

LABORATORY EVALUATION OF BORATE:AMINE:COPPER DERIVATIVES IN WOOD FOR FUNGAL DECAY PROTECTION

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Abstract. This study aimed to evaluate borate:amine:copper derivatives in wood for fungal decay protection as well as the permanence of copper and boron in wood. Each of four derivatives of borate:amine:copper prevented fungal decay in wood. Disodium tetraborate decahydrate (borax):amine:copper derivatives with 0.61-0.63% retention after water leaching prevented decay by *Gloeophyllum trabeum* (*Gt*) and with 0.64% retention prevented decay by *Trametes versicolor* (*Tv*). Leaching did not decrease decay resistance for either *Gt* or *Tv*. Disodium octaborate tetrahydrate (DOT):amine:copper derivatives with 1.14-2.93% retention after water leaching prevented decay by *Gt* and with 0.54-1.19% retention prevented decay by *Tv*. Leaching decreased decay resistance to *Gt* but not to *Tv*. Higher copper and boron in disodium borax:amine:copper derivatives contributed to more decay resistance to *Gt* and *Tv* than that of DOT:amine:copper derivatives as evidenced by elemental analysis. IR spectra of wood treated with 5% borate:amine:copper derivatives after water leaching showed increased absorption at 1632-1635 cm^{-1} compared with the control. This increased absorption was partly attributable to carbonyl of copper carboxylates from oxidation of hemiacetals of hemicelluloses and cellulose by copper (II) ions and carbonyls of copper (II) quinone methides by oxidation of guaiacols by copper (II) ions. It was also partly attributable to carbonyls of copper carboxylates from hemicelluloses and phenolates from lignin through ion exchange reactions. These oxidation and ion exchange reactions of copper with wood components may account for their efficacy and long-term performance.

Keywords: Borate:amine:copper derivatives, fungal decay protection, fixation of copper.

INTRODUCTION

Boron compounds, including boric acid, disodium tetraborate (borax), and disodium octaborate (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 efficacy of boric acid and borates against wood decay fungi, termites, and fire has been well established in wood products for the past 60 yr (Croft and Levy 1973; Lloyd 1997). The mechanisms of boric acid and borate inhibition to fungi and plants are not well investigated but are postulated to inhibit pentose pathway (Lee and Aronoff 1967). The tetrahydroxyborate ion acts by complexation with poly-ols and probably attacks decay fungi through

extracellular substrate sequestration, intercellular substrate sequestration, enzyme inhibition, and change in membrane function (Lloyd et al 1990) and interaction of borate in xylose moiety of the oxidized coenzymes NAD^+ , NMN^+ , and NADP^+ (Lloyd 1997). Borates are used in large quantities in building products in Asia and North America, in wood composites and pest control in North America, and in formulation of exterior and remedial treatments in Europe (Lloyd 1997). Because boric acid and borates are water-soluble, their use in outdoor wood products is 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 performed in recent years. Chromate copper borates

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(Ochrymowych and McOrmond 1978) performed well in field tests; however, chromium may not be used in products because of environmental concerns. Copper borates dissolved in ammonium hydroxide in wood (Johnson 1983; Johnson and Foster 1991) performed well after 6 yr in the field, but boron was leached from wood. Effectiveness of copper borates was attributed to permanence of copper in wood. Albumis protein borates (Thevenon et al 1997, 1998a, 1998b) were effective in 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 after water leaching showed effectiveness in laboratory fungal decay tests. This led us to prepare borate:amine:copper derivatives. Borate derivatives may form stable, leach-resistant compounds in wood through covalent bonding of boron with nitrogen in amines, which then forms a complex with copper (II).

Copper compounds are used for controlling algal growth, wood decay fungi, marine borers, and crop fungi and have been used successfully for more than a century (Richardson 1997). Copper oxidizes proteins, enzymes, and lipids and interferences with enzymatic processes (Eaton and Hale 1993; Rui and Morrell 1994).

This study aims to evaluate borate:amine:copper in wood for fungal decay protection as well as permanence of copper and boron in wood and to describe the complex formation of copper with wood components.

MATERIALS AND METHODS

Formulation

Four derivatives of borate:amine:copper were formulated using two borates, borax and DOT, and two amines, dicyandiamide and urea and copper sulfate penta hydrate, in a 1:2:4 molar ratio at four concentration levels (0.5, 1.0, 2.5, and 5%). Borate:amine:copper derivatives were dissolved in 8% ammonium hydroxide solution. Each borate derivative was prepared in a 1-kg solution (Table 1).

