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PERFORMANCE OF SELECTED COPPER AMINE BASED WOOD PRESERVATIVE SUPPLEMENTED WITH WOOD SWELLING AGENTS

Nejc Thaler, Miha Humar
University of Ljubljana, Biotechnical Faculty
Department of Wood Science and Technology
Ljubljana, Slovenia

Boštjan Lesar
Silvaprodukt D.O.O.
Ljubljana, Slovenia

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ABSTRACT

Copper amine based wood preservatives are currently the most important formulations for impregnation of wood in ground contact in Europe. One of the issues related to similar water based solutions is insufficient penetration to refractory wood species like Norway spruce (*Picea abies*). In order to address this issue, commercial copper ethanolamine based solution (Silvanolin, Silvaprodukt) was supplemented with five well known wood swelling agents (ammonia, ethylene glycol, DMSO, formic acid and triethanolamine) of three different concentrations (2.5 %, 5 % and 10 %). Spruce wood specimens were impregnated with those solutions, and uptakes of preservative solutions and depth of penetration was determined according to established procedures. Furthermore, Cu leaching according to the ENV 1250-2 (1994) protocol was determined as well. The results showed that triethanolamine and formic acid were found the most effective. They improved penetration of copper ethanolamine wood preservative to wood. On the other hand, addition of those two preservatives increased copper leaching from impregnated wood.

KEYWORDS: Copper, ethanolamine, *Picea abies*, refractory wood species, wood swelling agents, impregnation.

INTRODUCTION

Norway spruce (*Picea abies*) is one of the most important central European wood species (Leikola 1990). Due to its excellent ratio between mechanical properties and density it is frequently used for construction applications. However, spruce wood is classified as less durable material (EN 350-2, 1995); therefore it has to be impregnated with wood preservatives if used for load-bearing outdoor applications. At this point we face another limitation related to Norway spruce wood; it is extremely difficult to impregnate (EN 350-2, 1995), in fact, it is known as one of the most important refractory wood species (Militz and Homan 1993). This issue can be overcome via different ways, namely, with proper selection of preservative solution, with proper selection of impregnation procedure and with proper treatment of wood prior impregnation.

In order to overcome issues related to low impregnability of spruce and other refractory conifer wood species, and to limit use of organic solvents, supercritical impregnation was developed. In supercritical conditions, there is almost no surface tension (Morsing et al. 2005). However, there are two important drawbacks: price and cracks formation. Therefore, there are not many industrial processes using supercritical treatment. Furthermore there were some other solutions for improvement of impregnability developed. One of them is incising. Incising has long been used to increase the amount of transverse area exposed to potential preservative flow. The longitudinal pathways exposed on these transverse faces are far more receptive to preservative flow than are the radial or tangential surfaces (Morris et al. 1994). As a result, incising improves preservative penetration to the depth of the incision (Morrell et al. 1998). However, mechanical incising results in damaged surface of the treated wood as deteriorated visual appearance and deteriorated mechanical properties. The remaining holes in the wood after incising are also water traps and represent potential pathway for fungal colonisation. Therefore use of mechanical incising is not always desired.

In order to improve impregnability of the refractory wood species, wood swelling agents (WSA) were combined with a commercial copper-ethanolamine (Cu-EA) based preservative solution. The purpose of those chemicals was to swell wood and thus enable better penetration of preservative solutions to wood. WSA are of significant importance in diverse processes including: pulping, removal of extractives, dimensional stabilization as well as preservation and chemical modification (Mantanis et al. 1994). The phenomenon of swelling is characteristic of all elastic materials but differs somewhat for different types of materials. A solid is said to swell when it takes up a liquid and at the same time fulfils the following 3 conditions (Nageli 1854, Mantanis et al. 1994): a) Its dimensions are increased with an accompanying thermal change as a result of the taking up of another phase, b) It retains its homogeneity in microscopic sense, c) Its cohesion is diminished but not eliminated, that is, it becomes soft and flexible instead of hard and brittle. The swelling of wood and wood polymers in liquids is a complex process which is strongly influenced by both the solvent and the wood substrate. Mantanis and coworkers (1994) reported, that the maximum swelling of wood is mainly influenced by three WSA properties, the solvent basicity, the molar volume, and the hydrogen bonding capability. Furthermore it is believed that the cellulose is the major polymer responsible for wood swelling. During swelling, the voids in the wood structure opens, and this mechanism enables better penetration of wood preservatives to wood. New voids are new capillaries which improves liquid penetration to wood by capillarity mechanism. Water itself is wood swelling agent, therefore WSA agents that causes more prominent swelling than water shell be used. The purpose of WSA is not to reopen pits but to increase capillarity of the wood. However, the question that remained unsolved is the interaction between components of the wood preservative and WSA. This question is not the topic of this study and will be elucidated in one of the forthcoming contributions.

