

BORON IN WOOD PRESERVATION: PROBLEMS, CHALLENGES AND PROPOSED SOLUTIONS. AN OVERVIEW ON RECENT RESEARCH

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ABSTRACT

A short review is presented on boron as a wood preservative. Sessions include the kind of chemicals applied and the level of efficiency obtained against several kind of fungi and termites, the influence of wood species, the traditional problem of boron leachability if timber is simply impregnated with aqueous solutions of acid boric or borate, but that at the same time enables impregnation of less permeable wood species by slow diffusion of unseasoned timber, the application of boron in conjunction with polymer or proteins, claimed as increasing significantly the resistance to leaching, and, finally, a summary is made on the boron chemistry that can be explored for boron-in-wood fixation studies, an approach that has been already started to be followed by the authors.

RESUMO

É feita uma revisão sintética sobre o elemento boro como um agente preservador da madeira. Temas específicos incluem os tipos de produtos químicos de boro que são aplicados na madeira, o nível de eficiência anti-biodeterioração que tem sido possível atingir contra várias espécies de fungos, e contra as térmitas, o problema tradicional da lixiviação do boro, se forem aplicadas meramente soluções aquosas de ácido bórico ou de borato, os tratamentos por difusão lenta na madeira verde, alguns métodos que aplicam o boro em conjugação com polímeros ou proteínas para aumentar a resistência à lixiviação, e um sumário da química do boro sobre a qual pode ser baseada investigação sobre a fixação do boro na madeira, uma abordagem já iniciada pelos autores.

1. INTRODUCTION

The treatment of wood products to extend their service life, although often regarded as anti-ecological, because traditionally toxic chemical formulations have been applied to prevent degradation by biodeteriorating organisms (*e.g.* insects, fungi and sometimes bacteria), can, nevertheless, have ecological benefits. It is estimated that just in the United States the natural phenomenon of biodegradation of wood in service implies an additional forest cutting of more than 150.000 ha yearly (Barnes and Murphy, 1995). When extended worldwide, the loss of forested areas would be obviously even more significant, with respective loss of ecological benefits, especially considering

4 current concerns about global warming and the loss of biological diversity due to deforestation.

To these ecological disadvantage brought about when and where wood preservation is not an established practice, we must add economical losses. Giving just the example of Formosan subterranean termites (FST), it is estimated that they cause some US\$300 million in damage per year in the Greater New Orleans Metropolitan Area only, and for the whole U.S.A. the annual cost of replacing wood damaged only by the FST is estimated to be \$2 billion (Freeman et al., 2003).

Historically, the most common chemicals applied for the pressure treatment of wood in the wood-preserving industry have been creosote (which appeared on 1681), acid copper chromate (1928), pentachlorophenol (1931), chromated copper arsenate (CCA) (1933), ammoniacal copper arsenate (1939), inorganic borates for dip-diffusion (1950s), and more recently, non-arsenic and non-chromium systems (1990s). Although very efficient some of these formulation have been in extending the life of wood, the health hazard for treatment plants operators and the risk of environmental impact in soil and landscape is evident. Some of them involve arsenic or acid hexavalent chromium, and nowadays even copper is suspicious. To have an idea of the amount of chemicals involved, only in North America by the year 2000 the usage of CCA was 70,000 – 85,000 ton of active oxide (Preston, 2000).

For reasons explained below, and that make the reason of this paper, boron and borates are an exception in this pessimistic framing. This does not mean, however, that boron chemicals are at the present time the only solution to alleviate the anxiety of the consumer, or of the public opinion, in this subject matter. Other principles for wood preservation in the future are being investigated.

However, the foreseen of risks to environment is not straightforward. For example, chromated copper arsenate formulations (CCA), have been regarded as safe to use. Since time and conditions have been given in the treatment plant to fix the active elements, the loss, or leaching, of them to soil or water can be minimal. Moreover, they are highly effective: a pole of pine can last for 40 years, although an untreated one may be in service for only 2 years, at most. A problem persists, anyway. It is that, the end of service life of treated wood has to come some day, and it has to be replaced. Wood out of service that was treated with toxic chemicals is legally considered as a toxic residue, that needs proper disposal, that can be difficult and expensive, or maybe not already developed.

