

## **Boron in Wood Preservation A Review in its Physico-Chemical Aspects**

**Fernando Caldeira**

Associate Professor

CIAGEB - Research Centre on Global Changes, Energy, Environment and  
Bioengineering.

GAEA - Group of Environmental and Applied Ecology. Faculty of Science and  
Technology - Fernando Pessoa University. Praça 9 de Abril, 349, 4249-004 PORTO,  
Portugal

---

**Abstract.** A review is presented on the application of boron chemicals for the purpose of wood preservation that covers about the past 20 years and mostly the papers published in the journals of the wood science field. Topics developed here include the physical phenomena associated with the impregnation of wood with boron-chemical solutions, the issue of preventing leaching and/or fixing boron in wood to lengthen the effect of treatments and/or enable the application of wood and wood products in biodeterioration hazardous conditions, and the chemical and physical effects on wood of a combination of heat and boron treatments. Finally, as an essential condition for research aiming at developing more environment friendly and less risky methods for preserving wood with boron chemicals in a efficient way, a survey is made on boron chemistry pertinent to wood preservation.

**Key words:** Boron; preservation; wood; review

### **O Boro na Preservação da Madeira – Uma Revisão sobre os seus Aspectos Físico-Químicos**

**Sumário.** É apresentada uma revisão sobre a aplicação de produtos químicos de boro para a preservação da madeira, que cobre cerca dos últimos 20 anos e versa sobretudo artigos publicados nas revistas científicas da área das ciências da madeira. Os tópicos abordados incluem os fenómenos físicos associados à impregnação de madeira com soluções de boro, a questão de evitar o lixiviamento e/ou a fixação do boro na madeira para prolongar o efeito dos tratamentos e/ou possibilitar a aplicação de madeira e de produtos derivados de madeira em condições mais severas de biodeterioração, e os efeitos químicos e físicos na madeira dos tratamentos térmico e químico com boro combinados. Finalmente, como uma condição essencial para fazer investigação tendente ao desenvolvimento de métodos eficientes para tratamento de madeira com boro, mas que sejam ao mesmo tempo amigos do ambiente e que ponham poucos riscos à saúde humana, é feita uma abordagem à química do boro relevante para a preservação da madeira.

**Palavras-chave:** Boro; preservação; madeira; revisão

**Le Bore dans la Préservation du Bois – Une Révision sur ses Aspects Physico Chimiques**

**Résumé.** Nous présentons une révision sur l'application du bore dans la préservation du bois, qui couvre les vingt dernières années et presque tous les articles publiés dans les revues concernant le sujet de la science du bois. Les thèmes développés sont les phénomènes physiques concernant l'utilisation de solutions chimiques de bore, la prévention du lessivage et/ou la fixation du bore dans le bois pour prolonger l'effet des traitements et/ou pour rendre possible l'utilisation du bois et des produits dérivés du bois dans des conditions adverses du point de vue de la biodétérioration, et aussi les effets physiques et chimiques qui provoquent dans le bois des traitements qui combinent chaleur et bore. Finalement, on présente un résumé de la chimie du bore en ce qui concerne les procédés de conservation du bois, en tant que connaissance essentielle pour une recherche concernant des méthodes plus écologiques et moins dangereuses.

**Mots clés:** Bore; préservation; bois; révision

---

**Introduction**

BARNES and MURPHY (1995) pointed out that the goals of the wood preservation research community were to develop 1) new biocides with lower mammalian and eco-toxicity; 2) combination biocide systems that increase treatment effectiveness; and 3) innovative treatment technologies that reduce environmental impact. We can say that such objectives are still valid.

Still today there is a general afraid in the public opinion about the impact of wood preservation formulations on the environment and human health. Probably, what have been the most used formulations for the treatment of wood to be used in ground contact, namely CCA (chromium(VI)-copper-arsenic) preservatives, although very effective in lengthening the life of wood in service, they have also been developing a great concern. As a result, in Europe and North America arsenic has been banned from most of the applications for preserved wood. This means that market for CCA formulations was diminished

and new formulations have been developed to replace the former, with a similar efficiency if possible. Modifications already developed to such inorganic systems include replacement of part of the arsenic with zinc, as in ammoniacal copper zinc arsenate (ACZA) used in western North America, or the complete replacement of arsenic with boron, as in chromated copper borate (CCB) used in some parts of Europe. Also, chromium, as a heavy metal, has undergone close environmental scrutiny, thereby spurring efforts to replace or reduce its use in waterborne systems. Systems that rely on copper as a fungicide may also come under scrutiny in the future.

Boron-based systems are candidates for the future range of preservative formulations with lower environmental and health impacts. Boron compounds have been used for over 40 years in Australia and Europe. The principal compound being used in the United States is disodiumoctaborate tetrahydrate  $[\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}]$  (borax), which is soluble in water, is colourless,

and diffuses readily into green wood or can be pressure impregnated into dry wood. A retention of 2.7 kg/m<sup>3</sup> B<sub>2</sub>O<sub>3</sub> is specified by AWWPA (American Wood Preservers Association), and borates have been registered by the U.S. Environmental Protection Agency (EPA) as wood preservatives.

Boron compounds offer some of the most effective and versatile wood preservative systems available today, combining the properties of broad-spectrum efficacy and low acute mammalian toxicity (FREEMAN *et al.*, 2003). However, more recently (AUGUST, 2008) the European Commission decided to make an ATP - Adaptation to Technical Progress of Council Directive 67/548/EEC (the 30<sup>th</sup> ATP), and since then boric acid and disodium tetraborate decahydrate are classified as reprotoxic category 2. These boron chemicals are classified as substances toxic for reproduction category 2 for both fertility and developmental effects. The directive apply to them the risk phases R60 (may impair fertility) and R61 (may cause harm to the unborn child).

Products treated with borates include the following: lumber and plywood, oriented strandboard (OSB), siding, engineered wood, wood-plastic composites, millwork, windows, doors, furniture, telephone poles, railroad ties and log homes. However, the greatest use of boron has been remedial treatments. Fused borate rods, glycol solutions containing borates, and remedial bandage wraps for poles are all being used for remedial treatment.

Borates have favourable environmental characteristics, but their high susceptibility to leaching is the main obstacle to the widespread use of boron as a major component of broad-

spectrum wood preservatives.

This paper reviews recent developments in the area of the wood preservation with boron on its physico-chemical aspects: the treatability of wood with boron formulations, concerns and relative successes in fixing boron in wood; treatment of wood composites furnish, or wood composites themselves, with boron; effects of combining impregnation with boron solutions and heat treatments; and, as a background needed for the research in these topics, the basics on the boron chemistry with potential application in wood preservation.

