Termite resistance of wood treated with copper (II) compounds derived from tri- and dialkylamine-boric acid complexes

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Abstract

The objective of this investigation was to evaluate the toxicity to termites and the leaching stability of copper compounds derived from tri- and dioctylamine-boric acid complexes for protecting wood against termite attack. Water-insoluble copper N-methyldioctylamine or copper N-dioctylamine and copper borate were precipitated in wood by the reaction of N-methyldioctylamine or N-dioctylamine-boric acid complex with copper sulfate. Wood treated with these copper (II) compounds was resistant to subterranean termite attack in a modified nutritive supplement test. High or complete termite mortality occurred at 0.08 pcf (or 0.2%) for unleached, and 0.89 pcf (or 2%) for leached blocks. A notable advantage of the copper compounds over conventional wood preservatives was that termites readily acquired toxic doses by slight feeding on the treated wood; thus, unlike wood treated with conventional wood preservatives, these copper treatments might protect nearby untreated wood from termite attack.

The toxicity to micro-organisms of cationic and anionic alkyl and aryl compounds has been recognized for many decades and has been the subject of many investigations (3, 7, 8, 9, 12) since 1940. Because they are environmentally more acceptable than conventional wood preservatives, these agents have been investigated recently for protecting wood against wood-destroying organisms. Cationic alkyl compounds such as dialkylammonium compounds containing halides, acetates, or other anions (10, 11) and anionic alkyl and aryl compounds such as aryl and alkyl carboxylates containing copper ion (14) have been shown to be effective against wood-destroying fungi in laboratory soil-block tests. The increase in fungitoxicity of copper modified alkylammonium compounds has also been reported (4). The objective of this investigation was to evaluate the toxicity to termites and the leaching stability of wood treated with copper compounds derived from tri- and dialkylamine-boric acid complexes. The conversion of tri- and dialkylamine-boric acid complexes to copper compounds may have the advantages of decreasing water volubility and increasing fungi toxicity.

This paper reports on the resistance to termites of wood treated with the copper compounds derived from tri- and dialkylamine-boric acid complexes and discusses the advantages of this treatment. In unpublished results prior to this investigation, N-methyldioctylamine or N-dioctylamine-boric acid complex as well as other alkyl- and arylamine-boric acid complexes were evaluated for fungal toxicity. N-methyldioctylamine or the N-dioctylamine-boric acid complex was the most effective. These complexes which were incorporated into malt agar by the fungal growth method (13, 15) inhibited the brown-rot decay fungus *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. at a concentration of 0.01 percent (100 ppm). Further reaction of these complexes with copper sulfate to form the water-insoluble copper N-methyldioctylamine or copper N-dioctylamine and copper borate in wood were evaluated for fungal toxicity using *Gloeophyllum trabeum*. These results showed that wood treated with copper compounds derived from the N-dioctylamine-boric acid complex at 0.6 percent solution concentration had weight losses of 2.63 percent and 4.62 percent for unleached and leached samples, respectively. The effectiveness of the copper compounds in preventing the fungal attack on wood led to the investigation of the effect of these compounds on termite toxicity.

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Materials and methods

Chemical synthesis

Tri- and dialkylamine-boric acid complexes were synthesized as follows: Boric acid (2.47 g, 40 mmoles), dissolved in N, N-dimethylformamide (50 mL), was added to one equivalent of N-dioctylamine (9.66 g, 40 mmoles). The solution was stirred for 2 days at room temperature, which gave two layers. The bottom layer was isolated with a separatory funnel and mixed with distilled water to yield a white colloidal solution. This aqueous colloidal solution was extracted with chloroform and the aqueous layer was evaporated to dryness to obtain a white solid (7.59 g). The white solid was recrystallized from aqueous ethanol to yield white crystals: mp 32° to 33°C; ^{1}H NMR (d_6-acetone) 8,0.87 (bt, 6, CH_3), 1.30 (s, 24, CH_2), 2.06 (m, 3, H_3BO_3), 2.52 (bt, 4, NCH_2), 2.59 (s, 1, NH); IR (KBr) v_{max} 3380 (B-O-H), 2700 to 3000 (NH_2^+, 1310 to 1380 cm^{-1} (B-O).

