Sorption Properties of Wood Impregnated with Aqueous Solution of Boric Acid and Montan Wax Emulsion

Boštjan Lesar, Aleš Straže, Miha Humar

Department of Wood Science and Technology, Biotechnical Faculty, University of Ljubljana, Ljubljana, Slovenia

Received 5 February 2010; accepted 12 August 2010 DOI 10.1002/app.33196 Published online 23 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Nonbiocidal techniques for wood protection have become more and more important in the last few years. One of the possible treatments to enhance wood durability is use of water repellents. In this research, the influence of one of the possible water repellents, the montan wax emulsion, on the moisturizing and the sorption characteristics of impregnated wood was investigated. To achieve a better protection against wood decay fungi, wood was impregnated with montan wax emulsion enriched with boric acid. The equilibrium moisture content (MC) was monitored during the adsorption and the desorption processes at five levels of relative air humidity $(R\hat{H}_1 = \hat{20}\%, RH_2 = 33\%, RH_3 = 65\%, RH_4 = 88\%$, and $RH_5 = 98\%$). Water repellence efficiency was monitored in the chamber with high RH (87%) and during dipping in the water. Impregnated samples were also exposed outdoors in a covered position for 5 months to determine

INTRODUCTION

Wood is the most important biopolymer in the world. It is the most important natural material used for construction applications, but it is exposed to weathering and biotic decay. To slow down these processes, wood is frequently treated with polymers like surface coatings, waxes, oils, etc. Treatment of the wood with water repellents can influence the long-term properties of this material. Rain and dew water are causing surface erosion and leaching of wood components. Second, the moisture content (MC) of repellent-treated wood in service is reduced, and thus the risk of crack formation and biological degradation is lowered as well. It is well known that water repellent treatment lowers the MC of treated wood in water submersion tests considerably.¹ Furthermore, combinations of active ingredients such as fire retardants, biocides, or ultraviolet light protectants with water repellents prevented or at least limMC changes according to changes in outdoor humidity and temperature. The results showed that the sorption properties of the impregnated wood are strongly related to retention of preservative solutions after impregnation and its composition. Montan wax reduced equilibrium MC of the impregnated wood up to 25% (relatively), whereas specimens impregnated with combination of montan wax and boric acid resulted in decreased MC in some cases and in increased MC in some cases. The Guggenheim–Andersen–deBoer model of sorption isotherms was fitted to experimental data to explain the sorption mechanisms. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1337–1345, 2011

Key words: boron compounds; moisture content; montan wax; sorption; wood protection; adsorption; surfaces; coatings

ited their leaching.^{2–5} The most important water repellents used in the wood preservation are waxes, particularly paraffin waxes.^{6,7} Paraffin waxes find their second most important applications in wood industry after candle industry. The importance of use of waxes in wood industry is increasing in Europe in particular because consumers, due to increased environmental awareness, avoid biocidal-treated wood and wood from tropical forest. Therefore, industry is interested in development of alternatives, like treatment with waxes. There is at least one commercially operated treatment of wood with paraffin (Dauerholz in Germany).⁸ However, our experimental results clearly indicate that montan wax perform better than paraffin wax.⁹

Montan and carnauba waxes are one of the possible water repellent agents to be applied in the field of wood preservation, as well. Those waxes are among the most resistant waxes, and it should not be overseen that they have the ability of thin film formation. Montan and carnauba wax, as well as other waxes, are almost nontoxic and are used for variety of applications like fruit treatment to slow down fruit drying.¹⁰ Crude montan wax belongs to the group of the naturally occurring waxes of vegetable origin such as carnauba wax or candelilla wax. Montan wax is fossilized vegetable wax extracted

Correspondence to: M. Humar (miha.humar@bf.uni-lj.si). Contract grant sponsor: Slovenian Research Agency;

contract grant numbers: L4-0820-0481, P4-0015-0481.

Journal of Applied Polymer Science, Vol. 120, 1337–1345 (2011) © 2010 Wiley Periodicals, Inc.

from lignites, principally from the central German brown coal reserves west of the Elbe River. 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-chain acids. Other components such as free wax alcohols or ketones, paraffins, and terpenes are usually present in small quantities.¹¹ The wax is soluble in many organic solvents, particularly aromatic or chlorinated hydrocarbons, even on moderate heating. Montan wax is used in the form of flakes, powders, pastes with solvents, and aqueous emulsions.¹² One of the most important advantages of montan wax is its capability of forming thin-layer resistant films.¹³ Montan wax improves performance against wood decay fungi, but not sufficiently to be used for in-ground applications.¹⁴ However, wood impregnated with the preservative solutions, based on the montan wax and the boron compounds, is well protected against wood decay fungi in aboveground applications. Combinations of boron and montan wax have synergistic effect against the wood inhabiting fungi, and montan wax additionally reduces the leaching of boron compounds from impregnated wood.14

However, neither montan wax nor paraffin or synthetic waxes react with wood. They either form thin films on the surface of wood or on the surface of cell walls, or filled cell lumina with waxes, thus limiting water penetration to wood. Because they are insoluble in water, they do not leach from wood.¹⁵ However, it is reported that paraffin treatment in most of the cases does not prevent degradation processes, but only slows them down.