With this background, the goals for the research community on wood preservation are to develop 1) new biocides with lower mammalian and eco-toxicity; 2) combinations of biocide systems that increase treatment effectiveness; and 3) innovative treatment technologies that reduce environmental impact (Barnes and Murphy, 1995). In addition to this most pressing need, research

is also required to 1) improve the mildew and mold resistance of organic-biocide-based wood preservatives; 2) explore non-conventional methods of wood protection, like trapping and chemical modification, 3) explore the possibilities of wood preservatives derived from natural products, 4) improve their efficacy in ground contact; 5) reduce their cost; and 6) examine their effects on a host of wood properties, including corrosivity, paintability, gluability, electrical conductivity, strength, fire resistance, and ease of disposal and recycling (Evans, 2003).

Boron has been a candidate to meet these challenges. Boron has a low mammalian toxicity and low volatility; its aqueous solutions are colourless, odourless and non corrosive, are cost effective and effective as insecticides and fungicides (Nunes, 1997; Yalinkilic et al., 1999a). However, one restriction that borates have had in timber preservation has been a result of their natural solubility, that leads to the depletion of borates from treated wood under outdoor conditions, particularly at ground-contact, and with loss of biological resistance (Peylo and Willeitner, 1995; Lloyd, 1998).

Because of this, and even though borates had a promising start with timber treatments by dip-diffusion, after some years of application in Europe, their application was almost abandoned. This happened for a number of recognisable reasons but mainly because of problems with the supply and stocking of treated timber. Since the process was only suitable for application to green timbers and a long diffusion time was needed, orders had to be made months in advance and that was not very practical in terms of the construction market. At the same time LOSP (low organic solvent products) systems were being developed and they provided the industry with a convenient alternative to the boron diffused material.

To all the problems related above to the use of the traditional preservatives and the significant concerns about the use of volatile organic compounds, boron-based preservatives were re-discovered (Dickinson and Murphy, 1989). The renewed interest in boron as a wood preservative is mainly due to the need felt by the industry to find more operator and environmentally “friendly” preservative systems (Barnes et al., 1989).

Nevertheless, the leachability problems remained and for instance, in USA borate standards have only been issued by the American Wood-Preservers’ Association (AWPA) for (only) aboveground, protected uses.

The aim of this paper is to give a contribution to the question of making boron formulations more efficient for wood preservation, either in terms of fixation methods and long-term effectiveness, as well as preventing biodegradation by a broad range of organisms. The contribution from boron chemistry background and today research is seen as an important tool.

6 2. EFFICIENCY OF BORON AS A WOOD PRESERVATIVE

In terms of the timber industry, boron was initially considered for flame retardant treatments (Falck and Ketkar, 1934), but in the late 1940s the use of boron diffusion had spread in Australia and New Zealand where it gave reliable, effective and economical treatment of building timbers and plywood (Bunn, 1974, Cockroft and Levy, 1973). After 1950, considerable interest also developed in Europe (Findlay, 1956).

Primarily it was used for controlling infestations by the powder post beetle, *Lyctus sp.* either in solid wood or in plywood made of tropical hardwoods (Tamblyn and Gordon, 1950). It was also applied to control the common furniture beetle, *Anobium sp.* (Spiller and Denne, 1948; French, 1969) and later, as the knowledge of its efficacy developed, to prevent fungal attack (Harrow, 1950; Carr, 1958; Findlay, 1956, 1959) and to control termites (Gay et al., 1958; Tamblyn et al., 1959).

Aqueous solutions of boric acid/borax or of disodium octaborate tetrahydrate were applied almost exclusively by the “dip-diffusion” process. That is, unseasoned timber was dipped in a concentrated solution (e.g. 30%) of the preservative and then stored under non-drying conditions for several days or weeks for the preservative components to penetrate the timber by diffusion. Under suitable conditions, even timbers resistant to vacuum and pressure treatment could be fully impregnated by diffusion methods (Vinden, 1984; Dickinson and Murphy, 1989). An example can be the case of quaking aspen (*Populus tremuloides* Michx.). Puettmann and Schmidt (1997) had demonstrated that aspen boards, giving restricted drying conditions of high humidity and high temperature, can exhibit sufficient preservative loading at the core, sufficient for control of decay fungi and wood-destroying insects.