Table 1. Weight (g) of 5% borate:amine:copper in 1:2:4 molar ratio in 1-kg solution dissolved in 8% ammonium hydroxide.

Treatment ^a	Formulation ^b	
	Amine	Copper
B1A1 Cu	12.316	5.431
B1A2 Cu	12.711	4.003
B2A1 Cu	13.060	5.323
B2A2 Cu	13.470	3.922

^a B1, borax; B2, DOT; A1, dicyandiamide; A2, Urea; Cu, copper sulfate pentahydrate.

^b Weight (g) of 5% borate:amine:copper in a 1:2:4 molar ratio per 1-kg solution.

Impregnation

Each concentration (0.5, 1.0, 2.5, and 5%) of each borate:amine:copper solution was impregnated into wood by full cell pressure. For each concentration, 32 sapwood blocks in anatomical directions were used, including 20 blocks for fungal decay tests—10 loblolly pine (*Pinus taeda* L.) and 10 sweet gum (*Liquidambar styraciflua* L.). The remaining 12 blocks (6 loblolly pine and 6 sweet gum) were used for the weathering test. The treatment with one concentration for fungal decay and weathering tests is described subsequently.

Thirty-two sapwood blocks (16 loblolly pine and 16 sweet gum), 19 mm in all anatomical directions, were conditioned at 27°C and 30% RH for 3 wk and weighed. The blocks reached equilibrium moisture content after 3 wk. 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 concentration levels in 8% ammonium hydroxide solution (500 mL). After impregnation, the pressure was released and another 100 mL of solution was added. Treated blocks were soaked for 24 h. Blocks were then removed from the solution. Excess solution was wiped off, and blocks were weighed to determine the amount of solution absorbed. Blocks were then air-dried for 1 wk under a chemical hood. Half the blocks (16) were leached in distilled water (800 mL, 50 mL/block) for 6, 24, and 48 h and then every 24 h for 2 wk according to AWP A E10-91 (AWPA 1996). Leached and nonleached blocks

were conditioned at 27°C and 30% RH for 3 wk and weighed before fungal decay tests. Two fungi, *Gloeophyllum trabeum* (Gt), a brown-rot fungus, and *Trametes versicolor* (Tv), a white-rot fungus, were used in a 12-wk laboratory soil-block fungal decay test. Boric acid was used as a reference.

Weathering tests were used to determine the chemical losses caused by evaporation without presence of fungi. Six blocks (3 leached and 3 nonleached) from two species (loblolly pine and sweet gum) were placed in a soil-block decay bottle on top of a feeder strip not inoculated with fungal mycelia, and the bottles were placed in a growing chamber (27°C and 80% RH) for 12 wk. After 12 wk, the weathering blocks were conditioned at 27°C and 30% RH for 3 wk and weighed to determine weight loss caused by evaporation of volatile compounds from wood and dehydration of chemicals. Tables 2 and 3 show weight losses by decay fungi after correction for weathering losses.

Another 24 loblolly pine sapwood blocks (6 blocks, including 3 leached and 3 nonleached, for each derivative) were treated with 5% of each of four borate:amine:copper derivatives. The procedures and leaching were the same as described previously except one concentration (5%) was used. These blocks were used for elemental and IR analyses.

Chemical retention in the blocks is expressed in kilograms per cubic meter (kg/m^3) obtained by multiplying solution concentration with block weight. Chemical retention in wood for fungal decay tests is based on solution absorbed by blocks and conditioning at 27°C and 30% RH for 3 wk, before and after decay tests. Because too few data points (four concentrations) existed to establish a threshold relationship, nonlinear regression analysis to determine threshold retention would not be accurate (Steel and Torrie 1960; Nance and Amburgey 1976; Gezer et al 1999b). Weight losses greater than 2% were considered to be of fungal origin, and weight

Table 2. Effect of borate:amine:copper derivatives on weight losses of loblolly pine wood decayed by *Gloeophyllum trabeum* in a 12-wk soil-block fungal decay test of nonleached and leached specimens.

