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Fixation of Copper-Ethanolamine Wood Preservatives to Norway Spruce Sawdust

M. Humar,[a]* D. Žlindra,[b] F. Pohleven[a]

[a] *University of Ljubljana, Biotechnical faculty, Department of Wood Science and Technology, Jamnikarjeva 101, SI-1000 Ljubljana, Slovenia. Tel.: +386(0)14231161, Fax: +386(0)14235035, E-mail: miha.humar@bf.uni-lj.si.*

[b] *Slovenian Forestry Institute, Ljubljana, Slovenia.*

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Abstract

Despite of the fact that copper-ethanolamine based aqueous solutions have been used for wood preservation for almost two decades, the complete mechanism of Cu-ethanolamine fixation is not completely understood. In order to elucidate interactions between copper-ethanolamine aqueous solutions and wood, Norway spruce *(Picea abies)* sawdust was immersed to 19 different copper based formulations. These solutions besides copper(II) sulphate contains ethanolamine and quaternary ammonium compound, sodium borate and/or octanoic acid. pH of this mixture was monitored for 4 h. Immersed sawdust was put to filter paper and washed with 1 L of distilled water. Leached impregnated wood sawdust was than oven dried (103 °C) and kept in dark and dry place until copper and nitrogen content were determined and correlated to pH changes of sawdust-preservative suspension during impregnation. The result showed that presence of ethanolamine makes fixation of copper in wood more effective. Copper absorption to sawdust is affected by concentration of copper, pH of the preservative solution and correlates with pH decrease during impregnation well. Furthermore, we proved that copper and nitrogen absorption to Norway spruce wood are connected as well. Understanding of this mechanism will enable experts to develop preservatives with better performance against weathering and wood pests.

Keywords: copper(II) sulphate, amine, octanoic acid, wood, wood preservation, fixation, absorption

1. Introduction

Copper based preservatives are successfully applied for wood preservation for more than two centuries. They were combined with chromium compounds to enable fixation in wood and arsenic to improve performance against copper tolerant fungi and insects.[1] Due to arsenic toxicity, its use is not desired in the major part of European countries any more, thus it was generally replaced with boron.[2] However, the situation is currently changing even more with the introduction of the Biocidal products directive (BPD).[3] BPD directive will likely ban or radically limit use of chromium in wood preservatives, thus new solutions to enable copper fixation need to be developed. Similar trends are foreseen in North America as well.[4]

Amines seem the most appropriate replacement for chromium. Particularly ethanolamine is reported as the most promising amine source in several researches, and it is used already for some emerging preservative systems including alkaline copper quat (ACQ), copper dimethyl-dithio-carbamate (CDDC), copper hydroxyquinolinolate (Cu-HDO) and copper azole (CA).[5] However, fixation of copper-ethanolamine based preservatives is still not comparable to fixation of copper-chromium ones. Emissions of copper from wood impregnated with copper-amine preservatives can be reduced with proper copper-amine molar ratio and addition of different hydrophobic agents. Octanoic acid is one of the chemicals that significantly decrease copper leaching from impregnated wood.[6] This carboxylic acid has a multiplicative effect, beside hydrophobic, there are new less water-soluble complexes formed between copper-amine and octanoic acid in the preserved wood, resulting in decreased leaching. Additionally, octanoic acid has fungicidal effect itself, what results in improved quality of impregnated wood.[7]

Although copper-amine preservatives are utilized for approximately two decades, complete mechanisms of fixation are not resolved yet. The loss of amines due to volatilization of amines and the precipitation of insoluble copper salts was for many years thought to be the principal fixation mechanism, similar as at copper-ammonia preservatives.[8] Whilst this may be an important fixation mechanism for copper-ammonia-based preservatives, it cannot be the mechanism for copper-amine complexes as the amines have higher boiling points. Wood is a weakly acid substrate, in which functional groups, such as carboxyl groups and phenolic groups, are active sites for interactions with copper. Two types of reaction mechanisms for copper-ethanolamine fixation are proposed. In a ligand exchange reaction mechanism, copper-ethanolamine complexes exchange ligand with wood and release one or two amine molecules.[9] In the second possible reaction mechanism, non-charged species of copper-ethanolamine complexes are transformed into charged species during process of impregnation. Functional groups (carboxyl and phenolic groups) can react with the charged species to form a stable wood-copper-ethanolamine complex.[10] Copper fixation to wood was found to depend largely upon concentration and pH. We studied the influence of pH, pH decrease during impregnation, role of ethanolamine and other ligands on copper fixation.

