Synthesis and Evaluation of Dioctylaminoborate in Wood for Brown Rot Decay Protection

George C. Chen
Rebecca E. Ibach
USDA, Forest Service Forest Products Laboratory
Madison, Wisconsin

ABSTRACT

This study evaluated dioctylaminoborate in wood for fungal decay protection. Dioctylaminoborate was synthesized by refluxing dioctylamine and boric acid in 1:1 molar ratio in ethanol for 4 h. The product was characterized by proton Nuclear Magnetic Resonance Spectrophotometry (^{1}H- NMR) and Fourier Transform Infrared Spectrophotometry (FTIR).

Dioctylaminoborate prevented decay in loblolly pine (*Pinus Teada L.*) by the brown rot fungus, *Gloeophyllum trabeum (Gt)*. The leached specimens with chemical retention of 12.6% had weight loss of 1% by *Gt.* The non-leached specimens with chemical retention of 3.3% had weight loss of 0% by *Gt.* The control had a weight loss of 51.1% by *Gt.* Leaching of treated blocks decreased decay resistance to *Gt,* which required 12.6% to be effective.

Keywords: Dioctylaminoborate, fungal decay protection, synthesis.

INTRODUCTION

Boron compounds including boric acid, disodium tetraborate (borax) and disodium octaborate (DOT) are broad spectrum biocides (Pickard 1948), have low toxicity to mamals and aquatic life (Lloyd 1997), and have been used as fungicides, bactericides, herbicides, and fire retardants (Pickard 1948). The efficacy of boric acid and borates against wood decay fungi, termites, and fire are well established (Croft and Levy 1973; Lloyd 1997) and have 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 Norty America, and formulation of exterior and remedial treatments in Europe (Lloyd 1997). Because boric acid and borattes are water soluble, their uses for outdoor wood products are limited. Efforts to minimize borates leaching from wood products have been pursued for some time. These include impregnation of hydrophobic polymers such as polyethylene glycols, polyvinyl acetates and acrylic polymers (Murphy et al. 1995; Gezer et al 1999a; Williams and Bergstrom 2005), and forming complexes with copper ions (Johnson 1983; Johnson and Foster 1991). Howevcer, these borates remained leachable from the wood products.

In recent years, organoborates from albumin proteins (Thevenon et al 1997, 1998a, 1998b), borate esters (Carr et al. 2005) and aminoborates (Chen 2008) in treated wood after water leaching were effective against fungi in the laboratory soil-block fungal decay tests. This led to prepared dialkylaminoborate. The aminoborates may form stable, leach-resistant products in wood by introducing the hydrophobic dioctyl group. The aim of this study was to synthesize dioctylaminoborate and evaluate it in wood for fungal decay protection.

MATERIALS AND METHODS

Synthesis and characterization

Dioctylamine (22.76 g, 94.26 mmoles) and boric acid (5.83 g, 94,26 mmoles) in ethanol (200 ml) were refluxed for 4 h. Thin layer chromatography (silica gel 60 F254: RF 0.23, acetone) showed a complete conversion of dialkylamine to dioctylaminoborate in 3 h. The solvent was removed by a rotary evaporator to get the solid (25.59 g; 95.2%). The crude products were crystallized from acetone to give white crystals, mp. 146.5° to 148.5° C.

Dioctylaminoborate was charact4erized by an Advanced DPX250 Nuclear Magnetic Resonance Spectrophotometer (NMR), (Bruker Biospin Corporation, Biollerica, MA) using methanol-d4 (deuterium

methanol) as a solvent and a Galaxy series 5000 Fourier Transform Infrared Spectrophotometer (FTIR) (Unicam, UK) using KBr pellets.

Fungal Decay Tests

Impregnation

Four concentrations (0.5, 3.2, 6.4, and 12.9%) of dioctylaminoborate in methanol and boric acid in water were impregnated into wood by vacuum impregnation. The boric acid treated blocks were used as a comparison. Methanol was used as a solvent for dioctylaminoborate because of a lower boiling point than ethanol and distilled water for boric acid. For each concentration, 12 loblolly pine sapwood blocks were used for fungal decay tests. The treatment with one concentration for the fungal decay test is described below.

Twelve loblolly pine 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 500-ml bottle in a desiccator under vacuum at 1.07–1.33 kPa for 30 min and then impregnated with one of four concentrations. After impregnation, the pressure was released. The treated blocks were soaked in respective solvents for 24 h. The blocks were then removed from the solution. The excess solution was wiped off and the blocks weighed to determine the amount of solution absorbed. The blocks were then air-dried for 3 days under a chemical hood. Leaching of the blocks (6 blocks per concentration; 300 ml, 50 ml/block) was carried out according to AWPA M10-77 Standard (AWPA 1989) with replacement of water for 6, 24, 48, and then every 24 h for 2 weeks. The leached and non-leached specimens were conditioned at 27° C and 30% RH for 3 weeks and weighed before fungal decay tests.

