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Reducing leaching of boron-based wood preservatives – A review of research

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Abstract

Inorganic borates offer good protection to timber in most non-ground contact applications. The effective use of low solubility borates has not yet been achieved in the treatment of solid lumber. Interest in reducing the leaching of borates stems from their favorable environmental characteristics and broad spectrum efficacy. 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. We review research over the last two decades in laboratories around the world and classify all strategies employed into fifteen categories. For each strategy, resistance of the treated wood to wood destroying organisms, resistance to leaching, and potential applications are discussed. Published by Elsevier Ltd.

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1. Introduction

Because of its favorable environmental characteristics, wood preservation researchers have refocused on boron in the last two decades. Current standards (AWPA, 2007) allow for the use of borates in above-ground environments protected from rain wetting. Due to their broad spectrum fungicidal and insecticidal action, borates are considered more effective preservatives 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). Data on the leaching of borates has been gathered over the last 50 years. Inorganic boron systems offer

adequate protection to lumber in protected non-ground contact situations and more especially building applications (Williams, 1990, 1996; Williams and Amburgey, 1985). Years of field research in Hawaii and Japan support the conclusion that inorganic borates provide long term protection for structural timber (Grace et al., 2006; Tsunoda et al., 2006). 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 (Drysdale, 1994; Lloyd, 1995; Williams, 1996). 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 Willeitner, 1999).

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The balance between the disadvantages of preservative leaching and the benefits of preservative mobility is now more widely understood. As borate systems have expanded in use, efforts have continued to reduce leachability (Manning et al., 1997). Several strategies to reduce leaching and increase the potential range of products to cover the entire spectrum of wood preservation have been proposed. Previous reviews of boron compounds suggest that their future lies in the search to fix them within treated timber (Nicholas et al., 1990; Lloyd, 1995). A fixed preservative is described as one which when introduced in wood, satisfies the relevant leaching standard e.g. AWPA E11-97 (AWPA, 2007) and subsequent efficacy tests required for standardization. A treatment may not necessarily react with wood to meet these criteria (Lloyd et al., 2001). 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). Preservative properties of borates are primarily due to the tetrahydroxyborate ion $[B(OH)_4]^-$ ion formed upon exposure to water. The ion complexes with polyols of biological significance in wood destroying organisms through extracellular and intracellular substrate sequestration, enzyme inhibition, and change in membrane function. When the borate is complexed or immobilized, it has no effect on biological efficacy (Lloyd et al., 1990; Lloyd, 1998). Research has therefore been directed to partial fixation systems which conserve sufficient mobility to maintain preservative action (Pizzi and Baecker, 1996; Thévenon et al., 1999). Formulation of borates in forms other than simple inorganic aqueous solutions is beginning

to develop. Strategies that have been proposed or studied are listed in Table 1 and discussed in the following sections.

2. Surface treatments

Coating boron-treated wood with layers of varnish, resins and, hydrophobic wax to hinder moisture uptake is a common practice. An L-joint study by Forintek Canada revealed that borates perform well when painted and exposed to a leaching hazard. After 5 years, samples showed boron migration from the ends of the sample and complete protection against decay afforded by 0.02% BAE in the area of the joint (Manning et al., 1997). In another study, a three layer coating of nitrocellulose lacquer yielded good protection for disodium octaborate (DOT) treated pine (Mohareb et al., 2002). However, more studies reveal that surface coatings have a protective effect only during a distinct period depending on the thickness of the coating and may be useful only for a short term risk (e.g., during construction) (Peylo and Willeitner, 1995a,b, 1999). Even under coatings, boron is lost if moisture conditions are suitable for diffusion (above 20%). Three commercial water repellent coatings, an experimental polymer, and a latex paint applied to exteriors of framed storage buildings were all found to fail within 3 years (Sites and Williams, 1997). Coatings prevent leaching only if maintained regularly. In a 25-year study of rail units, Hedley and Page (2006) found units which had the most intact paint coating to have the highest level of residual boron.