2. Experimental

For treatment of wood sawdust 19 different aqueous solutions were prepared (Table 1). Most of the preservatives consisted of copper(II) sulphate and ethanolamine, with different additives: octanoic acid, quaternary ammonium compound and/or disodium octaborate tetrahydrate. Concentration of copper in those solutions was 0.5% (high concentration), 0.25% (medium concentration) or 0.125% (low concentration). These concentrations were selected, regardless to the concentration of active ingredients in commercial wood preservatives (c_{Cu} = 0.05 – 1.0%).

Norway spruce wood was milled in IKA A11 basic mill (Mesh 100). Afterwards, 10 g of sawdust was mixed with 50 g of formulation and immersed to this solution for four hours. pH of this mixture was monitored 1, 2, 5, 8 and 240 min after soaking, as evident from Figure 2. For pH measurement Metrohm 827 pH lab instrument was used. After immersion, impregnated sawdust was transferred to filter paper and washed with 1 L of distilled water. Leached wood was than oven dried (103 °C) and kept in dark and dry place.

Copper in wood was determined with atomic absorption spectrometer (AAS). About 0.15 g of dry specimen was digested with acid mixture (5 mL 65% HNO_3 and 1 mL 70% $HClO_4$) in closed polytetrafluoroethylene (PTFE) vessels and heated in a microwave oven. Copper was determined in specimen solutions with FLAAS (Varian SpectrAA Duo FS240).

Nitrogen and carbon content in untreated and treated Norway spruce sawdust was performed in three parallels. Approximately, 0.2 g of an oven dry sample was combusted in the oxygen atmosphere at 1350 °C in LECO 2000-CNS analyzer. Nitrogen was detected in the Thermo Combustion cell.

Table 1. Chemical composition of preservative solutions used.

Preservative solution	Concentration of preservative solution	c_{Cu} (%)	c_{EA} (%)	C_{OA} (%)	c_{quat} (%)	c_B (%)
CuS	High	0.5	0	0	0	0
	Medium	0.25	0	0	0	0
	Low	0.125	0	0	0	0
CuE	High	0.5	2.885	0	0	0
	Medium	0.25	1.442	0	0	0
	Low	0.125	0.721	0	0	0
CuEO	High	0.5	2.885	0.568	0	0
	Medium	0.25	1.442	0.284	0	0
	Low	0.125	0.721	0.142	0	0
CuEOQ	High	0.5	2.885	0.568	0.5	0.238
	Medium	0.25	1.442	0.284	0.25	0.119
	Low	0.125	0.721	0.142	0.125	0.059
CuEOQ-II*	High	0.5	2.885	0.568	0.5	0.238
	Medium	0.25	1.442	0.284	0.25	0.119
	Low	0.125	0.721	0.142	0.125	0.059
EA	High	0	2.885	0	0	0
	Medium	0	1.442	0	0	0
	Low	0	0.721	0	0	0
Water	/	0	0	0	0	0

* Difference between CuEOQ and CuEOQ-II is in its initial pH of preservative solutions used. The pH of CuEOQ-II of the highest concentration was adjusted using H_2SO_4 to the value of 8.80 in contrast to the initial pH of CuEOQ of the same concentration (9.53). EA – ethanolamine, OA – octanoic acid, quat – quaternary ammonium compound.

3. Results and Discussion

The most important aim of this research was to elucidate the properties of preservative solutions that influence copper absorption to wood. An aqueous copper sulphate solution was included into this experiment only for comparison. Most of the efforts will be focused on copper-ethanolamine based aqueous solutions.