Boron compounds are one of the oldest active ingredients for wood preservation that still remains on the market, even after introduction of biocidal products directive in the European Union. Their importance increased significantly. Boron compounds have low mammalian toxicity, but they are very effective against most of the wood pests. Their use is limited because their diffusibility and susceptibility to leaching. This is especially important when boron-impregnated wood is used for outdoor applications. It is important to consider that boron in impregnated wood is not bound at all; therefore, it tends to diffuse if concentration gradient and moist conditions are present.¹⁶ Because of only physical adsorption of boron compounds in wood, boron treatment does not influence the availability of hydrophilic hydroxyl groups in wood.17 Wood impregnated with boron compounds (boric acid [Ba]or borax) is more hygroscopic than untreated wood, particularly in high relative air humidity

(RH). The increase in equilibrium moisture content (EMC) of such wood depends on the type of wood preservative used, retention, and wood species.^{18,19} An EMC is problematic because of the more prominent leaching of active ingredients, creating favorable conditions for the growth of fungi, particularly molds, and because there are difficulties related to surface treatment and gluing of the moist wood.

To lower the EMC of the boron-treated wood, Babased aqueous solution was combined with the montan wax emulsion. To determine the effectiveness of preservative solution, three different tests were performed; conditioning in water or in a chamber with high RH, conditioning in chambers in the whole hygroscopic region during the adsorption and desorption processes, and monitoring of MC during outdoor exposure.

MATERIALS AND METHODS

Treatment solutions used

For impregnation of wood, the montan wax emulsion (LGE) (Samson, Slovenia) of two different concentrations 6% (LGE-A) and 12% (LGE-B), respectively, were used. Some solutions contained Ba as well ($c_B = 0.5\%$). The composition and the concentrations (dry content) of wax emulsions and boron compounds are shown in Table I.

Sorption properties

To determine the sorption properties, three types of tests were performed. In the first one, small impregnated wood specimens (SP) were conditioned in chambers with different RH. In the second set of experiments, slightly bigger specimens (EN 113) were submerged in water or conditioned in a chamber with high humidity, and their masses were monitored. In the third set of experiments, wood specimens were exposed outside, under a roof. MC of wood was determined gravimetrically based on the mass of impregnated specimens.

The first set of sorption experiment was performed on Norway spruce (*Picea abies*) specimens. Samples of $2.0 \times 2.0 \times 1.0$ cm (SP) dimensions were used in this experiment. Before vacuum impregnation (vacuum, 20 min; pressure, 90 min; and vacuum, 10 min) specimens (10 per preservative solution) were oven dried (40° C \pm 1°C for 3 days) and their masses were determined. In parallel, control specimens were dried according to the same procedure. For impregnation, two preservative solutions, montan wax emulsion (LGE-A) and montan wax emulsion with Ba ($c_B = 0.5\%$), were used. After impregnation, specimens were conditioned for 3 weeks at 25°C, 65% RH, and afterward oven dried (40° C \pm 1°C for