Table 1
Strategies proposed for reducing boron leaching

Item	Strategy/system	Proponents
1	Surface treatments	Peylo and Willeitner (1995a,b), Homan and Militz (1995), Mohareb et al. (2002), Hedley and Page (2006)
2	Envelope treatment (over-treatment)	Amburgey et al. (2003), Gauntt and Amburgey (2005)
3	Wood bulking resins and water repellants	Ramesh and Dodwell (1981), Yalinkilic et al. (1997), Cui and Kamdem (1999), Yalinkilic et al. (1999b), Mohareb et al. (2002), Hutter et al. (2004)
4	Organo boron compounds (boronic and borinic acids)	Liu et al. (1994), Yalinkilic et al. (1998a)
5	Precipitation of organo soluble salts within wood	Lin et al. (2001)
6	Combination of biocides and non-biocidal chemicals	Kartal and Green (2003), Kartal and Imamura (2003), Akbulut et al. (2004)
7	Metallo-borates	Schubert and Manning (1997), Lloyd et al. (2001), Furuno et al. (2003, 2006), Freeman and Amburgey (1997), Amburgey and Freeman (2000)
8	Ammoniacal and amine metallo-borates	Farber (1951), Malouf and Docks (1991), Shiozawa (1991), Barth and Hartner (1994), Walker (1997, 1999a,b, 2000), Walker et al. (2003), Lloyd and Fogel (2005)
9	Stabilized boroesters	Maynard (1993), Hedley et al. (2000), Humphrey et al. (2002), Carr et al. (2005)
10	Protein borates	Thévenon et al. (1998a,b, 1999), Thévenon and Pizzi (2003), Ratajczak and Mazela (2007)
11	Tannin auto condensation	Thévenon et al. (1998c,d, 1999), Pizzi and Baecker (1996)
12	In situ polymerization	Ozaki et al. (2001), Baysal et al. (2004), Cui and Kamdem (1999), Yalinkilic et al. (1998b), Yalinkilic et al. (1999b)
13	Vaporization of organic boron compounds and boric acid	Baysal and Yalinkilic (2005)
14	Boron-silicates	Du-Fresne and Campbell (1967), Kazunobu (1995), Slimak and Slimak (1998), Yamaguchi (2003), Yamaguchi (2005)
15	Physical modification of wood (compressive deformation)	Yalinkilic et al. (1999a), Baysal and Yalinkilic (2005)

Homan and Militz (1995) found that two layers of alkyd-based paint delayed boron loss. After 78 days leaching, only 3% boron from boric acid treated spruce was leached. However, when a deliberate saw cut was made on samples to simulate fracture of the coating film, 21% boron was lost within the same period.

2.1. Envelope treatment/over-treatment

Poor performance of wooden crossties in warm, humid areas has been attributed to use of species whose heartwood is not treatable with traditional preservatives which treat only the surface of the cell walls. Research by Amburgey et al. (2003), Gauntt and Amburgey (2005), Gauntt et al. (2006) and Jones et al. (2006) has shown that improved service life of crossties is achieved by treatment prior to air-seasoning with diffusible borates that penetrate the heartwood, followed by diffusion storage, air-seasoning, and with over-treatment with creosote to prevent loss of borate due to leaching. Little borate is lost from air-dried ties during creosote treatment. After 15 years of installation, ties continued to perform well and no decay or termite damage was observed in either the creosote dip- or pressure-treated ties. Reduced retentions of creosote may be used if ties are properly pre-treated with borates and stored to maximize diffusion during the drying process. There is a need to test other types of oil preservatives or solvent-based preservatives using this technique.

2.2. Wood bulking and rosin/resin treatments

Wood bulking involves swelling wood to its maximum dimension and retaining it at that dimension by depositing a bulking agent in the cell walls and cavities. It is economically prohibitive and may have a negative effect on wood strength properties. Physically restricting water access in wood by impregnating it with hydrophobic agents limits boron mobility without interfering with its bioactive nature. Lower water absorption and a reduction of void spaces can contribute to the immobility of boron. Use of water dilutable resins in a water miscible solvent to which a wood treating chemical is added deposits preservative and resin into the cell wall where it is converted to an insoluble form. The components must be comprised of molecules capable of entering voids in the cell wall and be converted to a more water insoluble form at ambient conditions either by itself or aided by other chemicals that act as catalysts (Ramesh and Dodwell, 1981; Mohareb et al., 2002; Hutter et al., 2004). Impregnating wood with an aqueous liquid dispersion or emulsion which contains a borate and rosin or rosin derivative simultaneously incorporates borate into wood and renders it hydrophobic. Suitable rosins include tall oil rosin, gum rosin, or wood rosin. Suitable rosin derivatives include hydrogenated rosins, formaldehyde-treated

rosins, dimerized rosin, polymerized rosin, rosin salts and esters (Hutter et al., 2004).