The absorption of copper to sawdust immersed to copper-ethanolamine solution was significantly more effective compared to sawdust treated with copper sulphate solution, only. More than two times higher copper concentrations were detected in copper-ethanolamine impregnated sawdust than in copper sulphate treated one (Table 2). This data prove that copper fixation is much more effective in the presence of ethanolamine, compared to the solutions without it, as there are new complexes formed between copper, ethanolamine and wood or its components.[10,11]

However, it was already reported, that concentration of copper in preservative solution influences copper absorption during impregnation.[9] Treatment of Norway spruce sawdust with aqueous solutions of the highest concentration resulted in the maximum copper concentrations in wood (Table 2). For example, after immersion of sawdust in solution CuE of the highest concentration (c_{Cu} = 0.5%), on average 8.25 ppm of copper was absorbed. On parallel samples, immersed to the same solution CuE of the four times lower concentration (c_{Cu} = 0.125%), 4.80 ppm of copper was determined in the impregnated sawdust (Table 2). From this value it can be easily calculated, that immersion of the sawdust into solution of four time higher concentration resulted in less than two times higher copper absorption. This indicates that the amount of fixation sites in wood is limited, and that absorption is relatively more effective at lower concentration. Similar relationships were determined at sawdust treated with other formulations as well (Table 2). However, from the graph where concentration of copper in preservative solution was plotted against concentration of copper in treated sawdust, it can be clearly seen that copper content in the preservative solution explains the relationship only partly (R = 0.84, Figure 1a). For example, If we compare the concentration of copper in wood, immersed to different copper-ethanolamine based solutions of the medium concentration (c_{Cu} = 0.25%), we see that the highest copper absorption was determined in sawdust treated with CuEOQ (7.20 ppm), aqueous solution of copper, ethanolamine, octanoic acid, boron and quaternary ammonium compound, and the lowest one at specimens treated with CuE, where approximately 13.5% less copper was absorbed (6.34 ppm, Table 2). This difference indicates that besides concentration, other parameters like composition and chemical properties of preservative solution significantly influence copper absorption as well. However, at wood treated with aqueous solutions where pH was artificially lo-

Table 2. Copper, nitrogen and carbon content in wood sawdust immerged to various preservative solutions for 4 h.

Preservative solution	Concentration of preservative solution	Carbon content (%)	Nitrogen content (%)	Copper content (ppm)
CuS	High	47.2	0.053	2.99
	Medium	47.5	0.055	2.46
	Low	49.4	0.060	2.00
CuE	High	47.4	0.369	8.25
	Medium	47.8	0.286	6.34
	Low	47.5	0.222	4.80
CuEO	High	49.4	0.397	8.30
	Medium	49.3	0.326	7.02
	Low	48.2	0.247	4.70
CuEOQ	High	49.5	0.523	8.12
	Medium	48.9	0.423	7.20
	Low	49.4	0.335	5.21
CuEOQ-II*	High	49.0	0.314	6.65
	Medium	48.7	0.259	5.11
	Low	48.9	0.174	2.72
EA	High	47.0	0.275	0.00
	Medium	49.2	0.258	0.00
	Low	49.1	0.217	0.00
Water	/	49.0	0.036	0.01

* Difference between CuEOQ and CuEOQ-II is pH of preservative solution. CuEOQ was used in its original pH (9.53). The pH of the solution CuEOQ-II of the highest concentration was adjusted using H_2SO_4 to the value of 8.80.