| | | | | | | Retention (kg/m ³) | | | |
|-----------------------|--------------------|----------------------------|------------------------|------------------------------|-----------------|--------------------------------|-------------|---------------|--|
| Preservative solution | Wax content (%) | Boron concentration (%) | Axial planes sealed | Type of samples ^a | Wood species | Preservative solution | Wax | Boric acid | |
| LGE-A | 6 | 0 | Yes | EN 113 | Spruce | 138 (21) | 16.5 (2.5) | 0.0 | |
| LGE-A | | 0 | No | EN 113 | Spruce | 696 (119) | 83.5 (14.3) | 0.0 | |
| LGE-A-Ba | | 0.5 | | | - | 598 (135) | 71.8 (16.2) | 2.99 (0.68) | |
| LGE-B | 12 | 0 | No | EN 113 | Spruce | 555 (162) | 66.7 (19.4) | 0.0 | |
| LGE-B-Ba | | 0.5 | | | | 595 (129) | 71.4 (15.5) | 2.97 (0.63) | |
| LGE-B | | 0 | Yes | EN 113 | Spruce | 159 (26) | 19.1 (3.1) | 0.0 | |
| LGE-B-Ba | | 0.5 | | | - | 154 (25) | 18.5 (3.0) | 0.77 (0.13) | |
| Ba | 0 | 0.5 | No | EN 113 | Spruce | 776 (69) | | 3.88 (0.35) | |
| Control | 0 | 0 | No | EN 113 | Spruce | 0 | 0 | 0 | |
| Control | 0 | 0 | Yes | EN 113 | Spruce | 0 | 0 | 0 | |
| LGE-A | 6 | 0 | No | EN 252 | Spruce | 178 (42) | 10.7 (2.5) | 0.0 | |
| LGE-B | 12 | 0 | | | - | 83 (26) | 10.0 (3.0) | 0.0 | |
| LGE-B-Ba | 12 | 0.5 | | | | 121 (13) | 14.5 (1.6) | 0.61 (0.06) | |
| Control | 0 | 0 | | | | 0 | 0.0 | 0.0 | |
| LGE-A | 6 | 0 | No | EN 252 | Beech | 402 (58) | 24.1 (3.5) | 0.0 | |
| LGE-B | 12 | 0 | | | | 236 (15) | 28.3 (1.8) | 0.0 | |
| LGE-B-Ba | 12 | 0.5 | | | | 264 (26) | 31.7 (3.1) | 1.3 (0.13) | |
| Control | 0 | 0 | | | | 0 | 0 | 0 | |
| LGE-B | 12 | 0 | No | SP | Spruce | 699 (30.4) | 83.8 (3.6) | 0.0 | |
| LGE-B-Ba | | 0.5 | | | | 677 (56.4) | 81.2 (6.8) | 3.4 (0.28) | |
| Control | | 0 | | | | 0 | 0 | 0 | |

TABLE IRetentions (n = 10) of the Preservative Solutions, Montan Wax, and Boric Acid in Vacuum/Pressure Treated
Specimens and in Wood Specimens Impregnated with Various Aqueous Emulsions of Montan Wax
(LGE-A, LGE-B, LGE-A-Ba, and LGE-B-Ba)

Standard deviation shown in parentheses.

^a Size of the specimens: EN 113, $1.5 \times 2.5 \times 5.0$ cm; EN 252, $2.5 \times 5.0 \times 50$ cm; and SP, $2.0 \times 2.0 \times 1.0$ cm.

3 days), and, then, the retention was gravimetrically determined. Retentions were expressed in kg/m^3 .

After drying, samples were conditioned at $20^{\circ}C \pm 0.5^{\circ}C$ at five different levels of RH, which were obtained with saturated salt solutions (CH₃COOK, RH = $20\% \pm 1\%$; MgCl₂·6H₂O, RH = $33\% \pm 1\%$; NaNO₂, RH = $65\% \pm 1\%$; ZnSO₄·6H₂O, RH = $88\% \pm 1\%$; H₂O, RH = $98\% \pm 1\%$), first in the adsorption and then in the desorption processes. A regression analysis was applied to fit the experimentally obtained data with the Guggenheim–Andersen–deBoer (GAB) sorption model.^{19,20} Sorption isotherms, according to the GAB model, exhibited good fitting of experimental data of various kinds of wood in the water activity range (*h*) 0.0–0.9.²¹ This model was used to predict MC of control and impregnated wood.

$$\frac{u}{u_0} = \frac{CKh}{(1 - Kh)(1 - Kh + CKh)} \tag{1}$$

In the above equation, u_0 , C, and K are the three free sorption parameters characterizing sorption properties of the material, u is wood MC, and h is water activity or RH fraction. The u_0 denotes MC corresponding to the monomolecular layer on the whole free surface of the material (on every free hydroxyl groups of wood one molecule of water is bonded). It is known that monolayer values decrease with increasing temperature.²¹ *K* constant is the measure of the difference of free enthalpy (standard chemical potential) of the sorbate (water) molecules in two states, the pure liquid and second sorption stage, the layers above the monolayer. It is always found that $K < 1.^{22}$ Other GAB energy constant *C* measures the difference of the chemical potentials of the sorbate (water) molecule in the upper sorption layers and in the monolayer.²²

For comparison and evaluation of hygroscopy of impregnated samples sorption quotient [eq. (2)] was determined:

$$s = \frac{\Delta u}{\Delta RH} = \frac{u_2 - u_1}{RH_2 - RH_1} \tag{2}$$

where, Δu is the change in wood MC between equilibrium states u_1 and u_2 and ΔRH is the difference between RH₁ and RH₂, where samples were conditioned.

The second set of sorption experiments was performed on Norway spruce (*P. abies*) wood specimens $(1.5 \times 2.5 \times 5.0 \text{ cm} \text{ [EN 113]})$, with end-sealed (epoxy coating) axial surfaces. Approximately 43% of the samples were unsealed before impregnation as evident from Table I. They were impregnated (vacuum, 20 min; pressure, 90 min; and vacuum, 10 min) with LGE-A, LGB-B, and LGE-A-Ba solutions (Table I).