Borates, in general, have proved to be effective fungicides at retentions of 2.0 kg/m³ or 0.5% (w/w) of boric acid equivalent (BAE) (e.g. Harrow, 1950; Becker, 1959; Turner et al., 1990; Tsunoda, 2001), though with some specific problems. For instance, they are usually quite effective in preventing the growth of sapstain fungi in green timber but cannot do the same with mould fungi. However, a mixture of borates with suitable co-biocides can prevent the growth of both kinds of fungi (Nunes, 1994; Amburgey, 1990; Byrne, 1990). As for soft rot fungi, they are also said to be boron tolerant (Williams and Amburgey, 1987) although the lack of efficacy might be linked with an eventual leaching of the borates. In a non leaching environment such as window joinery, the soft rots present are controlled with levels lower than the ones needed to control basidiomycetes (Dicker et al., 1983).

Termite testing with borates dates back several decades but has not been as comprehensive as the fungicidal testing (Drysdale, 1994) and a common feature of the termite studies has been the variability in toxic thresholds obtained with different combinations of test methods, termite and timber species. Efficacy against termites has been demonstrated in solid wood both in the field and in the laboratory since early days of research in this

field (Cockroft and Levy, 1973). Several researchers have carried out basic termite testing on the efficacy of several boron compounds either as wood or soil preservatives. Results from a number of tests with subterranean termites are summarised in Table 1.

Table 1: Examples of toxicity of boron compounds to subterranean termites

Termite Species	Feeding Material	Preservative	mrt		Comments	Reference
			BAE % w/w	other		
<i>Coptotermes formosanus</i>	Southern Yellow Pine	Timbor®		3.89 kg/m ³	above ground field tests in Hawaii and Florida	Preston et al., 1985 and Preston et al., 1986
	Several	Several	0.50		literature review	Harris, 1961
	Banak	Am-Bor-P®	0.09	1.44 kg/m ³	for 1% wood weight loss	Williams et al., 1990
		Am-Bor-S®	0.15	2.40 kg/m ³	“	<i>idem</i>
		Timbor®	0.18	2.88 kg/m ³	“	<i>ibidem</i>
	Spruce	Timbor®		> 2500 ppm	mortality 75.9%	Tokoro and Su, 1993
		Bora-care™		> 2500 ppm	mortality 91.7% (Surface treatment)	<i>idem</i>
	Douglas fir	Timbor®	1.02	0.85%	above ground field test (sequential exposure - 23 weeks)	Grace et al., 1992
		Timbor®	1.92	1.60%	like above (40 weeks)	Grace and Yamamoto, 1993
<i>Reticulitermes flavipes</i>	Southern Yellow Pine	Timbor®		3.89 kg/m ³	above ground field test	Preston et al., 1985
	Banak	Timbor®	0.33 > 0.17		no survival	Williams and Amburgey, 1987
		Am-Bor-P®	0.15	2.40 kg/m ³	for 1% wood weight loss	Williams et al., 1990
		Am-Bor-S®	0.12	1.92 kg/m ³	“	<i>idem</i>
		Timbor®	0.10	1.60 kg/m ³	“	<i>ibidem</i>
	filter paper	Timbor®		10000 ppm		Grace et al., 1990
	Spruce	Timbor®		> 2500 ppm	mortality 67.5%	Tokoro and Su, 1993
		Bora-care™		> 2500 ppm	mortality 94.7% (surface treatment)	<i>idem</i>
	Aspen waferboard	Timbor®		0.85%	mortality 100% (surface damaged; no choice and choice tests)	Myles, 1994

mrt = minimum recorded toxicity

8 The efficacy of novel boron treatments has also been evaluated for vapour boron on solid wood (pine and cryptomeria) but particularly on wood based products (Nunes, 1997; Tsunoda, 2001). A concentration of less than 1% BAE (boric acid equivalent) seemed sufficient to control biological attacks on composites.

3. BORON FIXATION STUDIES AND PROPOSALS

Although boron chemicals have been used to impregnate wood for more than 50 years, their fixation in wood, to prevent leaching under unprotected conditions from weather or soil, and ensure long term efficiency, has been a challenge for scientists, that lasts until today.

Traditionally, boron solutions have been applied in wood by dip-diffusion methods. This means that, although times needed to allow for diffusion of boron from surface to the core of timber members can be long, making such a treatment process low productive, on the other hand, it may enable to treat refractory wood species, that would not be feasible to treat by vacuum-pressure methods. That is the case of quaking aspen (*Populus tremuloides* Michx.), already referred.

Chen et al. (1997), after assessing the minimum diffusion time required for adequate diffusion penetration of borate, the effects of boron formulation and wood species on initial loading and subsequent borate diffusibility, and the relationship between wood liquid permeability and borate diffusibility, have concluded that more than 8 weeks of diffusion storage are needed for an adequate penetration of all four species studied (red oak (*Quercus rubra* L.), white oak (*Q. alba* L.), white ash (*Fraxinus americana* L.) and yellow-poplar (*Liriodendron tulipifera* L.).