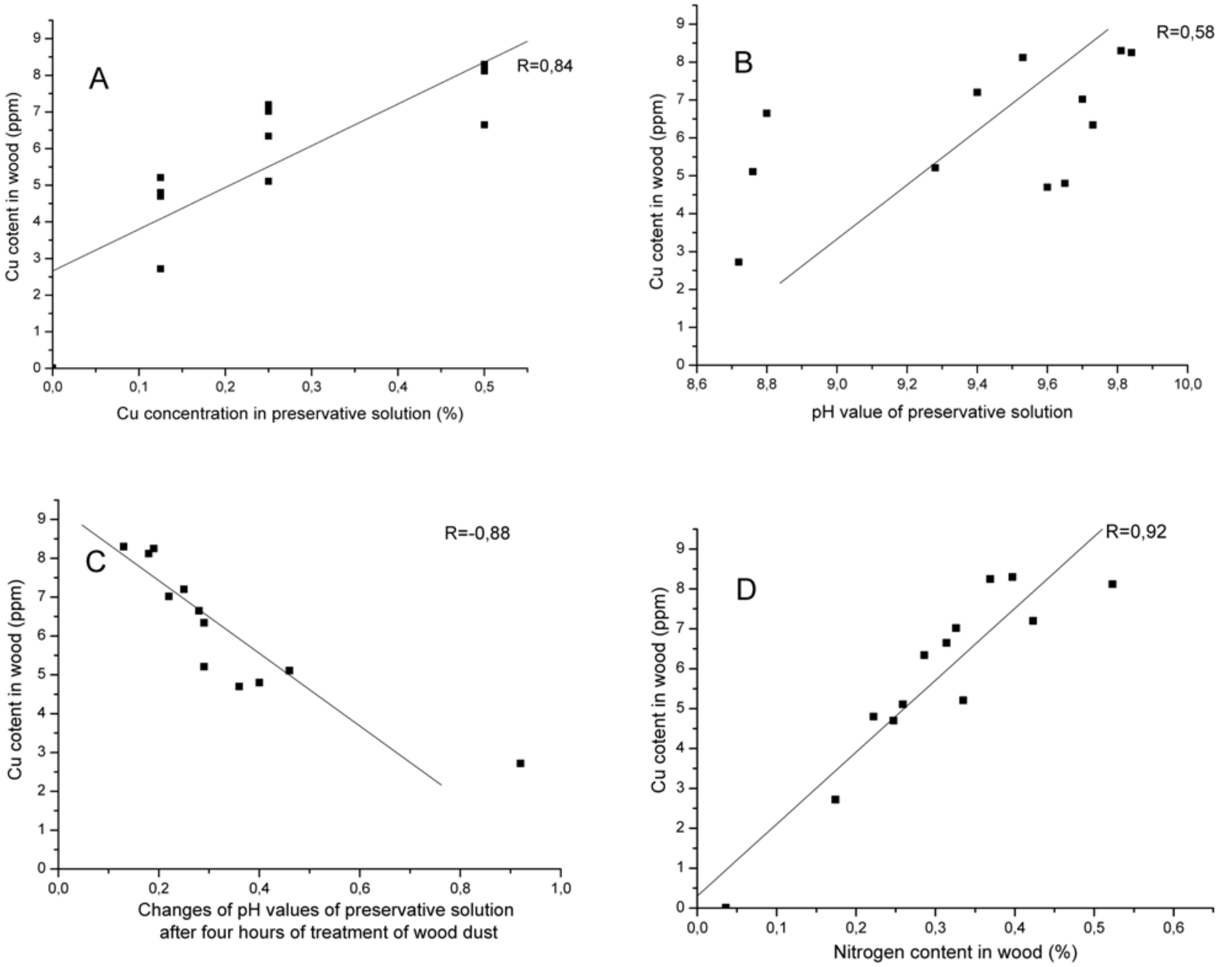

Figure 1. Correlations between copper content in immersed wood and preservative solution concentration (A), pH of preservative solution (B), changes of pH after 4 h of immersion (C) and nitrogen content in immersed wood (D).

wered, even lower copper contents were determined; therefore we further concentrate on influence of pH of treatments solution on copper absorption.

It was reported already that copper absorption is significantly influenced by the pH of preservative solution.[9] Therefore, we compared copper content in treated wood with pH of aqueous solutions used. From this relationship it can be clearly seen that, correlation between pH of the preservative solution and copper content is not significant (R = 0.58, Figure 1b), particularly if compared to correlation between copper concentration in preservative solution and copper content in wood (R = 0.84, Figure 1a).