Journal of Applied Polymer Science DOI 10.1002/app

After 4 weeks of air drying (25° C; 65°), the impregnated and control specimens were oven dried (40° C) for 3 days. Before drying, axial surfaces of unsealed specimens were sealed. Specimens dedicated to sorption monitoring were afterward transferred to the chamber with RH of 87%. The mass of the specimens was monitored daily for 6 weeks. On the other hand, specimens dedicated to water uptake analysis were immersed into distilled water. Masses of the specimens were monitored after predetermined periods, as shown in Figure 3(c,d,f), for 3 weeks.

Norway spruce and beech (Fagus sylvatica) specimens of 2.5 \times 5.0 \times 50 cm (EN 252) dimensions were used in the third part of the experiment. After drying ($103^{\circ}C \pm 2^{\circ}C$ for 24 h), samples were vacuum impregnated (vacuum, 30 min; pressure, 150 min; and vacuum, 10 min) with three different preservative solutions; LGE-A; LGE-B, and LGE-B-Ba (Table I). After 4 weeks of conditioning (25°C, 65% RH), samples were oven dried ($103^{\circ}C \pm 2^{\circ}C$ for 24 h) and then retention of active ingredients was gravimetrically determined. Those specimens were oven dried because they are considerably larger than other samples used. This reflects in slower drying rates compared with smaller specimens. Second, one of the objectives was to determine the dry content of retained wax because it is well known that chromatographic effect could take place, and, thus, there is less retained wax as it can be assumed from the quantities of retained solution. Control specimens were dried in parallel as well. Samples were exposed outside, under a roof (use class II). Masses of the specimens were monitored after predetermined periods for 5 months from February until June 2009. Outdoor temperature and RH were measured with EL-USB-2 data logger (Lascar Electronics, Whiteparish Salisbury, UK). This part of the investigation was also performed on 10 replicate specimens per solution/wood species.

RESULTS AND DISCUSSION

Composition of the preservative solution, wood species, and type of samples influence the retention of the preservative solutions considerably. In general, addition of montan wax negatively influences the uptake of aqueous solutions used (Table I).

Size of the specimens had a considerable influence on the retention of the preservative solutions as well. As expected, the highest average uptakes of preservative solutions was determined at SP specimens (688 kg/m³), followed by EN 113 specimens with unsealed surfaces (642 kg/m³), followed by EN 252 specimens (214 kg/m³), and the lowest retention was observed for EN 113 with end-sealed surfaces (150 kg/m³). Specific surface of the specimens was the most important factor that can explain the above-mentioned results. The highest uptake of preservative solution (776 kg/ m^3) among all specimens was observed for EN 113 specimens made of Norway spruce, impregnated with Ba aqueous solution only. Ba in this solution are small enough to penetrate into the cell wall.²³ In contrary, for EN 252 samples treated with montan wax emulsion (12% dry content), 10 times lower uptake (83 kg/m³) was observed. Two times higher loadings was measured at parallel specimens impregnated with montan wax emulsion containing 6% dry content (LGE-A) (178 kg/m^3) (Table I). The main reason for lower penetration of aqueous solutions that contained LGE emulsion was because particles in the emulsion are too big to penetrate into the cell wall, and, even more, they form a barrier on the surface of the cell wall and reduce penetration of the water into the cell wall. Similar results were obtained in previous research.¹⁴ The addition of Ba to LGE emulsions did not influence the loadings of the preservative solutions during impregnation process. On the other hand, influence of the wood species on the retention was the most prominent at the biggest EN 252 specimens. Uptakes of preservative solutions at beech specimens (EN 252) are two times higher than those at Norway spruce specimens. For example, beech specimens impregnated with LGE-A retained 402 kg/ m³, and spruce wood specimens treated with the same solution only retained 178 kg/m^3 (Table I). Described differences are a consequence of better impregnability of the beech wood because pits between cells in beech wood are bigger, and they are not aspirated as at spruce wood. Thus, montan wax emulsion can easily penetrate into the beech wood than into the spruce wood. However, beech wood is known to be more permeable than spruce wood.24 Therefore, composition of preservative solution did not have that prominent influence on loadings at beech wood specimens, as reported for spruce ones.