Treatment ^a	Solution concentration (% w/w)	Chemical retention (kg/m^3) ^b		Weight loss (%) ^c by <i>G. trabeum</i>	
		Nonleached	Leached	Nonleached	Leached
B1A1 Cu	0.5	2.38	2.36	0.2 (0.0)	0.2 (0.0)
	1.0	4.73	4.70	0.4 (0.1)	1.0 (0.0)
	2.5	11.67	11.84	0.7 (0.1)	0.7 (0.2)
	5.0	23.78	23.23	0.1 (0.2)	0.8 (0.2)
B1A2 Cu	0.5	2.37	2.35	0.5 (0.1)	1.1 (0.4)
	1.0	4.75	4.65	1.1 (0.2)	1.2 (0.4)
	2.5	11.78	11.49	0.9 (0.3)	0.3 (0.3)
	5.0	23.99	24.04	1.4 (0.3)	0.7 (0.3)
B2A1 Cu	0.5	2.37	2.36	0.2 (0.2)	20.3 (2.4)
	1.0	4.65	4.63	0.2 (0.1)	4.0 (0.8)
	2.5	11.75	11.90	0.7 (0.2)	0.1 (0.1)
	5.0	22.93	23.25	0.5 (0.1)	0.0 (0.1)
B2A2 Cu	0.5	2.30	2.31	0.9 (0.1)	8.2 (1.2)
	1.0	4.66	4.68	1.8 (1.0)	1.6 (0.9)
	2.5	11.29	11.44	0.3 (0.2)	0.7 (0.1)
	5.0	23.23	23.16	0.0 (0.0)	0.9 (0.1)
Boric acid	0.5	0.46		30.9 (2.9)	
	1.0	3.26		2.2 (0.9)	
	2.5	6.36		0.1 (0.1)	
	2.8	12.63		1.0 (0.2)	
Control				35.8 (0.1)	

^a B1A1 Cu, borax:dicyandiamide:copper; B1A2 Cu, urea:copper; B2A1 Cu, DOT:dicyandiamide:copper; B2A2 Cu, DOT:urea:copper.

^b Solution absorbed by blocks before and after treatments conditioned at 27°C and 30% RH.

^c Average of five replicates; values in parentheses are standard deviation.

Table 3. Effect of borate:amine:copper derivatives on weight losses of sweet gum wood decayed by *Trametes versicolor* in a 12-wk soil-block fungal decay test of nonleached and leached specimens.

Treatment ^a	Solution concentration (% w/w)	Chemical retention (kg/m ³) ^b		Weight loss (%) ^c by <i>T. versicolor</i>	
		Nonleached	Leached	Nonleached	Leached
B1A1 Cu	0.5	2.29	2.42	0.1 (0.0)	0.4 (0.2)
	1.0	4.64	5.04	0.2 (0.0)	0.0 (0.0)
	2.5	11.66	11.67	0.0 (0.0)	0.0 (0.0)
	5.0	24.32	23.78	0.8 (0.2)	0.4 (0.1)
B1A2 Cu	0.5	2.32	2.38	0.0 (0.0)	0.5 (0.2)
	1.0	4.39	4.65	0.0 (0.0)	0.2 (0.0)
	2.5	11.63	11.15	0.2 (0.1)	0.2 (0.0)
	5.0	24.17	24.12	0.7 (0.3)	0.1 (0.0)
B2A1 Cu	0.5	2.35	2.38	0.5 (0.1)	3.0 (1.3)
	1.0	4.79	4.69	0.2 (0.1)	0.0 (0.0)
	2.5	11.56	12.12	0.1 (0.0)	0.2 (0.0)
	5.0	23.50	23.87	0.0 (0.0)	0.2 (0.0)
B2A2 Cu	0.5	2.40	2.33	0.3 (0.3)	1.3 (0.3)
	1.0	4.76	4.61	0.0 (0.0)	0.2 (0.1)
	2.5	12.22	11.69	0.0 (0.0)	0.0 (0.1)
	5.0	23.66	523.31	0.0 (0.0)	0.0 (0.0)
Boric acid	0.1	0.46		1.4 (2.9)	
	0.7	3.23		1.5 (0.9)	
	1.4	6.39		0.6 (0.1)	
	2.8	13.73		0.0 (0.2)	
Control				33.8 (2.0)	

^a B1A1 Cu, borax:dicyandiamide:copper; B1A2 Cu, urea:copper; B2A1 Cu, DOT:dicyandiamide:copper; B2A2 Cu, DOT:urea:copper.

^b Solution absorbed by the blocks before and after treatments conditioned at 27°C and 30% RH.

^c Average of five replicates; values in parentheses are standard deviation.

losses less than 2% may include losses caused by chemical dehydration and wood extractive evaporation.