### Physics of the Treatment of Wood with Boron

Working with dry, incised or nonincised Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) and western hemlock (*Tsuga heterophylla* Raf.) Sarg.), MORRELL and LEBOW (1991) treated the lumber with disodiumoctaborate tetrahydrate and subjected it to dip or pressure treatments. They found that gross retentions and boron penetration were higher in pressure-treated material, particularly when the wood was incised. Higher retentions were achieved in dry lumber than were found in previous tests with green lumber, but boron penetration was generally lower in the dry material, probably because higher moisture contents improve boron diffusion without adversely affecting solution absorption.

An economical treatment schedule was arrived as for treating air-dried rubber wood (*Hevea brasiliensis* (HBK) Muell. Arg.) in a pilot plant cylinder: 15 minutes initial vacuum of 85 kPa, 15 min pressure of 1,000 kPa, and 5 min final

vacuum of 85 kPa (GNANAHARAN and DHAMODARAN, 1993). Treating with 3% BAE (boric acid equivalent) solution resulted in a dry salt retention of 13.1 kg/m<sup>3</sup>. Also, the green wood could be treated to required chemical retention by employing the above treatment schedule and by increasing the concentration of the treatment solution to 6% BAE. Latter, this treatment schedule was validated in a commercial wood treatment plant (DHAMODARAN and GNANAHARAN, 1994). Moreover, for *Eucalyptus grandis* (Hill) Maiden wood an economical treatment schedule was achieved, all similar with that described just before but with a pressure of 1,300 kPa (DHAMODARAN and GNANAHARAN, 2006). A dry salt retention (DSR) of 7.7 kg/m<sup>3</sup> was achieved using a 6% BAE solution. It was also found that neither the moisture content of wood nor the treatment schedule posed any problem as far as the treatability of *E. grandis* was concerned (DHAMODARAN and GNANAHARAN, 2007).

Japanese "dodai", used as sill plates for buildings, could be "shell-treated" or "completely penetrated" with borates using various pressure treating schedules and post-treatment diffusion methods (MORRIS *et al.*, 1996). The combination of treatment process and diffusion period selected would depend on the target penetration, analysis zone, or core loading required, and the species involved. For example, shell treatments of 80% at or exceeding 10-mm penetration were obtained in Pacific silver fir (*Abies amabilis* (Dougl.) Forbes) after a 2-hour pressure period. Western hemlock required a 2-hour pressure period and 2 weeks of diffusion. Complete penetration to core loadings of 1.2% BAE were obtained with Pacific

silver fir pressure treated for 6 hours and left for a 6-week diffusion period.

Actually, the fact that boron diffuses readily into green or moisten wood makes it suitable to treat refractory wood species, although diffusion can work on both ways: towards the inner side of wood, or after that, to outside if environment is wet. Experimental data on the diffusion of boron salt solutions (boric acid (H<sub>3</sub>BO<sub>3</sub>)/borax) in heartwood specimens of *Eucalyptus globulus* Labil. resulted in that the effective diffusion coefficients were in the order of  $2.6 \times 10^{-11}$  m<sup>2</sup>/s, and the effect of wood anisotropy was found negligible. The derived diffusion model could be extended to predict the immersion time required to achieve a given degree of salt loading, as a function of board thickness (MELO *et al.*, 1992).

The unsteady-state diffusion of boron through southern pine (*Pinus* spp.) was investigated at various moisture contents, temperatures, and treatment conditions (RA *et al.*, 2001). With this group of wood species, the fastest rates of diffusion were observed in the longitudinal direction, followed by the radial and the tangential directions. The longitudinal diffusion coefficients were 10 to 20 times larger than the radial diffusion coefficients, and the radial diffusion coefficients were 2 to 4 times larger than the tangential diffusion coefficients. The diffusion rate increased with time in all directions. The longitudinal diffusion rate increased rapidly with moisture content (MC), while a slow increase in the radial diffusion rate was observed at MCs above 90%. MC did not affect the rate of tangential diffusion within the range of MCs experimented (70-110%). The effect of temperature on boron diffusion rates

was more pronounced than the effect of MC. The diffusion rate increased with temperature, although slight direction-dependent differences were observed.

Constant radial diffusion coefficients of boron through southern pine were determined from the total amount of boron diffusing through wood and the amount of boron remaining on the wood surface after different diffusion periods (RA *et al.*, 2002). This method was presented as a potential way to easily predict the boron diffusion coefficients for dip-diffusion treatment. If the coefficients represent the difference among species characteristics, they might be useful as species indices. However, DAVIS and van HISE (2006) reported that their own investigation on the same issue gave substantially different diffusion coefficient values.

Investigation was also done on the diffusion of boron into southern pine used green, partially seasoned (air-dried, steam conditioned) or kiln-dried timber, which were subjected to a thermal treatment with 15% disodiumoctaborate tetrahydrate (DOT) solution (BARNES *et al.*, 1993). Results showed that effective treatment meeting the AWPAs minimum retention ( $2.72 \text{ kg/m}^3 \text{ B}_2\text{O}_3$ ) and penetration (64 mm or 85% of the sapwood) could be attained only with certain combinations of seasoning, treatment and diffusion storage. The best results in terms of both retention and penetration were obtained with material stored prior to treatment using a 10-minute hot bath time. Kiln-dried timbers could not be treated effectively.

The Spruce-Pine-Fir (SPF) species group is usually taken as difficult to penetrate with preservatives. The comparison of solution uptake and penetration of boron and copper from a

borax-copper (BC) preservative to that of boron in a disodium octaborate tetrahydrate (DOT) treatment and copper in a chromated copper arsenate (CCA) treatment revealed that, for all those wood species average solution uptake was consistently greater with the DOT solution than that with the BC and CCA solution (LEBOW *et al.*, 2005). Average boron penetration with DOT was also greater than for the BC solution.

The potential of thermal disodium-octaborate tetrahydrate (DOT) treatments as a measure for eliminating insects, fungi, and nematodes from Douglas-fir (*Pseudotsuga menziesii* Franco) logs was investigated (HE *et al.*, 1997). Logs were heated in DOT up to 3 hours at 80°C. Although conditions near the surface of the logs approached those considered lethal for most organisms (71°C for 60 min), temperatures in the pith were generally insufficient to eliminate established fungal infestations. Although boron levels near the surface were sufficient for fungal control, they declined rapidly below the surface; little residual boron was found in the wood at depths greater than 100 mm. Thus, thermal boron treatments may enhance protection of freshly sawn Douglas-fir logs, but they were suggested has not being used as the sole means of pest control for this wood species.

In terms of phytosanitation, it has been found that immersion in a hot borate solution achieved the heat treatment of green railway cross-ties in about 7 hours and significant borate retention was achieved (TAYLOR and LLOYD, 2009). Thus, hot borate immersion treatments could combine the benefits of heat treatment with the long-term advantages of borate treatment with little extra cost in U.S.A.