Furthermore, prominent differences between endsealed and unsealed EN 113 samples were noticed. There is no significant difference in loadings of the preservative solutions between EN 113 specimens with end-sealed axial surfaces and bigger EN 252 samples impregnated with the same preservative solution because both specimen types had approximately the same specific surface ratio. However, it is well known that wood is more permeable in axial than in transverse direction.²⁵ Therefore, at specimens with end-sealed axial planes, preservative solution had to penetrate through 15-100 less permeable radial and tangential planes.26,27 Our previously published experimental data²⁸ clearly indicate that the smallest SP samples and unsealed EN 113 samples are completely preserved with tested aqueous emulsions and solutions, whereas for EN 113 with end-sealed surfaces and for EN 252 samples, only

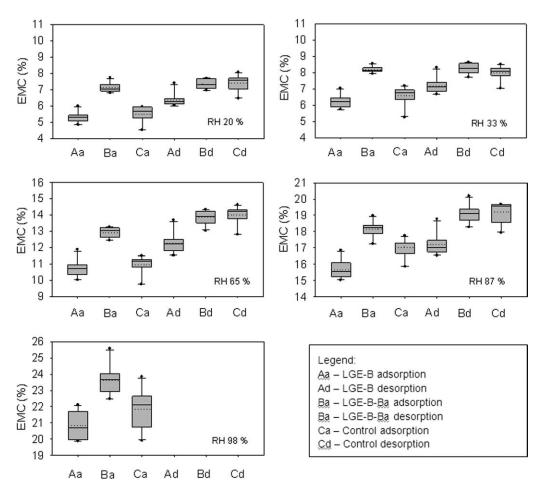


Figure 1 Box-and-whisker plots of the equilibrium moisture content (EMC) of control and impregnated Norway spruces specimens conditioned at five relative air humidity (RH) levels in the adsorption and desorption. Solid line is median, and dotted line is mean value.

the outer part of the specimens is treated, whereas the core remained almost unimpregnated.

However, the most important topic of our research was to elucidate how impregnation of wood with different combinations of montan wax emulsion and Ba influences sorption properties of impregnated wood. First set of sorption experiments was performed in chambers with different RH where Norway spruce specimens impregnated with LGE-B and LGE-B-Ba solution were exposed. Sorption isotherms of all impregnated and control samples have a characteristically sigmoid shape with hysteresis (Figs. 1 and 2). The graphs clearly show that the EMC in desorption process is always higher than that during adsorption at whole hygroscopic region. Hysteresis effect is greater for the control samples than for the impregnated ones. EMC of the samples impregnated with LGE-B was lower than EMC of control samples at all RH stages, for adsorption and desorption processes. For example, MC of montan wax (LGE-A)treated specimens was lowered by 3-9% in adsorption and by more than 10% in desorption process. It is presumed that the main reason for the reduced MC of LGE-A-treated specimens originates in the

hydrophobic effect of thin layer of montan wax on the wood surface and on the surface of the cell walls.^{2,6} Second reason for lower EMC was deposits

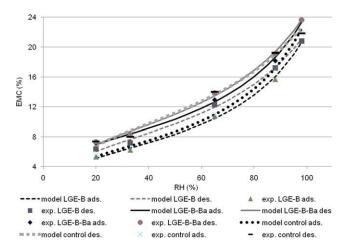


Figure 2 The average EMC of wood impregnated with aqueous emulsion of montan wax (LGE-B) and montan wax emulsion with boric acid (LGE-B-Ba) and control specimens (n = 10). GAB model fit curves are shown as well. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Journal of Applied Polymer Science DOI 10.1002/app

| | | Sorption quotient (s), hygroscopic region-RH (%) | | | | | GAB model | | |
|-----------------------|----------|--|-------|-------|-------|-------|-----------|----------|--------------------|
| Preservative solution | Sorption | 33–20 | 65–20 | 65–33 | 88–65 | 88–33 | K | С | u ₀ (%) |
| Control | А | 0.08 | 0.12 | 0.14 | 0.26 | 0.19 | 0.007604 | 19.94835 | 5.8 |
| | D | 0.05 | 0.15 | 0.19 | 0.23 | 0.20 | 0.006469 | 14.81227 | 8.6 |
| LGE-B | А | 0.07 | 0.12 | 0.14 | 0.21 | 0.17 | 0.00745 | 18.73971 | 5.7 |
| | D | 0.06 | 0.13 | 0.16 | 0.21 | 0.18 | 0.006863 | 17.13259 | 7.1 |
| LGE-B-Ba | А | 0.08 | 0.13 | 0.15 | 0.23 | 0.18 | 0.007201 | 37.19465 | 6.9 |
| | D | 0.07 | 0.15 | 0.18 | 0.23 | 0.20 | 0.006886 | 20.26673 | 7.9 |

TABLE IISorption Quotient (s) and the GAB Sorption Model Constants (K, C, and u_0) of Control Wood and Wood Impregnatedwith Emulsion of Montan Wax (LGE-B) and with Montan Wax Emulsion with Boric Acid (LGE-B-Ba) Conditioned in
Five Hygroscopic Regions in the Adsorption (A) and Desorption (D) Process

of montan wax in cell lumina and cell walls; wood cells were completely filled because of small dimension of samples and high retention.²⁸ On the other hand, EMC of specimens impregnated with LGE-B-Ba solution was higher than that of control ones, in average for 1.6% points (Fig. 1). The difference between LGE-B-Ba and control samples was approximately the same in the whole hygroscopic region. This is not in line with our previous research,¹⁹ where EMC's of Ba-impregnated wood were higher than the control ones only above 65% RH. However, the differences in EMC at desorption process of LGE-B-Ba-treated and control wood were not significant. It is supposed that higher adsorption EMC's of LGE-B-Ba-impregnated samples originates in hygroscopic properties of Ba¹⁹ and in formation of small crystals with several voids suitable for capillary condensation.^{29,30} Sorption quotient shows higher hygroscopicity of LGE-B-Ba-treated wood also (Table II).

