Technical Note

A Laboratory Test of the Leachability and Decay Resistance of Some Synthesized Borate Compounds

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Abstract

Quaternary ammonium tetraphenylborates (TPBs) and quaternary ammonium tetrafluoroborates were synthesized for the manufacture of leaching-resistant boron wood preservatives. The leachability of these boron compounds and the termite and decay resistance of wood treated with these compounds were evaluated. The boron leaching rate of wood treated with quaternary ammonium TPB formulations ranged from 2.1 to 6.7 percent, while that of quaternary ammonium tetrafluoroborate formulations ranged from 23.3 to 59.0 percent. Quaternary ammonium tetrafluoroborates performed better than quaternary ammonium TPBs in termite resistance and inhibition zone tests. Quaternary ammonium tetrafluoroborates could inhibit *Gloeophyllum trabeum* and *Phanerochaete chrysosporium* at all concentrations used in the laboratory inhibition zone test. Weight loss of masson pine (*Pinus massoniana*) sapwood treated with quaternary ammonium tetrafluoroborate solutions was 1.4 to 2.6 percent (*G. trabeum*) and 2.5 to 3.8 percent (by *Coriolus versicolor*) at preservative retentions around 7.0 kg/m^3.

Inorganic borates are effective and environmentally friendly wood preservatives, but they can only be used in indoor or protected applications because they can leach out from treated wood due to their water-soluble nature. Some research has focused on boron in the last two decades, looking at borates for exterior applications (e.g., Rainer 1993, Obanda et al. 2008). A two-stage treatment with sodium tetraphenylborate [$(C_6H_5)BNa$] and potassium chloride that forms insoluble salts of potassium tetraphenylborate was investigated by Lin et al. (2001). Good fixation of the boron compounds was observed after the leaching test, and they also showed an excellent antifungal activity against both *Coriolus versicolor* and *Tyromyces palustris*. However, other tetraphenylborates (TPBs) with low water solubility have not shown antifungal activity. Didecyldimethyl ammonium chloride (DDAC) and benzyldodecyldimethyl ammonium chloride (BAC), which are commonly used as components of alkaline copper quaternary wood preservatives, can react with both lignin and cellulosic compounds of wood cells and have some resistance to leaching (Jin and Archer 1991). Didecyldimethyl ammonium tetrafluoroborate (DBF, $[(C_{10}H_{21})_2N(CH_3)_2]^+BF_4^-$), a quaternary ammonium compound that contains two antifungal activity groups (quaternary ammonium and boric tetrafluoride [BF_4^-]), showed decay resistance against both *Fomitopsis palustris* and *Trametes versicolor,* even after a severe leaching test (Kartal et al. 2004). Evaluation of *Coptotermes formosanus* Shiraki resistance of wood treated with DBF showed adequate protection even after a 10-day severe weathering process. This suggests there may be adequate fixation of DBF for exterior applications (Kartal et al. 2005).

In this study, two borate compounds, benzyldodecyldimethyl ammonium tetrafluoroborate (BBF) and quaternary ammonium TPB were synthesized, and their structures were confirmed. The laboratory leaching performance of these borates and their fungicidal and insecticidal activity were evaluated with regard to their use as wood preservatives.

Experimental Methods

Synthesis of quaternary ammonium TPBs and quaternary ammonium tetrafluoroborates

Quaternary ammonium TPBs were synthesized through the reaction of 1 mol of TPB sodium aqueous solution and 1 mol of quaternary ammonium compound (Lin et al. 2001).

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The reaction was enhanced by stirring the mixture at 80°C for 3 hours. The crude products were precipitated upon cooling and then collected by filtration and recrystallization by acetone.

Quaternary ammonium tetrafluoroborates were synthesized through the reaction of 1.1 mol of tetrafluoroborate sodium aqueous solution and 1 mol of quaternary ammonium compound. The reaction was enhanced by stirring the mixture at room temperature for 3 to 5 hours. The crude products were extracted by ethyl acetate and then dehydrated by anhydrous sodium sulfate overnight. Finally, the products were obtained through filtration and subsequent evaporation of the solvent.

The quaternary ammonium compounds used were DDAC and BAC for each type.

Wood specimens and treatment

Sapwood of masson pine (*Pinus massonina*) was obtained from Anhui Province, China. The dimensions of specimens prepared for the impregnation treatment were 20 mm (tangential [T]) by 20 mm (radial [R]) by 20 mm (longitudinal [L]) for the leaching test; 20 mm (T) by 20 mm (R) by 10 mm (L) for the decay test; and 25 mm (T) by 25 mm (R) by 6 mm (L) for the termite resistance test.