Hickory (*Carya cordiformis* (Wangenh.) K. Koch) rounds, with the tight bark intact, were immersed for 10 minutes in a room-temperature solution of 24% BAE Tim-Bor (disodiumoctaborate tetrahydrate) or 26.8% BAE boric acid ( $H_3BO_3$ ), and then left plastic-wrapped for 8 weeks to allow for diffusion. The bark and the outer sapwood were penetrated by borate solutions, providing excellent protection from insect damage, as compared to controls (CASSENS and SCHMIDT, 1998).

Boards of a relatively refractory wood species, quaking aspen (*Populus tremuloides* Michx.) could be adequately treated with Tim-Bor (disodium octaborate tetrahydrate active ingredient) using traditional dip-diffusion methods (PUETTMANN and SCHMIDT, 1997). Under restricted drying conditions of high humidity and high temperature, a sufficient preservative loading was obtained for control of wood decay fungi and wood-destroying insects. For example, after 8 weeks of storage in controlled rooms of 86 and 92% RH (relative humidity), boards had core retentions of 0.04 to 0.37% BAE.

Studies on the minimum diffusion storage time required for adequate diffusion penetration of borate, on the effects of borate formulation and wood species on initial loading and subsequent borate diffusibility, and on the relationship between wood liquid permeability and borate diffusibility, were carried out with four wood species: yellow-poplar (*Liriodendron tulipifera* L.), red oak (*Quercus rubra* L.), white ash (*Fraxinus americana* L.), and white oak (*Quercus alba* L.) (CHEN *et al.*, 1997). Results indicated that more than 8 weeks of diffusion storage were needed for an adequate borate penetration for all four

species. Diffuse-porous wood treated better than ring-porous wood, and borate penetration into these samples was more closely related to radial permeability than longitudinal permeability.

Vapour boron treatment was applied in compressed and uncompressed states at high temperatures such as 180 and 200°C for 6-15 min, to wood specimens of Japanese cedar (*Cryptomeria japonica* D. Don) (BAYSAL and YALINKILIC, 2005). Results demonstrated that boric acid can be vaporized under heat and can be impregnated into wood. Success of the technique can be increased by increasing vapour pressure in a closed chamber. Such data have importance on dry wood treatment under heat by boron vapour with a little water presence which does not necessitate a further drying process.

To avoid the exposition of field cuts of treated wood to decay fungi, boron solutions were pressure injected into unprotected wood points and allowed then to diffuse (De GROOT and FELTON, 1998). The behaviour of several wood species was tested and compared.

The insertion of borate rods is also a known method to treat wood, or to remediate it, by a prolonged chemical diffusion around the point of insertion (RHATIGAN *et al.*, 2002). Other chemicals, like fluoride, can also be applied in wood by the same method.

The diffusibility of borate rods was investigated in three anisotropic directions using radiata pine (*Pinus radiata* D. Don) sapwood samples conditioned to 40 and 60% MC for 60 days (RA *et al.*, 2004). Wetter samples showed deeper penetration and higher concentrations of boron at the wood face adjacent to the borate rod. The deepest penetration of boron was observed in the longitudinal direction, followed by the

radial and the tangential directions.

KRABBENHØFT *et al.* (2004) formulated a set of equations governing the migration of dissolved boron in wood, as in remedial treatments with boron rods, for example. Equations were solved by the finite element method and results showing the effect of different treatment strategies were presented. Some conclusions were that rods should be placed as far away from the pole surface as possible; increasing the number of rods increases the maximum concentration in the critical points and the time over which a certain concentration is maintained; some improvement can be achieved by alternative rod placements.

As referred above, one of the common applications for boron are remedial treatments. BORA-CARE, 40% sodium octaborate tetrahydrate in glycol, was first developed in the United States. An investigation of the penetration of BORA-CARE at two different dilutions into four classes of southern pine wood, including old beetle-damaged wood with two different densities of exit holes, sound old wood and new wood, revealed that for all treatments percent BAE levels at all depths sampled were highest in beetle-damaged wood and sound, old wood (PUETTMANN and WILLIAMS, 1992). Compared with penetration of beetle-damaged wood, sound wood consistently treated less well.

The effects of glycol compounds on borate distribution were investigated using Douglas-fir heartwood blocks conditioned to 30-60% MC (FREITAG and MORRELL, 2002). The effect of glycol was more pronounced at 30% MC, although the results did not differ markedly from those with water addition. Results suggest that, while glycol can produce a

slight enhancement in borate diffusion, the added costs probably do not justify the use of this compound in place of water as a medium for enhanced diffusion.

MITSUHASHI *et al.* (2007), after assessing boron leaching during rainfall events with DOT pressure-treated Douglas-fir sawdust, small blocks and sections of boards, concluded that leaching was much quicker from sawdust and blocks, but much lower from boards. Hence, the researchers suggested that accelerated leaching methods are a poor predictor of loss from water diffusible systems.

The combination of boric acid and tall oil in a double impregnation treatment has given synergistic effects; i.e., decay resistance of wood against fungi was higher than that obtained with tall oil or boric acid alone (TEMİZ *et al.*, 2008).

### Boron Fixation Issues

Probably any time the role of boron as a wood preservative is discussed, it is referred the fact that, in traditional treatment methods as those pointed out above, boron is not fixed chemically to wood, and it will be leached out if wood in service is subjected to an wet environment. That is why research is active to find methods to fix boron in wood.

On the other hand, wood should perform well in dry conditions or when protected against moisture by finishes. Actually, this is what has been concluded by PEYLO and WILLEITNER (1995). They found that boron diffuses even at moisture contents below 20%. Thus, in their research work, leaching could not be affected by hydrophobic agents (resins and waxes) placed in the inner

surface of wood because diffusion still takes place in the cell wall. Surface coatings have some protective effect. Hence, it has been recommended that the best way to prevent leaching is the logistical protection by storing and using boron-treated wood under roof.

Based on results of high leachability and low kinetic constants, and on results for the adsorption isotherm of boric acid and wood, RAMOS *et al.* (2006) concluded that adsorption is the preferential mechanism for the bonding of boric acid on wood. Since this seems to be a physical adsorption (with weak forces acting like van der Waals and hydrogen bridges) and not a chemical adsorption, this makes easy the leaching of boron, increasing its tendency to go itself free from the wood. Moreover, YAMAUCHI *et al.* (2007), on their hand, found that  $B(OH)_3$  (boric acid) was the sole boron species observed in Japanese cedar (*Cryptomeria japonica* D. Don) sapwood blocks treated with aqueous or methanolic boric acid solutions, as information given by Raman spectroscopy and prompt gamma-ray analysis (PGA).