Schroeder (1982) patented a process where wood is treated with boric acid or trimethyl borate forming intermediate borate esters with hydroxyl groups of the cell wall and thereafter treating the wood with an aldehyde to effect aldehyde cross-linking of cell walls. Formaldehyde was preferred due to its effectiveness and low cost. Although boron-formaldehyde incorporations have shown remarkable improvements for decay and termite resistance, blocking of the OH-groups of the cell walls by cross-linking results in little reduction of boron leachability. Boron causes a decrease in the cross-linking efficacy of formaldehyde (Yalinkilic et al., 1997, 1999a). A major disadvantage is the special care that should be paid to formaldehyde toxicity. To address this problem, Yalinkilic et al. (1999a) added boric acid and phenylboronic acid (PBA) into aqueous solutions of non- or low-formaldehyde reagents; dimethylol dihydroxy ethyleneurea (DMDHEU), glutaraldehyde (GA), and glyoxal (GX). Although the complexes reduced boron leaching, boron decreased the cross-linking efficacy of GX and DMDHEU to the wood cell wall. After severe leaching, the retained boron did not show adequate termiticidal activity. However, PBA-addition to the reagents attained complete resistance against termites. Higher mass losses against *Tyromyces palustris* and *Coriolus versicolor* were recorded for PBA-GX combination treatments compared to PBA only treated wood possibly due to prior chemical complexation of the OH groups on PBA.

3. Organo boron compounds (OBC)

OBCs studied in wood preservation are boronic acids $RB(OH)_2$ and borinic acids R_2BOH . Aromatic boronic acids have greatly reduced solubility in water and leach resistance from wood due to the higher possibility of them interacting with the aromatic subunits of lignin and restricting access of water to the boron. Phenyl boronic acid (PBA) is the most widely studied OBC (Liu et al., 1994; Yalinkilic et al., 1998a, 1999a). PBA is stable to water and high temperature (Liu et al., 1994). Wood treated with 0.34% w/w PBA solution was found resistant to *T. palustris* and *C. versicolor*, even after running water leaching for 10 days (Yalinkilic et al., 1998a) and complete elimination of termite attack was accomplished with 1.0% PBA in leached specimens. PBA has two OH groups linked to the boron molecule and is connected to wood by bonds similar to those of boric acid. PBA-wood interaction is more stable because water access to boron is limited by the possible occupation of the OH groups by wood or other PBA molecules (Yalinkilic et al., 1998a). A dual treatment with PBA followed by vapor phase formalization improves dimensional stability and decay and termite resistance to a higher extent than PBA only (Yalinkilic et al., 1999a). The high cost of PBA

and all boronic acids hinders the commercialization of this process.

4. Precipitation of organo-borate salts

Another practical approach is the chemical complexation of a borate compound with an agent capable of forming a water-insoluble complex upon dehydration in wood (Baysal et al., 2004). The double treatment of tetraphenylborate sodium salt $[(C_6H_5)_4BNa]$ with potassium chloride was investigated by impregnating them into sapwood specimens of *Cryptomeria japonica* to form the insoluble salts of tetraphenylborate potassium (Lin et al., 2001). The reduction of boron retention in wood specimens after the leaching test indicated good fixation of the boron compounds. The double treatment also showed an excellent efficacy effect against both *C. versicolor* and *T. palustris* (Lin et al., 2001).

5. Combination of biocides and non-biocidal additives

Non-biocidal additives may give wood greater and/or broader protection than achieved with only the biocide. Treatment of wood blocks with DOT, boric acid, calcium borate, and NHA-Na (*N,N* 1,8-naphthalyl hydroxylamine) solutions in sequential processes reduces the susceptibility of boron to leaching (Kartal and Imamura, 2003; Kartal and Green, 2003). Blocks treated sequentially with the boron compounds and then 1% NHA-Na solutions showed 30% less boron leaching due to physical blocking of tracheids and ray parenchyma lumens or by co-precipitating with DOT. Kartal and Imamura (2003) and Akbulut et al. (2004) further showed that the existence of boron and NHA-Na in wood together gave a synergetic effect against fungi and termites. NHA-Na is thought to disrupt normal calcium cycling in fungal hyphae (Akbulut et al., 2004). Some additives do not enhance the performance of the borate due to incompatibility between the polymer and the boron solution. In a study of wood treated with an acrylic polymer and a borate, Murphy et al. (1995) found the extent of decay after leaching to be similar to the polymer only treated samples. After leaching, the polymer was the main decay preventive component. Polymer only treated samples performed better than untreated controls due to less moisture absorption, and the polymer masked receptor sites for fungal enzyme activity in wood cells walls or acted as a substrate for the fungi.

