

## **INFLUENCE OF MONTAN WAX EMULSIONS ON LEACHING DYNAMICS OF BORIC ACID FROM IMPREGNATED WOOD**

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### **ABSTRACT**

Boron biocides are one of the most frequently used components of commercial wood preservatives. They are very effective fungicides and insecticides, but they do not react with wood and thus leach from it in wet applications. In order to reduce leaching of boric acid, montan wax emulsion was introduced to the preservative solution. Spruce wood specimens were vacuum impregnated and afterwards leached according to the novel OECD and prCEN/TS 15119-1 procedures. Those two methods are non-continuous and are used for estimations of boron leaching from use class II and III applications. The results showed that addition of LGE emulsion does not reduce boron leaching significantly. Despite of the fact that both methods applied are non-continuous, it can be evident, that OECD procedure is much more severe than prCEN/TS 15119-1 one.

**KEY WORDS:** boric acid, leaching, montan wax emulsion, Norway spruce, wood preservation

### **INTRODUCTION**

Boron based compounds are one of the most important classical biocides, that remained on the market even after implementation of European Biocidal Product Directive (BPD 98/8/EC, 1998). Due to their broad spectrum of fungicidal and insecticidal properties, borates are considered more effective preservatives than copper and zinc ones, with the later two performing better only because of their fixation in wood, not their inherent fungicidal activity (Obanda et al. 2008). To inhibit growth of the fungi growing on nutrient medium, between 200 and 400 ppm of boron is necessary. In contrary, to inhibit growth of copper sensitive species 650 ppm and to inhibit growth of copper tolerant up to 1500 ppm of copper is required (Lesar and Humar 2009). Use of borates is limited due to their high mobility and good water solubility what results in

insufficient fixation. The solubility and mobility of borates allows them to treat wood species that are difficult to treat with copper-based preservatives. Even when not applied on the whole cross-section, they redistribute by diffusion if sufficient moisture is available in wood to provide one of the most effective preservation systems available today (Peylo and Willeitner 1999).

To increase the use of boron compounds as environmentally benign wood preservatives, several fixation systems have been developed to limit or decrease boron leaching. Some attempts have relied on limiting the water penetration of treated wood using water repellents, monomer and polymer systems (Kartal et. al. 2007). The most important solutions for limiting boron leaching are: combination of boron with glycerol/glyoxal (Taussaint-Davergne et al. 2000), vinyl monomers (Yalinkilic et al. 1999), silanes (Kartal et. al. 2007), alkydes (Peylo and Willeitner 1995), tall oil derivatives (Temiz et al. 2008). Despite numerous researches, there is no commercially solution available that could limit boron leaching below 25 %).

In our investigation boron was combined with montan wax. Our previous results showed, that montan wax acts synergistically with boric acid and improve its performance against fungi (Lesar et al. 2008). Crude montan wax belongs to the group of naturally occurring waxes of vegetable origin such as carnauba wax or candelilla wax. It is a mixture of chemical compounds that can be divided into three substance groups: waxes, resins and asphaltic substances. Like existing vegetable hard waxes such as carnauba wax, the pure wax substance in montan wax mainly consists of esters of long-chain acids with long-chain alcohols and free long chains acids. Other components such as free wax alcohols or ketones, paraffins or terpenes are usually present in small quantities (Matthies 2001). Montan wax is used in the form of flakes, powders, pastes with solvents, or aqueous emulsions (Heinrichs 2003). One of the most important advantages of montan wax is capability of forming thin-layer resistant films (Warth 1959). Therefore we anticipated that this thin film could limit water penetration and limit boron emissions from impregnated wood.

There are several standard methods developed to evaluate biocides emissions from impregnated wood. The oldest ones DIN 52172-2 (1972), EN 84 (1994) and ENV 1250-2 (1994) were based on continuous leaching, where specimens were in contact with water within the majority of the leaching procedure. Those standards were designed for testing of wood preservatives in ground contact like CCA or CCB. Boron based biocides are not used in such wet environments as copper based preservatives. Thus novel leaching procedures were developed in past years, as in most of the cases hydrophobic properties of wood can not be expressed if leached according to the continuous methods. The newly designed methods like OECD (2006) and prCEN/TS 15119-1 (2007) are designed for estimation of biocidal emissions from wood in use class III applications (above ground). Those standards are significantly less severe, as specimens are in water contact minor part of the leaching experiment. In present research, boron emissions from impregnated wood were evaluated using non-continuous methods to prove or reject hydrophobic effect of montan waxes.

