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PERFORMANCE OF BORON-ETHANOLAMINE-QUATERNARY AMMONIUM BASED WOOD PRESERVATIVES AGAINST LEACHING, WOOD DECAY AND BLUE STAIN FUNGI

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ABSTRACT

Importance of boron compounds is increasing due to their low environmental impact, high efficacy and fact that many other active ingredients have been removed from the market after introduction of the Biocidal products directive. Borates are very effective against wood decay fungi; unfortunately they leach out of wood in wet environment. In order to improve their fixation, solubility and efficacy, borax and boric acid were combined with ethanolamine and quaternary ammonium compound. Afterwards, Norway spruce (*Picea abies*) specimens were impregnated with aqueous solutions and exposed to three wood decay fungi *(Antrodia vaillantii, Gloeophyllum trabeum* and *Trametes versicolor*) according to EN 113 procedure. Half of the specimens were leached prior exposure. Fixation of testing formulation in samples was determined as proposed by ENV 1250-2 standard. In parallel efficacy against blue stain fungi (*Aureobasidium pullulans* and *Sclerophoma pithyophila*) were determined as well according to 152 EN standard. The results showed, that addition of ethanolamine slightly improves boron fixation. Wood impregnated with preservative solutions of the lowest concentration ($c_B = c_{quat} = 0.1\%$) was resistant against wood decay fungi. However, to ensure efficacy against blue stain fungi five or ten times more concentrated solutions needs to be used.

KEY WORDS: boron, ethanolamine, quaternary ammonium compound, fixation, Norway spruce, wood preservation

INTRODUCTION

Field of chemical wood preservation changed drastically in past years. Several classical active ingredients were removed from the formulation due to increased environmental awareness, only two boron based fungicides are allowed according to the Biocidal Products Directive (1998). Less than 40% of the biocides those were on the market before September 2006 remained on the list of the approved active compounds. Therefore, industry and other users looked for wood preservatives with low environmental impact. One of the remaining, active ingredients are boron compounds. Boron is on the first place very effective fungicide and insecticide. On the other hand toxicity (LD_{50}) of the boric acid and borax is similar to the toxicity of the table salt (NaCl) (Lloyd 1998), what increases the usefulness of the boron compounds in the field of wood preservation. Even more, boron has some fire retardant effect as well, therefore is recommended for protection of construction wood (Ramos et al. 2006).

High water solubility and good diffusibility of borates resulted in fact that borates are easily leached from impregnated wood, when treated wood is exposed to precipitations. Because of their non-fixed characteristics, boron preservatives are normally recommended for use in protected environments and are not recommended for use in use class three (above ground) or use class four (ground contact) (Baysal et al. 2006). Another weak point of borates is insufficient effectiveness against some moulds (Petrič et al. 2000). Thus boron compounds are usually used for protection of wood in use classes I and II (above ground, cowered) or they are added as co-biocides to copper based wood preservatives (Humar et al. 2004). The aim of this work was to prepare boron based aqueous solution, with addition of quaternary ammonium compounds (to improve fungicidal properties) and ethanolamine (to improve boron solubility) and test it against the most important wood decay and staining fungi.

MATERIAL AND METHODS

Preservative solutions

For experimentation two types of boron based solutions of three different concentrations were prepared. They consist of boron, ethanolamine and quaternary ammonium compound. As boron source boric acid and borax were chosen. As quaternary ammonium compound (quat), alkyl diethyl benzyl ammonium chloride (C12-C16) (CAS - 68424-85-1, Merck) was chosen. Those two compounds were chosen, as they are allowed according to the Biocidal products directive. Concentration of boron equals to quat concentrations. Namely, concentrations of 1, 0.5 and 0.1 % were chosen. Ethanolamine concentration was 10 times higher than boron concentration. Such concentration enable us suitable solubility of all components.

Leaching test

For leaching tests specimens made of Norway spruce (*Picea abies*) sapwood (1.5 × 2.5 × 5 cm) were vacuum impregnated with six different preservative formulations according to the EN 113 (ECS 1996) procedure. Average retention of preservative solution was 515 kg/m^3. After impregnation specimens were conditioned for four weeks according to the requirements of this standard.

Leaching was performed according to the modified ENV 1250-2 (ECS 1994) method. In order to speed up experiment, following two modifications were done: instead of five three specimens were positioned in the same vessels. Water mixing was achieved with shaking on shaking device instead of magnetic stirrer. To have three parallel leaching procedures, nine specimens per solution/

concentration/treatment were put in three vessels (three specimens per vessel). Afterwards, samples in the vessel were positioned with a weight. 300 g of distilled water were added and the vessel with its content was shaking with the frequency of 60 min^{-1}. Water was replaced daily for seven times in ten subsequent days. Leachates from the same vessel were collected and mixed together. Boron in the leachates was determined using inductively coupled plasma mass spectrometer (ICP-MS).