The purpose of our work was to find out how addition of different known wood swelling agents influence on the penetration of copper-ethanolamine based preservative solutions, and furthermore, how addition of wood swelling compounds influence leaching of Cu from impregnated Norway spruce wood.

MATERIAL AND METHODS

Experiments were performed on Norway spruce (*Picea abies*) heartwood wood samples of are predominately limited to heartwood. The quality and the orientation of the specimens followed the EN 113 recommendations (2004). Standard procedure enables comparison of the results with other laboratories. Average density of air-dry spruce wood was 420 $kg.m^{-3}$ (u = 6 %). Axial surfaces of the specimens were sealed with epoxy coating (Epolor Color). Sealant was applied with brushing.

For impregnation, a commercially available copper-ethanolamine based aqueous solution (Silvanolin, Silvaprodukt Slovenia) containing copper hydroxide (c_{Cu} = 0.25 %), ethanolamine (1.44 %), quaternary ammonium compound (alkyl diethyl benzyl ammonium chloride) (0.25 %), boric acid (c_B = 0.2 %) and carboxylic acid (0.2 %) was used (Humar and Pohleven 2008). This solution was supplemented with five different wood swelling agents (ammonia, ethylene glycol, DMSO, formic acid and triethanolamine) of three different concentrations (2.5 %, 5 % and 10 %). Those wood swelling agents were chosen due to well-known swelling properties reported in the literature (Mantanis et al. 1994). The pH value of the copper ethanolamine solutions was determined prior to impregnation.

For impregnation two different protocols were utilized. The first procedure (V) consists of 20 min of vacuum (0.02 MPa) and 1.5 h of soaking at normal pressure. The second procedure (V-P) was more severe and consists of 20 min of vacuum (0.02 MPa), 60 min pressure (0.8 MPa) and 5 min vacuum (0.02 MPa). Both methods are utilized in commercial applications. For each measurement five parallel specimens were utilized. After impregnation, uptake of preservative solutions and retention was determined gravimetrically. Later, the specimens were conditioned for four weeks, the first two weeks in closed chambers, the third week in half closed and the fourth week in open ones. Prior to further analysis, specimens were stored at 25°C, 65 RH. MC of the specimens was between 10 % and 12 %.

Impregnated specimens were cut at the middle with a circular saw. Depth of copper penetration in mixed radial and tangential direction was estimated on axial planes (specimens were not oriented due to recommendation of the standards, thus we were not able to determine the penetration in exact radial and tangential direction). 1 % aqueous solution of potassium hexaciano-ferrate was used as color reagent for copper (Humar and Lesar 2009). For boron penetration a color spot reagent comprising of two components: A saturated solution of salicylic acid in an ethanol (70 %) and HCl (30 %) mixture. The second component was ethanol extract of curcuma (*Curcuma* sp.). In the presence of boron, the wood is colored red, while the untreated part remained yellow (Theden and Kottlors 1965).