## MATERIAL AND METHODS

Samples ( $1.5 \times 2.5 \times 5$  cm) made of Norway spruce (*Picea abies*) were vacuum impregnated with different preservative solutions according to the EN 113 (1996) procedure. Preservative solutions consists of montan wax water emulsions (LGE – emulsion, Samson d.o.o., Slovenia) and boric acid ( $c_B = 0.1$  % or 0.5 %). For testing, two types of LGE emulsions were purchased. Emulsion LGE-A contain 6 % and emulsion LGE-B 12 % of montan wax. Specimens used for leaching have end sealed axial surfaces before impregnation( Tab. 1).

Tab. 1: Retention of wax and boron at vacuum impregnated and surface treated specimens. Axial surfaces of specimens were sealed before impregnation. Standard deviations are given in the parentheses

Wax type	CB	Retention kg.m <sup>-3</sup>	
		Wax	Boron
Without	0.1	0	0.19 (0.10)
	0.5	0	0.53 (0.29)
LGE-A	0.1	4.78 (1.84)	0.08 (0.03)
	0.5	5.10 (1.57)	0.43 (0.13)
LGE-B	0.1	7.71 (1.13)	0.06 (0.01)
	0.5	8.42 (2.26)	0.35 (0.09)
Surface treated with LGA-B	0.1	4.51 (0.58)	0.15 (0.05)
	0.5	4.74 (0.41)	0.63 (0.40)

Some specimens were impregnated with aqueous solution of boric acid, and afterwards brushed with montan wax type LGE-B. For leaching according to OECD procedure, all combinations of wax emulsions and boric acid were applied, while reduced quantity of preservative solutions were applied for protection of specimens leached in line with prCEN/TS 15119-1 (2007) standard (Tab. 2 and 4).

Tab. 2: Percentages of boron determined in leachates from boron impregnated wood determined according to the OECD (2006) procedure regarding the concentration of montan wax and boron. Standard deviations are given in the parentheses

Wax type	Leaching day										$\Sigma$
	CB	1	2	3	4	5	6	7	8	9	
	Leached boron (%)										
Without	0.1	38 (2)	10 (2)	6 (1)	4 (1)	3 (0)	2 (0)	2 (0)	2 (0)	2 (0)	67 (4)
	0.5	46 (2)	12 (2)	5 (1)	4 (0)	2 (0)	1 (0)	1 (0)	1 (0)	1 (0)	75 (3)
LGE-A	0.1	57 (3)	14 (5)	5 (22)	4 (1)	3 (0)	2 (0)	2 (0)	1 (0)	1 (0)	89 (5)
	0.5	47 (3)	11 (1)	5 (1)	4 (1)	2 (0)	1 (0)	1 (0)	1 (0)	1 (0)	75 (4)
LGE-B	0.1	60 (3)	12 (1)	4 (1)	3 (0)	3 (1)	2 (0)	2 (1)	1 (1)	0 (0)	86 (3)
	0.5	46 (6)	11 (1)	4 (1)	3 (0)	2 (0)	1 (0)	1 (0)	1 (0)	1 (0)	71 (7)
Surface treated with LGA-B	0.1	35 (4)	11 (2)	6 (2)	4 (0)	3 (0)	2 (0)	2 (0)	2 (0)	2 (0)	66 (6)
	0.5	26 (5)	11 (2)	6 (1)	3 (1)	2 (1)	2 (0)	2 (0)	2 (0)	1 (1)	55 (6)

Tab. 3: Moisture content of impregnated wood leached according to the OECD (2006) procedure at the end of each leaching cycle. Standard deviations are given in the parentheses

