

A Critical and Comprehensive Review of Boron in Wood Preservation

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ABSTRACT

Borates have played an ever-increasing role in the preservation of wood worldwide and especially in the USA since the voluntary cancellation of CCA for residential lumber use patterns in 2004. However, there has not been a review of the efficacy and performance of borates, especially Disodium Octaborate Tetrahydrate, outside of the AWWA Data Package submitted by Nicholas and Preston in 1988 and the Review by Drysdale in the IRG literature in 1994. The purpose of this publication is to have, in one location, the commonly referred to efficacy information on borates in wood preservation.

Keywords: Borates, efficacy, performance, leaching, depletion, toxicity, corrosion, environmental

INTRODUCTION - INORGANIC BORON

Elemental boron does not occur naturally, but combines with oxygen in a salt or ester of boric acid. Over 200 borate minerals exist but very few are commercially significant. Borates are used in the manufacture of fiberglass insulation, detergents, fertilizers, flame retardants, and wood preservatives. Inorganic borates have been used as wood preservatives for many years. Boric acid and borax were the first two to be used as preservatives and were constituents of several Celcure mixtures patented in 1933 (Cockcroft and Levy 1973). Borates available today offer a highly effective and flexible option for both stand alone and more specialized formulations and have received considerable attention in recent years. They include formulations prepared from sodium tetraborate, sodium pentaborate and boric acid, but the most common form is disodium octaborate tetrahydrate (DOT). DOT has the most widespread commercial use in North America (Groenier and Lebow 2006). It has higher water solubility allowing the use of higher concentrations and increasing mobility in wood (Lebow 2007).

The commercial potential of borate treatments was first identified in the 1930's. Interest in standalone borates as wood preservatives first arose in Australia and New Zealand where borates were recommended for insect control (Drysdale 1994). The first industrial treatments were carried out in 1949 using rapidly diffusing borate mixtures. Boron treatment was approved for exterior, above ground use in New Zealand in 1958. Borates were previously viewed as ineffective because the chemical was not fixed in wood. This limited the development and acceptance, of borates treatments to specific end uses and timber commodities (Drysdale 1994). Over the last two decades researchers have refocused on boron, due to the quest for a more operator and environmentally friendly, yet cost effective preservative (Barnes et al., 1989; Drysdale 1994) with studies more focused on improvements to the application methods and inclusion of borates in remedial treatments. Research continues to develop borate formulations that have increased resistance to leaching while maintaining biocidal efficacy (Lake and McIntyre 2006, Robinson et al. 2005). Borates are durable, do not breakdown into ineffective products, do not evaporate and although soluble, they do not

migrate far in soil (Currie 1997). Borate- treated wood is also odorless, colorless, and may be painted or stained.

Today borates have gained worldwide acceptance in vacuum pressure treatments and envelope treatments to construction timber. More recently finished joinery treatments have been commercialized using double vacuum technology and is now of particular interest where concern against organic solvent preservatives is increasing (Schoeman and Lloyd 1998). Current standards (AWPA 2008) allow for borates in above-ground environments protected from rain wetting. Due to their broad spectrum fungicidal and insecticidal action, borates are considered more effective than copper and zinc, with the later two performing better only because of their fixation in wood, not their inherent fungicidal activity (Lloyd et al. 2001).

DISODIUM OCTABORATE TETRAHYDRATE (DOT)

DOT is a stable, white, odorless, powdered chemical substance that is not flammable, combustible, or explosive and has low acute oral and dermal toxicity. The product itself is a flame retardant. It is sold under 'TIM-BOR®' ($\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$) and or 'BORA CARE®' (40% DOT in ethylene glycol) brands in the United States. 'SOLUBAR®' contains 98% DOT. DOT has a bulk density of 320- 480 kg/m³, a negligible vapor pressure at 20°C, solubility in water is 9.7% at 20°C, 34.3% at 50°C, melting point is 815°C, pH at 20°C is 8.3 (3 % solution) and 7.6 (10% solution) (MSDS 2007). For ease of comparison, boron compounds are often compared based on the "Boric Acid Equivalent" (BAE) which obviously is the amount of boric acid that could be formed from the subject compound. BAE is a standard unit of comparison of efficacy among borate compounds. Another standard unit of comparison that is typically used to express retentions in North America is "B₂O₃" or as Boric Oxide. A last convention is that in Australasia where the retentions are expressed as per cent on a mass/mass basis where the denominator is the mass of oven dried wood.

DOT has a higher solubility than borax and boric acid and contains more boron or B₂O₃ than either per unit mass. Boric acid contains 17.48% boron, borax has 11.4% while DOT (as TIMBOR) has 20.9%. Inorganic borates are diffusible, and with appropriate treating practices, can achieve excellent penetration in species that are difficult to treat with other preservatives. However, the borate in the wood remains water soluble and hence they are standardized by the AWPA for only applications not directly exposed to liquid water. Typical examples of satisfactory building construction use of DOT would be studs, rafters, sill plates (Nicholas and Preston 1988). Typical timber uses are described as framing or flooring used in dry or damp conditions (Drysedale 1994).

Strength test studies with borate treated wood shows that DOT does not degrade wood and in fact a slight increase in MOR values have been noted in borate treated wood (Nicholas and Preston 1988).

In termite studies, Tokoro and Su (1993b) estimated the oral toxicities (LD₅₀) of boric acid, TIM-BOR® and BORA-CARE® (40% DOT in ethylene glycol) and ethylene glycol (ca. 80% monoethylene and ca. 20% polyethylene glycol) and examined potential synergistic effects of the ethylene glycol in BORA-CARE® against *Coptotermes formosanus* and *Reticulitermes flavipes*. Boric acid is the least toxic for both termite species. Oral toxicities of BORA-CARE® were significantly higher (LD₅₀: 256.2 µg/g DOT and 304.9 mg/g BAE) than TIM-BOR® alone (LD₅₀: 408.2 µg/g DOT and 485.7 µg/g BAE); indicating a potential synergism of DOT by ethylene glycol in BORA-CARE®. Previous data indicated that the glycol carrier did not contribute significantly to the toxicity of the DOT/glycol mixture. Based on active ingredient DOT, BORA-CARE® was approximately 1.5 fold more toxic than TIM-BOR® for both termite species. At the highest concentration of ethylene glycol used 27% (w/w) there was insignificant termite mortality, showing no termiticidal effect. Hence ethylene glycol synergized DOT but the reason for the synergy is unknown.