5.1. Inorganic metal and borate combination (Metallo-borates)

Zinc borate (ZB) incorporated into composites offers much better leach resistance than soluble inorganic borates. It is impractical to treat solid wood with ZB because of its low solubility. Progress has been made by several researchers in the area of metallo-borates. Freeman and Amburgey (1997) studied a paste consisting of borax and amine solubilized copper naphthenate and applied it

to polyethylene backed wraps to below ground pole stubs. The stubs remained free of decay and termite damage after 12 years. It was hypothesized that copper borate complexes that formed in the wood were responsible for the long term protection. Three years later the complexes were found to be still effective in imparting protection to the timber (Amburgey and Freeman, 2000). Wood can be treated with inorganic borates and metal salts in two steps to form insoluble precipitates within wood. Dev et al. (1997) described a zinc borate treatment in which the wood is treated with solutions of borax and zinc chloride in sequential steps. In another study by Furuno et al. (2003) specimens were first impregnated with a saturated borax solution and then diffuse penetrated with Zn^{2+} ($ZnSO_4 \cdot 7H_2O$), Ca^{2+} ($CaCl_2$), or Pb^{2+} ($(CH_3COO)_2Pb \cdot 3H_2O$) solutions. Precipitates of the metallo-borates proved to be insoluble in water. The wood showed good resistance to *Fomitopsis palustris*, *Trametes versicolor* and *Coptotermes formosanus*. Despite the superb performance, the prospects of using lead as a preservative are limited because of environmental restrictions. These results were corroborated by Furuno et al. (2006) who evaluated metallo-borates formed by impregnating *C. japonica* with aqueous solutions of borax and then zinc sulfate or copper sulfate by double diffusion. In laboratory tests using *C. formosanus*, copper and zinc borate treated wood showed negligible weight loss with high termite mortality at a concentration of 3%. In field tests using *Macrotermes gilvus*, the borates at 5% showed little weight loss after 2 months and had enhanced resistance against *T. versicolor* and *F. palustris*. High cost of retreating and rehandling wood in two stages makes the commercial use of multi-stage processes unattractive.

Zirconium has no biocidal effect but has been investigated as a fixative for borates (Schubert and Manning, 1997; Lloyd et al., 2001). A dilute aqueous zirconium salt and borate are applied to wood in a single step and upon drying and removal of the ammonia content, zirconium is able to bond borate to wood components. Alternatively, the lumber is treated with the zirconium salt and then the boron compound, forming the composition within the wood structure (Schubert and Manning, 1997). The amount of borate retained increases as the concentration of zirconium oxide increases. Ammoniacal zirconium carbonate and potassium zirconium carbonate were found to produce similar levels of borate fixation and decay resistance, while zirconium oxychloride was found unable to fix borate. The minimum zirconium oxide concentration needed to inhibit leaching was 0.5%, when combined with 1.2% BAE or 1.0% when combined with 0.85% BAE. Fixation was optimized by heat treatment at 60 °C (Lloyd et al., 2001).

5.2. Ammoniacal and amine metallo-borates

Solutions of metallo-borates and acetic acid or ammonia can be chemically fixed in wood. Lloyd and Fogel (2005) patented a water borne leach-resistant borate preservative

formulation that contains ammonium or sodium borate, a source of co-biocide metal zinc and/or copper (metal oxide, metal carbonate or metal hydroxide), a volatile organic acid (formic, acetic or propionic acid), free ammonia, and ammonium salts to aid dissolution. In order to achieve a high concentration of metals and borate, it is necessary to use high concentrations of ammonia, resulting in excessive ammonia volatility and noxious fumes, creating undesirable worker exposure problems in large-scale operations and encouraging mold growth on treated timber. Several other United States patents propose the use of alkylammonium borates, tertiary amine oxides, or borate esters containing quaternary ammonium groups in wood preservation (Farber, 1951; Malouf and Docks, 1991; Shiozawa, 1991; Barth and Hartner, 1994; Walker, 1997; Walker, 1999a,b, 2000; Walker et al., 2003). Ethanolamine is reported as the most adequate amine source in several studies. Because these systems contain a metal cation with biocidal properties, determining the performance of a fixed borate could be difficult if the performance is masked by a biocidal cation (Lloyd et al., 2001).

Amine oxides enhance penetration, provide water-proofing properties to wood, improve leach resistance, and provide better dispersion of boron compounds. Preferred amine oxides include dodecyldimethylamine oxide, tridecyldimethylamine oxide, tetradecyldimethylamine oxide, or hexadecyldimethylamine oxide (Walker et al., 2003). Metal-free systems formulated with quaternary ammonium carboxylates (carboxylate quats) and quaternary ammonium borate (borate quats) in an aqueous solvent displayed greater resistance to leaching than inorganic systems (Walker, 1999a,b, 2000). The carboxylate and/or borate quat bonds to the wood directly or through hydrogen bonds to help anchor the quat. Examples of the quats used for this system are didecyldimethylammonium carboxylate and didecyldimethylammonium borate (Walker, 1999a,b). Water soluble ionene polymers when mixed with borates in certain proportions; provide a synergistic level of action in preventing fungal infestation in freshly cut timber. The mixture does not experience a reduction in fungistatic activity from leaching.