Wax type	Leaching day									
	cb	1	2	3	4	5	6	7	8	9
	Moisture content (%)									
Without	0.1	17 (3)	19 (3)	18 (3)	20 (3)	20 (2)	20 (2)	20 (2)	21 (2)	22 (2)
	0.5	14 (2)	16 (2)	16 (2)	17 (2)	18 (2)	19 (2)	18 (1)	19 (1)	21 (1)
LGE-A	0.1	14 (4)	17 (4)	17 (3)	19 (4)	20 (3)	19 (3)	19 (3)	20 (3)	23 (3)
	0.5	14 (4)	18 (4)	17 (3)	19 (4)	20 (3)	20 (3)	20 (3)	22 (3)	23 (3)
LGE-B	0.1	12 (1)	15 (2)	14 (2)	16 (2)	17 (2)	17 (2)	17 (3)	18 (2)	19 (2)
	0.5	13 (3)	16 (4)	15 (3)	17 (4)	18 (4)	19 (3)	18 (2)	20 (2)	21 (2)
Surface treated with LGA-B	0.1	14 (2)	18 (3)	17 (3)	19 (3)	20 (3)	21 (3)	20 (3)	22 (3)	23 (3)
	0.5	13 (3)	15 (2)	15 (2)	17 (3)	18 (3)	18 (2)	18 (2)	19 (3)	19 (2)

Tab. 4: Percentages of boron determined in leachates from boron impregnated wood determined according to the prCEN/TS 15119-1 (2007) procedure regarding the concentration of montan wax and boron. Standard deviations are given in the parentheses

Wax type	Leaching day										$\Sigma$
	CB	1	2	3	4	5	6	7	8	9	
	Leached boron (%)										
Without	0.1	3 (0)	6 (2)	4 (1)	5 (1)	6 (1)	6 (1)	4 (0)	3 (1)	2 (0)	39 (3)
	0.5	7 (1)	7 (1)	6 (3)	4 (2)	4 (0)	4 (0)	2 (0)	2 (1)	2 (0)	38 (4)
LGE-B	0.1	5 (2)	7 (3)	4 (0)	4 (2)	3 (2)	6 (0)	3 (0)	2 (0)	2 (0)	36 (2)
	0.5	8 (1)	7 (1)	6 (0)	5 (1)	4 (0)	4 (1)	2 (0)	1 (0)	1 (0)	39 (3)

Leaching was performed according to the OECD (2006) and prCEN/TS 15119-1 (2007) procedure. Those methods are non-continuous, thus the specimens were not immersed to water all the time during the leaching, but there are extensive drying periods included as well.

Both methods applied are relatively similar. In order to have comparable results, at both methods three specimens with end sealed axial surfaces were immersed to 300 mL of deionised water. Specimens leached according to OECD method were immersed to water for 1 hour, and air dried for 4 hours and afterwards immersed again for additional 1 hour. This cycle was repeated after two days, in total for nine times in three weeks lasting experiment. Similarly, prCEN/TS 15119-1 protocol prescribes shorter leaching cycles. Specimens are immersed to deionised water for 1 minute, and air dried for 2 hours and afterwards immersed again for 1 min and than dried (2 h) and immersed again (1 min). Leaching protocol prCEN/TS 15119-1 consists of nine above mentioned leaching cycles in three weeks in total. Water was collected after each set of cycle and boron content was determined using inductively coupled plasma mass spectrometer (ICP-MS). For each treatment, nine specimens leached in three parallel vessels was used. Moisture content of wooden specimens leached according to the OECD protocol was determined at the end of each leaching cycle.

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<sup>-1</sup>, auxiliary gas flow rate 0.7 L min<sup>-1</sup> and nebuliser gas flow rate 1.05 L min<sup>-1</sup>. 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<sup>-1</sup>) (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 (Al-Ammar et al. 1999). 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.

## RESULTS AND DISCUSSION

As a result of impregnation process, specimens retained between 64 and 193 kg.m<sup>-3</sup> of preservative solutions. Those values are rather low but it has to be considered, that axial surfaces of the specimens were sealed with epoxy coating. Secondly Norway spruce (*Picea abies*) wood is difficult to impregnate (Morrell and Morris 2002). The highest loadings were observed at specimens impregnated with aqueous solution without addition of wax (193 kg.m<sup>-3</sup>) and the lowest one at specimens that was impregnated with LGA-B solution with 0.1 % of boron. This clearly indicates that addition of montan wax emulsions reduces penetration of preservative solution to the spruce wood specimens. In dry specimens, between 0.06 and 0.63 kg.m<sup>-3</sup> of boron (equivalent 0.34 and 3.60 of H<sub>3</sub>BO<sub>3</sub> kg.m<sup>-3</sup>) remained in wood after impregnation (Tab. 1). Those retentions are sufficient to protect wood against most common basidiomycetes in use class II or III (Freitag and Morrell 2005, Lesar and Humar 2009).