Mechanism of action

In biological applications, boron is in the form of oxides as either boric acid or borates (Lloyd 1998). All borates convert to boric acid when they dissolve in acidic media such as in wood (pH 4-5). Boric acid in a 1% solution contains 0.56% B₂O₃; 1% borax contains 0.37% B₂O₃ while DOT (TIMBOR) contains 0.67% B₂O₃. Thus in treatment solutions one pound of DOT will deliver 0.67 pound B₂O₃ which is

equivalent to 1.195 pound boric acid equivalent (BAE). In solution boric acid acts as a Lewis acid accepting an OH⁻ to form the tetrahydroxyborate ion [B(OH)₄]⁻. The toxicity and therefore protection of timber is due to the complexation of [B(OH)₄]⁻ with polyols of biological significance in both wood attacking fungi and insects. The polyol compounds of biological significance include vitamins, co-enzymes with the oxidized co-enzymes NAD⁺, NMN⁺, NADP thought to be the most likely target (Lloyd 1998). Boric acid forms very stable complexes by rapid esterification and this has an effect on extracellular substrates, intracellular substrates, and membranes resulting in altered metabolism, interference with electron transport which eventually synthesis of protein, ATP or DNA/ RNA synthesis.

The efficacy of boron preparations depends mainly on the quantity of boron that is applied to wood irrespective of whether borax, boric acid or DOT is used. Concentration used determines boron content. To determine whether different borate salts elicit different responses in *C. formosanus*, workers were exposed to composite board samples of 0.88% zinc borate, 0.18% DOT, anhydrous boric acid and an untreated control. Activity and mortality data over 4 weeks suggested that the concentration of boron in the wood, rather than the associated salt, has an impact on termite feeding, and that anhydrous boric acid reduces termite feeding more rapidly than the other formulations tested (Gentz and Grace 2007). It is important that the form and formulation of the applied boron allows for the maximum production of free borate ions when in wood (Lloyd 1990; Lloyd 1998).

In termites, borates act as a stomach poison. Gut protozoa are susceptible, because boron is toxic to the cellulose-digesting organisms and leads to starvation of the host as well as systemic effects. Borates affect termites like a 'Bait toxicant'. Worker termites ingest small amounts of borates and transfer borate tainted food to other colony members leading to colony elimination. In addition borates exploit termites habit of keeping soil foraging tubes moist. Boron readily diffuses into moist soil tubes where many individuals contact boron and are discouraged from building more tubes or feeding (Williams 1997). Boron is toxic to termites even at 0.24% mass/mass (m/m) BAE and causes significant mortality, but termites are not deterred from attacking the timber even at retentions >2.0% m/m BAE, because borates have no repellent action. Higher retentions do not completely eliminate the possibility of minor cosmetic damage. Borates allow termites to 'graze' causing slight cosmetic change but not result in structural failure in buildings (Grace and Yamamoto 1993; Lloyd 1998; Grace and Campora 2005; Campora and Grace 2007).

In field tests, termites have investigated, and then avoided, those locations where borate-treated (rather than untreated) wood pieces were placed (Grace and Campora 2005). In long-term (three to eight week) laboratory choice tests termites fed less on borate-treated pieces than untreated samples (Ahmed et al. 2004; Kartal et al. 2004). In field tests similar results have been reported, with borate-treated lumber fed on less by termites than their untreated counterparts (Tsunoda et al. 2000; Grace et al. 1995; Tokoro and Su 1993). Borates accumulate in wood surrounding termite galleries suggesting that borate diffusion may be enhanced by termite activities such as construction of galleries with moisture and contaminated wood (Tokoro and Su 1993).

Effect of type of borate salt and formulation

Tokoro and Su (1993) examined the termiticidal effects of 'TIM-BOR®', and BORA- CARE®, surface-treated wood against subterranean termites, *C. formosanus* Shiraki, and *R. flavipes*. The borate formulation type affects efficacy. Termite penetration and wood consumption is significantly slowed in borate treated wood. Termite mortality was significantly higher for BORA CARE® with 91.7% for *C. formosanus* and 94.7% for *R. flavipes* while 'TIM-BOR®' had 75.9% for *C. formosanus* and 67.5% for *R. flavipes*. Both formulations did not hinder penetration by termites but slowed it down compared to penetration in untreated wood.

Gentz and Grace (2007) determined whether different borate salts elicit different responses in *C. formosanus* by exposing termite workers collected from field colonies in Hawaii, to composite board samples treated with different borate salt formulations. The treatments included zinc borate (ZB) (0.88% and 0.18%), DOT (ZB and DOT in a 60/40 and 80/20 ratio), anhydrous boric acid (B₂O₃) (60/40 and 80/20 ZB/B₂O₃), and an untreated composite board control. Activity and mortality data recorded over a 4-week period suggest the concentration of boron in the wood sample, rather than the associated salt, has a greater impact on termite feeding, and that anhydrous boric acid reduces termite feeding more rapidly than the other formulations tested.

Using ICP-AES techniques, Gentz and Grace determined that DOT consumption resulted in slightly higher boron concentrations than boric acid (324.2 and 306.3 mean $\mu\text{g/g}$ boron, respectively), and ZB 0.88% (170.0 $\mu\text{g/g}$) was intermediate between those two treatments and the control (30.2 $\mu\text{g/g}$). The DOT and B2O3 treatments were an order of magnitude greater than the composite board control.

Efficacy against Insects

DOT as an insecticide is effective against a wide variety of wood destroying insects including: powderpost beetles (Lyctidae) (Williams 1997); furniture beetles (Anobiidae); old house borers; longhorn beetles (Cerambycidae); subterranean termites (Reticulitermes, Coptotermes, Heterotermes) (Tokoro and Su 1993; Grace and Yamamoto 1992; Grace and Yamamoto 1993; Kartal et al. 2003); dampwood termites (Zootermopsis); drywood termites (Kaloterms, Incisitermes); and carpenter ants (Camponotus) (Jonge 1987; Lloyd 1997; Drysdale 1984). Early research demonstrating the performance of borates carried out in Europe was concerned primarily with problems caused by Hyloterpes bajulus and Anobium punctatum. Today a major use of borates is for protection susceptible sapwoods against Lyctus borers and Anobium attack.