The Agilent Technologies (Palo Alto, USA) HP 4500 quadrupole ICP-MS with Burgener Mira Mist nebuliser was used as a detection system for boron. The spray chamber temperature was 4°C. The plasma RF power was set to 1300 W. Plasma gas flow rate was 15 L min^{-1}, auxiliary gas flow rate 0.7 L min^{-1} and nebuliser gas flow rate 1.05 L min^{-1}. Sampler and skimmer cones were made of nickel.

Standard boron solutions for calibration curve were prepared by diluting a stock standard solution of boron (1000 mg L^{-1}) (Merck, Germany). Samples were diluted 50-fold with MQ water prior the analysis. The final standard and sample solutions contained 1% (v/v) of nitric acid. The memory effect (as a consequence of introduction of solutions with high boron concentration) was eliminated by washing the system with 20% (v/v) ammonia solution after each sample. The washout time was 60 seconds. Analytical grade nitric acid and ammonia solution (Merck, Germany) were used. NIST standard reference material 1643e (trace elements in water) was used to verify the accuracy of the measurements.

Percentages of leached boron were calculated from the amount of retained boron determined gravimetrically and amount of boron in collected leachates.

Wood decay test

The same specimens as prepared for leaching test were prepared for wood decay testing as well. This part of research was performed according to the EN 113 (ECS 1996) procedure. Following conditioning, the samples were leached according to the EN 84 procedure for 14 days (ECS 1994). Afterwards, the samples were oven dried (103°C), after which their masses were determined and then conditioned at 25°C, 65% RH. The samples were finally steam- sterilized prior to exposure to the fungi. Experiment was performed on five parallel specimens.

In order to determine resistance of impregnated wood against decay, two brown rot fungi (*Antrodia vaillantii* and *Gloeophyllum trabeum*) and one white rot fungus (*Trametes versicolor*) were used. Jars with PDA (Potato dextrose agar) medium were inoculated with small pieces of mycelium after which the wood samples (one each of treated and untreated) were placed on a plastic net in each inoculated jar. In parallel jars only control specimens were exposed in order to completely avoid influence of biocide on vitality of testing fungi. The samples were incubated in the growth chamber at 25°C, RH 75% for 16 weeks. After expose mycelia were carefully removed from the samples and mass losses were determined, and no correlation factors were considered. The experiment was replicated five times.

Blue stain testing

Blue stain test was done on pine (*Pinus sylvestris*) wood, because this wood is much more susceptible to staining than spruce wood. The experiment was performed according to the EN 152-1 standard (ECS 1996). The samples (1 × 4 × 11 cm) were brushed with all aqueous solutions to achieve final retention of approximately 300 g/m^2. After brushing, the samples were let to dry for three weeks, and afterwards were exposed to blue stain fungi (*Aureobasidium pullulans* and *Sclerophoma pithyophila*) for six weeks. After exposure the specimens were isolated and staining was visually evaluated. The samples were cut on three parts and penetration of hyphens from lower to upper (treated) part was measured, as well. Experiment was performed on five parallel specimens.

FTIR analysis

Fourier transform infra red (FTIR) analysis is perfect tool that enables us deeper understanding of fixation mechanism of biocides in wood. Therefore, FTIR spectra of control and impregnated specimens were measured. For this part of the research specimens were impregnated with the highest content of preservative solutions, only. A Perkin Elmer Spectrum One spectrometer was used for this study. IR spectra were measured using HATR (Horizontal Attenuated Total Reflection) technique. The HATR accessory ZnSe crystal (Perkin Elmer) was used. Specimens were positioned on the surface of the ZnSe crystal and 64 scans were performed at 1 cm^{-1}.

RESULTS AND DISCUSSION

Boron compounds have limited solubility in water (50 g/L for boric acid; 25.6 g/L for borax). Therefore, aqueous solutions with 1 % of boron can not be prepared. Addition of ethanolamine into the aqueous solution improves solubility of both boron compounds. Quaternary ammonium compound was added into this solution to improve fungicidal properties of this formulation. After mixing of these compounds, there were no precipitates observed. Formulations of boron, ethanolamine and quaternary ammonium compound were stable for at least six month.

