ISSN impresa 0717-3644
ISSN online 0718-221X
maderas CIENCIA Y TECNOLOGIA, 12(3):253-257, 2010
DOI 10.4067/S0718-221X2010000300009

ENVIRONMENTALLY FRIENDLY WOOD PRESERVATIVE SYSTEM BASED ON POLYMERIZED TANNIN RESIN-BORIC ACID FOR OUTDOOR APPLICATIONS*

Marie-France Thévenon[1], Gianluca Tondi[2], Antonio Pizzi[2]

ABSTRACT

Boron compounds are used as wood preservatives as they are both fungicide and insecticide, relatively inexpensive and environmentally acceptable. Nevertheless, in the field of wood protection, borates are only used for indoor non-exposed applications or in association with other biocides, due to their main disadvantage of being readily leachable from treated wood. To overcome this problem, boric acid was fixed into wood with condensed tannins and hexamine through a non-formaldehyde emission polymer network. Treated mixtures were tested with different proportions of mimosa tannins and hexamine, with and without co-added boric acid. The treated beech samples were leached and tested according to European Standard EN 113 against *Pycnoporus sanguineus* in tropical conditions. The systems had minimal boron depletion and good fungal decay efficacy, meeting the efficacy requirements of EN 113.

Thus, these associations could be envisaged to treat timber with insufficient natural durability for above ground outdoor use, and for a long service-life of the wooden commodities.
Keywords: Boric Acid, Tannins, Hexamine, Leaching, EN 113, *Pycnoporus sanguineus*

INTRODUCTION

Borates such as boric acid, borax or disodium octaborate tetrahydrate (DOT) have proved their efficiency for many years as wide spectrum wood preservatives (Lloyd 1997, Drysdale 1994). They have many advantages including being inexpensive, odourless, colourless and non flammable. They are also soluble in water allowing them to be introduced in wood by conventional methods like dipping-diffusion or vacuum-pressure treatments (Byrne and Morris 1997, Lebow and Morrell 1989). Boron compounds have been shown to have a lower human toxicity (Teshima *et al.* 2001, Usuda *et al.* 1998, Jansen *et al.* 1984) than for some animals' species (Hamilton and Buhl 1990, Maier and Knight 1991), and boric acid has been considered environmentally acceptable for many years. On the other hand, this high water solubility makes boron compounds easily leachable from treated wood and thus boron treated wood is not suitable for outdoor application (Lloyd 1998, Peylo and Willeitner 1997). The key issue to expand boron's use for wood protection appears to be their fixation into wood but allowing for sufficient mobility so they remain fungicidal (Obanda *et al.* 2008). Several different methods have been tried to decrease borate leachability from wood, including forming complexes of boron with flavonoid tannins (Pizzi and Baecker 1996). Another system involved a 2 step impregnation of copper, zinc and boron with tannins, with this system having good efficacy against wood destroying fungi (Scalbert *et al.* 1998). Water borne solutions of boric acid, gelatin and tannins can also be used to treat wood (Thevenon 1999). Gelatin, as a protein, can partially fix boric acid, and tannins can waterproof the protein-boric acid polymer leading to an insoluble network which minimized depletion of boron when treated wood is leached.

Another tannin system might be to harden a tannin resin with hexamine, a non emission substance when in presence of a fast reacting polyflavonoid tannin (Pichelin *et al.* 2006; Kamoun and Pizzi 2000 a,b; Kamoun *et al.* 2003). This paper presents some results obtained with tannin/hexamine/boric acid used as wood preservatives.

---

*This paper was originally presented at the 2010 EC-IAWS/ESTB7 meeting, Rabat-Morocco, March 2010, and has been updated.
[1]Wood preservation laboratory, UR40, CIRAD, TA B 40/16, 34398 Montpellier Cedex 5, France
[2]ENSTIB-LERMAB, Nancy University, 27 rue du Merle blanc, BP 1041, 88051 Epinal, France
Received: 08.06.2010 Accepted: 25.09.2010

MATERIALS AND METHODS

Beech (*Fagus sylvatica*) wood specimens, 50x25x15 mm^3, were treated with experimental wood preservatives. The different treatments used were (% w/w): (1) mimosa tannin extract in 10%, 20% and 35% solution and hexamine at 6% by weight on dry tannin extract weight; (2) mimosa tannin extract in 10%, 20% and 30% solution, with 5% boric acid on total tannin solution, and hexamine at 6% by weight on dry tannin extract. Dowanol (Dow Chemicals) (5% on dry tannin extract weight), a polyether, was added to the tannin solutions to decrease the viscosity of the tannin solution and facilitate wood penetration by the preservative solution.