Leaching was performed according to the modified ENV 1250-2 (1994) procedure. In order to speed up the experiment, two modifications were applied: Three specimens instead of five were placed in one (single) vessel and water mixing was achieved with shaking on a non-rotatory shaker instead of a magnetic stirrer. Nine specimens per concentration/treatment were put in three vessels (three specimens per vessel) to have three parallel leaching procedures. Afterwards, specimens in the vessel were positioned with a ballasting device that prevented them from floating. 300 g of distilled water was added and the vessel with its content was shaken with the frequency of 60 min^{-1}. Water was replaced six times in four subsequent days as proposed by standard ENV 1250-2 (1994). Leachates from the same vessel were collected and aggregated. Afterwards, atomic absorption spectroscopy (Varian SpectrAA Duo FS240) and XRF (TwinX, Oxford instruments) analysis of the leachates was performed at the end of first day and at the end of the experiment. Percentages of leached copper were calculated from the amount of retained copper determined gravimetrically and amount of copper in collected leachates.

RESULTS AND DISCUSSION

Addition of (WSA) into preservative solution influences their chemical composition and predominately pH value. pH value is one of the most important factors that influences fixation of copper-ethanolamine wood preservatives (Humar et al. 2007). In general, lower pH (around 8.5) of Cu-EA solutions resulted in better fixation. The most basic pH value was observed at Cu-EA solution supplemented with ammonia (10.91) and the lowest one was measured at Cu-EA in combination with formic acid (2.18) (Tab. 1). However, it should be considered that in this preservative solution the light blue color of the solution clearly showed that copper-ethanolamine complexes were not present.

Tab. 1: Influence of the wood swelling agent (WSA) on pH content of the copper ethanolamine solutions.

WSA	Conc. (%)	pH
Ammonia	10	10.91
DMSO	10	9.55
Ethylene glycol	10	9.05
Formic acid	10	2.18
Triethanolamine	10	9.91
/	/	9.21

During vacuum treatment spruce wood specimens retained in average 204 $kg.m^{-3}$ of Cu-EA preservative solution. Certain WSA have a positive impact on the retention (ethylene glycol, formic acid, triethanolamine), while the others have no influence (ammonia) or even negative one (DMSO) on the retention of the Cu-EA preservative solution during vacuum treatment. One of the reasons for negative influence of well-known swelling agent DMSO is possible new complexes formed between DMSO and ingredients in commercial solution (Tang et al. 2010). The highest retention was determined at Cu-EA with addition of triethanolamine. Spruce wood impregnated with Cu-EA solution with 2.5 % of triethanolamine or 10 % of formic acid retained 100 % more aqueous solution than parallel specimens impregnated with Cu-EA solution without additives (Tab. 2).

However, the results in Tab. 2 show that retention of the preservatives into Norway spruce is not always increasing with increasing concentrations of WSA. At triethanolamine supplemented Cu-EA it is clearly evident that with increasing triethanolamine concentrations, retention during vacuum treatment is even decreasing. To spruce wood impregnated with Cu-EA with 2.5 % of triethanolamine 423 $kg.m^{-3}$ of aqueous solutions penetrates, while only 177 $kg.m^{-3}$ of Cu-EA supplemented with 10 % of triethanolamine penetrates to parallel specimens. It seems like that there are some other phenomena influencing the uptake of preservative solution. Increasing concentrations of selected WSA might influence the chemical structure of preservative solution what negatively influence the uptakes. However, this issue needs to be addressed in one of the future studies. Similar relationship was evident at Cu-EA enriched with ethylene glycol as well. In contrary, the opposite relationship was noticed at Cu-EA with addition of formic acid (Tab. 2).

Tab. 2: Influence of various wood swelling agents (WSA) on the uptake and penetration of copper ethanolamine wood preservative during vacuum impregnation (V). Leaching of copper from impregnated wood was determined in line with ENV 1250-2 (1994) standard procedure. First leaching period corresponds to leaching during first day and the second leaching period corresponds to leaching during second, third and fourth day combined.