Sorption isotherms of the wood treated with montan wax emulsions and of the control unimpregnated wood, obtained according to the GAB model, exhibited good fitting of experimental data in the whole hygroscopic region (Fig. 2). Similar results were obtained also in the previous research.³¹ Examination of the GAB parameters in adsorption shows that the values of the monolayer MC u_0 are lower and those of the Guggenheim constant C are higher than for desorption (Table II). In terms of the sorption phenomenon, this means that during adsorption, although there are less sorption sites, they have a greater binding energy, with the multilayer molecules deviating from the free bulk water.²⁵ Comparison between treatments shows that at adsorption and desorption processes the highest monolayer MC (u_0) was that of samples treated with montan wax and Ba solution (LGE-B-Ba). This indicates that these samples have more available sorption sides, and that they have a greater binding energy, which is shown by a higher constant C at control and only montan-wax-treated samples.²⁵ For drying samples with higher C constant, more energy is needed, and, at wetting of these samples, more energy is loosen than at samples with lower Guggenheim constant *C*. Third, constant of GAB model *K* is just the measure of the difference of free enthalpy of the sorbate (water) molecules in two states and does not give any important information about material. On the basis of the reported results (Fig. 2), it can be concluded that the GAB model is suitable for the prediction of the MC of wood impregnated with montan wax and of wood treated with aqueous solution of montan wax emulsion and Ba.

Results of the moisture changes during dipping in water and during conditioning at high RH (87%) showed that the composition of preservative solutions and their retention have considerable influence on the sorption properties of the treated wood. Moisturizing of wax (LGE-A, LGE-B, LGE-A-Ba, and LGE-B-Ba)-impregnated unsealed specimens was slower compared with control specimens conditioned in the humid air and at the ones immersed in water. On the other hand, moisturizing of Ba-treated specimens was faster, and MC of Ba-treated wood was higher than MC of control specimens [Fig. 3(a-d)]. The samples impregnated with montan wax had lower MC than the control specimens [Fig. 3(a-d)]. Final MC of unsealed specimens impregnated with LGE-A solution, conditioned in chamber with 87% RH, was 11.4%, whereas approximately considerably higher MC was observed at control specimens (12.9%), and the highest MC was measured at Batreated samples (14.5%) [Fig. 3(a)]. Moreover, MC of LGE-B- and LGE-B-Ba-impregnated unsealed wood was around 11%, which is considerably lower than MC of control specimens (12.9%) [Fig. 3(b)]. Even more, EMC of control samples was reached at the 18th day, whereas the MC of LGE-B and LGE-B-Ba increased for 53 days, when the experiment was finished. Similar effect was observed for LGE-A-impregnated samples. However, rising of MC of LGE-A-Baimpregnated wood was faster and reached the same MC than control samples at the end of the conditioning in the humid atmosphere [Fig. 3(a)]. During dipping experiment, similar effect of moisturizing of control and impregnated samples to the effect during conditioning in humid environment was observed

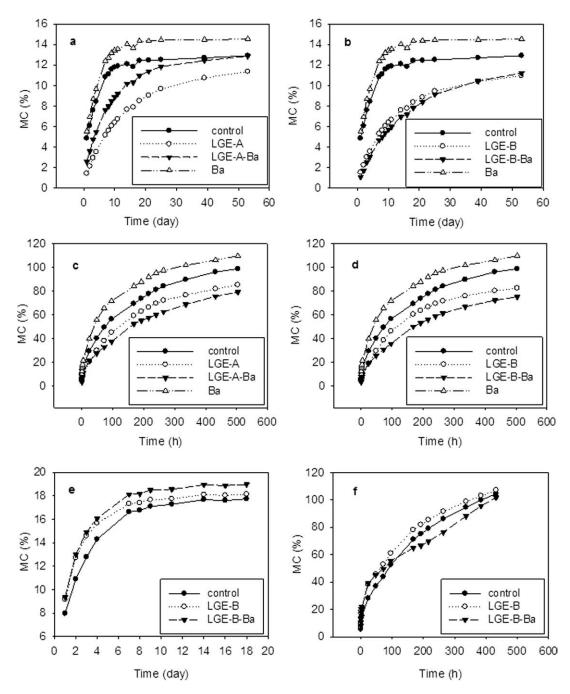


Figure 3 Changes in moisture contents (MC) of the EN 113 Norway spruce control specimens and specimens impregnated with preservative solutions based on montan wax emulsion with (LGE-B-Ba) or without (LGE-B) boric acid, or boric acid alone (Ba) in atmosphere with RH of 82% (a, b, and e) or during immersion in water (c, d, and f). The graphs a, b, c, and d show moisture contents of unsealed specimens and graphs e and f showed MC of sealed specimens.

