Laboratory Evaluation of Borate/Amine/Zinc Formulations in Wood for Fungal Decay Protection

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ABSTRACT

The goals of this study were to evaluate borate/amine/zinc formulations in wood for fungal decay protection as well as the permanence of zinc and boron in wood.

Wood treated with each of four formulations of borate/amine/zinc prevented or decreased fungal degradation after a 12-week AWPA Standard soil-block test. For non-leached specimens, wood treated with borax/amine/zinc formulations required retention of 1.2% to prevent decay by *Gloeophyllum trabeum* (Gt) and *Trametes versicolor* (Tv), whereas that of DOT/amine/zinc formulations required 0.6% to be effective. For leached specimens, only DOT/ dicyandiamide/zinc formulation prevented decay by both Gt and Tv but required high loading of 5.4 to 5.5% chemicals. The other three formulations were ineffective against both fungi.

Elemental analysis showed that decay protection of DOT/dicyandiamide/zinc formulation in wood after 2 weeks water leaching was attributed to higher boron and zinc contents than that of the other three borate/amine/zinc formulations. The leach-resistant zinc in the treated wood did not translate into effective decay protection compared with the copper formulations (Chen 2010).

Keyword: Borate/amine/zinc formulations, fungal decay protection

INTRODUCTION

Boron compounds including boric acid, disodium tetraborate decahydrate (borax), and disodium octaborate tetrahydrate (DOT) are broad spectrum biocides (Pickard 1948), with low toxicity to mammals and aquatic life (Lloyd 1997), and have been used as fungicides, insecticides, bactericides, herbicides, and fire retardants (Pickard 1948). The mechanisms of inhibition of boric acid and borates to fungi and plants are not well investigated but were postulated to inhibit the pentose pathway (Lee and Aronoff 1967), interfere with the production of phenolics and lignifications (Lewis 1980, Shorrocks 1990) and interact with the borate in xylose moiety of the oxidized coenzymes NAD^+, NMN^+ and $NADP^+$ (Lloyd 1997). The efficacy of boric acid and borates against wood decay fungi, termites and fire are well established (Croft and Levy 1973, Lloyd 1997), and boron has been used in wood products for the past 60 years. Borates are used in large quantity in building products in Asia and North America, wood composites and pest control in North America, and formulation of exterior and remedial treatments in Europe (Lloyd 1997). Because boric acid and borates are water soluble, their uses for outdoor wood products are limited. Efforts to minimize borate leaching from wood products by impregnating hydrophobic polymers, including polyethylene glycol, polyvinyl acetates, and acrylic polymers were not successful (Murphy et al. 1995; Gezer et al. 1999a; Williams and Bergstrom 2005). Research to find more leach-resistant borates for wood products has been pursued in recent years. Chromate copper borates (Ochrymowych and McOrmindl 1978) performed well in the field tests; however, chromium in the products may not be used in the future because of environmental concerns. Copper borates dissolved in ammonium hydroxide in wood (Johnson 1983; Johnson and Foster 1991) performed well after 6 years in the field, but boron was leached out from the wood. The effectiveness of copper borates was attributed to the permanence of copper in wood. Zinc and calcium borates have been used in wood composites for above-ground applications but have not been used for ground-contact wood products because they are less effective than copper wood preservatives (Larkin et al. 2008; Manning 2008). Albumin protein borates (Thevenon et al. 1997; Thevenon et al. 1998a; Thevenon et al. 1998b) were effective in the laboratory and field tests. Their long-term field performance remains to be assessed. Organoborates, including borate esters and aminoborates (Carr et al. 2005; Chen 2008) in treated wood, showed effectiveness in laboratory fungal decay tests after water leaching. This led us to

prepare borate/amine/copper formulations (Chen 2010) and borate/amine/zinc formulations. The borate formulations may form stable, leach-resistant compounds in wood through covalent bonding of boron with nitrogen in amines, which then forms a complex with zinc (II).