Characterization

Elemental analysis of copper and boron in loblolly pine treated with four derivatives from borate:amine:copper at the 5% level for both leached and nonleached as well as control specimens was performed with inductively coupled plasma (ICP). Nitrogen analysis of leached treated wood specimens was carried out by Galbraith Laboratory, Inc (Knoxville, TN) using combustion to convert the sample elements to simple gases, ie N₂, and analyzed using a Perkin-Elmer (Waltham, MA) 24000 Elemental Analyzer.

IR spectra in KBr of control and loblolly pine treated with 5% borate:amine:copper derivatives after 2 wk water leaching and dried over phosphorus pentaoxide (P₂O₅) for 4 wk were

obtained using a Mathson Galaxy series Fourier transform IR (FTIR) 5000 spectrophotometer. IR spectra were obtained with a transmittance method. Samples for IR analysis were prepared by cutting half the treated block into small pieces and then grinding the pieces in a Wiley mill to fine particles (passing 30 mesh) and then further grinding them to pass 60 mesh. The 60 mesh fine particles were used for IR analysis using KBr pellets. A baseline method (Colthup et al 1964a, 1964b) was used to compare intensity of IR absorptions at 2921-2924 cm⁻¹ (CH stretching) and 1632-1635 cm⁻¹ (C=O stretching).

RESULTS AND DISCUSSION

Weight losses of about 2% caused by fungal origin for reference compound boric acid (Tables 2 and 3) were in agreement with my past research (Chen and Ibach 2010) (0.7-1.4% for *Gt* and <0.1% for *Tv*) and with that reported by others (0.5-0.9% for *Gt* [Harrow 1950] and 0.2-0.3% for

Tv [Baechler and Roth 1956]). Borate:amine:copper derivatives in a 1:2:4 molar ratio in wood protected wood against fungal degradation. For loblolly pine treated wood decayed by *Gt* (Table 2), borax:dicyandiamide:copper derivative with a chemical retention of 0.6 and 0.63% had weight losses of 0.2 and 0.2%, respectively, for nonleached and leached wood; borax:urea:copper derivative with chemical retentions of 0.60 and 0.61% had weight losses of 0.5 and 1.1%, respectively, for nonleached and leached wood; DOT:dicyandiamide:copper derivative with chemical retentions of 0.59 and 2.93% had weight losses of 0.2 and 0.1%, respectively, for nonleached and leached wood; and DOT:urea:copper derivative with chemical retentions of 0.56 and 1.14% had weight losses of 0.9 and 1.6%, respectively, for nonleached and leached wood. These decay tests indicated that leaching decreased decay resistance slightly for DOT:amine:copper derivatives, which had weight losses of 20.3 and 8.2% with lowest retentions of 0.58 and 0.56%, respectively, for DOT:dicyandiamide:copper and DOT:urea:copper, but leaching did not affect the decay resistance of wood treated with borax:amine:copper derivatives.

For sweet gum treated wood decay by *Tv* (Table 3), borax:dicyandiamide:copper derivative with chemical retentions of 0.66 and 0.64% had weight losses from decay of 0.1 and 0.4%, respectively, for nonleached and leached wood. Borax:urea:copper derivative with chemical retentions of 0.63 and 0.64% had weight losses by decay of 0 and 0.5%, respectively, for nonleached and leached wood; DOT:dicyandiamide:copper derivative with chemical retentions of 0.61 and 1.19% had weight losses by decay of 0.5 and 0%, respectively, for nonleached and leached wood; and DOT:urea:copper derivative with chemical retentions of 0.59 and 0.59% had weight losses by decay of 0.3 and 1.3%, respectively, for nonleached and leached wood. This suggested that borax:amine:copper derivatives resisted water leaching, whereas DOT:amine:copper derivatives had decreased decay resistance after water leaching. Borax:amine:copper derivatives may form more stable copper borates than those of DOT derivatives as evidenced by ICP analysis (Table 4), which would result in more decay resistance.

The permanence of copper and boron in wood treated with 5% borate:amine:copper derivatives

Table 4. Retention of boron, copper, and nitrogen in wood in borate:amine:copper systems.