Chemical retention of the block is expressed as a percentage of chemical absorbed by the block. Retention of chemical in wood for fungal decay tests is based on the solution absorbed by the block. Nonlinear regression analysis could not be used (Steel and Torrie 1960; Nance and Amburgey 1976; Gezer et al. 1999b) because too few data points (4 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 the evaporation of extractives from wood.

RESULTS AND DISCUSSIONS

Synthesis and Characterization

Dioctylaminoborate was synthesized by refluxing dioctylamine and boric acid in 1:l molar ratio in ethanol for 4 h. A complete conversion of boric acid to dioctylaminoborate was reached after 3 h of reaction as shown by proton NMR and FTIR.

Proton NMR of dioctylaminoborate in methanol-d4 (deuterium methanol) showed the following characteristic protons (Figure 1): a triplet of methyl protons at 0.8 to 1 ppm, a singlet of six methylene protons at 1.4 ppm, a triplet of a-methylene protons adjacent to amino group at 2.6 to 2.85 ppm, and a singlet of 2 hydroxyl protons at 4.95 ppm.

FTIR of dioctylaminoborate in KBr (Figure 2) showed an intense absorption at 1350-1310 cm^{-1} attributable to the stretching of B-O bond and a strong absorption at 1468 cm^{-1} attributable to the stretching of B-N bond (Colthup et al. 1964).

The above Proton NMR and FTIR analysis indicated that dioctylaminoborate was formed by refluxing dioctylamine and boric acid in ethanol.

Fungal decay tests:

Soil-block fungal decay tests showed that dioctylaminoborate in wood prevented decay by the brown-rot fungus, *Gt* (Table 1). The non-leached specimens with chemical retention of 3.3% wood had weight loss of 0% and leached specimens with chemical retention of 12.6% had weight loss of 1%. Leaching of treated wood decreased decay resistance. Boric acid treated wood with chemical retention of 3.2% had weight loss by *Gt* of 0.1%, for non-leached specimens. The results indicate that dioctylaminoborate in wood was more effective than that of boric acid based on molar ratio. The control had 51.1% weight loss by *Gt,* and the solvent methanol had weight loss by *Gt* of 43.4%, indicating that solvent did not affect the decay tests. The above decay tests indicated that dioctylaminoborate in wood remained leachable. Additional research is

needed to prepare more stable and leach-resistant organoborates by increasing the hydrophobic property of the dialkyl groups from C8 to C16.

CONCLUSIONS

Dioctylaminoborate can be synthesized by refluxing dioctylamine and boric acid in ethanol as evidenced by proton NMR and FTIR analyses. Wood impregnated with dioctylaminoborate is as effective as that of boric acid against the brown rot fungus *Gt.* Leaching decreases decay resistance to a great extent. Additional research is needed to prepare more stable and leach resistant organoborates by increasing the dialkyl groups from C8 to C16.

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Table 1. Effect of dioctylaminoborate on weight losses of pine blocks exposed to *Gloeophyllum trabeum* in a 12-week soil-block fungal decay test.

Treatment"	Solution concentration (%)	Chemical retention (%)		Weight loss (%)[b] by *Gloeophyllum trabeum*			
		Non-leached	Leached	Non-leached		Leached	
Dioctylaminoborate	0.5	0.5	0.4	17.1	(1.6)	31.9	(4.3)
	0.7	3.3	3.1	0.0	(0)	16.1	(1.1)
	1.4	6.3	6.3	0.6	(0.1)	2.7	(0.5)
	2.8	12.6	12.6	1.7	(0.1)	1.0	(0.1)
Boric acid	0.1	0.1		20.2	(3.1)		
	0.7	0.9		0.1	(0)		
	1.4	1.8		0.4	(0.1)		
	2.8	3.4		1.7	(0)		
Solvent only (methanol)				43.4	(3.8)		
Control				51.1	(2.3)		

a. Dioctylaminoborate: methanol as a solvent; boric acid: distilled water as a solvent.
b. Average of five replicates, parenthesis are standard deviation.