Specimens were oven dried at 60°C for 72 hours and weighed. Six specimens were used for each treatment condition. After being kept under vacuum (8×10^3 Pa) for 30 minutes at room temperature, wood specimens were submerged in the borate solutions and maintained there at atmospheric pressure for 30 minutes. After treatments, specimens were reweighed to determine uptake of borate retention. The specimens were reconditioned at 20°C and 50 percent relative humidity for 2 weeks.

Leaching procedure

The leaching test was done according to American Wood Protection Association (AWPA) Standard E11-06 (AWPA 2010) with a minor modification. Four specimens per treatment were immersed in a beaker containing 100 mL of distilled water, and a vacuum (8×10^3 Pa) was applied for 20 minutes. After the vacuum was released, the specimens were kept in the distilled water at room temperature for 6 hours. The water was then exchanged with fresh water in which the specimens were kept for another 24 hours. This procedure was repeated for a total of 14 days. Boron content in the collected water was determined by inductively coupled plasma analysis.

Test of inhibition zone

A white-rot fungus *Phanerochaete chrysosporium* (PC) and brown-rot fungus *Gloeophyllum trabeum* (GT) were used. According to the test method from the Drug Compendium Appendix XI A of China (Drug Compendium Committees 2000), 6-mm filter papers were sterilized in petri dishes and then fully soaked in fungicidal formulations. Excess formulation was removed, and the treated filter papers were put into petri dishes containing potato dextrose agar (PDA). The surface of the media and the filter paper were fully covered with 1 percent (based on PDA weight) spore suspensions of the respective fungi. The petri dishes were then cultivated at 26°C to 28°C. After the fungus grew for 2 to 3 days and the hyphae were visible, the diameters of the inhibition zones were measured and calculated on the three replicates (petri dishes) for each formulation at each concentration test.

Termite resistance test

Untreated and treated wood specimens were exposed to subterranean termite (*C. formosanus*) according to the Japan Wood Preserving Association (JWPA) Standard JWPS-TW-P.1 (JWPA 2001). The test specimens were placed at the center of the plaster bottom of a cylindrical test container (60-mm diameter and 90-mm height). Three hundred sixty *C. formosanus* workers and 40 soldiers were introduced into each test container. The assembled containers were kept in a conditioning room with 25°C to 28°C and 75 to 80 percent relative humidity for 1 month. At the end of the test, the number of dead termites was recorded and weight losses of specimens were calculated.

Decay test

Treated and control specimens were exposed to the white-rot fungus *C. versicolor* (CV) and the brown-rot fungus GT according to Chinese Standard LY/T 1283-1998 (State Forestry Administration of the People's Republic of China 1998).

Fungal cultures were prepared by dissolution of 40 g of malt extract and 20 g of agar-agar in a 1,000-mL glass jar with distilled water. Glass jars were filled with about 70 mL of malt-agar medium and sterilized at 121°C for 20 minutes. The fungal strains were introduced on the sterilized solid medium. Wood specimens were sterilized by gamma ray introduced into the jars on a completely mycelium-covered surface. Jars were then placed in a 20°C, 70 percent relative humidity conditioning room for 16 weeks. Six replicates were done for each decay fungus and treatment.

Results and Discussion

Compounds confirmation

Each of the target compounds was confirmed by micro-elemental analysis. Elemental analysis determines the amount of an element in a compound. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis). It is accomplished by combustion analysis in which a sample is burned in an excess of oxygen, and various traps collect the combustion products—carbon dioxide, water, and nitric oxide. The masses of these combustion products can be used to calculate the composition of the unknown sample. Calculated values for didecyldimethyl ammonium TPB (DP) ($C_{46}H_{68}NB$) were C 85.55, H 10.61, N 2.17, and B 1.67. Measured values were C 85.83, H 10.67, N 2.27, and B 1.23. The melting point ranged from 90.58°C to 90.98°C.

Calculated proportions for benzyldodecyldimethyl ammonium TPB (BP) ($C_{45}H_{58}NB$) were C 86.65, H 9.37, N 2.25, and B 1.73, and measured proportions were C 86.78, H 9.41, N 2.22, and B 1.59. The melting point was 140.08°C to 141.38°C.

Calculated proportions for DBF ($C_{22}H_{48}NBF_4$) were C 63.91, H 11.70, N 3.39, and BF_4 21.00, and measured proportions were C 63.41, H 11.43, N 4.07, and BF_4 21.09. DBF is viscous liquid at room temperature.