As wood is acidic and it has a high buffering capacity,[12] the pH of preservative solution changes after treatment. Furthermore, during copper absorption, pH decreases due to liberation of protons as well.[13] In order to elucidate this decrease, pH of wood-preservative solution mixture was monitored 4 h after treatment. We consider this decrease during impregnation of considerable importance,

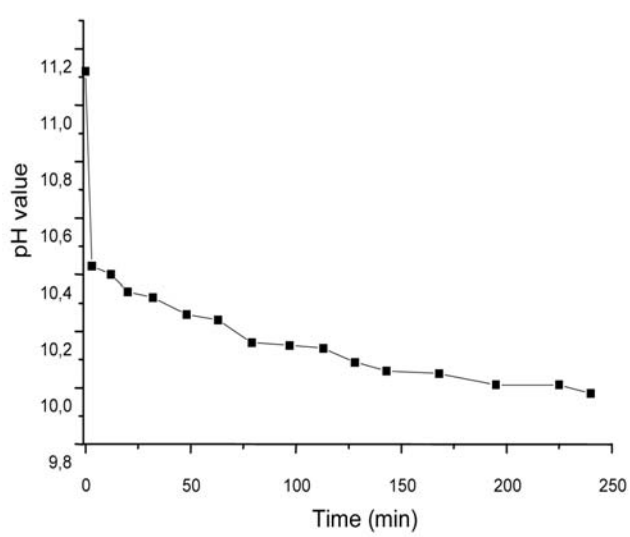

Figure 2. Changes of pH of ethanolamine (w_{EA} = 0.721%) spruce sawdust mixture during 4 h of soaking.

as fixation of some commercial copper-ethanolamine preservatives (copper hydroxyquinolinolate containing preservative, Cu–HDO) depends on pH change during impregnation. Cu–HDO is soluble at alkaline pH and precipitates when pH decreases below seven.[14] pH changes during immersion of wood sawdust to our preservative solutions as well. The most prominent changes in pH were determined immediately after treatment (Figure 2). In the majority of the treatments this decrease represents approximately 60% of total pH change. On the basis of the cited literature data we presume[13] that the reasons for the observed decrease of pH during additional few hours originates in proton-releasing cation-exchange reaction with hydroxyl and carboxylic acid groups and more or less stabilizes after four hours of soaking. Decrease at aqueous solutions of lower concentration, were more prominent in comparison to ones of highest concentration (Table 3). The most outstanding decrease was determined at aqueous solution of ethanolamine, following by copper ethanolamine solution and the lowest one at spruce sawdust treated with CuEO solution of the lowest concentration (0.13%, Table 3). In order to understand the meaning of decrease of pH during impregnation, pH of aqueous solution CuEOQ–II of the highest concentration was prior treatment additionally lowered from 9.53 to 8.8 using sulfuric acid (Table 3). During impregnation of wood sawdust with this solution, pH decreases even further. After 4 h of soaking of wood sawdust to solution CuEOQ–II of the lowest concentration, pH decrease of 0.92 was measured (Table 3). This was the highest decrease measured at copper-ethanolamine based solutions used in this experiment. It was more than three times higher than when a comparable aqueous solution CuEOQ of the same concentration was used. During immersion of sawdust to solution CuEOQ–II, pH decreases to such an extent that even copper precipitate was observed under microscope. When interactions between pH decrease and copper absorption was analyzed, very tight correlation (R = 0.88) was noticed. This correlation is tighter than the ones analyzed before (concentration or pH, Figure 1c).

Furthermore, beside the pH of preservative solution, ethanolamine plays important role in copper fixation as well. We were interested in, whether copper and ethanolamine absorption are connected. In order to elucidate this correlation, nitrogen content of wood were determined. But, it has to be taken into consideration that besides ethanolamine, quaternary ammonium compounds contributes to increased nitrogen content in wood as well.

At specimens treated with ethanolamine solution only (EA), generally lower nitrogen content was determined than at parallel copper-ethanolamine containing solutions. This difference was more prominent at spruce sawdust immersed to solutions of higher concentration. For example, in wood particles immersed to the most concentrated EA solution, 0.275% of nitrogen was measured in wood, while at parallel specimens immersed to solution

Table 3. pH of preservative solutions before and after four hours of immersion of wood sawdust.