Treatment retention	Boron (mg/g wood)	Copper (mg/g wood)	Nitrogen (mg/g wood)
Borax:dicyandiamide:copper (B1A1 Cu)			
(Theo) (NL)	2.56	15.22	
(Found) (NL) ^a	3.56 (139%) ^b	24.74 (163%) ^b	
(Found) (L) ^a	1.14 (32%) ^c	28.39 (115%) ^c	8.0
Borax:urea:copper (B1A2 Cu)			
(Theo) (NL)	2.82	16.55	
(Found) (NL) ^a	5.72 (203%) ^b	33.05 (200%) ^b	
(Found) (L) ^a	2.26 (46%) ^c	34.81 (105%) ^c	<5.0
DOT:dicyandiamide:copper (B2A1 Cu)			
(Theo) (NL)	4.98	14.65	
(Found) (NL) ^a	2.68 (54%) ^b	16.31 (113%) ^b	
(Found) (L) ^a	0.29 (11%) ^c	5.62 (35%) ^c	<5.0
DOT:urea:copper (B2A2 Cu)			
(Theo) (NL)	5.14	15.10	
(Found) (NL) ^a	2.67 (52%) ^b	17.70 (117%) ^b	
(Found) (L) ^a	0.37 (14%) ^c	4.98 (28%) ^c	<5.0
Control ^a	0.006	0.002	<5.0

^a Average of three replicates.

^b Percentage (%) based on theoretical values (block absorbed solution in 1, 2, 4 molar ratio).

^c Percentage (%) based on weight of chemical in non-leached specimens.

was evaluated by elemental analysis and EDXA (EDXA used for copper only). Elemental analysis (Table 4) showed that copper was retained quantitatively in leached specimens treated with borax:dicyandiamide:copper and borax:urea:copper derivatives; boron was retained at 32 and 46% for wood treated with borax:dicyandiamide:copper and borax:urea:copper derivatives, respectively. In leached specimens treated with DOT:dicyandiamide:copper and DOT:urea:copper derivatives, copper was retained at 35 and 28%, respectively, and boron was retained at 11 and 14%, respectively. More copper and boron were retained in wood treated with borax:amine:copper derivatives than with DOT:amine:copper derivatives, which contributed to more effective decay resistance of borax:amine:copper derivatives in wood than DOT:amine:copper derivatives. Copper in non-leached specimens (Table 4) was retained at 163 and 200% for borax:dicyandiamide:copper and borax:urea:copper, respectively, compared with 113 and 117% for DOT:dicyandiamide:copper and DOT:urea:copper, respectively. Boron was retained at 139 and 203% for borax:dicyandiamide:copper and borax:urea:copper, respectively, and 54 and 52% for DOT:dicyandiamide:copper and DOT:urea:copper, respectively. This indicated that borax was more reactive to form copper borates than was DOT.

Copper was retained more in leached specimens treated with 5% borax:dicyandiamide:copper (Table 4) than nonleached specimens, which was attributed to variability within specimens and copper determination. Similar results in copper determination were also reported in the literature (Johnson 1983). Table 4 shows that borax has formed more leach-resistant copper borates than has DOT, which also contributes to more decay resistance of borax derivatives compared with DOT derivatives. Nitrogen analysis (Table 4) of leached specimens treated with borax and DOT derivatives showed that dicyandiamide and urea were completely leached from treated wood, suggesting that aminoborates did not form. Apparently, the leach-resistant aminoborates that this study was looking for

were not achieved. The effectiveness of borate:amine:copper derivatives in wood against fungal degradation was attributed to fixation of copper to wood. Research is needed to develop leach-resistant aminoborates for wood, which will lead to metal-free boron wood preservatives.

IR spectra of leached loblolly pine treated with 5% borax:amine:copper and DOT:amine:copper derivatives (Fig 1b–e; Table 5) showed the following increased intensity of absorption at 1632–1635 cm^{-1} (Forziati et al 1951; Bellyamy 1954;

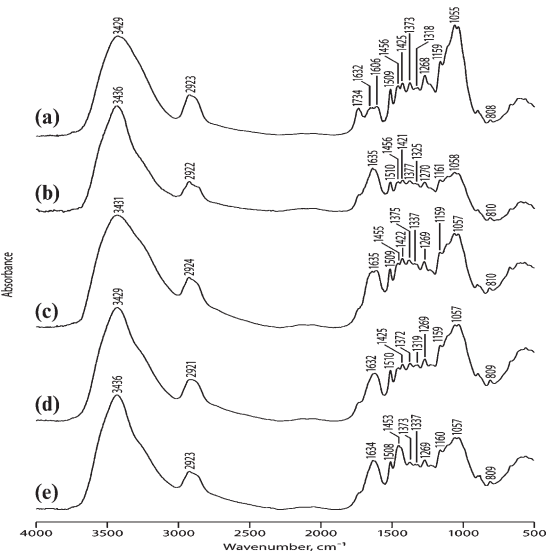


Figure 1. Fourier transform TIR of loblolly pine wood (a) and loblolly pine wood impregnated with B1A1 Cu (b), B1A2 Cu (c), B2A1 Cu (d), and A2B2 Cu (e).