Ten specimens for each case were treated by vacuum-pressure application (60 min at 10 mbar, introduction of the treatment solution, then 2 hrs at atmospheric pressure). The treatment was followed by 24 hours drying in oven at 103°C. After drying, half of the specimens were leached in 500 ml of water (1 vol of wood / 6.7 vol of water) at 20°C. The water was changed daily for 5 days. Once the samples were air dried, anhydrous weight of the samples (weight after drying at 103°C) was recorded after the treatment and the leaching, for the un-leached and leached samples respectively. This anhydrous weight was considered as “initial weight” for weight loss calculations (M0), and retention of the total treatment product was calculated after leaching.

The treated specimens were tested for resistance to biological attack according to the EN113, 1996, against *Pycnoporus sanguineus* (tropical brown rot, strain CTFT 270) grown on malt/agar medium (malt 40g/l, agar 20g/l). All wood specimens were sterilized by gamma radiations prior to fungal exposure. In each culture flask, one treated specimen and a control (untreated beech) were introduced. Virulence control was also performed on 6 untreated beech specimens. The specimens were incubated for 16 weeks at 27°C, 75% RH (tropical conditions to allow high fungal virulence). After this, the mycelium was removed and the specimens were weighted (M1) to determine their moisture content at the end of fungal exposure. The specimens were then dried at 103°C and their final weight was recorded (M2).

The following data were calculated, according to the formulas (1) and (2):

Humidity (end of fungal exposure, treated samples) % = [(M1 – M2)/M2] x 100 (1)

Weight loss % (treated samples) = [(M0-M2)/M0] x 100 (2)

RESULTS AND DISCUSSION

The results of the biological tests are shown in Table 1. The average mass loss of the specimens used for virulence controls was 35.47±6.86 %.

Table 1. Biological results of beech specimens treated with tannins + hexamine ± boric acid, unleached and leached, exposed to *Pycnoporus sanguineus (* Tannin+ hexamine +/- boric acid ** Standard deviation)*

Tannin solution (%)	Hexamine (%)	Boric Acid (%)	Total Retention* (kg/m³)	Moisture content at the end of the test (Std dev)** Treated (%)	Average Mass loss (Std dev)** Treated samples (%)	Average Mass loss (Std dev)** Controls samples (%)
Not leached						
10	0.6	-	56.4	75.25(13.61)	33.23(2.03)	43.30(3.92)
20	1.2	-	95.9	78.46(18.89)	25.36(2.37)	47.44(7.04)
35	1.8	-	140.8	71.76(4.96)	6.46(0.71)	38.17(4.28)
Leached						
10	0.6	-	46.0	47.88(7.99)	31.93(0.82)	34.81(3.61)
20	1.2	-	77.8	55.96(2.55)	31.91(4.10)	37.03(1.51)
35	1.8	-	110.9	61.55(7.05)	30.40(1.39)	32.85(1.24)
Not leached						
10	0.6	5	56.2	63.27(5.60)	3.42(0.96)	45.78(4.66)
20	1.2	5	98.2	56.95(4.78)	3.95(0.15)	41.16(2.68)
30	1.8	5	125.9	51.44(3.95)	4.38(0.12)	42.79(1.49)
Leached						
10	0.6	5	46.6	36.94(2.86)	1.69(0.17)	35.46(2.40)
20	1.2	5	84.9	48.12(13.21)	1.74(0.54)	36.33(3.70)
30	1.8	5	109.1	43.90(2.62)	2.26(0.10)	33.19(2.58)

The formulations based on condensed tannin (mimosa tannin extract) and hexamine only can be considered as the matrix without the presence of any active ingredient. They provide a slight protective effect only when tannins are used at 35% and for unleached samples.

The formulations based on the complex formed by boric acid with condensed mimosa tannin being networked and hardened by reaction with hexamine induce a high biological resistance to the wood, considering the severity of this test (the virulence of the fungus being very strong). For the formulations containing boric acid, and for each mimosa tannin concentration, the non-leached specimens present a higher average mass loss than the leached ones. This is probably due to some leaching with no correction factors determined (according to EN113 standard). For each formulation and concentration, the correction factor corresponds to the average mass loss of treated specimens (at least 4 specimens) on malt/agar medium only, which would have account for non-fungal mass loss due to leaching.

The chemical mechanism(s) of these systems are still to be explored, but it is clear that the resinification of the hydrophobic tannin + hexamine system greatly reduces leaching of the boric acid. The boric acid is then still most non-covalently bonded to the tannin resin but retains sufficient mobility that allows it to work as a fungicide.