PIZZI and BAECKER (1996) presented a boron fixation mechanism based on a reaction in which boric acid induces autocondensation of flavonoid tannins. The boric acid is partly fixed to the network by the autocondensed tannin in the wood but conserves sufficient mobility to maintain its preservative action. Apparent reaction rate constants with very simple model compounds are presented as well as results of accelerated termite field tests. It was concluded that, at the low retentions used experimentally, it should not be suited for ground contact applications but only for aerial, non-ground contact

ones. Further work revealed that preservative systems based on the cross-linking and hardening of condensed tannins by hexamine, where boric acid is complexed onto the network, markedly slow down the leaching of boron (THEVENON *et al.*, 2009). Testing with basidiomycetes fungi also have shown that such treatment enhanced wood durability, before and after leaching.

Wood preservatives based on protein borates, obtained by just mixed water solutions of protein and boric acid, as well as in the case of premanufactured protein borate salts, were shown to greatly retard the leaching of boron from treated timber (THEVENON *et al.*, 1997). Just premixed albumin plus boric acid, premanufactured albumin borate, and soja protein plus boric acid, all showed good preservative performance. A salt is formed with the protein, which is then insolubilised by heat-induced coagulation. From results of biological tests, these preservatives could be classified as long-term, wide-spectrum, ground-contact, heavy-duty wood preservatives. Further studies were carried out on the chemical mechanism that occurs, and on preservative efficiency (THEVENON *et al.*, 1998). With the obtention of  $^{11}B$  NMR (nuclear magnetic resonance) spectra of the reaction products present in solutions of boric acid and protein such as albumin, it was found that at acid pHs only the undissociated  $H_3BO_3$  occurs, while at alkaline pHs it occurs the species  $[B(OH)_4]^-$ ,  $[B_3O_3(OH)_4]^-$  and  $[B_3O_3(OH)_5]^{2-}$  (THEVENON and PIZZI, 2003). Application of heat causes a relative increase in the proportion of the latter two signals indicating both an increase of charged structures in solution and of the proportion of boron ions having reacted



with the protein.

In experiments with aspen (*Populus tremula* L.) and Scots pine (*Pinus sylvestris* L.), although the depth of the penetration of a solution mixture of globular protein and boric acid was smaller than the depth of penetration of the ingredients in the isolated form, which was attributed to the formation of a protein-borate salt, a given vacuum-pressure method ensured deep penetration in wood (MAZELA *et al.*, 2007).

The rate of boron retention in cellulose, lignin and wood powder of Scots pine (*Pinus sylvestris* L.) by using denaturing properties contained in reaction solutions and the reactivity of wood and those wood components with protein borates was assessed (RATAJCZAK and MAZELA, 2007). The method of protein denaturation (thermal and chemical with tannic acid were investigated) played the crucial role in the rate of boron retention, and the type of protein had also a significant effect.

Boron treatment of wood was combined with vinyl polymerisation to improve leaching resistance of boron, as well as dimensional stability, biological and fire resistance of wood (YALINKILIC *et al.*, 1998). Boric acid was impregnated into wood specimens (*Cryptomeria japonica* D. Don) prior to vinyl monomer impregnation in the presence of a catalyser and a crosslinker. Polymerization was conducted by heat radiation. Latter on, scanning electron microscope (SEM) observations suggested how controlled-but-continuous boron leaching might have occurred in accelerated weathering tests (YALINKILIC *et al.*, 1999a). An "enveloping" treatment of boron deposited in cell walls by an effective bulking process was found essential for

better immobility.

Experiments with several other non- or low-formaldehyde crosslinking reagents (dimethylol dihydroxy ethyleneurea, glutaraldehyde and glyoxal), and comparison of boric acid and phenylboronic acid as preservatives, concluded that boric acid was appropriate to be added to the used crosslinking agents in such service conditions where decay risk is high, while phenylboronic acid combinations should be preferred if termite damage prevails (YALINKILIC *et al.*, 1999b). Furfuryl alcohol, when polymerised mixed with borates, not only considerably improved antismoulding efficiency of Japanese cedar and Scots pine, but also retarded boron leaching, suggesting the possibility of longer protection of treated wood in service (BAYSAL *et al.*, 2004).

A phenol-formaldehyde (PF) resin, where the phenol was partly substituted with pyrolysis oil derived from softwood bark, was prepared to penetrate wood and immobilize copper and boron in wood cells (MOURANT *et al.*, 2009). A reduction of up to 25 times in leaching of boron was achieved, as compared to control samples, on a total weight basis.

Wood-mineral composites were made by introducing inorganic substances into wood using the water glass (sodium silicate)-boron compound system (double treatment) (FURUNO and IMAMURA, 1998). This is a method for the formation of insoluble inorganic substances in wood and, after the leaching procedure, the composites showed generally excellent termite resistances.

GEZER *et al.* (1999) succeeded in imparting resistance to boron leaching by a sequential treatment with sodium

borate and then with polyethylene glycol (PEG). However, after leaching tests they defended that, although results suggested that bulking agents may enhance the resistance of boron to leaching, it may be a temporary effect, possibly as a result of PEG depletion. BAYSAL *et al.* (2006) also found that PEG-400 not even restricted boron leaching but showed to increase it; however, among other agents (water repellents) tried to restrict water access to wood, and hence boron leaching, styrene was the most effective monomer.

Mixtures of glycerol/glyoxal and boric acid showed to be a preservative system for hazard class III, capable of improving not only durability but also the dimensional stability of timber treated with them (TOUSSAINT-DAUVERGNE *et al.*, 2000).

A double treatment of tetraphenylborate sodium salt  $[(C_6H_5)_4BNa]$  with potassium chloride (KCl) or tetramethylammonium bromide  $[(CH_3)_4NBr]$  can be a method to form insoluble salts of tetraphenylborate tetramethylammonium or tetraphenylborate potassium in wood (LIN *et al.*, 2001). The reduction of boron retention in treated wood specimens after the water leaching test was very small, showing the good fixation of boron compounds in wood.

Preliminary results indicated that formulations based on borate with zirconium additive are probably suitable for use in exterior aboveground and possibly ground contact situations (LLOYD *et al.*, 2001). The treatment solution contained disodium octaborate tetrahydrate and zirconium oxide, in the form of ammonium zirconium carbonate. The fixation was optimised by heat treatment at 60°C, and the maximum fixation was found at the highest pH

level experimented (pH 10) of the treating solution.

A combination of a silicic acid monomer aqueous solution with boric acid proved to be another method for boron fixation in wood, as there was little leaching of agent in leaching tests (YAMAGUCHI, 2002). Field tests during three rainy seasons (about 6 months in total) in three years demonstrated that the silicic acid:boric acid agent had a high water resistance ability worthy of application in the outdoors (YAMAGUCHI, 2003).