In New Zealand, to protect against Anobiids a minimum of 0.1% BAE for softwoods and 0.2% BAE for hardwoods on a dry wood basis of the core (the central one ninth of the cross-sectional area) is recommended. Approximately double this level is required for control of Lyctids (Schoeman and Lloyd 1998). The toxicity threshold of boric acid for egg larvae of Hyloterpes bajulus is 0.3-0.4 kg/m^3 . The values are somewhat lower in the case of the egg larvae of Anobium punctatum. Because borates act as stomach poisons, they have a very slow effect on the larvae of both beetle species because the larvae are able to survive a period of four weeks without any food intake. 0.36 kg/m^3 boric acid is sufficient to achieve 100% extermination of Hyloterpes bajulus. Against larvae of Anobium punctatum, 100% extermination is achieved with 0.043% BAE.

In recent years there has been an increased interest in boron treatments as an option for protection of structural timbers used in termite risk areas. Drysdale (1994) reviewed efficacy data for both fungi and termites relevant to this end-use. Borates are used for protection of new construction as either a stand alone treatment or as a supplement to soil treatment against termites. A retention higher than that needed to control boring beetles is usually needed for the control of termites (Table 1)

Table 1. Biological reference values for DOT as determined by EN tests

Test/target organism(s)	Retention		
	DOT, kg/m^3	DOT, pcf	%BAE
EN113/Basidiomycetes	0.8	0.05	0.16
EN20-2/Lyctus	1.0	0.063	0.20
EN47/Hyloterpes	0.7	0.044	0.14
EN49-2/Anobium	0.3	0.019	0.06
EN117/Termites	5.6	0.35	1.12
EN330/L-Joint Field Test	0.8	0.05	0.16

(Schoeman and Lloyd 1998)

Termite testing of borates dates back several decades. Several workers report efficacy studies in Australia, North America and Hawaii. Borate efficacy data for termite control is influenced by variations in test methodology, timber species and termite species. Multiple exposure techniques have demonstrated borates effectiveness against Formosan termites (Grace et al., 1992; Grace et al., 1993) and are backed up

by other studies in various parts of the world (Grace et al., 1995; Grace et al., 1997; Peters and Fitzgerald 1997). Commercial retentions recommended for protection against termites are usually in excess of 1% BAE equal to 4.5 kg/m³ depending on timber density (Schoeman and Lloyd 1998).

Laboratory results indicate that the minimum treatment required to protect against termite attack and damage was >1.0% m/m BAE (Ahmed et al. 2004). A retention of 1.09% m/m BAE in Matai wood is required to eliminate *Nasititermes exitiosus*, while 0.05-0.11% BAE was required for *C. lacteus*. A higher retention of 0.46-0.56% w/w BAE was required for *C. acinaciformis*. *Nasititermes exitiosus* are more tolerant to borates than *Coptotermes* species. Control of dampwood termites (*Zootermopsis angusticollis*) has been achieved at a retention of 0.52-1.2 TIMBOR[®] (0.5% m/m BAE equivalent) and 0.15% m/m for the drywood termite (*Cryptotermes domesticus*) (Drysdale 1994). More recently there has been considerable interest in the control of *C. formosanus* and *R. flavipes* (the eastern subterranean termite) (Grace and Yamamoto 1992; Grace and Yamamoto 1993; Preston et al., 1985, 1986; Williams et al., 1990). Investigations have covered remedial type treatments and efficacy after treatment of refractory species e.g., Douglas fir heartwood (Drysdale 1994). A paper by Williams and Amburgey (1987) reports 0.3% m/m BAE for adequate protection against *R. flavipes* (Kollar) in pine in laboratory tests and >0.54% BAE is needed to protect *C. formosanus* (Kartal et al. 2003). Minimizing feeding damage by field populations of Formosan termites requires 2.0% BAE. A retention of 5 kg/m³ is required in South Africa while 6 kg/m³ in Hawaii against Formosan termites (Lloyd 1997).

In a rigorous field test protocol, Grace and Yamamoto (1993) pressure-treated Douglas-fir boards with DOT retentions of 0 (controls), 0.88, 1.23, 1.60, or 2.10% (m/m) and sequentially exposed them to four active field colonies of *C. formosanus* in an above-ground field test for 10 weeks in Hawaii. Samples were placed in contact with each colony for 10 weeks, with weight losses determined between exposures, for a total exposure period of 40 weeks. Feeding activity differed among termite colonies, with the controls having mean weight losses of 1.3-15.1% during each individual 10-week exposure. The two lower borate retentions (0.88 and 1.23% DOT) had virtually equal efficacy. Feeding was negligible at the two higher borate retentions (weight losses during each 10-week period ranging from 0.7-1.3% with 1.60% DOT, and 0.3-0.9% with 2.10% DOT. Total cumulative wood weight losses over the 40 week exposure were: 10.2% (0.88% DOT), 8.7% (1.23% DOT), 3.6% (1.60% DOT), and 2.4% (2.10% DOT). The degree of cosmetic damage was negatively correlated with DOT retention, with wood treated with the highest retention of 2.1% DOT (2.52% BAE) having extremely shallow feeding depressions ('termite tasting') on the wood surface and a cumulative weight loss of only 2.4% after 10 weeks. Increasing damage of DOT treated wood can occur from repeated exploratory attacks by different termite colonies, although each attack may be of brief duration, a scenario that may only occur over a period of many years for wood in service. Under conditions of high Formosan termite hazard, wood treated with greater than 1% DOT can be expected to provide protection from serious structural damage, higher retentions minimize although not completely eliminate the possibility of minor cosmetic damage to the wood surface (Grace and Yamamoto 1993).

Grace et al. (2006) report eight years of field study results from a protected above-ground field test in Hawaii simulating the large sill plate (dodai are typically 4 by 4 in. in cross section) used in Japanese housing construction. Field tests were established in Hawaii and Japan (both sites support active Formosan subterranean termites, *C. formosanus* Shiraki) to examine the efficacy of DOT at 2% and 3% BAE shell and through treatments. In Hawaii, CCA at 4 kg/m³ and ACZA at 4 kg/m³ were included in the test. DOT gave comparable performance to CCA and ACZA. All wood treatments performed well, with mean visual damage ratings ranging from 10 (ACZA) to 8.2 (DOT, 2% BAE shell treatment) on the AWP 0-10 scale after six years. Results supported the hypothesis of delayed deterrence from termite exposure to these non-repellent treatments. In contrast, untreated control boards were completely destroyed within two years. These results support the use of DOT, CCA or ACZA treatments to protect sill plates (dodai) from termite attack. Neither DOT nor CCA are repellent to termites, so minor damage is not unexpected. In the case of DOT, the lack of progression of attack beyond a rating of 7 after the second year of field exposure, despite the location of each of these samples within the test array immediately adjacent to untreated controls that were completely destroyed within a single year, is consistent with the "delayed deterrence" hypothesis.