Kartal et al. (2004) evaluated the effect of 2% didecyldimethyl ammonium tetrafluoroborate wood preservative (DBF) $[(C_{10}H_{21})_2N(CH_3)_2]^+BF_4^-$ incorporated with acryl-silicon type resin emulsion on decay and termite resistance. DBF is a quaternary ammonia compound that contains boric tetrafluoride (BF_4^-) as a counter ion. The anionic emulsion contains stable silicon groups and carboxylic end groups making it stable in water. Wood blocks showed decay resistance against both *F. palustris* and *T. versicolor* even after severe leaching. Evaluation of *C. formosanus* resistance of wood treated with DBF without the acryl-silicon resin showed adequate protection even after a 10-day severe weathering process suggesting adequate fixation of DBF in wood, and it could be used for exterior applications (Kartal et al., 2005).

5.3. Stabilized boron esters and other complexes

Boric acid esters or borate esters have been used to deliver boric acid into wood using a number of processes which include: solutions of boron esters for remedial and diffusible treatment of wood, solid boron esters for remedial treatments, vapor treatments using low boiling point esters (i.e. trimethyl borate) and solutions of boron esters for light organic solvent preservatives treatment (Romero et al., 1995). Boron esters are soluble in organic solvents and hydrolyze to boric acid on exposure to water. They all have similar reactions which are important for the development of wood preservation chemicals. These reactions include hydrolysis, alcoholysis, and reaction with amines, acids, aldehydes, ketones, acetals, hydroxides, halogen compounds, silicone compounds, nitriles, metals, organometallic reagents, sulphur compounds, oxidation, and reduction (Romero et al., 1995). Borate esters of various glycols have been used in several applications for many years (Carr et al., 2005). Hydrolysis of boron esters caused by water molecules supplying electrons to the electrophilic boron atom poses a frustrating attribute and has a major impact on wood treatments. The cleavage occurs between the B–O bond rather than the O-alkyl group (Kristen and Vinden, 2000).

Complexing boric acid or boronic acids with selected ligands, thus modifying its chemical behavior and enabling of certain physical properties has been tried and a range of complexes have been prepared and characterized in biological tests and accelerated weathering. Previous studies indicated that complexation leads to loss of the activity of boron (Lloyd et al., 1990; Lloyd, 1995). However, this is not the case with complexes examined by some authors (Humphrey et al., 2002; Mohareb et al., 2002; Carr et al., 2005). This implies that the choice of ligand is critical and complexation of boron as an approach to enhancing resistance to leaching merits further investigation. Hydrolytically stable borate esters with biocidal properties include trialkyl amine borates, trialkanolamine borates (borate salts of triethanolamine or triisopropanolamine), monoalkanolamide borates, and esters of carbamates containing polyhydroxyl substitutes on the nitrogen atom. Bulking of the boron atom with large molecular weight radicals results in better hydrolytic stability. Ligands are chosen with the intention of producing complexes that resist hydrolysis, unlike those formed from simple alcohols that hydrolyze on contact with water. Mixtures of boric acid/DOT, glycerol, and glyxocal pressure impregnated into wood results in less boron leaching due to formation of complexes that progressively hydrolyze to release boric acid and impart durability and dimensional stability (Tous-saint-Dauvergne et al., 2000; Mohareb et al., 2002). The principle involves building a polymeric network within the wood that may be covalently bonded to the wood matrix and progressively release boric acid by hydrolysis. Formation of lipophilic borate esters is a promising approach. Mohareb et al. (2003) investigated the leachabil-

ity of six boron ester compounds derived from fatty acids. Scots pine sapwood vacuum treated at different concentrations of boron ester were tested. The esters were more resistant to leaching than DOT. Assays confirmed efficacy of the esters against *C. versicolor*, *Coniophora puteana*, *Gloeophyllum trabeum*, and *Poria placenta* after 16 weeks.