Wood blocks treated sequentially with boron compounds (disodium octaborate tetrahydrate (DOT), boric acid or calcium tetraborate, and then with 1.0% NHA-Na (N'-n-(1, 8-Naphthyl) hydroxylamine) solutions showed about 30% less boron leaching (KARTAL and IMAMURA, 2004). The interpretation for this result is a possible boron precipitation after NHA treatments.

Surface treatment of wood using acryl-silicon type resin including didecyl dimethyl ammonium tetrafluoborate (DBF) at 2%-concentration provided lasting protection against wood degradation owing to the amount of DBF remaining in the wood after a 10-cycle severe weathering process (HWANG *et al.*, 2005). Further investigation for preservative efficacy against brown-rot and white-rot fungi and termites suggested that DBF was a promising treatment to be used outdoors (KARTAL *et al.*, 2006).

A new chemical compound (ABO) combining the water repellence of oleic acid and the biocidal effect of boric acid, linked by ammonia, and which synthesis was validated by FTIR (Fourier-transformed infrared spectroscopy), enabled to retain after weathering about

half of the boron initially impregnated in Japanese cedar (LYON *et al.*, 2007). Hence, the action of ABO was seen as providing a water resistant inner coating.

Several aminoborates, prepared by refluxing boric acid with a diol in solvent N,N-dimethylformamide, and that were characterised by PMR (proton magnetic resonance spectroscopy), FTIR (Fourier-transform infrared spectroscopy) and elemental analysis were able to impart protection against brown- and white-rot fungi after 2-weeks water leaching (CHEN, 2008).

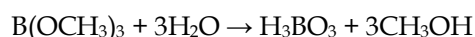
A new type of chemical modification of wood was developed and applied to functionalise wood with organoboron compounds (NAMYSLO and KAUFMANN, 2009). Such wood modification consists in the covalent attachment of metalloids substituents via a benzotriazolyl-activated benzoic acid to wood hydroxyl groups. Modified wood (beech wood, spruce wood and pine sapwood) yielded weight percent gain values from 14% to 31%. Biodeterioration tests are, then, needed.

#### **Preservative Treatment of Wood Composites with Boron Chemicals**

As they are made of wood, wood composites also suffer in general from susceptibility to decay. Therefore, when intended for exterior use it is desirable that wood composites were preservative-treated in some way. However, common methods for the treatment of solid wood cannot be applied. Namely when chemical aqueous solutions are considered, they would swell wood particles of which the wood composite is made, ultimately disrupting the bonds and giving it without physical integrity. An exception are composites bonded

with water resistant binders, like phenol-formaldehyde (PF) or methylenediisocyanate (MDI) resins, but the question of biological decay is still maintained and such boards will show a degree of permanent swelling. Another possibility is the pre-treatment of the boards furnish with preservative, prior to drying, mattress forming, and pressing. But the preservative agent must be chosen with care, as it may interfere with resin curing, giving a material with poor physical properties. Solvent-based preservatives would lead to solvent losses in a time when VOC's (volatile organic compounds) emissions are under strong scrutiny, as it is the present.

The application of the chemical preservative in gaseous form is a possibility to avoid the above mentioned drawbacks. Trimethyl borate (TMB) can be applied in the vapour phase as a preservative treatment for wood-based board materials. Deposition of boric acid in wood results from the combination of TMB with moisture present on or within the wood cell walls, according to the following equation:



MURPHY and TURNER (1989) tested this treatment in chipboard, medium density fibreboard (MDF), aspen waferboard and oriented strandboard (OSB). Chemical penetration was influenced by treatment time, moisture content, board density, particle size and, possibly, species composition. But, under appropriate conditions, complete penetration could be achieved in relatively short treatment times. Such treatments could reach levels appropriate for protection against biological attack and fire, with no significant effect on modulus of rupture

(MOR), internal bond strength (IB), or bond durability (HASHIM *et al.*, 1994). Stiffness was increased by treatment. Also, the levels of water swelling, mass increase after water soaking, hysteresis over a range of 30 to 90%, and dimensional changes associated with changes in relative humidity, were not affected by the boron treatment (HASHIM *et al.*, 1997). TSUNODA (2001) extended this type of treatments to solid wood, with no difference of effectiveness between vapour-boron and liquid boron treatment.

An investigation on the variability of bending and tensile properties of LVL (laminated veneer lumber), OSB and MDF (medium-density fibreboard) treated with vapour boron and manufactured on North America showed that mill location significantly affected property values while treatment level caused only significant reductions at the highest treatment level (EARNEST and MURPHY, 2005). The significance of mill location was attributed mainly to wood species differences.

KREBER *et al.* (1993) investigated the effects of boron loading level (0 to 15% BAE) on the strength development rates of small phenol formaldehyde-to-wood (Sitka spruce, *Picea sitchensis* (Bong.) Carr.) test bonds. All levels of boron pretreatment hastened initial strength development rates. But levels above 7.5% BAE had diminishing effects on isothermal rates, with possible decreases at very high levels (15% BAE).

The addition of boric acid to melamine-urea-formaldehyde (MUF) glue formulations enabled the incorporation of relatively high quantities of boron without reducing the mechanical properties of poplar (*Populus* sp.) LVL (BRIDAUX *et al.*, 2001). Such

addition method allowed good diffusion of boron in veneers and a certain amount of gradual boron diffusion durable in veneers under the action of leaching waters.

Fibreboard panels made from pine (*Pinus nigra* Arnold *var. pallasiana*) and beech (*Fagus orientalis* Lipsky) treated with N'-N-(1,8-naphthalyl) hydroxylamine sodium salt (NHA-Na) plus borax, with urea-formaldehyde (UF) resin as a binder, showed no reduction in MOR or MOE (modulus of elasticity), with a small reduction in IB, but giving no problem in meeting standards (AKBULUT *et al.*, 2004).

### Heat Treatment and Boron Chemical Treatments

Results from research on heat treatment of wood generally agree by a strong correlation between wood acidity and thermal degradation. 0.1 M sodium borate solution has a pH of the order of 9. A preliminary borate impregnation of wood before a mild heat treatment has been suggested to reduce the severity of strength loss during heat treatment, such a reduction that has been ascribed to the buffering effect of the alkali of the borate solution (AWOYEMI and WESTERMARK, 2005). Such a mitigating effect increased from a concentration of sodium borate of 0.1 to 0.3 M, and higher from this until 0.5 M did not produce significant differences as assessed by MOR and MOE (AWOYEMI, 2008).

However, it was found that heat treatments of Japanese cedar sapwood had no effects on boron release after boric acid (BA) and di-sodium octoborate tetrahydrate (DOT) impregnations; i.e. all boron was leached from wood specimens during a 10-day weathering period

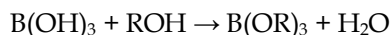
(KARTAL, 2006). But, the same research concluded by a kind of synergistic effect between heat and DOT treatments as far as white-rot decay and termites are concerned. Furthermore, if heat treatment decreases water absorption, on the other hand boron- and heat-treated wood specimens showed increased water absorption due to the hygroscopic properties of BA and BOT (KARTAL *et al.*, 2007).