The goals of this study were to evaluate borate/amine/zinc in wood for fungal decay protection and the permanence of zinc and boron in wood.

MATERIALS AND METHODS

Formulation and impregnation of borate/amine/zinc formulations in wood

Formulation

Four formulations of borate/amine/zinc were carried out using two borates: borax (disodium tetraborate decahydrate) and DOT (disodium octaborate tetrahydrate) and two amines: dicyandiamide and urea, and zinc sulfate hepta-hydrate in 1:2:4 molar ratio at four concentration levels (0.5%, 1.0%, 2.5%, and 5%). The borate/amine/zinc formulations were dissolved in 8% ammonium hydroxide solution. Each borate formulation was prepared with 1,000-g solution (Table 1).

Table 1. Weight in grams of 5% borate/amine/zinc in 1:2:4 molar ratio in 1000-g solution dissolved in 8% ammonium hydroxide

	Formulation		
Treatment[a]	Borate	Amine	zinc
B1A1Zn	11.220	4.945	33.835
B1A2Zn	11.545	3.635	34.820
B2A1Zn	11.920	4.860	33.225
B2A2Zn	12.260	3.570	34.175

[a]B1: Borax, B2: DOT, A1: dicyandiamide, A2: Urea; Zn: zinc sulfate hepta-hydrate.

Impregnation

Each of the above four concentrations (0.5, 1.0, 2.5, and 5%) from four borate/amine/zinc formulations was impregnated into wood by vacuum pressure. For each concentration, 32 sapwood blocks were used, which included 20 blocks consisting of 10 loblolly pine (*Pinus teada* L.) and 10 sweet gum *(Liquidambar styraciflua L.*) for fungal decay tests and the remaining 12 blocks (6 loblolly pine and 6 sweet gum blocks) were used for elemental analysis. The treatment procedure for one concentration for fungal decay is described subsequently.

Thirty-two sapwood blocks (16 loblolly pine blocks and 16 sweet gum blocks), 19 mm in all anatomical directions, were conditioned at 27° C and 30% relative humidity (RH) for 3 weeks and weighed. The blocks reached equilibrium moisture content (EMC) after 3 weeks conditioning. They were placed in a 1-L beaker in a desiccator under vacuum at 0.27-0.4 KPa for 30 min and then impregnated with one of four concentrations in 8% ammonium hydroxide solution (500 ml). After impregnation, the pressure was released and another 100 ml of solution was added. The treated blocks were soaked for 24 h. The blocks were then removed from the solution. The excess solution was wiped off and the blocks were weighed to determine the amount of solution absorbed. The blocks were then air-dried for one week under a chemical hood. Leaching of the blocks (16 blocks; 800-ml, 50 ml/block) was carried out according to AWPA E10-91 Standard (AWPA 1996) with changing water for 6, 24, and 48 h and then every 24 h for 2 weeks. The leached and non-leached blocks were conditioned at 27° C and 30% RH for 3 weeks and weighed before fungal decay tests. The treated and control blocks were exposed to two fungi, Gt and Tv, for 12 weeks in an incubation room at 25 to 27° C and 65 to 75% RH according to the AWPA Standard E10-91. Chemical retention of the blocks is expressed as weight percent gain (WPG), which is obtained by multiplying the concentration of solution by the weight of the solution absorbed by the block. Non-linear regression analysis to determine the threshold retention could not be used (Steel and Torrie 1960; Nance and Amburgey 1976; Gezer et al. 1999b) because too few data points (four concentrations) existed to establish a threshold relationship. Weight losses over 2% were considered to be of fungal origin, and weight losses below 2% may include losses from dehydration of chemicals and evaporation of wood extractives from wood.

Characterization

Elemental analysis of zinc and boron in loblolly pine treated with four formulations from borate/amine/zinc at 5% level for both leached and non-leached specimens as well as control was carried out using Inductively Coupled Plasma (ICP). Nitrogen analysis of leached specimens of above treated wood was carried out by Quantitative Technologies, Inc. (Whitehouse, New Jersey) using combustion to convert the sample elements to simple gases, such as N_2, and analyzed using a PerkinElmer 2400 Elemental Analyzer (PerkinElmer, Waltham, Massachusetts).

