treated wood placed in contact with the ground, and the consequence of vulnerability to copper tolerant fungi for WPMs stored above ground is unclear. In contrast, many of the formulations provided significantly better protection than ZnN when yellow poplar was exposed to the white-rot fungi *T. versicolor* and *I. lacteus*. A wood species divergence also occurred in termite exposure, where many of the test formulations were more effective than ZnN in protecting pine, but less effective than ZnN in protecting yellow poplar. However, in the latter case weight losses from termite feeding were still relatively low for the higher solution concentrations evaluated. Increasing the dip time from one to three minutes, as was evaluated with two formulations, provided no increase in protection for either wood species or any test organism. An on-going field test with these formulations and wood species, and recently initiated laboratory tests with plywood, are expected to provide additional information on the efficacy of these dip treatments.

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