### Elements of Boron Chemistry Relevant to Wood Preservation

As the hydroxyl group is the most abundant functional group in wood, any study aiming at finding conditions for boron chemical species to become covalently bonded to wood needs to disclose which conditions give rise to a reaction between a given boron species and hydroxyls.

There are many types of organic derivatives containing boron-oxygen bonds, the chief examples being those containing trigonal boron: the orthoborates,  $B(OR)_3$ ; the acyl borates,  $B(OCOR)_3$ ; the peroxy borates,  $B(OOR)_3$ ; and the boronic acids,  $RB(OH)_2$ , all of which are best considered to be derivatives of boric acid (COTTON and WILKINSON, 1995).

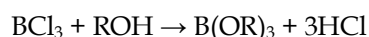
Boric acid is readily converted to alkyl or aryl orthoborates,  $B(OR)_3$ , by condensation with alcohols in the presence of sulphuric acid:



Boric acid ( $B(OH)_3$ ) and borates ( $B(OH)_4^-$ ) form very stable complexes with 1,2-diols. The concentration of boric acid can be determined by complexation with a diol such as glycerol, followed by titration with NaOH.

Boron trifluoride ( $BF_3$ ) is one of the strongest Lewis acids known and reacts readily with most Lewis bases, such as ethers, alcohols, amine or water to give adducts. An adduct is defined as a product of a direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components, with formation of two chemical bonds and a net reduction in bond multiplicity in at least one of the reactants. The resultant is considered a distinct molecular species.  $BF_3$  is widely used to promote organic reactions.

Even the weakest of Lewis bases will form adducts with the trihalides of boron. Ethers, amines, phosphines, alcohols, anions, carbon monoxide, and the like all form adducts by donation of an electron pair to boron:



### Discussion

For decades boron has been the topic of many research projects for wood preservation. Also, saying that boron is an effective chemical to impregnate wood with its aqueous solutions resulting then wood more resistant to biological decay, is not new. Moreover, the fact that common boron chemicals, namely boric acid and borax, give effective wood preservation formulations, combining the properties of broad spectrum efficacy and low acute mammalian toxicity, makes boron-based wood preservation systems even more interesting. Furthermore, it is not new that boron aqueous solutions diffuse readily into wood making possible to treat refractory wood species.

However, it seems that it is the issue of boron fixation in wood that draws the

attention of the research in the field. One cannot say that there is still no system where boron is fixed, or immobilised, in wood. There have been several reports, as referred above, that present chemical systems giving rise to boron immobilisation in wood. One feature common to all of these systems is that boron chemicals alone have not been fixed into wood. Together with boron chemicals, wood has been impregnated for that purpose together with tannins, protein, vinyl monomers, formaldehyde-based crosslinking agents, etc., and even chemical modification has been made to functionalise wood with boron compounds. But no wood scientist has made use of the background in boron chemistry available today, for a more efficient and scientific research. Collaboration between wood scientists and inorganic chemists is then advisable.

Without doubt that research results reporting on new methods for boron fixation/immobilising of boron in wood are welcome. However, the challenge nowadays is to validate such chemical systems with scale up, and after that, a further validation in economic terms. Then, we can say that we have a boron fixation system that has value nowadays; i.e., that can be transferred to the industry making profit and creating or maintaining jobs.

### Symbols

ACZA - ammoniacal copper zinc arsenate preservative  
AWPA - American Wood Preservers Association  
BA - boric acid

BAE - boric acid equivalent  
CCA - chromium(VI)-copper-arsenic preservative  
CCB - chromium-copper-borate preservative  
DBF - didecyl dimethyl ammonium tetrafluoborate  
DOT - disodium octaborate tetrahydrate  
DSR - dry salt retention  
EPA - U.S. Environmental Protection Agency  
FTIR - Fourier-transform infrared spectroscopy  
IB - internal bond strength  
LVL - laminated veneer lumber  
MC - moisture content  
MDF - medium-density fibreboard  
MDI - methylenediisocyanate resin  
MOE - modulus of elasticity  
MOR - modulus of rupture  
MUF - melamine-urea-formaldehyde resin  
NHA - N'-n-(1,8-Naphthalyl) hydroxylamine  
NMR - nuclear magnetic resonance spectroscopy  
OSB - oriented strandboard  
PEG - polyethylene glycol  
PF - phenol-formaldehyde resin  
PGA - prompt gamma-ray analysis  
PMR - proton magnetic resonance spectroscopy  
SEM - scanning electron microscope  
SPF - Spruce-Pine-Fir species group  
TMB - trimethyl borate  
UF - urea-formaldehyde  
VOC - volatile organic compounds