Maynard (1993) patented a method of preparing a borate organic complex anion containing a salt. The method involves reacting an organic complexing agent, preferably an alcohol, with boric acid to produce a complex ion which is further reacted with a cationic species. 'Tebbacop' (Tetrakis boronato bis aquo copper II) a formulation based on this method contains spiro-borate complexes of derivatised 2-hydroxybenzyl alcohol. Tebbacop is synthesised by transmetallation of the sodium salt of a complex aromatic spiroboronate using a source of Cu^{2+} ions. The spiroboronate is prepared from borate and a substituted polyhydric aromatic alcohol (Maynard, 1993; Hedley et al., 2000). The complex promotes the solubilisation of Cu^{2+} in hydrocarbon solvents with the species formed assumed to be an ion-pair between the spiro-borate and Cu^{2+} in a 2:1 ratio. Humphrey et al. (2002) prepared and characterized three spiro-borates complexes (non-copper analogues of 'tebbacop'). First was tetrabutylammonium bis(salicylato)borate $\text{NBu}_4[\text{B}(\text{sal})_2]$ prepared from boric acid, tetrabutylammonium hydroxide, and salicylic acid. The second tetrabutylammonium bis(2-hydroxymethylphenolato) borate, $\text{NBu}_4[\text{B}(\text{hba})_2]$ was prepared from boric acid, tetrabutylammonium hydroxide, and 2-hydroxymethylphenol. The identity of the third complex was confidential. The precipitated complexes were resistant to hydrolysis. They were screened against boron tolerant basidiomycetes, *Gloeophyllum abietinum* and *Perenniporia tephropora*, and the termite *Coptotermes acinaciformis*. All complexes inhibited fungal and termite activity more effectively than the same concentration of boric acid. $\text{NBu}_4[\text{B}(\text{sal})_2]$ treatment retained 36% boron in wood after an accelerated weathering study; $\text{NBu}_4[\text{B}(\text{hba})_2]$ retained 7% while boric acid only treatment retained 2%. The difference in boron retention despite similarity in physical properties of the complexes indicates that the choice of ligand is critical in borate complexes. Carr et al. (2005) evaluated the anti-fungal, termiticidal, and resistance to leaching of the borate ester tetra-*n*-butylammonium bis(*ortho*-hydroxymethylphenolato)borate $\text{NBu}_4[\text{B}(\text{o-hmp})_2]$, its sodium salt, $\text{Na}[\text{B}(\text{o-hmp})_2]$ and boric acid. $\text{NBu}_4[\text{B}(\text{o-hmp})_2]$ had the highest activity and limited water solubility. These esters would be expected to reduce anti-fungal activity on account of unavailability of the borate ion but, the anti-fungal activity was not compromised but actually enhanced.

5.4. Vaporization of organic boron compounds and boric acid

Vapor boron treatment (VBT) of wood composites by trimethyl borate integrates the drying and treatment processes. Dimensional stability of wood is assured and the

process requires small working volumes of chemical though it has not been adopted into the market due to the high cost of trimethyl borate and working difficulties with methanol. Baysal and Yalinkilic (2005) vaporized borax at high temperatures followed by impregnation into wood. Vapor treatment with borax in a closed chamber without mechanical compression to wood resulted in increased leach resistance of boron. In addition to reduced leaching, VPT has been found not to result in deleterious effects on bending and tensile properties of OSB, MDF and LVL at low retentions of ~1% BAE (Barnes and Murphy, 2004). For both OSB and MDF high boron loadings lead to reduced bond strengths. Water absorption and thickness swelling are not affected by the treatment (Barnes and Murphy, 2005). Barnes et al. (2004) also showed that treating composites with VBT reduces the tool wear associated with machining.

6. In situ polymerization

To reduce leaching of boron, attempts have relied on limiting water penetration of wood using monomer and polymer systems. The wood cell wall is impregnated with monomers which are then polymerized in situ resulting in swelling of the cell wall which increases the dimensional stability. Ozaki et al., 2001 treated *C. japonica* and *Pinus caribaea* blocks with a mixture of furfuryl alcohol and boron compounds (boric acid, ammonium borate, and ammonium baborate – a type of polyborate compound with more than one boron atom in the structure). The combination of furfuryl alcohol and boric acid did not improve boron leachability as all of the boron was leached after ten cycles. The combination of furfuryl alcohol and ammonium borate and ammonium baborate improved boron retention even after severe leaching, indicating the formation of more stable compounds (Ozaki et al., 2001). In a similar study in which Baysal et al. (2004) treated wood with furfuryl alcohol and the same three borate compounds, there was a drastic reduction in boron leached and greater resistance to termites and decay fungi for all three compounds as compared to samples treated with boric acid only. The treatment did not entirely halt the mobility of boric acid and efficacy was maintained. Furfuryl alcohol a sufficiently small polar molecule is a polymerizing chemical that causes wood to permanently swell. Polymerization is accomplished using a catalyst, heat, or penetrating radiation. Borates also have a catalytic effect on the polymerization.

