Miha Humar, Marko Petrič, Franc Pohleven

Leaching of copper from wood treated with copper-based wood preservatives

Izluživanje bakra iz drva tretiranog zaštitnim sredstvima na osnovi bakra

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ABSTRACT • *Copper-based preservatives are widely used for wood protection. Traditionally, copper salts were combined with chromium, as chromium fixes copper into wood and thus prevents leaching of these preservatives. Since carcinogenic nature of chromium compounds is well known, several European countries intend to ban or limit the use of chromium in wood preservatives. Therefore, our aim was to find proper substitutes for chromium. Amines seem very efficient in fixing copper into wood. Leaching of copper significantly depends on various factors such as copper source, amine ligand, molar ratio Cu:N and pH of treatment solutions. Copper carboxylates in aqueous solution of ethanolamine were found promising for further research and use.*
Key words: *Copper based wood preservatives, copper leaching, copper(II) octanoate, copper(II) sulphate, ethanolamine*

SAŽETAK • *Zaštitna sredstva na osnovi bakra uvelike se rabe u zaštiti drva. Tradicionalno, bakar se miješao s kromom jer krom fiksira bakar u drvo i tako sprječava izluživanje tih zaštitnih sredstava. Kako je kancerogena priroda kromskih smjesa dobro poznata, nekoliko europskih zemalja namjerava zabraniti ili ograničiti uporabu kroma u sredstvima za zaštitu drva. Stoga je naš cilj pronaći odgovarajuću zamjenu za krom. Čini se da su amini vrlo djelotvorni u fiksaciji bakra u drvo. Izluživanje bakra znatno ovisi o različitim čimbenicima kao što su izvor bakra, aminski ligand, molekularni odnos Cu:N, te pH u sredstvima za razrjeđivanje. Bakreni karboksilati u vodenom razrjeđivaču etanolaminu pokazali su se*

Autori su, redom, asistent, docent i profesor na Oddelku za lesarstvo Bitoehniške fakultete Univerze v Ljubljani, Slovenija.Rad je u neznatno izmijenjenom obliku predstavljen na konferenciji *Drvo u graditeljstvu – tradicija i budućnost* u Zagrebu, u travnju 2001.
Authors are an assistant, an assistant professor and a professor, respectively, at the Wood Department of the Biotechnical Faculty of the University of Ljubljana, Slovenia. This article is a slightly altered version of a paper presented at the conference *Wood in Construction - Tradition and Future* in Zagreb, in April 2001.

obećavajućima za daljnja istraživanja i uporabu.

Ključne riječi: *zaštitna sredstva na bazi bakra, izluživanje bakra, bakrov(II) oktanat, bakrov(II) sulfat, etanolamin*

1. INTRODUCTION AND LITERATURE OVERVIEW
1. UVOD I PREGLED LITERATURE

Copper-based preservatives were introduced shortly after Bouchery had patented a sap displacement method for treatment of freshly felled timber using copper sulphate. From 1838 onwards, many copper-containing timber-preserving products were developed (Hughes 1999). These products had an important drawback; copper did not get fixed into wood and was prone to leaching out of wood. This problem was resolved by introducing fixed water-borne preservatives. Heinrich Bruning discovered that normally soluble metal salts could be made insoluble, or fixed inside wood, by adding large quantities of chromium (Richardson 1993). Additional fungicidal and insecticidal properties were achieved by adding arsenic into the formulation. In relatively low concentrations, copper is quite toxic to fungi, bacteria and algae. On the other hand, it is less toxic to plants. It is even one of the seven micronutrients essential for proper development of higher plants (Gupta 1979, Jin and Archer 1991, Richardson 1997).

In recent years, the use of copper compounds for biocidal purposes has increased. The reasons are the following: copper compounds are relatively safe, development of pathogens has been minimal (pathogens show an increased tolerance against organic fungicides after extended period of use) and, thirdly, there has been an increase in government regulations and restrictions (or outright banning) of alternative products due to their toxicological or environmental impacts (Richardson 1997). By the year 1995, the world usage of copper/chromium containing formulation was estimated to be about 120.000 tonnes of active components. Thus, production of chromium/copper treated lumber is estimated to be around 15 million m^3 (Preston 2000).