In a similar test Tsunoda et al. (2006) simulated the sill plate of the Japanese houses at a the termite field test site in Japan where two economically important termite species [(*C. formosanus* Shiraki and *Reticulitermes speratus* (Kolbe)] are established. DOT treated hem-fir samples (*Tsuga heterophylla* and

Abies amabilis (Dougl.) of 4 x 4 x 20 in. (105 x 105 x 500 mm) size were placed on concrete blocks 7.5 in. (190 mm) above the ground surface and were protected from weather. The test samples were pressure treated at target levels of 2% BAE and 3% BAE. Samples were annually inspected for termite attack and decay and visually rated (AWPA standard). All treated samples remained free from decay after 10 years' exposure. Slight progress in termite attack was observed on a few treated samples including four samples with target retention of CCA 4 kg/m³. Treatment at 3% BAE performed as well as CCA 4 kg/m³ after 10 years with a mean rating of 9.5. Although mean ratings of termite attack on the treated samples ranged from 8.8 to 9.6, statistical analysis showed no significant differences among all treatments.

Peters and Fitzgerald (1998) conducted field assays with two Australian subterranean termites *Coptotermes acinaciformis* and the giant northern termite *Mastotermes darwiniensis* to determine response to borate treated slash pine *Pinus elliotti*. Wood blocks were placed in lunch boxes and attached to infected trees and responses determined by mass loss over 5-10 weeks. In another assay treated blocks were placed on concrete brick assemblies in above ground weather protected situations in an area with high termite hazard. There were apparent differences in the feeding behavior of the two termite species and total prevention of termite damage was not achieved. Borate retentions in excess of 1.2 and 1.4% BAE were necessary to prevent significant damage by *C. acinaciformis* and *M. darwiniensis*, respectively.

Borates are known to be good wood treatments, but many structures are built with non-wood materials. Smith and Lloyd (2004) evaluated the ability of borate glycols to prevent termite tubing over non-wood materials. Concrete was selected as a common inert construction material. Concrete was considered the most aggressive material to test, due to its high alkalinity and its ability to inactivate many termiticides, and the Formosan subterranean termite was selected because it is considered one of the most difficult termite species to control. Glycol borate treatment on concrete restricted the ability of termites to construct tubes. Exploratory tubes were less than 8 in. (200 mm) in length and the treatment caused near complete termite mortality. Glycol borates protect cellulosic materials within structures not built from wood. Over the last five years, the use of glycol borates has become widespread in the United States with over 150,000 homes now treated. It is also estimated that 15% of new construction treatments will be with glycol borates in 2004 (Smith and Lloyd 2004). Borates are toxic to termites when placed in soil, but removal by leaching prevents commercial soil treatments. It can be concluded from the results of this work that a termite toxic barrier can still be achieved in a structure in the absence of wood, by simply treating above ground foundation and other construction materials. Examples of non wood structures would include brick and block or concrete poured homes, or commercial buildings in many parts of the world.

While termites use wood as a food, carpenter ants do not; they create galleries to rear their young and forage outside the nest for food. This makes them difficult to control. They attack wood in a variety of environments, including pressure-treated wood. The threshold for carpenter ant deterrence remains unknown. 1.5% BAE on wood treated remedially with borates is effective at repelling carpenter ants (Lloyd 2003). For utility poles in areas of intense ant pressure, borate rods may deter ant infestation. Morrell and Schneider (1995) found borate levels of 0.94% BAE 8.9 in. (225 mm) away from the treated zone after one year in Douglas-fir poles treated with fused borate rods. These suggested that boron levels approach those necessary to repel carpenter ants. A spray test revealed reduced colony activity one month after treatment, and the colony appeared to be dead after 6 months with no evidence of reinfestation and one year (Mankowski 2007).

Efficacy against Fungi

The effectiveness of borates against basidiomycetes has been demonstrated in service and in laboratory studies by many workers. Organisms tolerant to copper, arsenate, pentachlorophenol, creosote and tri-butyl tin oxide have been tested against borates. These include *Coniophora puteana*, *Coriolus versicolor*, *Poria* spp., *Gloeophyllum trabeum* and *Lentinus lepidius*. Wood treated to a minimum retention of 3.2 kg/m³ (BAE) will be protected from both decay fungi and insects. Various studies have determined that 1.5 kg/m³ BAE is required to inhibit decay (McCutcheon et al. 1992). DOT is more effective than boric acid and borax against decay fungi because it contains a higher proportion of boron and the borate ion is more readily available (Jonge 1987).

As yet, no wood decaying basidiomycetes have been reported to be tolerant against borates at normal preservative retention (Dickinson and Murphy 1989; Amburgey 1990; Lloyd 1998; Schoeman and Lloyd

1998). No brown rot fungi are known to have developed resistance to boron although this can occur with copper or arsenic containing preservatives (Drysdale 1994). The data on efficacy of borates as fungicides date back 70 years ago. A toxic threshold from pure laboratory tests on pine species indicate a retention of <0.4% m/m BAE (2.0 kg/m³) will prevent the onset of decay by a number of fungal species. Findlay (1956) found a toxic threshold of 0.1-0.3% w/w BAE (0.5-1.6 kg/m³) in a wood block test method which tends to give lower values than those obtained by the soil block jar test. Baechler and Roth (1956) established a toxic threshold of 0.17-0.27% w/w BAE (<1.28 kg/m³) for southern pine in a soil jar test with three decay fungi while Jacquoit et al (1960) reported a 0.2-0.37% w/w retention to prevent decay in Scots pine blocks. A New Zealand study performed in 1960, showed a toxic threshold of 0.74 kg/m³ TIM-BOR[®] (0.9 kg/m³ boric acid) for pine to prevent decay of *Lentinus lepideus*, *Coniophora cerebella* and *Poria vaillantii* and 0.61-1.24 kg/m³ (0.1-0.2% m/m BAE) for *Lenzites trabea*. Williams and Amburgey (1987) found banak (*Virola* spp.) was protected from decay by 0.4-0.5% m/m.