Vinyl monomers are used in wood modification by filling the capillaries, vessels and other void spaces after being polymerized in wood. Yalinkilic et al. (1998b) studied *C. japonica* initially treated with boric acid and then impregnated with vinyl monomers (styrene and methylmethacrylate) after air-drying. The wood had five times less boron release compared to that solely treated with boric acid and acquired perfect dimensional stability. However, the necessary monomer loading required to achieve an acceptable level of boron immobility was too high. To address

this problem, Yalinkilic et al. (1999b) included mechanical hot compression during in situ polymerization of the monomers (at 60–90 °C) in composites pretreated with boric acid. Volume reduction of cell lumens under compression reduced the amount of monomer uptake while stimulating the penetration. Boron leaching was considerably lower.

Cui and Kamdem (1999) synthesized a polyester borate by refluxing low molecular weight polyethylene glycol (PEG-400) with boric acid. The relatively stable and colorless ester was dissolved in 4,4'-methylenediphenyl isocyanate (MDI) and used to pressure-treat *Pinus* sp. Boron loss after leaching tests was negligible. The isocyanate group bonds to wood better than the polyester borate which hydrolyses in water. The treated wood also showed good efficacy against cultures of *G. trabeum*, *P. Placenta*, *P. ostreatus*, and *I. lacteus*.

6.1. Protein borates

Boric acid can be partially fixed to timber by forming an association with animal and vegetable proteins, which is then insolubilized by heat induced coagulation to form complexes and acid–base salts (Thévenon et al., 1998b, 1999; Ratajczak and Mazela, 2007). Egg albumin, collagen, casein, and soya flour all form insoluble complex networks by protein gelation or coagulation. This mechanism while retarding leaching leaves small amounts of boron free to diffuse and exercise activity. Biological tests on leached wood showed good performance against basidiomycetes (Thévenon et al., 1998b, 1999). Proteins complex with boric acid to form salts and complexes because they contain hydroxyl, amine groups and the peptidic links secondary amido groups –NH–CO– which present mildly alkaline behavior (Thévenon et al., 1998a,b; Thévenon and Pizzi, 2003). Protein coagulation insolubilizes protein boron complexes and good performance has been demonstrated. The performance of the protein borate and the nature of the coagulum vary with relative proportions of boric acid and polyborate ions present in the treating solution under different pH conditions. Albumin at an acidic pH provides a more durable performance than at alkaline pH because the relative proportion of covalent bonds between boric acid and protein is higher at the lower pH. In the alkaline range, ionic charge interactions are more easily hydrolyzable by the presence of the solvent. At pH < 7, the protein coagulates with boric acid moieties attached to suitable alkaline sites on the protein. The boron compound does not form bridges between different sites of the protein but is only a pendant group grafted onto it. At alkaline pH, polyborate bridges between different sites of the protein are ionic and hydrolyzable (Thévenon and Pizzi, 2003). Ratajczak and Mazela (2007) further showed that protein–boron retention was 3–4 times higher on cellulose than on lignin possibly because the aromatic acyclic lignin system is less susceptible to the action of amino acid groups.

6.2. Tannin auto condensation

The low toxicity of tannins prevents their use as wood preservatives on their own. However, they fix biocides because of their excellent chelating properties. Pizzi and Baecker (1996) describe a mechanism in which boric acid is used to induce autocondensation of flavonoid tannins, leading to the formation of a network of solid autocondensed tannin throughout the wood structure to which the borate is partially fixed. The polymer of low water solubility may or may not be covalently bonded to the wood component. Co-impregnation in a two step treatment of copper, zinc, and boron with tannins met the European standard for protection against rot (Scalbert et al., 1998). A tripartite system with water borne solutions of boric acid, gelatin, and tannins retained boron in wood after a leaching test due to partial fixation of boron by the gelatin and the tannins induced water proofing of the protein leading to the formation of an insoluble polymer network (Thévenon et al., 1998d).

6.3. Physical modification of wood

Compressive deformation of wood is achieved by heating under certain conditions. Compression to a permanent state is densification and reduces the volume of void spaces in wood for liquid uptake. In addition, heating and steaming for compression might induce favorable chemical changes of boron (Yalinkilic et al., 1999b; Baysal and Yalinkilic, 2005). Reduction in boron leaching of steam-compression of boric acid treated wood at 171–200 °C may be due to a chemical conversion of boron (formation of trimeric hydroxyborate ion through dehydration and hydration reactions and/or formation of metaboric ester with the water molecules) in wood (Yalinkilic et al., 1999a).