RESULTS AND DISCUSSIONS

Borate/amine/zinc formulations in 1:2:4 molar ratio in wood protected or decreased fungal degradation (Table 2, 3). Loblolly pine treated with borax/dicyandiamide/zinc formulation (Table 2) at chemical retentions of 1.2 and 5.7 % had weight losses by Gt of 0.4 and 3%, respectively, for non-leached and leached wood. Borax/urea/zinc formulation with chemical retentions of 2.9 and 5.6% had weight losses of 0.1 and 4%, respectively, for non-leached and leached wood. DOT/dicyandiamide/zinc formulation with chemical retentions of 0.6 and 5.5% had weight losses of 2 and 0.4%, respectively, for non-leached and leached wood. DOT/urea/zinc formulation with chemical retentions of 0.6 and 5.3% had weight losses of 1.0 and 2.9%, respectively, for non-leached and leached wood. The above decay tests indicated that leaching decreased greatly the decay resistance for borax/amine/zinc formulations.

Sweet gum treated with borax/dicyandiamide/zinc formulation decayed by Tv (Table 3) with chemical retentions of 1.2 and 5.8% had weight losses of 0.2 and 9.3%, respectively, for non-leached and leached wood. Borax/urea/zinc formulation with chemical retentions of 1.2 and 5.5% had weight losses of 0.5 and 7.1%, respectively, for non-leached and leached wood. DOT/dicyandiamide/zinc formulation with chemical retentions of 0.6 and 5.4% had weight losses of 0.7 and 1.6%, respectively, for non-leached and leached wood. DOT/urea/zinc formulation with chemical retentions of 0.6 and 5.7% had weight losses of 0.3 and 2.3%, respectively, for non-leached and leached wood. This suggested that leaching greatly decreased decay resistance for all four formulations and only the DOT/Dicyandiamide/zinc formulation prevented decay. This formulation, however, required high loading of chemicals. The leached specimens treated with all four formulations had high weight losses (15 to 47%) for both Gt and Tv (Tables 2, 3). The high weight losses attributed to dehydration and evaporation of treated chemicals in wood will be reflected on both non-leached and leached specimens. However, the weight losses of non-leached specimens after decay were very low (0.3 to 2.4%) for all four formulations decayed by Tv (Table 3) and also for 3 formulations decayed by Gt (1 to 2.5%) (Table 2) except for B1A1Zn treatment (10%). The results imply that high weight losses are in the decay origin rather than being attributed to dehydration or evaporation of chemicals in wood. Borate/amine/zinc formulations are less effective than borate/amine/copper formulations (Chen 2010).

Elemental analysis showed that all four formulations of borate/amine/zinc in leached wood have similar zinc contents ranging from 9.9 and 9.8 mg/g wood for borax/dicyandiamide/zinc and borax/urea/zinc, and 10.5 and 9.3 mg/g wood for DOT/dicyandiamide/zinc and DOT/urea/zinc formulations (Table 4). The leach resistance of zinc in treated wood did not translate into effective decay protection compared with borate/amine/copper formulations (Chen 2010). The zinc in wood treated with these formulations may be unable to form stable complexes with wood components, as evidenced by high loading of about 1% to be effective against fungi for leached specimens. Copper in leached specimens treated with borax/amine/copper formulations were higher (2.8 to 3.5%) than zinc in wood treated with borate/amine/zinc formulations (about 1 %) but were lower for wood treated with DOT/amine/copper formulations (0.5 to 0.6%) (Chen 2010). This implies that the ability of copper or zinc to complex with wood components rather than the amount of insoluble copper or zinc in wood plays an important role in the effectiveness and long-term performance of copper or zinc against wood decay. The mechanism of copper-complexed wood is based on the inability of fungal enzymes to metabolize the copper-modified wood substrate rather than being based on toxicity to prevent fungal decay. Research using better swelling solvents for wood may help to improve complex formation between zinc preservatives with wood components.