CONCLUSIONS

Wood preservatives based on the cross-linking and hardening of condensed polyflavonoid tannins by hexamine, onto which boric acid is added and complexed, had greatly reduced boron leaching. Further, wood treated with these combinations had increased fungal durability before and after leaching according to European standard EN 113. Further work with this system might lead to environmentally-benign wood protection systems.

REFERENCES

Byrne, A.; Morris, P.I. 1997. Recent Research in Boron Treatment of Canadian Wood Species. *The Second International Conference on Wood Protection with Diffusible Preservatives and Pesticides, Forests Products Society* 55-61

Drysdale, J.A. 1994. Boron Treatments for the Preservation of Wood. A review of Efficacy Data for Fungi and termites. *The International Research Group on Wood Preservation. Stockholm, Sweden.* Doc IRG/WP 94-30037

European Norm. 1996. EN113. Wood preservatives. Method for determining the protective effectiveness against wood destroying Basidiomycetes. Determination of toxic values.

Hamilton, S.J.; Buhl, K.J. 1990. Acute toxicity of boron, molybdenum and selenium to Fry of Chinook salmon and Coho salmon. *Archives of Environmental Contamination and Toxicology* 19: 366-373

Jansen, J.A.; Andersen, J.; Shou, J.S. 1984. Boric acid single dose pharmacokinetics after intravenous administration to man. *Archives of Toxicology* 55:64-67

Kamoun, C.; Pizzi, A. 2000a. Mechanism of hexamine as a non-aldehyde polycondensation hardener, Part 1, Mechanism. *Holzforschung Holzverwertung* 52(1):16-19

Kamoun, C.; Pizzi, A. 2000b. Mechanism of hexamine as a non-aldehyde polycondensation hardener, Part 2: recomposition of intermediate reactive compound. *Holzforschung Holzverwertung* 52(3):66-67

Kamoun, C.; Pizzi, A.; Zanetti, M. 2003. Upgrading of MUF resins by buffering additives – Part 1: hexamine sulphate effect and its limits. *Journal of Applied Polymer Sci*ence 90(1): 203-214

Lebow, S.T.; Morell, J. 1989. Penetration of boron in Douglas-fir and western hemlock lumber. *Forest Products Journal* 39(1): 37-70

Lloyd, J.D. 1997. International borate status of borate preservative systems. *The second international conference on wood protection with diffusible preservatives and pesticides* 45-54

Lloyd, J.D. 1998. Borates and their biological applications. *The International Research Group on Wood Preservatio, Stockholm, Sweden.* Doc IRG/WP 98-30178

Maier, K.J.; Knight, A.W. 1991. The toxicity of waterborne boron to *Daphnia magnia* and *Chironomus decorus* and the effect of water hardness and sulphate on boron toxicity. *Archives of Environmental Contamination and Toxicology* 20: 282-287

Obanda, N.D.; Shupe, F.T.; Barnes, M.H. 2008. Reducing leaching of boron based wood preservatives – A review of research. *Bioresource Technology* 99: 7312-7322

Peylo, A.; Willeitner, H. 1997. Leaching of Boron more than 3 years after exposure. *The International Research Group on Wood Preservation, Stockholm, Sweden*. Doc IRG/WP 97-30143

Pichelin, F.; Nakatani, M.; Pizzi, A.; Wieland, S.; Despres, A.; Rigolet, S. 2006. Thick wood panels bonded industrially with formaldehyde free tannin adhesives, *Forest Products Journal* 56(5): 31-36

Pizzi, A.; Beacker, A. 1996. A new boron fixation mechanism for non-toxic wood preservatives. *Holzforschung* 50: 507-510

Scalbert, A.; Cahill, D.; Dirol, D.; Navarrete, M.A.; de Troya, M.T., Van Leemput, M. 1998. A tannin/copper preservation treatment for wood. *Holzforschung* 52:133-138

Teshima, D.; Taniyama, D.; Oishi, R. 2001. Usefulness of forced diuresis for acute boric acid poisoning in an adult. *Journal of clinical Pharmacy and Therapeutics* 26: 387-390

Thevenon, M.F. 1999. Formulation of long-term, heavy-duty and lowtoxicwood preservatives. Application to the associations boric acid-condensed tannins and boric acid-proteins. *Ph.D. Thesis, University of Nancy I,* France

Usuda, K. ; Kono, K. ; Orita, Y. ; Dote, T.; Iguchi, K.; Nishiura, H.; Tominaga, M.; Tagawa, T.; Goto, E.; Shirai, Y. 1998. Serum and urinary boron levels in rats after single administration of sodium tetraborate. *Archives of Toxicology* 72 (8): 468-474