Since carcinogenic nature of chromium compounds is well known (Barceloux 1999), several European countries (Netherlands, Norway, Belgium, Germany, Denmark and Slovenia) intend to ban the use of chromium in wood preservatives. Some other countries (Finland, Sweden and Belgium) allow use of chromium preserved wood only for purposes that are classified as hazard class IV (Pohleven 1998, Humar and Petrič 2000). However, some of the wood preservatives of the new generation will probably be based on copper compounds. In the new generation of wood preservatives, chromium will be displaced with other chemicals that prevent leaching, or copper will be in such a form which can prevent leaching out of wood.

1. 1. Leaching procedures
1. 1. Postupci izluživanja

There are several methods for determining the leaching of wood preservatives out of wood. Generally, they can be divided into two groups. European standard EN 1250 (ECS 1994) and American standard AWPA A11-93 (AWPA 1998) prescribe leaching from wooden cubes. The only difference between the mentioned methods is in the size of samples and the periods of water renewal. On the other hand, according to the old German standard (DIN 52 172), leaching was determined from samples that were cut into 3 mm thin layers after fixation of a wood preservative. This method is much more severe than leaching from wooden blocks.

1. 2. Leaching of classical and novel copper based preservatives
1. 2. Izluživanje klasičnih i novih zaštitnih sredstava na bazi bakra

Hughes (1999) compared the leaching of classical and novel copper containing wood preservatives (Table 1).

Copper in wood, impregnated with copper(II) sulphate, showed the weakest fixation in wood. Almost 66% of copper was leached out of wood. This result was not surprising, since it is well known that copper(II) sulphate does not react with wood or its components (Richardson 1993, Eaton and Hale 1993, Humar *et al.* 2001). Copper in this form is just adsorbed through cation exchange into wood (Hughes 1999). However, when comparing the leaching of various copper compounds, it has to be taken into account that copper fixation depends largely upon the solution concentration used (Zhang and Kamdem 2000).

As expected, the presence of chromium prevents leaching of copper (Table 1). Nevertheless, as mentioned above, the researchers would like to find suitable substitutes for chromium, as it is regarded as non-suitable due to its toxicity (Pohleven

1998, Barceloux 1999, Humar and Petrič 2000).

Amines seem suitable substitutes for chromium. Leaching of copper from copper/amine or copper/ammonia treated wood was higher than from copper/chromium treated wood, but still significantly slighter compared to copper(II) sulphate treated wood (Table 1). From these results it can be concluded that amines prevent leaching of copper from wood. Although ammonia is highly effective at fixing copper, it does not seem suitable due to unpleasant ammonia emissions and poor surface appearance of copper/ammonia preservative treated wood (Humar and Petrič 2000).

Despite the fact that a commercial importance of copper/amine products is increasing, a mechanism of fixation of these preservatives into wood is still not completely understood. Copper fixation in amine/copper preservative systems is thought to operate by several different complex reactions. Jin and Archer (1991) classified them into three distinct groups: ion exchange between copper/amine ions and carboxyl groups of lignin hemicelullose complex (Jin *et al.* 1990, Dagarin *et al.* 1996), formation of hydrogen bonds between an amine nitrogen and cellulose hydroxyl group (Thomas in Kringstad 1971, Walker *et al.* 1993) and formation of insoluble salts after evaporation of an amine (Hartford 1972). Evaporation of amines and precipitation of insoluble copper salts cannot be the important mechanism for fixation of amine-copper complexes as amines are relatively low volatile. Amines chemically react with wood, or at least their major part does not evaporate from it (Ruddick and Xie 1995, Humar and Petrič 2000, Zhang and Kamdem 2000b). During this reaction, significant amounts of oxygen are consumed (Humar *et al.* 2000). From the changes of FTIR spectra it was proposed that ethanolamine mainly reacts with $^{-}$C=O groups in $^{-}$COOH groups of hemicelluloses and 1, 3, 4 substituted benzene ring groups in lignin complex (Humar and Petrič 2000).

1. 3. Influence of amine ligand type on leaching of copper
1. 3. Utjecaj vrste aminskog liganda na izluživanje bakra

In their paper, Zhang and Kamdem (2000a) evaluated the effect of amine ligand on copper hydroxide leaching. The molar ratio of Cu:N was 1:4, being the same at all formulations. They used three different amines (Table 2). It was shown that the role of amine ligands in copper fixation is important, as amine species can affect stability, polarity and solubility of copper amine complexes (Zhang and Kamdem 2000a). According to the results present in Table 2, the differences in copper leaching are small, but it can be seen that with the increase of molecular weight of a ligand less copper was absorbed during impregnation, and consequently, less copper was leached out of wood.