Table 5. Relative intensity of IR peaks of C=O (1632–1635 cm^{-1}) and C-H (2921–2925 cm^{-1}) of loblolly pine treated with 5% borate:amine:copper derivatives after a 2-wk water leaching.

Treatment	Relative intensity of IR peak ^a	
	C=O (1632–1635 cm^{-1})/C-H (2921–2925 cm^{-1})	
Control	0.96	
B1A1 Cu	1.04 (8.3%) ^b	
B1A2 Cu	1.04 (8.3%)	
B2A1 Cu	1.02 (6.3%)	
B2A2 Cu	1.05 (9.4%)	

^a Baseline method.
^b Percentage (%) increased in C=O absorption compared with untreated pine (control).

Zhbankov 1966; Davidson 1967) compared with the control (Table 5): B1A1 copper (Cu) (8.3%), B1A2 Cu (8.3%), B2A1 Cu (6.3%), and B2A2 Cu (9.3%). Both borax:amine:copper derivatives (B1A1 Cu and B1A2 Cu) had the same number (8.3%), whereas DOT:dicyandiamide:copper (B2A1 Cu) and DOT:urea:copper (B2A2 Cu) were 6.3 and 9.3%, respectively. The increased intensity of absorption at $1632\text{--}1635\text{ cm}^{-1}$ was partly attributed to ion exchange reactions of carboxylates from hemicelluloses and phenolates from lignin as well as to carbonyls of copper carboxylates from polysaccharides and copper quinone methides from lignin. This indicated that oxidation of hemiacetals of hemicelluloses and cellulose by copper (II) to carboxyls and oxidation of guaiacyls to quinone methides (Forziati et al 1951; Bellyamy 1954; Zhbankov 1966; Davidson 1967) took place, which then formed complexes with copper (II) to form copper carboxylates and copper quinone methides.

IR spectra of wood treated with 5% borate:amine:copper derivatives after water leaching did not show strong absorption of B-N ($1330\text{--}1465\text{ cm}^{-1}$) because no aminoborates were formed and B-O absorption of borates ($1310\text{--}1380\text{ cm}^{-1}$) was too weak to characterize (Fig 1b–e) (Colthup et al 1964a, 1964b).

Many studies have reported that copper (II) formed complexes with carboxylates of hemicelluloses and phenolates of lignin through ion exchange reactions (Cooper 1991; Thomson and Pasek 1997; Kamdem and Zhang 2000; Staccioli et al 2000; Zhang and Kamdem 2000). However, fixation of copper with wood in copper amine systems was not as effective as that of CCA systems (Zhang and Kamdem 2000; Waldron et al 2006). Leaching of copper from treated wood remained a problem (Lebow 1996; Hingston 2002; Morsing 2003; Tascioglu et al 2005). More research is needed to optimize the fixation of copper in copper amine systems. These ion exchange reactions only describe complex formation between lignin- and carboxyl-containing hemicelluloses but did not involve cellulose and noncarboxyl-containing hemicelluloses. Cellulose and noncarboxyl-containing hemicelluloses

will form complexes with copper (II) ion through oxidation of hemiacetals to carboxyls, which then complex with copper (II) ions as postulated in this article. This complex formation between wood polymers and copper ion contribute to the efficacy and long-term performance of copper wood preservatives in the field.

Research is needed to investigate the reaction of each wood component with copper (II) and to study how it responds to fungal enzymatic degradation. Understanding this will help maximize fixation of copper to wood and minimize non-fixed copper leaching into the environment.