This procedure was also used to yield a white solid (7.63 g) of N-methyldioctylamine-boric acid complex. The white solid was recrystallized from aqueous ethanol to give a syrup: ^{1}H NMR (d_6-acetone) δ 0.87 (bt, 6, CH_3), 1.30 (s, 24, CH_2), 2.03 (m, 3, H_3BO_3), 2.13 (s, 3, NCH_3), 2.28 (bt, 4, NCH_2); IR (KRr) v_{max} 3380 (B-O-H), 2330 to 3000 (NH^+), 1310 to 1380 cm^{-1} (B-O).

Treating solutions and wood blocks

Tri- and dialkylamine-boric acid complexes were dissolved in distilled water at a concentration of 0.005 percent (50 ppm) and formed colloidal solutions at or above 0.01 percent (100 ppm). Both complexes were prepared as aqueous solution at two concentration levels (0.1% and 1%). Four treating solutions were prepared from two complexes. Each treating solution was prepared as follows: A 1 percent aqueous solution of the complex containing two equivalents of copper sulfate was prepared by adjusting the pH to 2.75 with 6N hydrochloric acid to dissolve a small portion of the insoluble compound. A 0.1 percent treating solution was then prepared from 1 percent solution by dilution.

Sample blocks of southern yellow pine sapwood *(Pinus sp.) were* prepared according to the AWPA Standard (M12-72) (1). The blocks were 2.54 centimeters square by 0.65 centimeter, the 2.54-square centimeter face was in the radial section (radial longitudinal surface) and cut from the same board. The blocks had four to six annual rings per inch with smooth surfaces and no visible defects and were conditioned at 26.7°C (80°F) and 30 percent relative humidity (RH) to equilibrium moisture content (EMC) (4 days).

Impregnation and leaching

Impregnation and leaching of the wood blocks were performed according to the AWPA Standard (M10-77) (2). Six conditioned blocks were placed under vacuum at 50.9 mm (2 in.) mercury for 45 minutes. They were then impregnated with one of the four aqueous solutions (70 mL) containing a tri- or dialkylamine-boric acid complex and copper sulfate in 1:2 molar ratio. After impregnation, the blocks were soaked in the treating solution for 1 day. The external solution was then adjusted to pH 7.5 with concentrated ammonium hydroxide to allow maximum precipitation and maintained at pH 7.5 for an additional day. After soaking, the blocks were washed three times with 100 mL of distilled water and then conditioned at 26.7°C (80°F) and 30 percent RH. Three of the blocks per treatment were leached in 50 mL of distilled water for 2 weeks, and three of the control blocks were not leached.

Termite feeding

Termites for this study were collected at Janesville, Wis., and maintained at 25°±1°C prior to use. Each treated block was exposed to 1.0 g termites (natural caste mixture averaging 244.7 undifferentiated functional workers, 2.3 soldiers, and 0.7 nymphs).

We evaluated the termite resistance of the treated wood by a slightly modified nutritive supplement method (5) using an untreated paper pulp block (0.3 by 0.2 by 2.5 cm in size; about 0.5 g) made from a commercial pine paper pulp sheet as the nutritive supplement. A leached or unleached wood block was placed in a covered cylindrical plastic box (5.0 by 3.8 cm) along with a supplemental food block. Each wood or pulp block was moistened with 2 mL of deionized water immediately prior to inclusion of the termites. These units were stored in a BOD incubator (25° ± 1°C) for 4 weeks; they were only removed for inspections at about 3-day intervals and another 2 mL of deionized water was added after 2 weeks. During inspections, microbial contamination, termite feeding behavior, and mortality were recorded. After 4 weeks, the final conditioned weight of the treated block and the final live weight of termites were recorded.

The weight of surviving termites and weight loss of treated blocks were analyzed by one-way analysis of variance ($p= 0.05$). The values were transformed to arc sine for the analysis but were given as untransformed values in Table 1. Differences among treatments were compared by Duncan's new multiple range test ($p= 0.05$).

Results and discussion

A preliminary evaluation of termite toxicity showed that wood treated with copper compounds derived from tri- and dialkylamine-boric acid complexes at 0.08 pcf (0.2% concentration) could also prevent attack by *Reticulitermes flavipes* (Kollar) and cause complete termite mortality.