7. Boron–silicon compounds

Experiments on reactions of wood with silicon compounds to mimic the high natural durability of silicate containing wood species such as *Dicorynia guyanensis* and *Syncarpia glomulifera* have met with limited success (Militz et al., 1997). Applications of silicates have been done in combinations with other biocides or in wood modification. Soluble alkali metal silicates have been employed as agents to reduce boron leaching in numerous studies (Du-Fresne and Campbell, 1967; Kazunobu, 1995; Slimak and Slimak, 1998; Yamaguchi, 2003, 2005). Silicic acid and boric acid impregnated into wood in a single step showed high resistance to termites and decay by *F. palustris* and displayed high water resistance. A silicon element is substituted and a boron element built into the crystal lattice of silicic acid preventing leaching of boron from the wood (Yamaguchi, 2003). Alkali silicate compounds are soluble and various methods have been proposed to insolubilize them in wood. The silicate is selected from sodium, potassium, lithium, cesium, rubidium or ammonium silicate. Du-Fresne and Campbell (1967) showed that wood can be impregnated

with a solution containing a silicate and borate and then treated with sufficient carbon dioxide for about 8 h to form a silicon dioxide polymer. Atmospheric air is insufficient because of low percent CO₂. The fire resistance of the wood was retained even after severe weathering. This study did not test against wood degrading organisms. Soluble sodium silicate in intercellular structures of cellulosic material can be polymerized to an insoluble form by infusion of radiant heat, electrical current, microwaves, lasers, or high temperatures for short periods of time. The process may cause destruction of the interior structure of the wood (Slimak and Slimak, 1998). Solubility of sodium silicate may also be reduced by treating wood in a second step with a soluble metal salt (e.g., CaCl₂) which penetrates the voids and reacts in situ to form a hydrated water insoluble metallic silicate (Kazunobu, 1995). Kazunobu (1995) patented a formulation comprising a preservative component selected from a copper, zinc, a boron compound or mixtures thereof, a volatile basic compound, sodium silicate, and water. Sodium silicate is made insoluble in a second treatment with a soluble salt. Thus, boric acid, copper, and/or zinc components are confined in the wood.

8. Borates as additives in other formulations

The limitation of borates for non-leaching applications has to some extent been overcome by use of formulations where boron is one ingredient in a mixed preservative formulation. Boron compounds are frequently used as additives to improve efficacy of copper-based preservatives especially against copper tolerant fungi. Wood impregnated with copper-ethanolamine and boron has shown reduced copper fixation in leaching studies but improved performance against the copper tolerant fungus *Antrodia vaillantii* (Pohleven and Humar, 2006). Borates have played a successful role as co-biocides in formulations such as copper chrome boron (CCB) seen as a suitable alternative to CCA (Lloyd, 1995). The magnitude of boron leached from CCB treated wood is higher than that of copper and chromium (Peylo and Willeitner, 1997, 1999). Although less boron is leached from ammoniacal copper borate (ACB), there is more boron leached compared to copper (Johnson and Gutzmer, 1978; Johnson and Foster, 1991). Although the boron in zinc borate is more resistant to depletion than in sodium borates, the boron will deplete over time while the zinc component is much more resistant to depletion. ZB hydrolyses to zinc oxide and boric acid. The zinc oxide stays in the wood while boric acid is leached (Laks and Manning, 1995). The first copper azole formulation (type A) contained 49% copper, 49% boric acid, and 2% tebuconazole. The more recent, type B formulation does not contain boric acid and is comprised of 96% copper and 4% tebuconazole (Lebow, 2004). Laboratory and field tests have shown that borates do not protect wood adequately against molds (fungi Imperfecti) and soft-rot fungi (Ascomycetes) and hence must be formulated with co-biocides to protect against this fungi (Amburgey, 1990).

9. Conclusions

Data on the leaching of borates has been gathered over the last 50 years. Stand alone inorganic boron systems offer adequate protection to lumber in non-ground contact situations and building applications. Most of the research in attaining reduced leaching is aimed at expanding the user classes of borates. 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. Use of borates in exterior applications is likely to prove commercially significant in future. The physical and chemical properties of borates render them suitable for formulation as stand alone preservatives and allows them to make 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. 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 crossties. This treatment option has been commercialized and borate pretreated ties are used in AWP hazard zones 4 and 5 (Gauntt and Amburgey, 2005; Jones et al., 2006). Establishment of niche systems is another option likely to be taken by the industry. This implies 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. 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.

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