Calculated proportions for BBF ($C_{21}H_{38}NBF_4$) were C 64.45, H 9.79, N 3.58, and BF_4 22.18, and measured proportions were C 64.35, H 9.39, N 4.28, and BF_4 21.98. The melting point for BBF was 77°C.

Boron leachability

The boron leaching rate was less than 6.7 percent for DP- and BP-treated wood, while it was about 57.8 to 59.0 percent for DBF-treated wood and 23.3 to 35.0 percent for BBF-treated wood (Table 1). The results also showed that the higher the retention of a formulation in the wood, the lower the boron leaching rate from the wood. DP and BP had a much lower leaching rate than DBF and BBF, possibly because of the low water solubility of DP and BP.

A two-stage treatment, first with TPB sodium salt solutions and then with 2.0 percent tetramethylammonium bromide or KCl solutions, showed generally excellent leaching resistance (5% to 12%; Lin et al. 2001). However, the high cost of retreating and rehandling wood in two stages makes the commercial use of multistage processes unattractive.

In earlier studies, DDAC was added to the borate solution to protect the lumber against stain and mold during the short diffusion storage or on rewetting in service. Since DDAC and BAC are surfactants that can decrease surface tension and improve the wettability of wood, they can also increase penetration of borate (Morris and Byrne 1997). Because DBF and BBF have the same cations as DDAC and BAC, respectively, it is anticipated that they will increase penetration of tetrafluoroborates into the wood as the surface tension is decreased. DBF contains fluoroborate ion in its structure, which is known to be more resistant to water than the chlorine found in DDAC.

Test of inhibition zone

The antifungal activity was evaluated through measure of the inhibition zone diameter (in millimeters). All four formulations appeared to be effective for inhibiting the two decay fungi at a concentration of 1 percent (Table 2). DP was effective at inhibiting GT and PC at the 1 percent concentration, but it was not effective against PC at the concentrations of 0.01 and 0.1 percent. BP only inhibited GT and PC at the higher concentration of 1 percent. DBF and BBF could inhibit both fungi at all test concentrations.

Previous studies showed that the fixation of boron may prevent leaching, but it may also result in loss of biological efficacy (Lloyd et al. 1990). DBF and BBF had partial fixation, which may conserve sufficient mobility to maintain fungicidal activity.

Table 1.—Boron leaching rate.

Preservative[a]	Concentration (%)	Retention, mean ± SD (kg/m^3)	Boron leaching rate, mean ± SD (%)
DP	2.0	10.5 ± 0.5	2.7 ± 0.3
	1.0	5.1 ± 0.2	6.7 ± 0.8
BP	2.0	10.2 ± 0.4	2.1 ± 0.5
	1.0	4.9 ± 0.2	5.9 ± 0.9
DBF	2.0	12.1 ± 0.6	57.8 ± 3.9
	1.0	6.2 ± 0.3	59.0 ± 4.2
BBF	2.0	12.5 ± 0.5	23.3 ± 2.6
	1.0	6.8 ± 0.1	35.0 ± 3.1

[a] DP = didecyldimethyl ammonium tetraphenylborate; BP = benzyldodecyldimethyl ammonium tetraphenylborate; DBF = didecyldimethyl ammonium tetrafluoroborate; BBF = benzyldodecyldimethyl ammonium tetrafluoroborate.

Table 2.—Antifungal activity of the borate compounds by inhibition zone.[a]

Preservative	Concentration (%)	Diameter of inhibition zone, mean ± SD (mm)	
		GT	PC
DP	0.01	8.9 ± 0.2	0.0 ± 0.0
	0.10	17.9 ± 0.4	0.0 ± 0.0
	1.00	17.5 ± 0.7	10.1 ± 0.3
BP	0.01	0.0 ± 0.0	0.0 ± 0.0
	0.10	0.0 ± 0.0	0.0 ± 0.0
	1.00	22.5 ± 1.0	14.7 ± 0.5
DBF	0.01	13.4 ± 1.3	15.6 ± 0.8
	0.10	26.2 ± 0.8	21.6 ± 1.1
	1.00	33.1 ± 1.4	27.4 ± 0.9
BBF	0.01	11.4 ± 0.7	12.8 ± 0.6
	0.10	41.5 ± 0.4	20.3 ± 0.8
	1.00	55.6 ± 2.1	23.6 ± 1.2

[a] GT = *Gloeophyllum trabeum*; PC = *Phanerochaete chrysosporium*; DP = didecyldimethyl ammonium tetraphenylborate; BP = benzyldodecyldimethyl ammonium tetraphenylborate; DBF = didecyldimethyl ammonium tetrafluoroborate; BBF = benzyldodecyldimethyl ammonium tetrafluoroborate.