WSA	Conc.	Density	Uptake	Penetration of Cu	Penetration of B	Leached Cu 1st period	Leached Cu 2nd period	Total leached Cu
	(%)	(kg.m^{-3})		(mm)		(%)		
Ammonia	2.5	430	189	1.3	1.7	1.7	2.4	4.1
	5	402	217	1.8	2.0	1.5	1.6	3.0
	10	403	198	1.8	2.8	2.1	10.6	12.7
DMSO	2.5	412	96	0.6	1.4	5.5	3.5	9.0
	5	420	111	0.9	1.5	3.3	2.2	5.5
	10	411	103	0.7	1.3	2.9	1.7	4.5
Ethylene glycol	2.5	424	244	1.9	4.6	10.8	8.2	19.0
	5	421	254	1.1	2.3	9.6	8.0	17.6
	10	407	151	1.6	2.5	21.8	8.5	30.3
Formic acid	2.5	420	220	2.3	5.3	17.6	17.1	34.7
	5	426	265	6.7	7.4	13.0	11.9	24.9
	10	415	455	7.5	10.0	37.9	28.5	66.4
Triethano lamine	2.5	403	423	4.9	7.4	11.4	12.6	24.0
	5	414	203	2.1	2.6	16.7	13.1	29.8
	10	421	177	2.3	3.0	21.3	15.5	36.8

However, when uptake and penetration data are compared, there is clear evidence of tight correlation between these two parameters (r^2 = 0.68). Where higher uptakes of Cu-EA solutions were determined there was better penetration to the Norway spruce wood specimens determined as well (Fig. 1). Consequently, the best Cu penetration was determined at specimens impregnated with Cu-EA solution supplemented with 10 % of formic acid (7.5 mm), and the lowest one at Cu-EA in combination with 2.5 % of DMSO (0.6 mm). At this point it needs to be considered, that axial surfaces of the specimens were sealed, and preservative solutions penetrates in radial and tangential directions only.

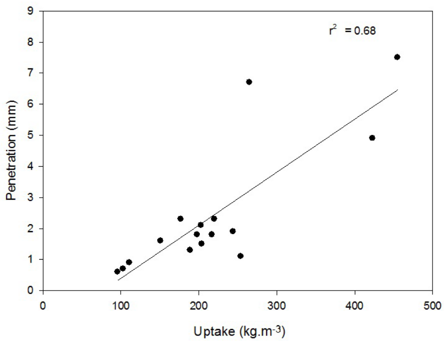

Fig. 1: Correlation between uptakes of WSA supplemented Cu-EA aqueous solutions and Cu penetration at vacuum treated Norway spruce specimens.

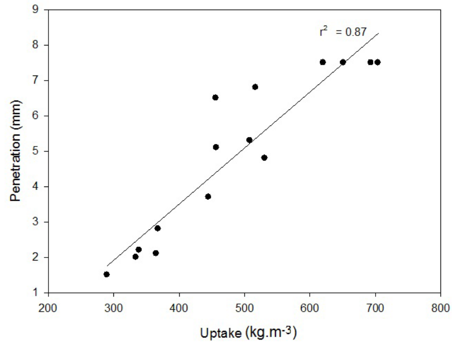

Fig. 2: Correlation between uptakes of WSA supplemented Cu-EA aqueous solutions and Cu penetration at vacuum-pressure treated Norway spruce specimens.

Similar results were determined at vacuum-pressure impregnated spruce wood. As expected, there were considerably better uptakes determined during vacuum-pressure impregnation compared to vacuum one. During vacuum-pressure process spruce wood uptakes 496 $kg.m^{-3}$ of Cu-EA based solution in average while considerably lower uptakes were noticed at parallel Cu-EA vacuum impregnated material (219 $kg.m^{-3}$) (Tabs. 2 and 3).

However, control vacuum-pressure treated specimens retained 445 $kg.m^{-3}$ of testing solutions. Similarly as reported, some WSA (ammonia, formic acid, triethanolamine) have positive impact on the uptake while other WSA (DMSO, ethylene glycol) have negative impact on the uptake of preservatives. The highest uptake was determined at spruce wood specimens impregnated with Cu-EA in combination with 10 % of formic acid (704 $kg.m^{-3}$) and 2.5 % of triethanolamine (693 $kg.m^{-3}$).