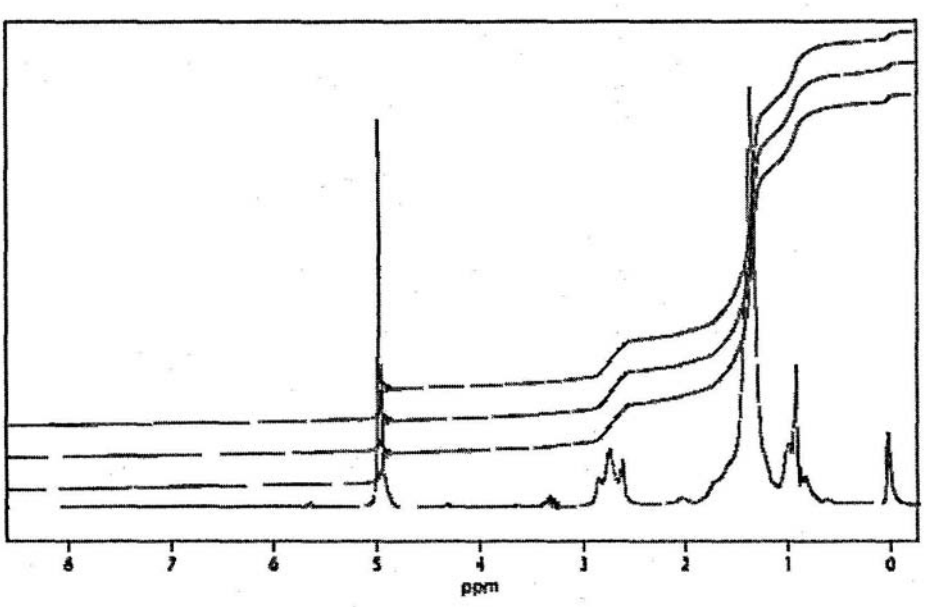

Figure 1. Proton nuclear magnetic resonance (^{1}HNMR) spectra of dioctylaminoborate.

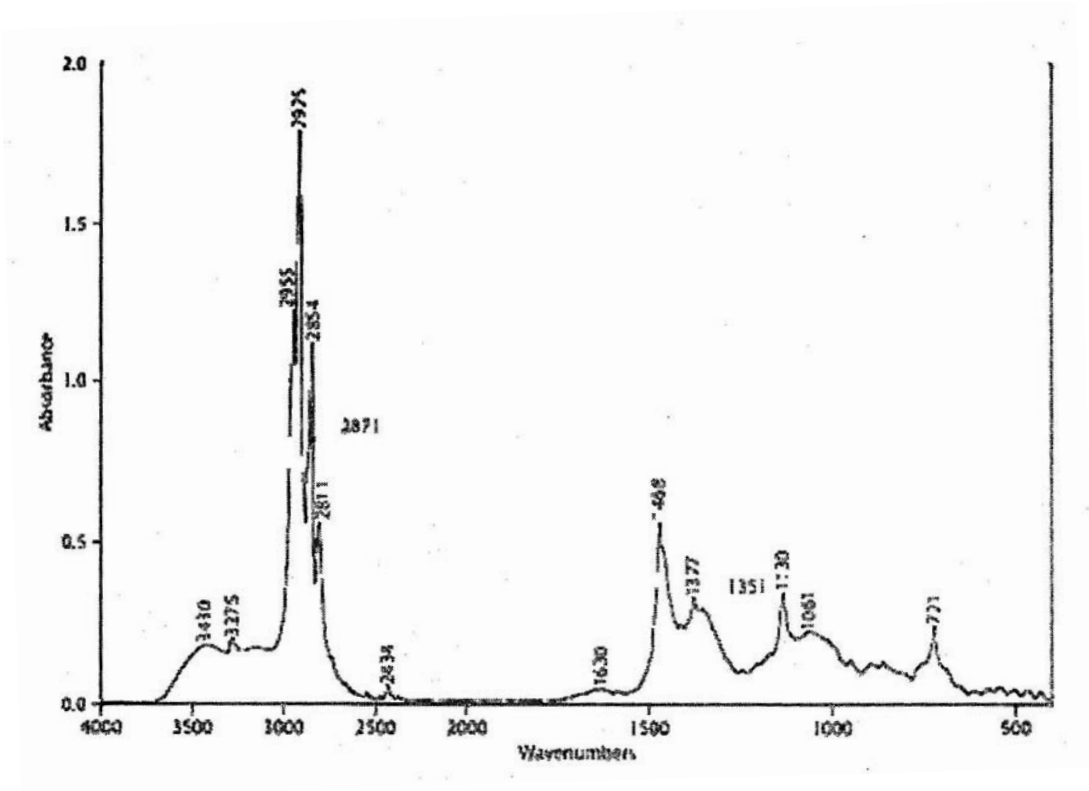

Figure 2. Fourier transform infrared (FTIR) spectra of dioctylaminoborate.

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