Raman spectroscopic studies revealed that, when wood is treated with aqueous boric acid solution, $B(OH)_3$ is the dominant form in the boron species present in wood, and this can be classified into two groups: 1) one group comprise the microcrystalline state of $B(OH)_3$ precipitated in lumens, and the other comprises the $B(OH)_3$ units penetrating the cell wall (Yamauchi and Doi, 2003).

Pizzi and Baecker (1996) have presented a boron fixation mechanism based on a reaction of the autocondensation-type induced by boric acid on flavonoid tannins. As argued by the authors, the boric acid is partly fixed by the network of the autocondensed tannin in the wood but conserves sufficient mobility to maintain the preservative action. Accelerated termite field tests indicated an increase in permanence of boron in wood with consequent preservative durability between 3 and 6 times.

A boron-based treatment of wood regarded as long-term, wide-spectrum, ground-contact suitable, and heavy duty, with performances comparable to CCA, has been presented by Thevenon et al. (1997). The principle is simple,

and just premixed albumin plus boric acid, premanufactured albumin borate, and soja protein plus boric acid, all showed good preservative performance and much retarded leaching of boron. The mechanism seems to lie on the formation of a salt with the protein which is then insolubilised by heat-induced coagulation.

Other combined treatment, impregnation of wood specimens with sodium borate or boric acid, followed by impregnation with polyethylene glycol (PEG), resulted in a significantly increased resistance to boron leaching (Gezer et al., 1999), although authors suspected that the PEG effect may be temporary. More research on this topic is needed.

Lin et al. (2001) succeeded in a very small reduction of boron retention in wood after water leaching tests, and excellent decay-resisting effect at low boron retention, after the double treatment of tetraphenylborate sodium salt with potassium chloride, or tetramethylammonium bromide, to form insoluble salts of tetraphenylborate tetramethylammonium or tetraphenylborate potassium.

Other properties than just biodeterioration resistance were improved by a combined treatment of boron with vinyl monomer polymerisation (Yalinkilic et al., 1998). Wood specimens were impregnated with boric acid, followed by impregnation again with styrene, methylmetacrylate and their mixtures, in the presence of a catalyser and a crosslinker, and polymerisation was conducted by heat radiation. Treated wood exhibited lower water absorption, considerably delayed boron leaching, became resistant to two decay fungi and a termite, and more resistance to fire.

Boric acid (BA) and phenylboronic acid (PBA) were added into aqueous solutions of dimethylol dihydroxy ethyleneurea (DMDHEU), glutaraldehyde (GA) and glyoxal (GX), to obtain some synergistic effects (Yalinkilic et al., 1999b). Although the benefits in dimensional stability of wood were not consistent for all those 3 chemicals, BA was found appropriate to be added to the used cross-linking agents in such service conditions where decay risk is high while PBA combinations should be preferred if termite damages prevail.

Still in line with combined treatments for combined effects, a proposed treatment combines glycerol/glyoxal and boric acid mixtures capable of improving not only the durability but also the dimensional stability of timber (Toussaint-Dauvergne et al., 2000). Preliminary laboratory tests indicate dimensional stabilisation and inhibition of fungal growth, although no data on boron leaching resistance were reported and, hence, more extensive studies are needed.

Wood composites can also be turned more biodeterioration resistant with boron. Bridaux et al. (2001) added borates to the gluing formulation of poplar veneer LVL. The melamine-urea-formaldehyde (MUF) formulations were mixed with various concentrations. No significant reduction of physical

10 properties was measured and a 0.8% retention of boron was measured after intensive water leaching. However, no fire nor decay resistance data were obtained in this study.

If the description above has always involved aqueous solutions of boron, it can also be applied on a gaseous form, which presents advantages in given situations. Tension forces at the liquid-air and liquid-wood interfaces may be eliminated, and the low permeability of pit membranes may no longer be a problem, enhancing transverse movement. Also, densified wood composites (e.g., particleboard, MDF, OSB, etc.) would not swell and lower their physical properties, if aqueous boron treatments were made after manufacturing. Hashim et al. (1997) treated several kinds of wood composites with trimethyl borate in the vapour phase. Its reaction with the wood moisture would yield boric acid and methanol. The test retentions represented levels appropriate for protection against biological attack and fire, and the treatment did not significantly affect the physical properties of the boards. Tsunoda (2001) applied the same gaseous treatment to wood, finding no difference in effectiveness between vapour-boron and liquid-boron, regarding resistance to decay fungi and subterranean termites.