As part of a research program on the potential use of borates by the Canadian wood products industry, Forintek initiated an L-joint test of untreated and borate-diffusion treated hem-fir (western hemlock and amabilis fir) in 1990. The treated material had a low initial retention of only 0.2% BAE. The borate treated L-joints showed no signs of decay for 7 years, and after 10 years only 12% showed signs of decay. None had failed. In contrast 93% of the untreated L-joints showed signs of decay after 10 years and two thirds had failed. These field test results confirm those obtained from practical experience, considering that the L-joint test represents a higher leaching and biodeterioration hazard than a window (Morris 2000).

Hedley (2006) gave results of a study on above ground tests of rail units and L-joints established at the NZ Forest Research Institute (now Scion) between 1967 and 1980 to monitor performance of boron treatment painted with a three-coat paint system in relation to that of untreated and CCA-treated timber. Results showed that even without any maintenance of the paint coats, boron treatment to retentions used at the time test were established considerably extended service life compared with that of untreated test units. After 35 years' exposure, painted boron treated rail units had a greater Index of Condition than unpainted CCA-treated units. Losses of boron from leaching were substantial in all tests, highly likely to have been the result of lack of maintenance of the paint coats. Dickinson and Murphy (2000) report results of a study of millwork (joinery) treated with borates 23 years ago and in service in residential flats and surveyed and analyzed for boron content. The levels of boron still present were sufficient to prevent decay. None of the windows surveyed showed any decay despite the fact that moisture and sapwood contents were conducive to decay.

Stand alone DOT has limited protection against molds (Micales-Glaeser et al. 2004). Borates have proven effective in controlling sapstain but not mold (Fungi imperfecti) (Buthcher and Preston 1978). Borates are more effective against staining fungi at high pH, hence DOT is less effective than borax or boric acid against staining fungi (Lloyd 1998). More soluble mixtures are used to achieve the normal commercial concentrations required and penetrate refractive species. Toxic thresholds for sapstain are 2.0 kg/m³ BAE. Only high concentrations of DOT 1.97% BAE noticeably retard mold growth in species such as *Cladosporium cladosporioides*, *Penicillium brevicompactum*, and *Stachybotrys chartarum* (Micales-Glaeser et al. 2004). Borates are less effective against molds because under conditions suitable for them, the wood is green or moist and contains large amounts of glucose and fructose, which complex with the boric acid making it unavailable to complex with the polyols of biological significance in the fungi (Lloyd et al. 1990).

The fungitoxic properties of chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, CTL) in an aqueous dispersion, DOT (40% glycol solution and a 98% wettable powder, and DDAC in an 80% was examined alone and in combination, against four molds commonly associated with indoor air quality problems: *Aspergillus niger*, *Cladosporium cladosporioides*, *Penicillium brevicompactum*, and *Stachybotrys chartarum*. DOT in both forms was very effective against *A. niger*, but provided only sporadic protection against other fungi and no single fungicide provided total control of all four fungi on wood. DOT (8.5 m/m %)+ DDAC (1.0 m/m %) totally prevented or greatly reduced growth of *A. niger*, *P. brevicompactum* and *S. chartarum*. *Cladosporium cladosporioides* was the most difficult organism to control, but even this was achieved when DDAC was increased to 1.0% with DOT. The most consistent control of discoloration, sporulation, and growth of the fungi was obtained with the combination of DOT and CTL. CTL provided the best single-agent protection (Micales-Glaeser et al. 2004).

Nicholas and Preston (1988) summarized toxic threshold values for borate treated wood against insects and fungi and the data is presented in Tables 2 and 3.

Table 2. Approx. toxic threshold values (BAE equivalent) for borate treated wood exposed to Fungi in the soil block test.

Wood	Fungus	Approximate toxic threshold	
		kg/m ³	lbs/ft ³
Southern Pine	<i>Lentinus lepideus</i>	1.3-1.9	0.08-0.121
Southern Pine	<i>Lentinus trabea</i>	1.-2.0	0.08-0.124
Southern Pine	<i>Poria vaporaria</i>	0.6-1.3	0.039-0.081
Oak	<i>Polystictus versicolor</i>	1.8-3.0	0.11-0.185
Oak	<i>Lenzites trabea</i>	1.8-2.9	0.11-0.184
Oak	<i>Poria vaporaria</i>	0.8-1.1	0.047-0.067
Oak	<i>Lentinus lepideus</i>	0.54-1.4	0.034-0.088
Oak	<i>Coniophora puteana</i>	0.5-0.73	0.033-0.045
Oak	<i>Serpula lacrymans</i>	0.4-0.5	0.025-0.031
Radiata Pine	<i>Coniophora cerebella</i>	0.7-1.4	0.045-0.09
Radiata Pine	<i>Poria vaporaria</i>	0.7-1.4	0.045-0.09
Radiata Pine	<i>Lenzites trabea</i>	1.4-2.2	0.09-0.135

(Source: Nicholas and Preston 1988)

Table 3. Approx. toxic threshold values (BAE equivalent) for borate treated wood exposed to insects

Wood	Insect	Test method	Approximate toxic threshold	
			kg/m ³	lbs/ft ³
Banak	<i>R. flavipes</i>	ASTM D 3345	1.9	0.12
Radiata Pine	<i>Anobium</i>	Observations from treated wood	0.2	0.01
Radiata Pine	<i>Lyctus</i>	Observations from treated wood	0.8	0.05
Corsican Pine	<i>Anobium</i>	Egg laying and larval survival	0.4	0.024
Corsican Pine	<i>Hylotrupes</i>	Newly hatched larvae	0.4	0.024
Southern Pine	<i>C. formosanus</i> and <i>R. flavipes</i>	Above ground	2.0	0.125

(Source: Nicholas and Preston 1988)

Standards and treatments methods

A variety of methods are used to apply borates depending on the required amount of borate to be delivered. Borates are diffusible and may be applied on freshly felled timber by brushing and spraying or pressure treatment. Active ingredients diffuse into wood using moisture available in wood or moisture brought in by insects like termites. Injection methods to inject liquid or foam are used primarily for termite infested wood. Paste like injection tubes are used to control wood destroying fungi and control of deep seated beetle infections is most effectively achieved by injecting solutions in drilled holes or by use of the borate glycol formulation.