Our results proved that boron, does not react with wood, and therefore leaches from wood considerably. From the data presented in Tab. 2 is evident, that between 38 % and 46 % of retained boron is leached from wood during the first leaching cycle of OECD protocol, consisting of two one hours' immersion phases. However, after three weeks of non-continuous OECD leaching, in average 67 % of boron leached from specimens impregnated with the lowest and 75 % of boron was released from the spruce wood specimens impregnated with the boric acid based solution of the highest concentration. However, leaching performed according to the prCEN/TS 15119-1 was less severe (Tab. 4). During first leaching cycle, consisting of three one minutes' immersion phases, between 3 % and 8 % of retained boron was leached, only. This is 5 to 10 times less than observed during first OECD leaching cycle. Furthermore, at the end of leaching prCEN/TS 15119-1 procedure, between 36% and 39% of boron emitted from impregnated wood (Tab. 4). This final value was approximately two times lower than observed at the end of OECD procedure. If those values are compared to other, continuous leaching procedures, it can be seen, that those methods are less severe than continuous leaching protocols. Literature data revealed (Lesar et al. 2008), that from the specimens leached in line with EN 84 (1984) and ENV 1250 guidelines, considerably higher portion of boron was leached. Namely, from specimens impregnated with aqueous solution containing 0.1 % of B, all boron released from the specimens.

It was expected, that addition of montan wax into aqueous solution of boric acid will reduce boron leaching from impregnated specimens. From the data presented in Tab. 2 and 4 it can be evident, that in certain conditions addition of montan wax into boron based aqueous

solutions does not reduce leaching of boron from impregnated wood. Even more in the first stages of leaching, addition of montan wax has even a negative effect on boron leaching. We presume that the reason for this occurrence resulted in the fact, that more viscose LGE based aqueous solutions did not penetrate that depth as less viscose boric acid based solutions without LGE emulsion. Boron on the surface of LGE/boric acid based aqueous solutions was therefore more exposed to leaching than boron in the centre of the spruce wood specimens impregnated with aqueous solution of boric acid, only. It was even more surprising, that in certain cases addition of LGE emulsion to boron based aqueous solutions have even considerably negative influence on release of boron from impregnated wood. If we compare leaching data with moisture content of wooden specimens after each leaching cycle (OECD procedure only), it can be seen that specimens impregnated with aqueous solutions containing waxes have slightly lower moisture content (Tab. 3). Another interesting observation is that very prominent diffusion appeared at relatively dry specimens. From specimens with average moisture content between 13 % and 14 %, during first day of leaching, between 46 % and 60 % of boron was leached. Perhaps the reason for this originates in fact, that surface of the specimens, where the majority of the boron was present, has considerably higher moisture content than interior of the specimens. However, we were not able to determine the moisture content of the outer part, but of the whole specimens only. Another reason for prominent emissions of boron from leached specimens is fact that the surface of specimens was drying after each leaching cycle, what resulted in mass flow of the water with dissolved boron from interior to the surface of leached specimens.

Part of the specimens, were after impregnation with boron based aqueous solutions surface treated with montan wax. Those specimens were leached according to the OECD procedure only. Retention of wax applied with surface treatment is comparable to the specimens treated with preservative solutions based on montan wax emulsion LGE-A. However, there was considerable difference between those two treatments. At surface treated specimens, the major part of the wax was present on the surface of the specimens, while at vacuum treated specimens deeper penetration of wax was achieved. It seems like that wax introduced into the surface of spruce wood specimens formed a barrier that limit boron leaching. Surface treatment with montan wax reduced emissions from specimens treated with the highest concentration of boron for more than 25 % (Tab. 3). Similar effect of surface applied water repellents is reported by (Peylo and Willeitner 1995) as well.

## **CONCLUSIONS**

Despite of the fact that prCEN/TS 15119-1 leaching procedure is less severe than OECD method, both methods lead us to similar conclusion. Considerable portions of boron are leached from wood in the first leaching cycles, already. The addition of montan wax emulsion to boric acid aqueous solution does not reduce leaching of boron compounds from spruce wood, unfortunately.