Preservative solution	Concentration of preservative solution	Initial pH of preservative solution	Final pH of preservative solution mixed with wood dust	Difference between initial and final pH
CuS	High	4.18	3.12	1.06
	Medium	4.47	3.22	1.25
	Low	4.6	3.35	1.25
CuE	High	9.84	9.65	0.19
	Medium	9.73	9.44	0.29
	Low	9.65	9.25	0.4
CuEO	High	9.81	9.68	0.13
	Medium	9.7	9.48	0.22
	Low	9.6	9.24	0.36
CuEOQ	High	9.53	9.35	0.18
	Medium	9.4	9.15	0.25
	Low	9.28	8.99	0.29
CuEOQ-II *	High	8.8	8.52	0.28
	Medium	8.76	8.3	0.46
	Low	8.72	7.8	0.92
EA	High	11.57	10.68	0.89
	Medium	11.33	10.28	1.05
	Low	11.12	9.98	1.14
Water	/	6.15	4.85	1.3

* Difference between CuEOQ and CuEOQ–II is in its initial pH of preservative solutions used. The pH of CuEOQ–II of the highest concentration was adjusted using H_2SO_4 to the value of 8.80 in contrast to the initial pH of CuEOQ of the same concentration (9.53).

that besides the same amount of ethanolamine contains copper (CuE), almost 35% higher nitrogen content (0.369%) was determined in sawdust (Table 2). We presume that the reason for the observed increase originates in formation of copper-ethanolamine complexes in wood. As wood sawdust was oven-dried at 103 °C prior to the analysis, it is expected that most of free, non-reacted ethanolamine was either leached out from wood or evaporated, thus only fixed ethanolamine remained in wood.[15] An addition of octanoic acid increases copper and nitrogen absorption even better. Approximately 45% higher nitrogen content were determined in sawdust immersed to solution CuEO of the highest concentration compared to dust immersed to ethanolamine solution of the same concentration. This confirms that there are new complexes formed between octanoic acid and amine as well.[7] In sawdust that was immersed to solution CuEOQ, that besides copper, ethanolamine contains quaternary ammonium compound as well, the highest nitrogen and copper amounts remained, indicating that copper forms complexes not only with ethanolamine but with quaternary ammonium compound as well. At specimens that were immersed to solution to the same solution, but of lower pH CuEOQ–II, lower nitrogen and copper concentrations were analyzed (Table 2), At the end, correlation between copper and nitrogen absorption was determined (Figure 1d). Our analysis showed, that correlation between copper and nitrogen content in wood is 0.92, what is the most significant correlation determined in this experiment. This data confirmed that not only ethanolamine, but quaternary ammonium compound as well influences copper fixation.

4. Conclusions

Fixation of copper in wood is much more effective in the presence of ethanolamine. Copper absorption to sawdust is tightly correlated to concentration of active ingredients and pH decrease during impregnation. Furthermore, it was proven that copper and nitrogen absorption to Norway spruce sawdust are related as well.

5. Acknowledgements

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Povzetek

Baker-etanolaminske pripravke uporabljamo za zaščito lesa že skoraj dvajset let. Kljub temu, mehanizem vezave teh pripravkov v les še ni v celoti pojasnjen. Z željo osvetliti interakcije med vodnimi raztopinami bakrovega(II) sulfata in etanolamina smo smrekovo *(Picea abies)* žagovino namočili v devetnajst različnih kombinacij bakrovih vodnih raztopin. Poleg bakrovega(II) sulfata so ti zaščitni pripravki vsebovali še etanolamin in kvartarno amonijevo spojino ter bor ali oktanojsko kislino. Ves čas impregnacije smo spremljali vrednost pH sistema. Po štirih urah namakanja smo žagovino stresli na filtrirni papir in sprali z destilirano vodo. To impregnirano žagovino smo nato posušili pri 103 °C. Zatem smo v prahu določili vsebnost bakra in dušika. Ti dve vrednosti smo nato primerjali s spremembo vrednosti pH med impregnacijo. Rezultati so potrdili, da etanolamin močno izboljša vezavo bakrovih spojin na funkcionalne skupine lesa. Ugotovili smo, da je absorpcija bakra v les v povezavi z koncentracijo bakra v zaščitnem pripravku, vrednostjo pH sistema in spremembo vrednosti pH med impregnacijo. Nadaljnje smo potrdili, da sta absorpcija bakrovih spojin in dušika ravno tako tesno povezani. Ta dejstva so pomembna za razvoj novih učinkovitejših zaščitnih pripravkov za les.