Nitrogen analysis of leached specimens treated with these formulations showed that borates and amines did not form boron-nitrogen bond because nitrogen contents (6 to 13 mg/g wood) were close to the untreated wood (5 mg/g wood) (Table 4).

Higher boron content of wood treated with DOT/amine/zinc formulations (0.14 to 0.21 mg/g wood) than wood treated with borax/amine/zinc formulations (0.06 to 0.10 mg/g wood) (Table 4) contributed to more effectiveness against both the brown- and white-rot fungus. Zinc retained more in leached specimens treated with all of four 5% borate/amine/zinc formulations (Table 4) than non-leached specimens. This may be attributed to the sulfate salts (sodium sulfate, ammonium sulfate) present in the non-leached specimens, which leads to lower values of zinc determination. A similar result in lower copper determination was reported in the literature (Chen 2010; Johnson 1983).

CONCLUSIONS

Wood impregnated with each of four formulations of borate/amine/zinc prevented or decreased decay by fungi. Only specimens treated with DOT/dicyandiamide/zinc formulation after 2 weeks water leaching prevented decay by both the brown and white rot fungus. Borate/amine/zinc formulations are less effective than borate/amine/copper formulations against decay fungi, probably attributable to their inability to form stable complexes with wood components. Additional research is needed to improve complex formation of zinc with wood components.

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Table 2. Effect of borate/amine/zinc formulations on weight losses of loblolly pine wood decayed by *Gloeophyllum trabeum* in a 12-week soil-block fungal decay test of non-leached and leached specimens.

Treatment[a]	Solution concentration (%, w/w)	Chemical retention (%,w/w)[b]		Weight loss (%)[c] by *G. trabeum*			
		Non-leached	Leached	Non-leached		Leached	
B1A1Zn	0.5	0.6	0.6	10.0	(5.7)	31.6	(1.8)
	1.0	1.2	1.2	0.4	(0.1)	47.2	(8.3)
	2.5	3.0	2.9	0.0	(0.0)	23.7	(1.6)
	5.0	5.6	5.7	0.9	(0.2)	3.0	(0.7)
B1A2Zn	0.5	0.6	0.6	2.5	(1.3)	38.7	(3.4)
	1.0	1.2	1.2	2.2	(0.4)	42.6	(1.6)
	2.5	2.9	2.9	0.1	(0.3)	19.3	(2.7)
	5.0	5.5	5.6	1.4	(0.2)	4.0	(0.8)
B2A1Zn	0.5	0.6	0.6	2.0	(0.5)	34.5	(1.2)
	1.0	1.2	1.2	0.9	(0.4)	43.0	(2.8)
	2.5	2.8	2.9	0.4	(0.3)	20.1	(4.5)
	5.0	5.4	5.5	0.4	(0.1)	0.4	(0.1)
B2A2Zn	0.5	0.6	0.6	1.0	(0.3)	33.9	(1.3)
	1.0	1.1	1.2	1.0	(0.4)	43.3	(1.8)
	2.5	2.9	2.9	0.1	(0.6)	20.8	(2.0)
	5.0	5.9	5.3	0.5	(0.1)	2.9	(1.6)
Boric acid	0.1	0.1		30.9	(2.9)		
	0.7	0.3		2.2	(0.9)		
	1.4	0.6		0.1	(0.1)		
	2.8	1.2		1.0	(0.1)		
Control				46.30	(0.4)		

[a] B1A1Zn: borax/dicyandiamide/Zinc; B1A2Zn: borax/urea/Zinc; B2A1Zn: DOT/dicyandiamide/zinc; B2A2Cu: DOT/urea/Zinc.
[b] Solution absorbed by blocks before and after treatments conditioned at 27°C and 30% RH.
[c] Average of five replicates, parenthesis are standard deviation.