Formulation (c_{Cu}=0,3%) *Formulacija (c_{Cu}=0,3%)*	Copper loss Gubitak bakra (%)
Copper sulphate Bakrov sulfat	66,1
Chromated copper (CC) Kromatirani bakar (CC)	2,3
Chromated copper arsenate (CCA) Kromatirani bakrov arsenat (CCA)	1,7
Ammoniacal copper Amonijačni bakar	8,6
Amine copper Aminski bakar	7,1

Table 1. *Copper loss from impregnated Pinus sylvestris after 14 days of leaching according to modified EN 84 (Hughes 1999). • Gubitak bakra iz impregnirane bijele borovine Pinus sylvestris nakon 14 dana izluživanja prema modificiranoj normi EN 84 (Hughes 1999).*

Amine ligand Aminski ligand	Copper loss Gubitak bakra [%]
Ethanolamine Etanolamin	24
2-methylamino-ethanol 2-metilamino-etanol	23
N-dimethyl-ethanolamine N-dimetil-etanolamin	20

Table 2. *Copper loss from impregnated southern pine (c_{Cu}=1,0%) after 8 days of leaching according to AWPA A11-93 (Zhang and Kamdem 2000a). • Gubitak bakra iz impregnirane američke južne borovine (c_{Cu}=1,0%) nakon 8 dana izluživanja po metodi AWPA A11-93 (Zhang and Kamdem 2000a).*

The other important factor influencing leaching of copper from copper/amine treated wood is the copper/amine molar ratio. Generally, higher molar (*e.g.* Cu : N = 1 : 8) ratios means more copper leaching (Hughes 1999). However, we have to be very careful with generalisations. A higher copper/amine molar ratio means also better penetration. Consequently, if better copper retention is achieved, more copper can leach out of the wood.

2. MATERIALS AND METHODS
2. MATERIJAL I METODE

The leaching of copper was determined according to the European standard EN 1250 (ECS 1994). The specimens made of Norway spruce (*Picea abies* Karst) (5,0 cm x 2,5 cm x 1,5 cm) were impregnated with different copper based preservatives and masses of retained solution were determined. For purposes of comparison, the specimens impregnated with distilled water were used. The samples were vacuum impregnated according to the standard EN 113 (ECS 1989). Then they were left to dry in a closed vessel for two weeks, in a half-closed vessel for the next, third week, and in an open vessel for the fourth week. After drying and conditioning, we sealed the end grains of the samples with a two-component epoxy coating. Then we put five specimens per each treatment into a beaker and positioned them with ballasting device. After that, we added 500g of water and put a beaker with contents on a magnetic stirrer. The water was replaced six times, as described in the standard EN 1250 (ECS 1994). Afterwards, AAS analyses of water were performed and percentages of leached copper were calculated. The experiment was performed in three parallel leaching procedures for each treatment.

3. RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3. 1. Influence of pH on copper(II) sulphate leaching
3. 1. Utjecaj pH faktora na izluživanje bakar (II) sulfata

Table 3. *Influence of pH value of Cu(II) sulphate solution on leaching of copper from Norway spruce samples • Utjecaj pH vrijednosti otopine bakrovog (II) sulfata na izluživanje bakra iz uzoraka od smrekovine*

pH of a solution pH otopine	Copper loss Gubitak bakra [%]
1,59	26,2
2,61	32,9
3,60	49,8
4,68	16,1

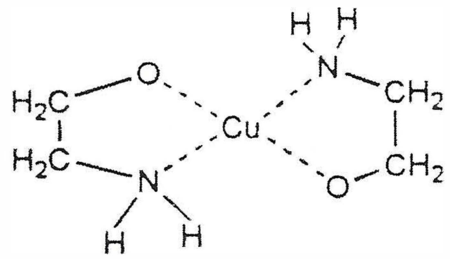

Figure 1. *Copper ethanolamine complex (Zhang and Kamdem 2000b)*

Table 4. *Leaching of copper (c_{Cu}=0,75%) from samples made of Norway spruce • Izluživanje bakra (c_{Cu}=0,75%) iz uzoraka od smrekovine*

Copper source Izvor bakra	Copper loss Gubitak bakra %
Copper(II) octanoate + ethanolamine	12,2
Copper(II) sulphate + octanoic acid + ethanolamine	12,6
Copper(II) sulphate + ethanolamine	22,2

