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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