Inorganic boron is also standardized as a pressure treatment for a variety of species of softwood lumber used out of contact with the ground and protected from water. With the use of heated solutions, extended pressure periods, and diffusion periods after treatment, borax is able to penetrate relatively refractory species such as spruce. LVL panels may be treated by adding the borate during the gluing process. Akbulut et al. (2004) also showed that water-soluble boron compounds have little or no effect on the bonding performance of urea-formaldehyde resin. Table 4 shows typical applications for DOT according to AWPAs use categories. It should be noted that Above Ground, weather protected use is listed only within the ICC-ES framework and not within the AWPAs.

Table 4. Typical applications for TIM-BOR® (DOT)

Service conditions	AWPA use category	Typical applications
Above ground, interior dry uses	UC1	Interior construction, furnishings, and millwork
Above ground, interior damp uses	UC2	Interior beams, flooring, framing. Millwork and sill plates
Above ground, weather protected exterior applications may be exposed to occasional sources of moisture	UC3A*	*Coated millwork, siding, trim *EnviroSafe ICC-ES ESR only, Not currently AWPAs Ratified and promulgated

Use of DOT in Diffusion Treatments

The solubility and mobility of borates allows them to treat wood species that are difficult to treat with copper based preservatives. Even when not applied on the whole cross section, they redistribute by diffusion if sufficient moisture is available in wood to provide one of the most effective preservation systems available today (Lloyd 1995; Lloyd and Manning 1995; Peylo and Welleitner 1999).

The conventional dip diffusion requires extensive holding periods (up to 6 weeks) while stacking and wrapping to allow adequate penetration. Turner and Conradie (1995) describe a boron based wood preservative (Totim B- 40% BAE) for the treatment of green timber. Totim B is a high viscosity wax emulsion containing a supersaturated solution of DOT that permits the use of borates in H3 class situations. Designated for dip diffusion of full cross-section in a range of timber sizes, the product seals the timber with a thin film of wax immediately after dipping thus retarding drying while the borate diffuses into the wood. The wax eliminates the need for block stacking and wrapping and the 6-week diffusion period. Dipped timber can be utilized within 8 hours after treatment. The wax also provides a water repellent coating to reduce boron loss caused by leaching. A conventional surface coating maintenance program may be required if the borates are to be used under H3 conditions.

Borate rods can be used to protect inner untreated heartwood portion of utility poles from internal decay. Highley et al. (1996) monitored the diffusion of boron from fused DOT rods over 42 months in CCA-treated Douglas-fir transmission poles. The BAE was estimated by the curcumin/salicylic acid color test on increment cores removed from the poles. Moisture content of the poles was always above 20%. Diffusion of boron increased until 18 months then decreased slightly at 30 and 42 months. Boron was

almost always detected downward from the treatment holes at a distance of 10 in. (250 mm). Likewise, boron was usually detected laterally from the insertion hole at a distance of 3 in. (76 mm). Movement of boron upward from the insertion holes was poor, often nil and not exceeding 2 in. (50 mm). Thus, because of the variable penetration of boron in the Douglas-fir heartwood, untreated areas are present that are susceptible to decay. Remedial treatments of CCA-treated poles in service with incipient soft rot with boron rods, boron/glycol solution, boric acid paste, copper/creosote paste and a commercial product Dinitrophenol, fluoride chrome and copper/ DFCK paste applied by injection. A good spread of borates was shown after 28 months. The results concerning the micro-flora after 28 months were encouraging for boron rods and boric acid paste (Henningsson et al., 1988).

While under conditions of higher moisture content, relatively good liquid diffusion of the borate is observed in the grain direction, diffusion perpendicular to the grain is minimal and glue lines largely hinder liquid transport/diffusion. Militz (1991) evaluated the diffusion of anhydrous DOT (Biokil Timbor rods) and bifluorides (Woodpil 55 and woodcap B.V) containing ammonium and potassium bifluoride from preservative rods in laminated beams from spruce, pine and larch. The rods were placed in a 62mm deep hole with a diameter equal to that of the pill. After 3 and 6 months chemical indicators were used to access diffusion of each component. After 6 months the diffusion of the bifluorides was, in all species 5 times larger than the diffusion from DOT rods. The bifluorides were not hindered by the glue-lines. The diffusion of the borate was poor, mainly perpendicular to the grain and was hindered by the glue-line. Bifluorides diffuse in conditions where no moisture is present in the wood through gas diffusion. Gas diffusion progresses better in the grain direction but is also very strong perpendicular to the grain and finds little hindrance through the glue lines. Borates on the other hand, show little or no gaseous diffusion hence the slight diffusion perpendicular to the grain and through glue lines.

Use in Joinery

Although window joinery is recognized as a Use Category UC3B application (above ground and exposed to weathering), boron treatments have been shown to be effective remedial treatments for joinery. Target borate retention levels of 0.8-1.5 kg/m³ for remediation of window joinery is described as inhibitory for fungal growth while 2-3 kg/m³ is necessary to achieve toxic retention (Drysdale 1994).

A survey and analysis of boron content in joinery treated with borates 23 years earlier and in service in residential flats by Dickinson and Murphy (1998) showed that the levels of boron still present were sufficient to prevent decay. None of the windows surveyed showed any decay despite the fact that moisture and sapwood contents were conducive to decay. Moisture content readings showed the presence of timber above the fiber saturation point, in the lower joint regions of the ground floor windows but no obvious evidence of decay in any of the windows examined despite the windows having been at risk from decay as described in European H3. The levels of boron remaining was similar to the accepted toxic values for decay fungi (0.2% BAE) and it seemed likely that the windows will continue to give good decay free service for some years to come.