CONCLUSIONS

Borate:amine:copper derivatives in a 1:2:4 molar ratio in wood protected wood against fungal degradation. For borax:dicyandiamide:copper and borax:urea:copper in wood after 2 wk water leaching, retentions of 0.61–0.63% prevented decay by *Gt* and retentions of 0.64% prevented decay by *Tv*. Leaching did not decrease decay resistance. For DOT:dicyandiamide:copper and DOT:urea:copper derivatives, retention of 1.14–2.93% prevented decay by *Gt* and 0.59–1.19% prevented decay by *Tv*. Leaching of wood treated with DOT:amine:copper derivatives decreased decay resistance to *Gt* but did not decrease decay resistance to *Tv*. The increased effectiveness of borax:amine:copper derivatives against decay fungi compared with DOT:amine:copper derivatives was attributed to higher retention of copper and boron in borax derivatives than in DOT derivatives as evidenced by elemental analyses. Nitrogen analysis of leached specimens treated with borax and DOT derivatives showed that dicyandiamide and urea were completely leached out from treated wood, indicating that aminoborates were not formed. The effectiveness of borate:amine:copper derivatives was attributed to fixation of copper to wood. Research is needed to develop leach-resistant aminoborates in wood, which could lead to metal-free boron wood preservatives. Results of 8-yr field tests of stakes treated with borate:amine:copper derivatives will be reported in the future.

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REFERENCES

- AWPA (1996) Standard method of testing wood preservatives by laboratory soil-block cultures. E10-91. American Wood Preservers' Association, Birmingham, AL.
- Baechler RH, Roth HG (1956) Laboratory leaching and decay tests on pine and oak blocks treated with several preservatives salts. *Proc American Wood-Preservers' Association* 52:24-34.
- Bellyamy LJ (1954) The infrared spectra of complex molecules. Pages 161-177 in Bellyamy, LJ, ed. II. Carboxylic acids. John Wiley & Sons, Inc., New York, NY.
- Carr JM, Duggan PJ, Humphrey DG, Tyndall EM (2005) Enhanced anti-fungal activity of the organo-soluble borate ester, tetrabutyl ammonium bis (ortho-hydroxy methyl phenolato) borate. *Aust J Chem* 58(1):21-25.
- Chen GC (2008) Synthesis and evaluation of aminoborates derived from boric acid and diols for protecting wood against fungal and thermal degradation. *Wood Fiber Sci* 40(2):248-257.
- Chen GC, Ibach RE (2010) Laboratory evaluation of borate/amine/zinc formulations in wood for fungal decay protection. *Proc. Am Wood Prot Assn* 106:139-145.
- Colthup NB, Daly LH, Wiberley SE (1964a) Chapter 2. Experimental considerations. Pages 37-39 in Colthup NB, Daly LH, Wiberley, eds. *Introduction to infrared and raman spectroscopy*, Academic Press, New York.
- Colthup NB, Daly LH, Wiberley SE (1964b) Chapter 12. Compounds containing boron, silicon, phosphorus, sulfur, or halogen. Pages 219-318 in Colthup NB, Daly LH, Wiberley, eds. *Introduction to infrared and raman spectroscopy*. Academic Press, New York
- Cooper PA (1991) Cation exchange adsorption of copper on wood. *Wood Protect* 1:9-14.
- Croft C, Levy JF (1973) Bibliography on the use of boron compounds in the preservation of wood. *J Inst Wood Sci* 8:28-37.
- Davidson EA (1967) Carbohydrate chemistry. Holt, Rinehart and Winston Inc., New York, NY, 447 pp.
- Eaton RA, Hale MD (1993) Wood: Decay, pests and protection. Chapman & Hall, London, UK. 520 pp.
- Forziati FH, Rowen JW, Plyler EK (1951) Spectrophotometric determination of carboxyl in cellulose. *J Res Natl Bur Stand* 46(4):288-291.
- Gezer ED, Micheal JH, Morrell JT (1999a) Effect of glycol on leachability and efficacy of boron wood preservatives. *Wood Fiber Sci* 31(2):136-142.
- Gezer ED, Yalinkilic MK, Kizilkaya K, Micheal JH (1999b) Estimation of preservative toxic threshold retention from laboratory decay tests: A new method. *Wood Sci Technol* 33:63-71.
- Harrow KM (1950) Toxicity of water-soluble wood preservatives to wood-destroying fungi. *New Zeal J Sci* B31(5):14-19.
- Hingston JA (2002) Leaching of copper based preservatives in aquatic environments. PhD thesis, Faculty of Life Science, University of London, London, UK.
- Johnson BR (1983) Field trials with ammoniacal copper borate wood preservatives. *Forest Prod J* 33(9):59-63.
- Johnson BR, Foster DO (1991) Field trials with ammoniacal copper borate. *Forest Prod J* 41(9):37-38.
- Kamdem DP, Zhang J (2000) Contribution of wood components on the absorption of copper amine. International Research Group on Wood Protection, Document No. IRG/WP 00-30216. Stockholm, Sweden.
- Lebow S (1996) Leaching of wood preservative components and their mobility in the environment. Summary of pertinent literature. Gen Tech Rep FPL-GTR-93. USDA For Serv Forest Prod Lab, Madison, WI. 36 pp.
- Lee S, Aronoff S (1967) Boron in plants: A biochemical role. *Science* 158:798-799.
- Lloyd JD (1997) International status of borate preservative systems. Pages 45-54 in *Proc Second International Conference on Wood Protection with Diffuse Preservatives and Pesticides*. Forest Products Society, Madison, WI.
- Lloyd JD, Dickinson DJ, Murphy RJ (1990) The probable mechanisms of action of boric acid and borates as wood preservatives. International Research Group on Wood Protection, Doc No IRG/WP/90-1450. Stockholm, Sweden.
- Morsing N (2003) Leaching of active components from preservative treated timber. Status after approximately 4 months out-door exposure. Document No. IRG/WP 03-20276. International Research Group on Wood Protection, Stockholm, Sweden.
- Murphy RJ, Barnes HM, Gray SM (1995) Decay and soil depletion studied with polymer/boron preservative systems. *Forest Prod J* 45(9):77-81.
- Nance WL, Amburgey TL (1976) Statistical analysis of data from laboratory decay tests. *Proc American Wood Preservers' Association* 72; 161-171, GA.
- Ochrymowych J, McOrmond RR (1978) Performance of pole-diameter posts treated with various preservatives during a quarter century of testing at Orange Park, Florida test plot. *Proc American Wood Preservers' Association* 74:190-213.
- Pickard MH (1948) Boron oxides, boric acid, and borates. In RE Kirk and DF Othmer, eds. Pages 600-622, *Encyclopedia of chemical technology*. Vol. 2. The Interscience Encyclopedia Inc., New York, NY.