Table 3. Effect of borate:amine:Zinc formulations on weight losses of sweet gum wood decayed by *Trametes versicolor* in a 12-week soil-block fungal decay test of non-leached and leached specimens.

Treatment[a]	Solution concentration(%, w/w)	Chemical retention (%, w/w)[b]		Weight loss (%)[c] by *T. versicolor*			
		Non-leached	Leached	Non-leached		Leached	
B1A1Zn	0.5	0.6	0.6	2.4	(0.7)	4.2	(1.2)
	1.0	1.2	1.2	0.2	(0.1)	10.7	(0.5)
	2.5	3.0	3.0	0.3	(0.1)	9.6	(1.4)
	5.0	5.8	5.8	0.5	(0.1)	9.3	(1.5)
B1A2Zn	0.5	0.6	0.6	5.5	(1.9)	15.1	(1.0)
	1.0	1.2	1.2	0.5	(0.1)	9.7	(0.8)
	2.5	2.9	2.9	0.3	(0.2)	7.1	(1.8)
	5.0	5.9	5.5	0.7	(0.3)	7.1	(0.9)
B2A1Zn	0.5	0.6	0.6	0.7	(0.1)	12.0	(1.2)
	1.0	1.2	1.2	0.1	(0.1)	9.8	(0.8)
	2.5	2.8	2.8	0.1	(0.1)	9.1	(2.70)
	5.0	5.7	5.4	0.6	(0.1)	1.6	(0.7)
B2A2Zn	0.5	0.6	0.6	0.3	(0.0)	10.8	(1.0)
	1.0	1.2	1.1	0.0	(0.0)	7.6	(0.8)
	2.5	2.8	2.7	0.8	(0.8)	5.7	(1.4)
	5.0	5.6	5.7	0.4	(0.1)	2.3	(1.3)
Boric acid	0.1	0.1		1.4	(2.9)		
	0.7	0.3		1.5	(0.9)		
	1.4	0.6		0.6	(0.1)		
	2.8	1.3		0.0	(0.2)		
Control				33.8	(2.0)		

[a] B1A1Zn: borax/dicyandiamide/zinc; B1A2Zn: urea/zinc; B2A1Zn: DOT/dicyandiamide/zinc; B2A2Zn: DOT/urea/zinc.
[b] Solution absorbed by the blocks before and after treatments conditioned at 27°C and 30% RH.
[c] Average of five replicates, parenthesis are standard deviation.

Table 4. Retention of boron, zinc and nitrogen in wood in borate/amine/zinc systems by solution absorption and chemical analysis.

	Retention				
Treatment	Boron (mg/g wood)		zinc (mg/g wood)		Nitrogen (mg/g wood)
B1A1Zn					
Solution absorbed (NL)[a]	0.62		1.84		
Analyzed (NL)[a]	0.99		9.58		
Analyzed (L)[a]	0.10	(10%)[c]	9.86	(103%)[c]	13
B1A2Zn					
Solution absorbed (NL)[b]	0.61		1.85		
Analyzed (NL)[a]	0.73		7.71		
Analyzed (L)[a]	0.06	(8%)[c]	9.8	(1 27%)[c]	10
B2A1Zn					
Solution absorbed (NL)[b]	0.6 1		1.73		
Analyzed (NL)[a]	1.65		7.87		
Analyzed (L)[a]	0.21	(13%)[c]	10.5[c]	(133%)[c]	6
B2A2Zn					
Solution absorbed (NL)[b]	0.66		1.86		
Analyzed (NL)[a]	1.52		8.20		
Analyzed (L)[a]	0.14	(9%)[c]	9.25	(113%)[c]	9
Control[a]	0.006		0.06		< 5.0

[a]Average of three replicates; corrected for boron and zinc in untreated wood.

[b]Percentage (%) based on block absorbed borate/amine/zinc solution in 1:2:4 molar ratio.

[c]Percentage (%) based on wt. of chemicals in non-leached specimens. NL is non leached; L is leached

PROCEEDINGS

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