External joinery can be successfully treated with diffusible preservatives in aqueous solutions with suitable treating and drying schedules and relevant treatment requirements, taking into account the specific properties of diffusible preservatives. The most critical problem is the drying time with a drying time of a few days preferred. Kiln drying schedule (developed for organic solvent preservatives) result in deformations - bowing of tenons and checks in the end grain (Jermer and Lloyd 2000). Factory finished window joinery components were treated with an aqueous borate preservative to investigate penetration and retention levels, associated drying times; and the potential impact of using a water-based treatment on finished items. It was found that by using borates applied by light double vacuum schedules, it was possible to meet standards for penetration and retention and air dry components within 48 hours and avoid significant negative impact usually associated with aqueous treatments of joinery. This indicates that it is possible to replace organic solvent carried preservatives with water-borne technology in finished joinery products especially noting the move from solvent to aqueous systems (Jermer and Lloyd 2000).

Corrosivity

Metal connectors, anchors, and fasteners will corrode and may lose load carrying capacity when installed in corrosive environments or exposed to corrosive materials. There are many environments and

materials which may cause corrosion including preservative-treated wood. Increased corrosion from some preservative-treated woods is a new issue with little historical data. DOT has a pH of 8.3 at 20 °C as a 3.0% solution and a pH of 7.6 as a 10.0% solution. It is considered non-corrosive. Borate treated wood is compatible with metal fasteners. Wood treated with DOT is less corrosive to carbon steel and galvanized steel than CCA oxide treated wood. Borates also exhibit extremely low corrosion to aluminum, copper and brass (Barnes et al., 1984).

Mankowski and Manning (2006) report on a corrosion test conducted in accordance with AWWA E-12-94 to compare wood treated with ACQ (0.4 pcf), copper-azole (CA, 0.10 pcf), and DOT (0.28 pcf) and untreated wood (Table 3). Four metals Aluminum, Brass, Steel and Zinc Galvanized Steel (HDG) were used. The samples were placed in an environmental chamber maintained at 49 °C and 90% relative humidity for 45 days. For aluminum, wood treated with ACQ and CA caused high levels of corrosion compared to DOT and untreated wood. Brass was relatively unaffected by contact with any treated wood. Mild steel in contact with untreated wood and DOT treated wood had much lower corrosion rates than wood treated with ACQ or CA. These two preservatives caused very high levels of corrosion in this metal. Galvanized steel showed very low corrosion for untreated and DOT treated wood and was higher for ACQ and CA treated wood. Wood treated with DOT will have little effect on metal fasteners used in contact with this type of preservative treated wood. Simpson Strong-Tie have also performed corrosion tests with borate treated wood and showed that testing on DOT treated wood generally indicates corrosion rates less than seen with CCA-C treated wood (Simpson Strong-Tie Bulletin 2008).

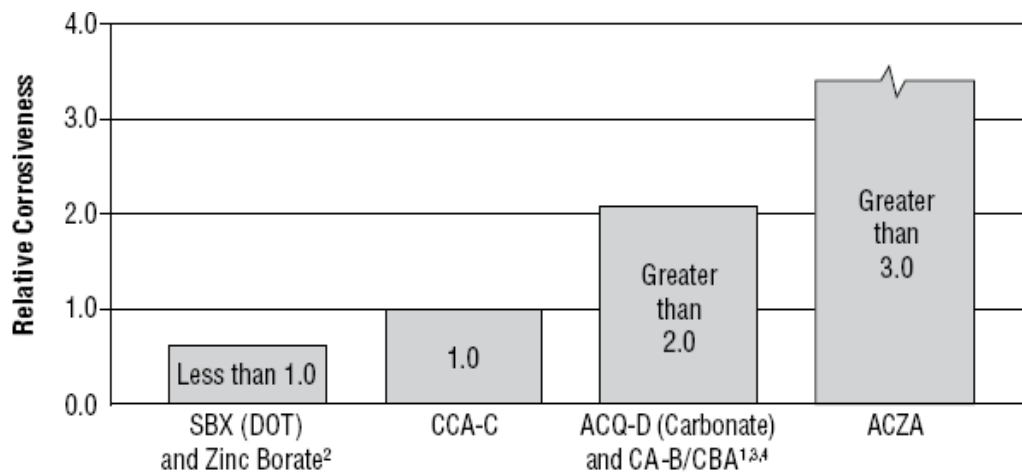
Table 5. Corrosion (mpy) of four metals exposed to untreated, DOT, ACQ, and CA treated wood for 45 days at 49 °C and 90% RH.

	Aluminum		Brass		Mild Steel		Galvanized Steel	
	(mpy)	STDEV	(mpy)	STDEV	(mpy)	STDEV	(mpy)	STDEV
Untreated	.06	.01	.04	.01	13.5	2.1	0.55	0.33
SBX	.03	.1	.03	.01	10.4	4.6	.3	.24
ACQ	27.7	16.4	.24	.07	31.3	5.6	6.7	1.2
CA	19.7	15.1	.24	.07	37.6	16.4	6.6	1.8

Source: Mankowski and Manning (2006)

Figure 1 compares the average relative corrosiveness of several treatments to the corrosion which occurred with CCA-C treated wood. The numbers shown are an average of the results of G90 and G185 continuous hot-dip galvanized steel samples based on AWWA E12 accelerated testing.

Figure 1. Relative corrosiveness of treatments to HDG



Source: Mankowski and Manning (2006)

Permanence and leaching

Stand alone inorganic boron systems offer adequate protection to lumber in non-ground contact situations and building applications. The effective use of low solubility borates has not yet been achieved in the treatment of solid lumber. Data on the leaching of borates has been gathered over the last 50 years and field tests have shown rapid retention depletion of borate from wood in ground situations. Monitoring of treated timber above ground has shown insufficient loss to cause concern for the durability of the timber (Drysedale 1994). Timber framing treated with borates have reported no failures in service. Because of solubility and depletion of borates from treated wood, stand alone borates have been restricted to for use in interior situations or where protected by coatings such as painted external joinery/millwork. However the continued mobility is considered beneficial and allows cross-sectional protection from envelope application methods (Schoeman and Lloyd 1998).