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## REFERENCES

1. Al-Ammar, A., Gupta, R.K., Barnes, R.M., 1999: Elimination of boron memory effect in inductively coupled plasma-mass spectrometry by addition of ammonia. *Spectrochimica Acta Part B* 54: 1077-1084
2. Biocidal Products Directive, 98/8/EC. Official Journal of the European Communities 1998, L 123: 1-63
3. DIN 52172-2, 1972: Prüfung von Holzschutzmitteln; Beschleunigte Alterung von geschütztem Holz, Auswaschbeanspruchung für die Bestimmung der ausgewaschenen Wirkstoffmenge
4. ENV 1250-2, 1994: Wood preservatives. Methods for measuring losses of active ingredients and other preservative ingredients from treated timber – Part 2: Laboratory method for obtaining samples for analysis to measure losses by leaching into water or synthetic sea water
5. EN 113, 1989: Wood preservatives. Determination of the toxic values against wood destroying basidiomycetes cultured an agar medium.
6. EN 84, 1994: Wood preservatives: Accelerated ageing of treated wood prior to biological testing – Leaching procedure
7. prCEN/TS 15119-1, 2007: Durability of wood and wood-based products. Determination of emissions from preservative treated wood to the environment - Part 1: Wood held in the storage yard after treatment and wooden commodities exposed in Use Class 3 (not covered, not in contact with the ground). Laboratory method
8. Freitag, C., Morrell, J.J., 2005: Development of Threshold values for boron and fluoride in non soil contact applications. *Forest Products Journal* 55(4): 97-101
9. Heinrichs, F.L., 2003: Montan wax. In: Ullman's encyclopedia of industrial chemistry, Vol. 39 –chapter 3. Eds. Bhonet M. Wiley-VCH, Weinheim, Pp. 154-159
10. Kartal, N.S., Hwang, W.J., Yamamoto, A., Tanaka, M., Matsumura, K., Imamura, Y., 2007: Wood modification with a commercial silicon emulsion: Effects on boron release and decay and termite resistance. *International Biodeterioration and Biodegradation* 60(3): 189-196
11. Lesar, B., Humar, M., 2009: Re-evaluation of fungicidal properties of boric acid, Holz als Roh und Werkstoff, in press
12. Lesar, B., Kralj, P., Humar, M., 2008: Montan wax improves performance of boron-based wood preservatives, *International Biodeterioration and Biodegradation*, doi: 10.1016/j.ibiod.2008.10.006, in press
13. Lesar, B., Kralj, P., Žlindra, D., Kancilija, V., Humar, M., 2008: Comparison of standard procedures for estimation of biocides leaching from impregnated wood, *Zbornik gozdarstva in lesarstva* 86: 59-64
14. Matthies, L., 2001: Natural montan wax and its raffinates. *European Journal of Lipid Science and Technology* 103: 239-248
15. Morrell, J.J., Morris, P.I., 2002: Methods for improving preservative penetration into wood: a review. The International Research Group on Wood Preservation, IRG Document No: IRG/WP 02-40227
16. Obanda, D.N., Shupe, T.F., Barnes, H.M., 2008: Reducing leaching of boron-based wood preservatives – A review of research *Bioresource Technology* 99(15): 7312-7322
17. OECD Guideline for testing of chemicals, 2006: Estimation of Emissions from preservative treated Wood to the Environment: Laboratory Method for Wood held in Storage after Treatment and for Wooden Commodities that are not covered, and are not in Contact with Ground

18. Peylo, A., Willeitner, H., 1995: The Problem of reducing Leachability of Boron by Water Repellents. *Holzforschung* 49: 211-216
19. Peylo, A., Willeitner, H., 1999: Five years leaching of boron. The International Research Group on Wood Preservation. IRG/WP/99-30195
20. Taussaint-Davergne, E., Solounganga, P., Gerardin, P., Loubinoux, B., 2000: Glycerol/glyoxal: A new boron fixation system for wood preservation and dimensional stabilization. *Holzforschung* 54: 123-126
21. Temiz, A., Alferdsen, G., Eikenes, M., Terziev, N., 2008: Decay resistance of wood treated with boric acid and tall oil derivatives. *Bioresource Technology* 99: 2102-2106
22. Warth, A.H., 1959: The chemistry and Technology of Waxes. Reinhold Publishing cooperation, New York, 2 pp.
23. Yalinkilic, M.K., Imamura, Y., Takahashi, M., Yalinkilic, A.C., 1999: In situ polymerization of vinyl monomers during compressive deformation of wood treated with boric acid to delay boron leaching. *Forest Products Journal* 49: 43-51

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