- Richardson HW (1997) Handbook of copper compounds and applications. Marcel Dekker, New York, NY. 423 pp.
- Rui C, Morrell JJ (1994) Assessing biocide effects on protoplasts of wood decay fungi. *Wood Fiber Sci* 26(2):205-211.
- Staccioli G, Sturaro A, Rella R (2000) Cation exchange capacity tests on some lignocellulosic materials highlight some aspects of the use of copper wood preservative. *Holzforschung* 54(2):133-136.
- Steel RGD, Torrie JH (1960) Principles and procedures of statistics. McGraw-Hill Book Company, Inc., New York, NY, pp. 332-345.
- Tascioglu C, Cooper PA, Ung T (2005) Rate and extent of adsorption of ACQ preservative components in wood. *Holzforschung* 59(5):574-580.
- Thevenon MF, Pizzi A, Haluk JP (1997) Non-toxic albumin and soy protein borates as ground-contact wood preservatives. *Holz Roh Werkst* 55(5):293-296.
- Thevenon MF, Pizzi A, Haluck JP (1998a) Albumin borates: A new non-toxic, wide spectrum, ground-contact wood preservative. International Research Group on Wood Protection, Doc No IRG/WP/98-3016., Stockholm, Sweden.
- Thevenon MF, Pizzi A, Haluck JP (1998b) Proteinborates as non-toxic, long term, wide-spectrum, ground contact wood preservatives. *Holzforschung* 52(30):241-248.
- Thomson S, Pasek EA (1997) Amine copper reaction with wood components: Acidity versus copper adsorption. International Research Group on Wood Protection, Doc No. IRG/WP 97-30161, Stockholm, Sweden.
- Waldron L, Cooper PA, Ung TY (2006) Prediction of long-term leaching potential of preservative treated wood by diffusion modeling. *Holzforschung* 59:581-588.
- Williams LH, Bergstrom TB (2005) Boron-treated expanded polystyrene insulation units native subterranean termites damage after 3 years field exposure. *Forest Prod J* 55(3):56-60.
- Zhang J, Kamdem DP (2000) FTIR characterization of copper ethanolamine-wood interaction for wood preservation. *Holzforschung* 54:119-122.
- Zhbankov, RG (1966) Chapter V. Oxidation products of cellulose. Salts of oxidation products of cellulose. Pages 117-129 in Zhbankov, eds. *Infrared spectra of cellulose and its derivatives*. Consultant Bureau, New York, NY.