The pH value of a solution has an important influence on copper(II) sulphate fixation and consequently on its leaching. It seems that there are two mechanisms of fixation of copper from a copper(II) sulphate based solution. Copper is not soluble near neutral pH values. Therefore, if we treat spruce blocks with copper(II) sulphate solution with such a pH that copper(II) is on the verge of solubility (*e.g.* pH = 4,7), pH of this solution in wood increases insufficient acidic values and copper hydroxide is precipitated. Similarly, the buffer capacity of wood takes a prominent part in changing the pH of the preservative solution (Albert *et al.* 1999). Copper hydroxide is not soluble in water and it cannot leach out of the preserved wood. This is well seen from Table 3. The treatment of wood with the copper(II) sulphate highest pH solution (pH = 4,68) resulted in a significantly reduced leaching of copper, compared to the leaching of copper from wood impregnated with Cu(II) sulphate solution with a pH value of 3,60. We presume that the reason for this phenomenon is due to copper precipitation mentioned above. The other reason might be a cation exchange. Timber is a week cation exchanger and copper reacts by ion exchange with acidic groups (Hughes 1999, Humar *et al.* 2001). The cation exchange capacity of wood largely depends on pH of a treatment solution. When pH of a solution increases (*e.g.* from 3,6 to 4,68), more acidic groups become dissociated and may be responsible for additional exchange sites and thus more copper can be adsorbed and stronger copper complexes were formed (Rennie *et al.* 1987).

The highest leaching of copper was found at the samples treated with a solution of pH 3,60. (Table 3). On the other hand, lower pH resulted in better fixation. This result, however, does not correlate with the literature data and the above explanations . We must say that, for the time being, we are not able to explain these results

3. 2. Influence of octanoic acid on leaching of copper from copper ethanolamine treated wood
3. 2. Utjecaj oktankse kiseline na izluživanje bakra iz drva zaštićenog bakar etanol aminom

Water-borne Copper carboxylates are considered as the new, promising wood preservatives. The best results were obtained with copper(II) octanoate. It is a complex of copper with a linear, saturated octanoic acid (Pohleven *et al.* 1994). Copper(II) octanoate is not soluble in water, but it dissolves well aqueous amine solution. Cu ions are prone to form complexes with ethanolamine through amino and hydroxyl groups. It is suggested that copper in aqueous solution of ethanolamine is co-ordinated to two nitrogen atoms and two oxygen atoms as seen from Figure 1. This assumption was well supported also by our recent results (EPR, polarimetry, colormetry, ...) (Humar *et al.* unpublished).

The main goal of our leaching experiments with copper/ethanolamine solutions was to clarify whether it is reasonable to use a presynthesized copper(II) octanoate in the copper(II) octanoate – water – ethanolamine system, or whether we could achieve the same results with a combination of copper(II), octanoic acid and ethanolamine. The leaching results showed that there was no statistically significant difference between these two systems (Table 4). In both cases, approximately 12.5% of copper was leached (Table 4). This is an important result, as we could save substantial costs by using these components (copper(II) sulphate and octanoic acid) instead of synthesised copper(II) octanoate. Furthermore, these results confirmed an important role of octanoic acid. More than 22% of copper was leached from the wood treated with a preservative solution of copper(II) sulphate and ethanolamine without octanoic acid. This is almost twice more than at the wood impregnated with copper-based solutions with octanoic acid (Table 4). We presume that octanoic acid has a hydrophobic effect, or that there are some complexes formed between copper, octanoic acid and ethanolamine, which influence copper leaching.

Also, some other results (EPR, polarimetry, colormetry, etc) confirmed our assumption that there is no difference between copper(II) octanoate/ethanolamine aqueous solution and copper(II) sulphate/octanoic acid/ethanolamine containing aqueous solution.

Copper/amine based preservatives are commercially available products. They are introduced as Wolmanit CX, Tanalith E, Impralit KDS, Kuproflorin, ... These preservatives are now estimated to have sales over 1000 tones per year in Europe (Hughes 1999).

4. CONCLUSIONS
4. ZAKLJUČCI

One of the biggest disadvantages of copper-based preservatives is the fact that copper does not get fixed into wood so it can be easily leached out. By adding chromium the problem can be resolved. As chromium is regarded as non-suitable, we wanted to find another way for fixing copper. From the results presented in the paper, we can conclude that amines seem suitable substitutes for chromium. According to our results and the quoted literature, it can be seen that leaching of copper from copper/amine preserved wood is influenced by amine source, pH-value of the preservative solution, copper amine molar ratio, concentration, etc. What we have found out is that we can achieve the same leaching results with the preservative using components copper(II) sulphate and octanoic acid, instead of synthesised copper(II) octanoate in ethanolamine aqueous solution.

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