[Fig. 3(c,d)]. With one exception, MC of LGE-A-Baand LGE-B-Ba-impregnated wood was lower than MC of specimens impregnated only with montan wax (LGE-A and LGE-B), but the differences were not significant. After 500 h of dipping in water, LGE-B-Baimpregnated specimens reached MC of 75%, LGE-B specimens reached MC of 82%, and even higher MC was determined for control samples (99%). The highest MC (109%) was determined for Ba-impregnated specimens [Fig. 3(c,d)]. The results of this study clearly show that the addition of LGE emulsion lowers MC and EMC of impregnated wood. Even more, montan wax emulsion retains positive influence on the MC even in the presence of Ba. MC of wood treated with montan wax emulsion and Ba is lower than that of wood treated with Ba only [Fig. 3(a–d)]. MC of wood treated with Ba is generally higher than control or than LGE-treated wood. The reasons for higher MC of Ba-treated wood were explained in the previous

Journal of Applied Polymer Science DOI 10.1002/app

paragraphs. Additionally, possible explanations for lower MC of montan wax-treated wood are similar to those stated before. Namely, wood surface of waxtreated wood is more hydrophobic, which particularly slowed down moisturizing in the first hours of exposure. Second, montan wax forms thin-layer resistant film¹³ on the wood surface and acts as barrier. Third, deposits of montan wax and Ba form in the cell lumina, which physically reduce space for water accumulation.² All above-mentioned facts are valid for specimens with unsealed axial surfaces, where high retention of wax emulsions were achieved. Conversely, specimens with end-sealed axial surfaces retained approximately three to four times less LGE-based emulsions. It can be clearly seen from Figure 3(e,f) that low quantity of retained wax had no significant influence on MC of impregnated wood. It seems that montan wax, which remained on the surface of the test specimens, was not sufficient to form a barrier that would limit water penetration to the treated wood. It is presumed that wax treatment is suitable for impregnation of more permeable wood species than Norway spruce like Scots pine, radiata pine, beech, etc.

Similar effect as for spruce wood specimens with sealed axial surfaces was evident for bigger (EN 252) Norway spruce specimens, too. As mentioned previously, retention of wax emulsions at EN 113 samples with sealed axial surfaces and EN 252 ones was comparably low. It is supposed that low loadings of emulsion had no influence on MC of Norway spruce specimens exposed in outdoor application. (However, it has to be considered that those specimens were not exposed to the rain.) All wax-treated spruce specimens had MC comparable to the MC of control specimens. This is clear evidence that loadings of wax need to be sufficient to reduce the MC of impregnated wood. On the other hand, two times higher retentions of LGE emulsion and Ba were achieved at beech wood EN 252 specimens; thus, it was presumed that there will be more considerable influence of wax treatment on MC of impregnated beech wood. It can be seen from Figure 4 that MC of treated and untreated control wood was related to RH. At the beginning of the experiment, MC of all impregnated samples was around 3%, whereas MC of control samples was 4.3%. This difference in MC increased during the experiment. After 5 months, MC of impregnated samples with LGE-A and LGE-B was 9.5%, MC of LGE-B-Ba was 20% higher, and MC of control specimens was 35% higher (Fig. 4). It is believed that the main reason for this difference originates in the wax treatment of wood. Montan wax can influence the MC of wood, if it is applied in sufficient loadings. Detailed mode of action is described in the previous sections. Furthermore, it should be considered that those bigger specimens were dried at 103°C before outdoor exposure. Dry-

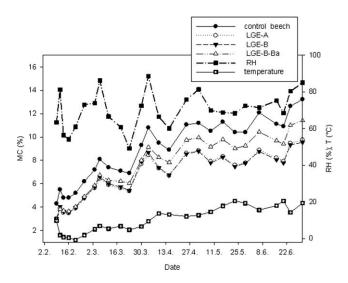


Figure 4 The monitored RH and MC changes of the control and impregnated beach wood EN 252 specimens exposed outdoors, covered application for 5 months, between February and June 2009.

ing of wood at this temperature causes some depolymerization of hemicellulose, which results in lower MCs compared with nondried wood.³²