## References

- AKBULUT, T., KARTAL, S.N., GREEN III, F., 2004. Fiberboards treated with N'-N-(1,8-naphthalyl)hydroxylamine (NHA-Na), borax, and boric acid. *Forest Prod. J.* **54**(10): 59-64.
- AWOYEMI, L., WESTERMARK, U., 2005. Effects of borate impregnation on the response of wood strength to heat treatment. *Wood Sci. Technol.* **39**(6): 484-491.
- AWOYEMI, L., 2008. Determination of optimum borate concentration for alleviating strength loss during heat treatment of wood. *Wood Sci. Technol.* **42**(1): 39-45.
- BARNES, H.M., MURPHY, R.J., 1995. Wood preservation – The classics and the new age. *Forest Prod. J.* **45**(9): 16-26.
- BARNES, H.M., LANDERS Jr, R.W., WILLIAMS, L.H., 1993. Thermal treatment of southern pine timbers with borates. *Forest Prod. J.* **43**(3): 31-34.
- BAYSAL, E., SONMEZ, A., COLAK, M., TOKER, H., 2006. Amount of leachant and water absorption levels of wood treated with borates and water repellents. *Bioresource Technol.* **97**(18): 2271-2279.
- BAYSAL, E., YALINKILIC, M.K., 2005. A new boron impregnation technique of wood by vapor boron of boric acid to reduce leaching boron from wood. *Wood Sci. Technol.* **39**: 187-198.
- BAYSAL, E., OZAKI, S.K., YALINKILIC, M.K., 2004. Dimensional stabilization of wood treated with furfuryl alcohol catalysed by borates. *Wood Sci. Technol.* **38**: 405-415.
- BRIDAUX, V., CHARRIER, B., FAUROUX, N., CHARRIER, F., GONCALEZ, J., 2001. Addition of boron based compound in the LVL glueline: effect on the mechanical properties and the leaching of boron. *Holzforsch* **55**(5): 559-562.
- CASSENS, D.L., SCHMIDT, E.L., 1998. Use of borate compounds to prevent insect damage to furniture hickory rounds with the bark intact. *Forest Prod. J.* **48**(3): 36-37.
- CHEN, P.Y.S., PUETTMANN, M.E., WILLIAMS, L.H., STOKKE, D.D., 1997. Treatment of 8/4 hardwood lumber with borate preservatives. *Forest Prod. J.* **47**(6): 63-68.
- CHEN, G.C., 2008. Synthesis and evaluation of aminoborates derived from boric acid and diols for protecting wood against fungal and thermal degradation. *Wood Fiber Sci.* **40**(2): 248 – 257.
- COTTON, F.A., WILKINSON, G., GAUS, P.L., 1995. *Basic Inorganic Chemistry*. John Wiley & Sons, Inc., Chichester, UK, 1995.
- DAVIS, K.A., van HISE, J.R., 2006. Comment on: Predicting boron diffusion in wood from surface sorption. *Forest Prod. J.* **56**(6): 38-39.
- De GROOT, R.C., FELTON, C.C., 1998. Distribution of borate around point source injections in dry wood members. *Holzforsch.* **52**(1): 37-45.
- DHAMODARAN, T.K., GNANAHARAN, R., 1994. Commercial scale trial of an economical schedule for boron impregnation treatment of green rubber wood. *Holz Roh-Werks.* **52**: 323-324.
- DHAMODARAN, T.K., GNANAHARAN, R., 2007. Boron impregnation treatment of Eucalyptus grandis wood. *Bioresource Technol.* **98**(11): 2240-2242.
- DHAMODARAN, T.K., GNANAHARAN, R., 2006. An economical treatment schedule for boron impregnation of Eucalyptus grandis wood. Commercial trial of partially dried material. *Holz Roh- Werks.* **64**(1): 80-81.
- EARNEST, H.M., MURPHY, R.J., 2005. Bending and tensile properties of vapor boron-treated composites. *Wood Fiber Sci.* **37**(3): 379-383.
- FREEMAN, M.H., SHUPE, T.F., VLOSKY, R.P., BARNES, H.M., 2003. Past, present, and future of the wood preservation industry. *Forest Prod. J.* **53**(10): 8-15.
- FREITAG, C.M., MORRELL, J.J., 2002. Effect of glycol on movement of borate from fused borate rods. *Forest Prod. J.* **52**(6): 68-74.

- FURUNO, T., IMAMURA, Y., 1998. Combinations of wood and silicate. Part 6. Biological resistances of wood-mineral composites using water glass-boron compound system. *Wood Sci. Technol.* **32**: 161-170.
- GEZER, E.D., MICHAEL, J.H., MORRELL, J.J., 1999. Effects of glycol on leachability and efficacy of boron wood preservatives. *Wood Fiber Sci.* **31**(2): 136-142.
- GNANAHARAN, R., DHAMODARAN, T.K., 1993. A pilot plant investigation of boron treatment of rubber wood: arriving at an economical treatment schedule. *Holz Roh-Werks.* **51**: 279-282.
- HWANG, W.J., KARTAL, S.N., SHINODA, K., IMAMURA, Y., 2005. Surface treatment for preventing decay and termite attack in wood using didecyl dimethyl ammonium tetrafluoroborate (DBF) incorporated with acryl-silicon type resin. *Holz Roh-Werks.* **62**(5): 378-385.
- HASHIM, R., MURPHY, R.J., DICKINSON, D.J., DINWOODIE, J.M., 1997. The physical properties of boards with vapor boron. *Forest Prod. J.* **47**(1): 61-66.
- HASHIM, R., MURPHY, R.J., DICKINSON, D.J., DINWOODIE, J.M., 1994. The mechanical properties of boards with vapor boron. *Forest Prod. J.* **44**(10): 73-79.
- HE, W., SIMONSEN, W.J., CHEN, H., MORRELL, J.J., 1997. Evaluation of the efficacy of selected thermal boron treatments in eliminating pests in freshly peeled Douglas-fir logs. *Forest Prod. J.* **47**(3): 66-70.
- KARTAL, S.N., IMAMURA, Y., 2004. Effects of N'-N-(1,8-Naphthalyl) hydroxylamine (NHA-Na) and hydroxynaphthalimide (NHA-H) on boron leachability and biological degradation of wood. *Holz Roh-Werks.* **62**(5): 378-385.
- KARTAL, S.N., HWANG, W.-J., IMAMURA, Y., 2007. Water absorption of boron-treated and heat-modified wood. *J. Wood Sci.* **53**(5): 454-457.
- KARTAL, S.N., HWANG, W.-J., SHINODA, K., IMAMURA, Y., 2006. Laboratory evaluation of boron-containing quaternary ammonia compound, didecyl dimethyl ammonium tetrafluoroborate (DBF) for control of decay and termite attack and fungal staining of wood. *Holz Roh-Werks.* **64**(1): 62-67.
- KARTAL, S.N., 2006. Combined effect of boron compounds and heat treatments on wood properties. Boron release and decay and termite resistance. *Holzforsch.* **60**(4): 455-458.
- KRABBENHØFT, K., HOFFMERYER, P., BECHGAARD, C.G., DAMKILDE, L., 2004. Finite element analysis of boron diffusion in wooden poles. *Wood Fiber Sci.* **36**(4): 573-584.
- KREBER, B., HUMPHREY, P.E., MORRELL, J.J., 1993. Effect of polyborate pre-treatment on the shear strength development of phenolic resin to stika spruce bonds. *Holzforsch.* **47**: 398-402.
- LEBOW, S., HATFIELD, C., ABBOTT, W., 2005. Treatability of SPF framing lumber with CCA and borate preservatives. *Wood Fiber Sci.* **37**(4): 605-614.
- LIN, L., FURUNO, T., KATOH, S., 2001. Leachability and decay resistance of tetraphenylborate salt-treated wood. *Holzforsch.* **55**(4): 355-357.
- LLOYD, J.D., FOGEL, J.L., VIZEL, A., 2001. The use of zirconium as an inert fixative for borates in preservation. *32nd Annual Meeting of IRG - The International Research Group on Wood Preservation. Section 3 - Wood Protection Chemical.* Document IRG/WP 01-30256
- LYON, F., PIZZI, A., IMAMURA, Y., THEVENON, M.-F., KARTAL, S., GRIL, J., 2007. Leachability and termite resistance of wood treated with a new preservative: ammonium borate oleate. *Holz Roh-Werks.* **65**(5): 359-366.