As reported at vacuum treated material, there was tight correlation determined between penetration and uptake of preservative solution at vacuum-pressure treated spruce wood as well ($r^2 = 0.87$) (Fig. 2). Therefore it is reasonable, that the best penetration was determined at spruce wood impregnated with Cu-EA in combination with triethanolamine and formic acid (Tab. 3). Those specimens were completely soaked up with the preservative solutions.

One of the goals of this research was to investigate the influence of the WSA on the uptake and penetration of copper ethanolamine based solutions. The second goal was to determine the performance of this treatment. As copper is known as effective biocide, there is no fungicidal test included in this preliminary experiment. On the other hand, it is well known that chemical composition of Cu-EA based solutions considerably affects the fixation (Zhang and Kamdem 2000). Therefore, copper fixation in wood impregnated with various Cu-EA treatments is elucidated herein.

As expected, wood swelling agents influence copper fixation. Some have positive aspect on the fixation like ammonia or certain concentrations of DMSO. On the other hand, addition of formic acid, ethylene glycol and triethanolamine considerably increased copper leaching from impregnated specimens (Tabs. 2 and 3). The highest leaching was determined at specimens impregnated with combination of formic acid or triethanolamine. From those specimens in average

Tab. 3: Influence of various wood swelling agents (WSA) on the uptake and penetration of copper ethanolamine wood preservatives during vacuum-pressure impregnation (V-P). Leaching of copper from impregnated wood was determined in line with ENV 1250-2 (1994) standard procedure. First leaching period corresponds to leaching during first day and the second leaching period corresponds to leaching during second, third and fourth day combined.

WSA	Conc.	Density	Uptake	Penetration of Cu	Penetration of B	Leached Cu 1st period	Leached Cu 2nd period	Total leached Cu
	(%)	(kg.m^{-3})		(mm)		(%)		
Control	/	428	445	3.7	6.4	1.5	0.7	2.2
Ammonia	2.5	403	517	6.8	9.1	1.0	1.4	2.4
	5	406	457	5.1	7.1	0.9	1.5	2.4
	10	406	531	4.8	8.3	1.0	2.0	3.0
DMSO	2.5	416	334	2.0	4.0	1.2	1.3	2.6
	5	414	290	1.5	2.6	1.1	1.5	2.5
	10	421	508	5.3	7.3	1.3	2.3	3.6
Ethylene glycol	2.5	420	339	2.2	3.2	8.9	4.4	13.4
	5	427	365	2.1	3.4	8.6	9.2	17.9
	10	414	368	2.8	5.5	1.8	1.2	3.0
Formic acid	2.5	412	620	7.5	10.0	9.9	11.5	23.0
	5	413	651	7.5	10.0	8.1	8.3	17.7
	10	421	704	7.5	10.0	8.3	3.9	12.2
Triethano lamine	2.5	439	693	7.5	10.0	5.2	13.7	18.9
	5	435	456	6.5	10.0	13.2	14.0	27.2
	10	432	651	7.5	8.6	13.5	23.1	36.6

around 30 % of retained copper was leached. Those results are somehow expectable. Addition of the formic acid to Cu-EA solution changed the chemistry of the solution. There was no copper amine complexes present any more. On the other hand, at solution containing triethanolamine, there was to high copper-amine ratio. As can be resolved from the cited literature, high copper amine ratios resulted in insufficient fixation of copper amine based preservative solutions (Zhang and Kamdem 2000, Humar et al. 2005).

CONCLUSIONS

Addition of certain wood swelling agents to copper ethanolamine solutions considerably improves uptake and penetration of aqueous solutions. Among tested wood swelling agents, formic acid and triethanolamine were found the most effective. Unfortunately, some swelling agents resulted in weekend fixation of copper, therefore there are some further investigations required to optimize the composition of copper amine based preservatives.

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Nejc Thaler, Miha Humar
University of Ljubljana
Biotechnical Faculty
Department of Wood Science and Technology
Jamnikarjeva 101
Si-1000 Ljubljana
Slovenia
Phone: +38613203638
Corresponding author: miha.humar@bf.uni-lj.si

Boštjan Lesar
Silvaprodukt D.O.O.
Dolenjska Cesta 42
1000 Ljubljana
Slovenia