CONCLUSIONS

Retention of preservative solutions was influenced by concentration (viscosity) of the preservative solution, the wood species used, and type (specific surface) of the samples. However, concentration of montan wax in the solution had minor effect on the total amount of retained wax. Specimens impregnated with the lower concentration of montan wax retained approximately the same amount of wax as specimens impregnated with the higher concentration. The amount of retained montan wax determined the hydrophobic effect and sorption properties. The more wax was introduced into the wood specimens, the lower was EMC. To the contrary, the MC of Batreated wood was higher than that of the control wood, and MC of wood impregnated with combination of Ba and montan wax, after conditioning at chamber with 87% RH, dipping experiment, and outside exposition, was lower than that of the control wood. In some cases, the MC content of wood treated with montan wax and Ba was even lower than the MC of only montan wax treated wood. The lower MC of treated wood is particularly important from the practical point of view. Leaching of boron compounds from the wood with lower MC is considerably reduced. Second, lower MC of treated wood offers less suitable conditions for mold and fungal growth and increases the performance of such wood.

The authors thank the technical support of Żiga Melanšek, Tomaž Grof, and Boris Hafner.

References

- 1. Donath, S.; Militz, H.; Mai, C. Holzforschung 2006, 60, 40.
- Rowell, R. M.; Banks, W. B. Forest Products Laboratory General Technical Report, FPL-50; Forest Products Laboratory: Madison, WI, 1985.
- Williams, R. S.; Feist, W. C. Forest Products Laboratory General Technical Report, FPL-109; Forest Products Laboratory: Madison, WI, 1999.
- Zahora, A. International Research Group for Wood Preservation Document no. IRG/WP 00-40159; International Research Group for Wood Preservation: Stockholm, Sweden, 2000.
- 5. Mai, C.; Militz, H. Wood Sci Technol 2004, 37, 453.
- 6. Banks, W. B. Wood Sci Technol 1973, 7, 271.
- Schultz, T. P.; Nicholas, D. D.; Ingram, L. L. Holzforschung 2007, 61, 317.
- Anonymous. 2010. Available at: http://www.dauerholz.de/. Accessed 15 December 2009.
- 9. Lesar, B.; Humar, M. Eur J Wood Wood Prod, to appear.
- 10. Anonymous. 2005. Available at: www.basf.de. Accessed 15 December 2009.
- 11. Matthies, L. Eur J Lipid Sci Technol 2001, 103, 239.
- Heinrichs, F. L. In Ullman's Encyclopedia of Industrial Chemistry, 3rd ed.; Bhonet, M., Ed.; Wiley-VCH: Weinheim, 2003.
- 13. Warth, A. H. The Chemistry and Technology of Waxes; Reinhold Publishing Corp.: New York, 1959.
- 14. Lesar, B.; Kralj, P.; Humar, M. Int Biodeterior Biodegrad 2009, 63, 306.

- 15. Berninghausen, C.; Rapp, A.; Welzbacher, C. Patent WO2005025824, 2005.
- Lloyd, J. D. International Research Group for Wood Preservation, Document no. IRG/WP 30178; International Research Group for Wood Preservation: Stockholm, Sweden, 1998.
- 17. Pizzi, A.; Baecker, A. Holzforschung 1996, 50, 507.
- White, R. H.; Dietenberger, M. A. Wood Handbook, Wood as an Engineering Material; Forest Service, Forest Products Laboratory: Madison, WI, 1999.
- 19. Lesar, B.; Gorišek, Z.; Humar, M. Dry Technol 2009, 27, 94.
- 20. Blahovec, J.; Yanniotis, S. Food Bioprocess Technol 2008, 1, 82.
- 21. Krupinska, B.; Strommen, I.; Pakowski, Z.; Eikevik, T. M. Dry Technol 2007, 25, 1459.
- 22. Timmermann, E. O. Colloid Surf A: Physiochem Eng Aspects 2003, 220, 235.
- 23. Dawson, H. B.; Czipri, J. J. Wood Protect 1991, 1, 55.
- 24. Anonymous, European Committee for Standardization, Paris. Standard EN350-2. 1994.
- Skaar, C. Water in Wood; Syracuse University Press: New York, 1972.
- 26. Pallin, M. A.; Petty, J. A. Wood Sci Technol 1981, 15, 161.
- 27. Tarmian, A.; Perre, P. Holzforschung 2009, 63, 352.
- 28. Lesar, B.; Zupančič, M.; Humar, M. Les/Wood 2008, 60, 320.
- 29. Humar, M. Les/Wood 2006, 58, 348.
- 30. Mangel, A. J Therm Anal Calorim 2000, 62, 529.
- Krupinska, B.; Strommen, I.; Pakowski, Z.; Eikevik, T. M. Dry Technol 2007, 25, 1463.
- 32. Fengel, D.; Wegener, G. Wood—Chemistry, Ultrastructure, Reactions; Walter de Gruyter: New York, 1989.