Through chemistry-based studies on the treatment of maritime pine (*Pinus pinaster* Ait) with aqueous solutions of boric acid and borate, Ramos et al. (2004) found for acid boric a higher kinetic constant and lower leachability than for borate. Results of adsorption isotherms suggest that physical adsorption, not a chemical reaction, seems to be the preferential mechanism for bonding of boron on wood, and that the adsorption of boric acid (pH=5.5) is faster and stronger (low leachability) than the uptake of borate.

In fact, in our research to develop any methods for boron fixation in wood we follow a chemistry-based approach, either by making use of the existing background in the field, of which the next session is a summary, or by developing ourselves a contribution for such knowledge.

4. BORON CHEMISTRY RELEVANT TO WOOD PRESERVATION

Boron, the fifth element in the periodic table, has a highly diverse and interesting chemistry (Greenwood and Earnshaw, 1984). Much of the interest in B chemistry arises from the electron deficiency of its compounds. With three valence electrons it can form three bond pairs, leaving an unfilled p orbital in the valence shell (Power and Woods, 1997) that gives boron the ability to accept electron pairs (Lewis acidity). This is why boron has a high affinity to oxygen.

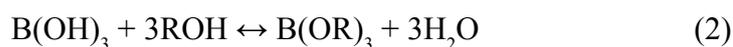
Boron is not an abundant element but it is widely distributed in both the lithosphere and hydrosphere. High B content soils are associated with recent volcanism. In nature, boron is always bounded to oxygen as borates, less often as boric acid and rarely as BF_4 .

Boric acid is normally obtained from borax ($\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{OH}$) and consists of $\text{B}(\text{OH})_3$ units bounded by hydrogen bridges. It is a weak acid and act as a Lewis acid accepting OH^- .



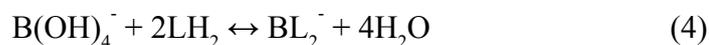
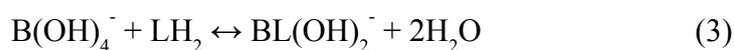
At low concentrations ($<0.025 \text{ M}$) only the mononuclear species $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ are present in solution. At higher concentrations polynuclear ions are formed (Cotton and Wilkinson, 1988).

Boric acid reacts with alcohols in accordance with the following reaction:



The reaction may be driven to completion by removal of water in accordance with Le Chatelier's principle. This can be due by addition of a hydrocarbon, e.g. benzene or toluene, to form an azeotrope which may be removed by distillation. A wide variety of boric acid esters can be synthesised in this way (Power and Woods, 1997). With polyhydroxialcohols, or carboxylic acids with *cis*-hydroxi groups, boric acid forms very stable complexes 1:1 or 1:2.

Boron, in the form of borate, reacts with carbohydrates to form anionic complexes:



where LH_2 is a 1,2 diol.

Formation of complexes is only possible if the two hydroxyl groups are favourably positioned. So, borate complexes are easily obtained with ligands that have two hydroxyl groups in a *cis* position. Reactions of boron with cyclic sugars are more difficult than reactions with aliphatic compounds.

The reactions described above are of great interest for wood preservation because they can also occur with hydroxyl surface groups of wood polysaccharides producing chemically fixed boron and decreasing boron leachability. Although it is important that boron conserves a certain mobility to maintain the preservative action and, at the same time, decreasing its leachability.

5. CONCLUSIONS

There is an extensive experience on boron as a wood preservative, when applied simply as aqueous solutions of boric acid or borate (about toxic thresholds, any resistant biodeteriorating organisms, conditions of application, leachability rates, durability of timber, etc.). There is no doubt that boron chemicals, and methods to apply them, are at the heart of the nowadays trend of research to develop environment friendly preservatives,

12 with low social impact. The main challenge is to impregnate timber with boron in any form or by any method, alone or concomitantly with other chemicals to obtain a synergistic effect, so that timber is efficiently protected, for a long time, and in unprotected outdoor conditions, against the main biodeterioration organisms. Some methods have already been published, but until now no-one reached industrial application. It seems that this is the course of research on this specific field but, these days, with an ultimate validation by a commercial application. This poses other orders of technical problems and of decision criteria. There is a lot of scope for research, and to develop and make use of boron chemistry related to wood chemistry.

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