- MAZELA, B., DOMAGALSKI, P., MAMONOVA, M., RATAJCZAK, I., 2007. Protein impact on the capability of the protein-borate preservative penetration and distribution into pine and aspenwood. *Holz Roh-Werks*. **65**(2):137-144.
- MELO, R., CESPEDES, J., ZAROR, C., 1992. Diffusion of boron salts in heartwood specimens of Chilean-grown *Eucalyptus globulus*. *Wood Protection* **2**(1): 9-14.
- MITSUHASHI, J., LOVE, C.S., FREITAG, C., MORRELL, J.J., 2007. Migration of boron from Douglas-fir lumber subjected to simulated rainfall. *Forest Prod. J.* **57**(12): 52-57.
- MORRELL, J.J., LEBOW, S.T., 1991. Borate treatment of seasoned western hemlock and Douglas-fir lumber. *Forest Prod. J.* **41**(1): 27-29.
- MORRIS, P.I., BYRNE, A., MINCHIN, D.R., 1996. Achieving "shell" or "complete" penetration of western hemlock and Pacific silver fir with borates by pressure/diffusion treatments. *Holz Roh-Werks*. **46**(3): 51-55.
- MOURANT, D., YANG, D.-Q., LU, X., RIEDL, B., ROY, C., 2009. Copper and boron fixation in wood by pyrolytic resins. *Bioresource Technol.* **100**(3): 1442-1449.
- MURPHY, R.J., TURNER, P., 1989. A vapour phase preservative treatment of manufactured wood based board materials. *Wood Sci. Technol.* **23**: 273-279.
- NAMYSLO, J.C., KAUFMANN, D.E., 2009. Chemical improvement of surfaces. Part 1: Novel functional modification of wood with covalently bound organoboron compounds. *Holzforsch.* **63**(5): 627-632.
- PEYLO, A., WILLEITNER, H., 1995. The problem of reducing the leachability of boron by water repellents. *Holzforsch.* **49**(3): 211-216.
- PIZZI, A., BAECKER, A., 1996. A new boron fixation mechanism for environment friendly wood preservatives. *Holzforsch.* **50**(6): 507-510.
- PUETTMANN, M.E., SCHMIDT, E.L., 1997. Boron diffusion treatment of aspen lumber stored under various relative humidities. *Forest Prod. J.* **47**(10): 47-50.
- PUETTMANN, M.M., WILLIAMS, L.H., 1992. Penetration of southern pine floor joists by borate/glycol formulations. *Wood Protection* **2**(1): 29-34.
- RA, J.-B., CHO, J.-S., SONG, Y.-S., KIM, G.-H., 2004. Diffusion of boron from borate rods in radiata pine. *Forest Prod. J.* **54**(5):81-84.
- RA, J.B., BARNES, H.M., CONNERS, T.E., 2002. Predicting boron diffusion in wood from surface sorption. *Forest Prod. J.* **52**(10): 67-70.
- RA, J.B., BARNES, H.M., CONNERS, T.E., 2001. Determination of boron diffusion coefficients in wood. *Wood Fiber Sci.* **33**(1): 90-103.
- RAMOS, A.M., CALDEIRA JORGE, F., BOTELHO, C., 2006. Boron fixation in wood: studies of fixation mechanisms using model compounds and maritime pine. *Holz Roh-Werks*. **64**(6): 445-450.
- RATAJCZAK, I., MAZELA, B., 2007. The boron fixation to the cellulose, lignin and wood matrix through its reaction with protein. *Holz Roh-Werks*. **65**(3): 231-237.
- RHATIGAN, R.G., MORRELL, J.J., FREITAG, C.M., 2002. Movement of boron and fluoride from rod formations into Douglas-fir heartwood. *Forest Prod. J.* **52**(11/12): 38-42.
- TAYLOR, A., LLOYD, J., 2009. Phytosanitation of railway crossties with a borate solution immersion treatment. *Forest Prod. J.* **59**(4): 76-78.
- TEMIZ, A., ALFREDSEN, G., EIKENES, M., TERZIEV, N., 2008. Decay resistance of wood treated with boric acid and tall oil derivatives. *Bioresource Technol.* **99**(7): 2102-2106.
- THEVENON, M.-F., TONDI, G., PIZZI, A., 2009. High performance tannin resin-boron wood preservatives for outdoor end-uses. *European J. Wood and Wood Prod.* **67**(1): 89-93.

- THEVENON, M.-F., PIZZI, A., 2003. Polyborate ions' influence on the durability of wood treated with non-toxic protein borate preservatives. *Holz Roh- Werks.* **61**: 457-464.
- THEVENON, M.-F., PIZZI, A., HALUK, J.-P., 1998. Protein borates as non-toxic, lon-term, wide-spectrum ground-contact wood preservatives. *Holzforsch.* **52**(3): 241-248.
- THEVENON, M.-F., PIZZI, A., HALUK, J.-P., 1997. Non-toxic albumin and soja protein borates as ground-contact wood preservatives. *Holz Roh- Werks.* **55**: 293-296.
- TOUSSAINT-DAUVERGNE, E., SOULOUNGANGA, P., GÉRARDIN, P., LOUBINOX, B., 2000. Glycerol/glyoxal: a new boron fixation system for wood preservation and dimensional stabilization. *Holzforsch.* **54**(2): 123-126.
- TSUNODA, K., 2001. Preservative properties of vapor-boron treated wood and wood-based composites. *J. Wood Sci.* **47**: 149-153.
- YALINKILIC, M.K., IMAMURA, Y., TAKAHASHI, M., YALINKILIC, A.C., 1999a). *In situ* polymerization of vinyl monomers during compressive deformation of wood treated with boric acid to delay boron leaching. *Forest Prod. J.* **49**(2): 43-51.
- YALINKILIC, M.K., GEZER, E.D., TAKAHASHI, M., DEMIRCI, Z., ILHAN, R., IMAMURA, Y., 1999b. Boron addition to non- or low-formaldehyde cross-lonking agents top enhance biological resistance and dimensional stability of wood. *Holz Roh- Werks.* **57**: 351-357.
- YALINKILIC, M.K., TSUNODA, K., TAKAHASHI, M., GEZER, E.D., DWIANTO, W., NEMOTO, H., 1998. Enhancement of biological and physical properties of wood by boric acid-vinyl monomer combination treatment. *Holzforsch.* **52**(6): 667-672.
- YAMAGUCHI, H., 2002. Low molecular weight silici acid – inorganic compound complex as wood preservative. *Wood Sci. Technol.* **36**:399-417.
- YAMAGUCHI, H., 2003. Silicic acid:boric acid complexes as wood preservatives. Ability of treated wood to resist termites as combustion. *Wood Sci. Technol.* **37**: 287-297.
- YAMAUCHI, S., SAKAI, Y., WATANABE, Y., KUBO, M.K., MATSUE, H., 2007. Distribution of boron in wood treated with aqueous and methanolic boric acid solutions. *J. Wood Sci.* **53**(4): 324-331.

Entregue para publicação em Junho de 2010

Aceite para publicação em Outubro de 2010