Termite resistance test

All treated wood specimens showed higher termite mortality than the untreated samples (Table 3). Termite mortality decreased when the retention of the preservatives decreased. Ammonium TPBs showed less termite resistance than ammonium tetrafluoroborates.

Kartal et al. (2004) evaluated the effect of 2 percent DBF incorporated with acryl-silicon–type resin emulsion on decay and termite (*C. formosanus*) resistance. It was found that only a high concentration of the preservative solution (2%) could provide partial protection against the termites. The higher termite mortality was observed in the specimens treated with higher concentration solutions. These results suggest that this preservative solution is a slow-acting preservative and may act as termite repellent rather than a termiticide (Kartal et al. 2004, 2005; Hwang et al. 2006).

Decay test

The antifungal activity of the TPB compounds, as measured by inhibition zones, were quite weak, so they were not included in the decay test. The average weight loss of masson pine sapwood samples treated by DBF and BBF solutions was 1.4 to 2.6 percent (by GT) and 2.5 to 3.8 percent (by CV) with retention around 7.0 kg/m^3, while the average weight loss of BAC-treated sapwood was 11.5 percent (GT) and 9.7 percent (CV) with a similar retention (Table 4). The average weight loss of untreated wood was 60.7 percent (GT) and 43.1 percent (CV).

These data suggest that DBF and BBF preservatives in treated wood with retentions of 7.0 kg/m^3 or greater could protect wood used outdoors against both fungal decay and termite attack. For further study, other properties such as toxicity to mammals and field tests of DBF and BBF should be examined before their commercial use.

Conclusions

1. A series of quaternary ammonium TPB and quaternary ammonium tetrafluoroborate were synthesized. The

Table 3.—Results of laboratory termites test.[a]

Preservative[b]	Retention (kg/m^3)	Termite level[c]	Weight loss (%)	Mortality rate of termites (%)
DP	26.0 ± 1.2	8.5 ± 0.5	13.8 ± 0.3	100.0 ± 0.0
	8.9 ± 0.5	7.5 ± 0.4	16.9 ± 1.0	99.3 ± 0.2
BP	18.8 ± 0.8	8.5 ± 0.6	13.3 ± 0.4	100.0 ± 0.0
	6.8 ± 0.3	7.0 ± 0.3	25.6 ± 1.2	96.6 ± 0.5
DBF	22.9 ± 0.9	10.0 ± 0.0	8.6 ± 0.6	100.0 ± 0.0
	9.8 ± 0.1	9.7 ± 0.2	10.2 ± 0.2	98.1 ± 0.1
	4.8 ± 0.1	8.3 ± 0.2	12.8 ± 0.5	87.9 ± 1.4
BBF	23.9 ± 0.8	10.0 ± 0.0	8.9 ± 1.0	100.0 ± 0.0
	10.1 ± 0.3	9.5 ± 0.0	10.8 ± 0.3	96.9 ± 0.8
	6.1 ± 0.1	8.0 ± 0.5	12.0 ± 0.6	82.7 ± 1.2
BAC	21.9 ± 0.6	10.0 ± 0.0	8.7 ± 0.7	100.0 ± 0.0
Untreated control	—	4.0 ± 0.8	30.3 ± 1.6	37.8 ± 4.9

[a] Values are means ± standard deviations.
[b] DP = didecyldimethyl ammonium tetraphenylborate; BP = benzyldodecyldimethyl ammonium tetraphenylborate; DBF = didecyldimethyl ammonium tetrafluoroborate; BBF = benzyldodecyldimethyl ammonium tetrafluoroborate; BAC = benzyldodecyldimethyl ammonium chloride.
[c] Termite level: 10 = nonvisible destruction in the surface of the specimen; 8 = moderate destruction, the area of destruction in a transverse section of the specimen is 3 to 10 percent; 4 = serious destruction, the area of destruction in a transverse section of the specimen is 50 to 75 percent.