Boron is extremely diffusible in wood. It is well known, that boron does not fixate in wood and therefore it is extremely prone to leaching in wet environments. Those properties reflect in rather extensive boron leaching. In laboratory conditions, in average between 60 and 70% of boron is leached from impregnated wood treated with boric acid (Peylo and Willeitner 1995). From specimens impregnated with our testing formulations, between 46.9 and 59.7% of boron was leached from wood. Boron fixation was influenced by concentration and composition of preservative. Aqueous solutions where boric acid was used as boron source performed better than the ones based on borax. In average, from wood treated with preservative formulation BxEQ_55.8% of boron was leached, while more than 10% lower leaching rates were determined from spruce impregnated with BaEQ_(Tab. 1). However, if we compare leaching of tested preservative systems, particularly those based on boric acid, with literature data (Peylo and Willeitner 1995), it can be concluded that addition of ethanolamine into preservative formulation does not decrease boron fixation, but even slightly improves it (Tab. 1). Furthermore, the higher leaching rates were determined at wood block impregnated with solutions of the lowest boron concentration (c_B = 0.1%). This is rather unusual observation, as in most of the other biocides like copper, leaching increases with increasing concentration (Zhang and Kamdem 2000, Humar et al. 2007).

Identification of interactions between preservative solutions and wood, FTIR spectroscopy were used. FTIR spectra of wood impregnated with boron-ethanolamine and ethanolamine based solutions only were comparable, indicating, that changes in wood appears as a result of interactions of ethanolamine with wood. Any influence of boron and quaternary ammonium compounds on wood can not be resolved from the FTIR spectra. Data shown in Fig. 1 confirms, that the most of the changes in impregnated wood can be seen on peaks assigned to hemicelluloses (1737, 1268, 1100, 1056 cm^{-1}) and lignin (1601, 1268 cm^{-1}) (Fig. 1) (Michell 1989). Those changes are result of the lignin and hemicelluloses depolymerisation induced by ethanolamine (Humar et al. 2007). This depolymerisation resulted in higher number of available active sites for boron absorption. At specimens impregnated with more concentrated solutions, more prominent depolymerisation appears. Therefore, there were more active sites formed, and consequently lower boron leaching was observed (Tab. 1). However, ethanolamine

does not depolymerise cellulose (Claus et al. 2004), which is the most important absorption site for boron (Ramos et al. 2006), therefore it had no negative impact on boron fixation.

Tab. 1: Boron leaching from Norway spruce wood specimens impregnated with different boron (borax - Bx, Boric acid – Ba; ethanolamine – E; quat - Q) based aqueous solutions

Preservative solution	$c_B = c_{QUAT}$ [%]	Boron leaching [%]
BxEQ	0.1	59.7
	0.5	53.0
	1	54.6
BaEQ	0.1	50.8
	0.5	50.6
	1	46.9

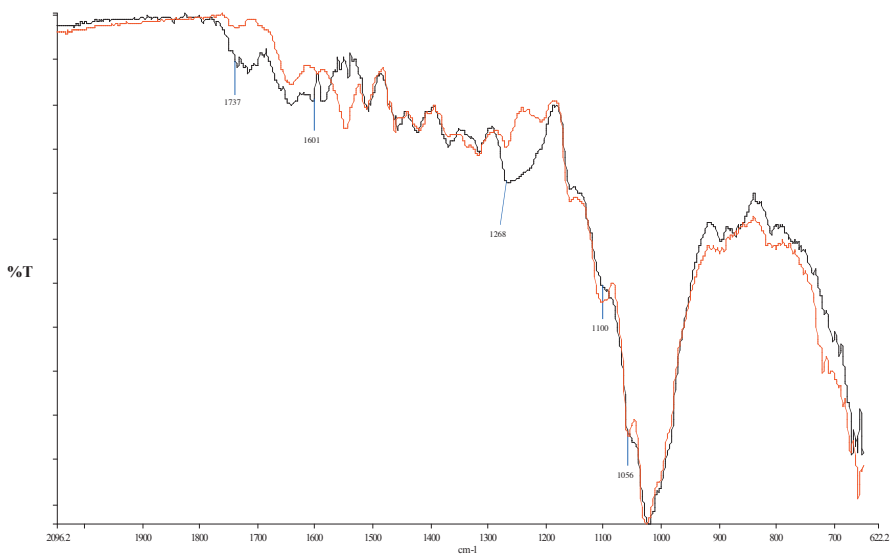

Fig. 1: FTIR spectra of unimpregnated Norway spruce wood (black) and of spruce wood impregnated with aqueous solution of boric acid, ethanolamine and quaternary ammonium compound ($c_B = c_{QUAT} = 1.0\%$)