Weight losses of treated blocks and termite survival (Table 1) showed the significant effects of the treatments on termites. The unleached wood blocks at both retentions (0.08 and 0.89 pcf) of the two copper compounds containing tri- and dialkyl complexes had small weight losses (0.2% to 0.3%), and no termites survived for 4 weeks in test units containing them. These results were significantly different at the 0.05 confidence level from the 14.2 percent weight loss and 92.7 percent survival with untreated control blocks, but not from each other. Nevertheless, the termites survived longer in test units containing blocks treated to lower retention (22 or 26 days) than in those containing blocks treated to the higher retention (13 to 15 days).

Results after leaching the treated blocks revealed some loss of resistance to termite attack and toxicity to termites. At the high retention with both copper com-

TABLE 1. — *Percentage weight loss of blocks and survival of Reticulitermes flavipes exposed to leached and unleached wood treated with copper salts derived from tri- or dialkylamine-boric acid complexes.*

Compound	Solution concentration[a]	Retention[a]	Weight loss of blocks[b]		Termite survival[c]	
			Unleached	Leached	Unleached	Leached
	(%)	(pcf)	(%)			
Copper salt of N-methyldioctylamine-boric acid complex	0.2	0.08	0.2 A	6.1 C	0(22 days) A	75.2 B
	2	0.86	0.3 A	0.2 A	0(13 days) A	0.3[d] A
Copper salt of N-diocytylamine-boric acid complex	0.2	0.08	0.2 A	10.3 D	0(26 days) A	89.4 B
	2	0.89	0.3 A	0.2 A	0(15 days) A	1.0[d] A
Control			14.2 B		92.7 B	

[a]Concentrations of tri- or dialkylamine-boric acid complex containing two equivalents of copper sulfate.
[b]Figures are averages of three replicates. Means with the same capital letter are not significantly different at the 0.05 level.
[c]Based on final live biomass; parentheses indicate average days to complete mortality. Means with the same capital letter are not significantly different at the 0.05 level.
[d]Trialkyl derivative: Two replicates exhibited complete termite mortality. The third replicate had a few living termites (0.8%). Dialkyl derivative: Two replicates showed complete termite mortality. The third replicate had a few living termites (2.9%).

pounds, the weight loss of blocks remained low (0.2%); and slight survival of termites with both copper compounds (0.3% or 1%) occurred in only one of the three replicates. At the lower retention, there was greater weight loss of blocks (6.1% or 10.3%) and survival (75.2% or 89.4%); but the copper compounds containing dialkyl complex had greater block weight loss (10.3%; $p = 0.05$) than the copper compounds containing trialkyl complex (6.1%). The toxic effect of water-insoluble copper compounds in treated blocks after leaching was attributed to copper tri- or dialkylamine and copper borate. These water-insoluble copper compounds were precipitated in wood by the reaction of copper sulfate with the tri- or dialkylamine-boric acid complex. Our emphasis in this investigation was to convert tri- or dialkylamine-boric acid complex in wood to less water-soluble copper compounds and evaluate these copper compounds as a whole to termite toxicity. No efforts were devoted to evaluating termite toxicity of the individual copper compound.

These results demonstrate that copper compounds containing tri- and dialkyl complexes were effective at the 0.89 pcf retention level in suppressing termite attack and survival, even after water leaching. The leaching appeared to cause a 10-fold loss of effectiveness, because after leaching, the 0.89 pcf retention was similar in effectiveness to the 0.08 pcf retention before leaching. The leaching loss may be due to the extraction of unreacted copper sulfate in the treated wood because the copper sulfate in the treating solution was one equivalent in excess of tri- or dialkylamine-boric acid complex. The leaching loss may also be attributed partially to the water volubility of copper borate because copper borate was soluble to some extent in distilled water which was slightly acidic (PH = 5.70).

The copper compounds may have an advantage over conventional preservatives, such as pentachlorophenol. In the nutritive supplement test, although termite attack on test blocks and supplemental food blocks was slight, the termites accepted the treated wood well enough to acquire toxic doses of the compounds even though there was adequate supplementary nutrient to avoid such feeding on treated wood. Such slight but effective acceptance of the treated wood is similar to the slight but effective acceptance of mirex-treated baits in field tests (6). This palatability of the toxic wood indicates that the copper compounds in wood may also protect nearby unprotected wood by killing termites, whereas conventional preservatives are readily crossed over by termites to reach untreated wood.

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