Despite leaching concerns several studies show that wood retains sufficient boron to prevent attack by basidiomycetes. Studies have shown that borate treated wood in ground contact shows improved service life in comparison to untreated timber. Loss of borates occurs to a serious degree only when timber remains wet throughout its cross-section for long periods while also having an external sink for boron migration. A reduced loss rate occurs as retention approaches a level too low to drive diffusion. This occurs above the toxic limit for decay (Drysedale 1994; Lloyd 1995; Williams, 1996). For leaching to occur, there must be source of water and then entry of that water into wood. Dry wood does not wet easily and in the event of the timber becoming wetted, this in itself will not result in leaching. Penetration of water can be prevented by good building practices (Drysedale 1994). Above ground tests of rail units and L-joints show that the average life of boron-treated L-joints compared to untreated L-joints was extended from 4.8 years to between 14.6 (at 1.6 kg/m³) and probably 21-22 years (at 4.5 kg/m³). After 35 years, painted boron treated rail units had a greater Index of Condition than unpainted CCA treated units (Hedley and Page 2006). In another above ground field test, 3% BAE performed as well as CCA at 0.25 pcf (4 kg/m³) after 10 years with mean rating of 9.5. Statistical analysis showed no significant differences among Borate and CCA treatments (Tsunoda et al. 2006).

DOT is more soluble than Borax and slightly loses more boron after leaching tests. McCutcheon et al. (1992) observed that borax treated pitch pine block samples retained boron levels above 0.2% BAE after leaching by submersion for one month. Polybor[®], a formulation containing DOT, and Boracol[®] had less than 0.2% BAE retained. The restriction of borates to indoor applications has been overcome by use of more complex formulations where boron is just one active ingredient in a formulation containing two or more e.g., in CCB.

Interest in reducing the leaching of borates stems from their favorable environmental characteristics and broad spectrum efficacy. Obanda et al (2007) reviewed research over the last two decades in laboratories around the world and classified all strategies employed into fifteen categories. While little or no commercialization has taken place with most of these “fixed” borate systems, there have been major advances in the understanding and approach to developing strategies aimed at reducing leaching. It is now understood that the key to extending the use of borates to cover the entire spectrum of wood preservation is improving their permanence in wood while retaining efficacy by retaining limited mobility of the borate. The balance between the disadvantages of preservative leaching and the benefits of preservative mobility is now more widely understood. Previous studies show that while fixing boron may prevent leaching, it may lock the boron resulting in loss of biological efficacy (Lloyd et al. 1990). Research has therefore been directed to partial fixation systems which conserve sufficient mobility to maintain preservative action (Pizzi and Baecker 1996; Thevenon et al. 1997).

Use of borates in exterior applications is likely to prove commercially significant in future. Future efforts will likely focus on envelope treatment of wood with boron compounds and retreating it with an oil based formulation after drying and conditioning to prevent boron leaching. Although this may be expensive and result in undesirable surface properties, this technology is already being practiced for cross-ties used in AWP Use Categories 4 and 5 situations (Gauntt and Amburgey 2005; Jones et al. 2006). Establishment of niche systems specifying inorganic boron salts used for the building industry and more complex borate based formulations and/or multi component systems that are appropriate for ground and exterior applications is another option. There will likely be a wider range of types and retentions of boron-based preservatives and the use of non-biocide additions to borate formulations to improve permanency will increase (Obanda et al., 2007).

Synergistic effects and formulations

Borates are frequently used in combination with other biocides to increase efficacy against mold and soft rot. In tests with unseasoned lumber when borates are mixed with co-biocides, such mixtures are very effective for preventing growth of both sapstain and mold (Amburgey 1990). The borate physical and chemical properties make borates suitable as standalone preservatives or borates can be components of more complex formulations in combination with copper, chromium, quaternary ammonium, or organic ligands. Boron-based systems therefore offer a totally flexible option. There has been a massive increase in the number of boron formulations on the market. The potential range of products is almost infinite and end use applications could cover the entire spectrum of wood preservation. Formulations now range from being a primarily boron-based formulation to a formulation that contains some amount of boron. The overall efficacy of such compounds may rely more on the other compounds than the borate itself. The advantages of boron preservatives may not be retained as it will result in a change in the mechanism of action and mammalian toxicity. The drive to keep wood preservative costs low may hinder the development of sophisticated (and relatively expensive) treatments as treated wood must maintain its cost advantage over steel and concrete (Obanda et al., 2007).

Copper remains the primary biocide component used to protect wood used in contact with the ground or fully exposed to the weather, but preservatives containing boron or organic biocides are gaining importance for more protected applications (Lebow 2007). Borates improve efficacy of oxine copper (Myers 1989; Morris et al. 1999) and triazoles (Luo et al. 2005). Borate and DDAC (1.0 w/w %) are efficient in totally prevented or greatly reducing growth of *A. niger*, *P. brevicompactum* and *S. chartarum* (Micales-Glaeser et al. 2004). Borax used together with NHA-Na has been shown to have a synergistic effect against fungi *F. palustris* and *T. versicolor* and subterranean termite *C. formosanus* (Akbulut et al. 2004).

Borates provide effective treatment against soft rot in laboratory Petri dish tests but in wood blocks, have been shown to provide inadequate protection most likely due to leaching of the borates. Lack of efficacy of borates to mold and soft rot fungi may partly explain the relatively poor performance of borate treated wood in ground contact. As with molds, tests where borates are mixed with co-biocides indicate that such mixtures are very effective for preventing growth of soft rot (Amburgey 1990). Replacing arsenic in CCA with boron, resulted in better protection of birch specimens against soft rot than specimens treated with CCA. The results of this and other studies indicate that the presence of copper in formulations

containing borates may be the key to increasing resistance of borate treated wood to soft rot fungi (Amburgey and West 1989; Amburgey and Freeman 2000).

SUMMARY AND CONCLUSIONS

Borates are especially good wood preservatives for the protection of wood from decay fungi and a wide variety of insects, including all species of termites. The single drawback of borates, like borax and boric acid and DOT, is that they can also be readily leached from wood under certain conditions. Some published work has shown that even when all borate is leached from wood and is no longer detectable by normal methods, the previously treated borate wood has somewhat of a “sterilized effect” and is still not attacked by wood destroying insects or decay fungi. To date, only one environmental screening test has shown negative health results on borates and this study indicated high ingestion levels of water soluble sodium borates may lead to testicular atrophy in some mammals, but not cancer or DNA interruption. The two levels of borates, as their B₂O₃ equivalents currently specified by both the AWP and other worldwide organizations should protect wood, in a non-leaching environment for many decades. Detection of boron, using wet-chemistry reagents such as curcumin, is readily done as is the analysis of treating solutions and treated wood. Continued work on the “fixing” of borates with an inexpensive, safe, and environmentally benign compound to limit their mobility and make them highly resistant to leaching is still one of the searches for the “holy grail” in wood preservation.

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