However, the most important question related to tested preservative solution is their effectives against targeted wood decay fungi. All used fungi species were vital and control specimen's loss mass of 37.2% at *Gloeophyllum trabeum*, 26.6% at *Antrodia vaillantii* and 22.2% at *Trametes versicolor*, respectively (Tab. 2). All tested solutions even the ones of the lowest

concentration successfully preserved wood against tested wood decay fungi. None of the impregnated wood specimen did lose more than 3% of their initial masses (Tab. 2). Therefore, we can conclude, all tested formulations completely fulfil requirements of the EN 113 standard (1996). Furthermore, even two weeks of leaching (artificial ageing) of the impregnated wood did not influence the resistance of impregnated wood against wood decay fungi. This confirms that remaining biocides (boron and quaternary ammonium compounds) are sufficient to protect wood against tested wood decay fungi. But, it should not be overlooked that even ethanolamine has some influence on the growth of the wood decay fungi, and contributes to the effectiveness of the tested preservative solutions (Humar and Lesar in press). Fortunately, nitrogen introduced into wood via impregnation (ethanolamine) does not stimulate fungal growth. On the basis of this data, we presume that tested preservative solutions could be used at lest for preservation of wood in use class 3 (above ground applications). Effectiveness of this preservative in such conditions will be confirmed in ongoing field testing. After two years of lap joint testing according to procedure described by Rapp and Augusta (2004), there are no signs of decay observed until now.

Tab. 2: Mass loss of control and impregnated Norway spruce (Picea abies) specimens exposed to wood decay fungi for 16 weeks according to EN 113 procedure. Half of the specimens were leached (EN 84) before fungal exposure. (borax - Bx, Boric acid – Ba; ethanolamine – E; quat - Q)

Preservative solution	Leached	$c_B = c_{QUAT}$ [%]	Wood decay fungi		
			G. trabeum	*A. vaillantii*	*T. versicolor*
			Mass loss [%]		
BxEQ	No	0.1	-0.6	0.8	0.5
		0.5	-0.1	0.3	0.5
		1	-0.1	0.7	0.9
	Yes	0.1	0.8	1.3	0.6
		0.5	0.6	1.2	0.9
		1	1.0	1.2	1.0
BaEQ	No	0.1	0.2	0.5	0.1
		0.5	0.3	0.0	0.1
		1	0.4	0.7	0.5
	Yes	0.1	0.3	0.6	0.5
		0.5	0.1	0.4	1.5
		1	0.0	0.3	1.4
Control	No	/	37.2	26.6	22.2

Tested preservative solutions are not effective only against wood decay but against blue stain fungi as well. After six weeks control specimens were completely covered by stains, and

therefore marked with estimation 3. To ensure appropriate protection of pine sapwood against blue stain organisms, preservative solution of higher concentrations ($c_B = c_{QUAT} = 0.5 – 1.0\%$) should be used, than for protection against wood decay fungi. Specimens brushed with solution of the lowest concentration BxEQ, and exposed to blue stain fungi, were graded with mark 2.4 and effectiveness of solution BaEQ of the same concentration against blue staining were estimated with 1.2 (Tab. 3), what indicates that the surface of treated specimens were not as stained as of the control ones, but there was still considerable portion of surface discoloured. There are several reasons for lower effectiveness against blue stain fungi. Firstly specimens exposed to blue stain fungi were brushed only while specimens exposed to decay fungi were vacuum impregnated, and secondly boron is well known to be less effective against blue stains (Becker 1959), what reflects from our results as well.

Tab. 3: Influence of boron-ethanolamine-quat preservative solutions on blue staining of pine (Pinus sylvestris) wood

Preservative solution	$c_B = c_{QUAT}$ [%]	Visual estimation of surface	Depth of hyphen penetration (mm)
BxEQ	0.1	2.4	10
	0.5	0	1-2
	1	0	1-2
BaEQ	0.1	1.2	10
	0.5	0.2	2-3
	1	0	1-2
Control	/	3	10

CONCLUSIONS

Addition of quaternary ammonium compounds and ethanolamine into boron based aqueous solution significantly improves its solubility and slightly improves its fixation in wood. Norway spruce wood impregnated with these solutions is well protected against wood decay fungi even after artificial ageing (leaching). Boron, quaternary ammonium compounds and ethanolamine based aqueous solutions are effective against blue stain fungi as well. However, for protection of wood against blue stain fungi, higher concentrations of active ingredients should be used than for protection against wood decay strains.

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