Table 4.—Result of laboratory decay test.[a]

Preservative	Concentration (%)	Retention, mean ± SD (kg/m^3)	CV weight loss, mean ± SD (%)	GT weight loss, mean ± SD (%)
DBF	1.0	7.0 ± 0.1	2.5 ± 0.2	1.4 ± 0.0
	2.0	14.8 ± 0.3	0.3 ± 0.0	0.0 ± 0.0
BBF	1.0	7.2 ± 0.2	3.8 ± 0.1	2.6 ± 0.1
	2.0	14.8 ± 0.3	3.2 ± 0.2	1.2 ± 0.0
BAC	1.0	6.6 ± 0.1	9.7 ± 0.5	11.5 ± 0.4
Untreated	—	—	43.1 ± 3.8	60.7 ± 5.9

[a] CV = *Coriolus versicolor*; GT = *Gloeophyllum trabeum*; DBF = didecyldimethyl ammonium tetrafluoroborate; BBF = benzyldodecyldimethyl ammonium tetrafluoroborate; BAC = benzyldodecyldimethyl ammonium chloride.

compounds were confirmed by micro-elemental analysis and melting points.

2. The laboratory leaching results showed that boron leaching rate for wood treated with quaternary ammonium TPB formulations was less (2.1% to 6.7%) than wood treated with quaternary ammonium tetrafluoroborate formulations (23.3% to 59.0%).
3. Quaternary ammonium tetrafluoroborates inhibited test fungi at all test concentrations in a laboratory inhibition zone test, while quaternary ammonium TPBs showed a smaller inhibitory effect on the two fungi tested.
4. Quaternary ammonium TPBs showed partial termite resistance in all tested retentions. A higher retention level of quaternary ammonium tetrafluoroborates (>10 kg/m^3) appeared to have complete termite resistance.
5. At a retention level of about 7.0 kg/m^3, the weight loss of masson pine sapwood treated with quaternary ammonium tetrafluoroborate solutions was less than 3.0 percent.

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Literature Cited

American Wood Protection Association (AWPA). 2010. Standard method of determining the leachability of wood preservatives. AWPA E11-06. *In:* Annual Book of AWPA Standards 2010. AWPA, Birmingham, Alabama. pp. 393–395.

Drug Compendium Committees in Ministry of Health of the People's Republic of China. 2000. The Antibiotics Microorganism Method. Drug Compendium of the People's Republic of China. Appendix XI of Second part. People's Medical Publishing House, Beijing.

Hwang, W. J., S. N. Kartal, and Y. Imamura. 2006. Evaluation of new quaternary ammonium compound, didecyldimethylammonium tetrafluoroborate (DBF) in comparison with DDAC: leachability and termite resistance tests. *Eur. J. Wood Wood Prod*. 64(2):111–116.

Japan Wood Preserving Association (JWPA). 2001. Laboratory test method to evaluate effectiveness of termiticides for pressure treatment and performance requirements of the treated materials. JWPS-TW-P.1. JWPA, Tokyo.

Jin, L. and K. Archer. 1991. Copper based wood preservatives: Observations on fixation, distribution and performance. *Proc. Am. Wood Preserv. Assoc*. 87:169–184.

Kartal, N. S., W. Hwang, and Y. Imamura. 2005. Preliminary evaluation of new quaternary ammonia compound, didecyl dimethyl ammonium tetrafluoroborate for preventing fungal decay and termite attack. IRG/WP 05-30375. International Research Group on Wood Protection Secretariat, Stockholm.

Kartal, N. S., W. Hwang, K. Shinoda, and Y. Imamura. 2004. Decay and termite resistance of wood treated with boron-containing quaternary ammonia compound, didecyl dimethyl ammonium tetrafluoroborate (DBF) incorporated with acryl-silicon type resin. IRG/WP 04-30334.

International Research Group on Wood Preservation Secretariat, Stockholm.

Lin, L., T. Furuno, and S. Katoh. 2001. Leachability and decay resistance of tetraphenylborate salt- treated wood. *Holzforschung* 55:355–357.

Lloyd, J. D., D. J. Dickinson, and R. J. Murphy. 1990. The probable mechanisms of action of boric acid and borates as wood preservatives. IRG/WP/90-1450. International Research Group on Wood Preservation Secretariat, Stockholm.

Morris, P. I. and A. Byrne. 1997. The effect of DDAC on the penetration of borates into western hemlock. *Forest Prod. J*. 47(4):71–73.

Obanda, D. N., T. F. Shupe, and H. M. Barnes. 2008. Reducing leaching of boron-based wood preservatives—A review of research. *Bioresour. Technol*. 99:7312–7322.

Rainer, J. B. 1993. Borates as wood preservatives—An environmental, health and safety perspective. IRG/WP 93-50001-03. International Research Group on Wood Preservation Secretariat, Stockholm.

State Forestry Administration of the People's Republic of China. 1998. Method of laboratory test for toxicity of wood preservatives to decay fungi. LY/T 1283-1998. State Forestry Administration of the People's Republic of China, Beijing.