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Influence of carboxylic acids on fixation of copper in wood impregnated with copper amine based preservatives

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Abstract The importance of copper/amine based preservatives is increasing. Leaching of copper from wood preserved with these solutions is still higher than leaching from wood impregnated with copper chromium ones. In order to decrease leaching, different carboxylic acids (octanoic, 2-ethylhexanoic, decanoic) were added to copper/amine/boron aqueous solutions. An experiment of leaching of copper from Norway spruce was performed according to the modified standard procedure (EN 1250). Results confirmed that carboxylic acids significantly improve copper fixation. The best fixation was determined in specimens impregnated with the preservative solutions consisting of copper, ethanolamine, boric acid and octanoic acid. From such wood, only 1.6% of copper was leached.

Introduction

In the last century copper biocides were mainly combined with chromium and arsenic or boron to improve its fixation and resistance against insects. However, the use of chromium in wood preservatives is foreseen to be significantly limited or even banned in several European countries. In order to use copper as fungicide in the future, new solutions to improve Cu fixation were developed.

Ammonia was found to be a very effective copper fixative long time ago, but due to its emissions this formulation never came into extensive commercial use. Later, ammonia was replaced with amines; particularly ethanolamine was found a very effective copper fixative (Zhang and Kamdem 2000). Nowadays, ethanolamine is a component of several copper based wood preservatives that

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are available in the market. This includes copper-quat, copper dimethyl-dithiocarbamate and copper azole. Copper–amine relationship significantly influences the performance of the preserved wood. In the previous researches, it was figured out that copper–amine molar ratio significantly affects the penetration, fixation and performance of the preservative (Zhang and Kamdem 2000).

However, leaching of copper from copper/amine preserved wood is still higher compared to wood impregnated with copper/chromium formulation. In earlier papers it was reported that the presence of octanoic acid significantly decreases the leaching of copper from preserved wood (Humar et al. 2003). In order to elucidate the leaching of copper from wood preserved with different combinations of copper, amines and carboxylic acids, the present research was carried out.

Materials and methods

Treatment solutions

To determine the influence of carboxylic acids on leaching of copper from impregnated wood, 90 different aqueous solutions were prepared. Among these, 30 formulations that exhibited good solubility and did not have precipitates were chosen (Table 1). Preservative solutions that were investigated consisted of copper(II) sulphate, amine, carboxylic acid and boric acid. Concentration of Cu in the solution was 1% in all the investigated solutions. Three different amines (ethanolamine, diethanolamine, triethanolamine) and also three carboxylic acids (octanoic, 2-ethylhexanoic, decanoic) were used for the preparation of the solutions as well (Table 1).

Impregnation

Specimens (1.5×2.5×5.0 cm) made of Norway spruce (*Picea abies*) were vacuum impregnated according to the EN 113 procedure (ECS 1989) with different preservative solutions listed in Table 1. The treatment of the wood specimens resulted in a solution uptake of about 400 kg/m^3. Later, the specimens were conditioned for 4 weeks, the first 2 weeks in closed chambers, the third week in half closed and the fourth week in open ones. Prior to leaching, specimens were stored at 25°C, 65% RH.

Leaching procedure

Leaching was performed according to the modified EN 1250 (ECS 1994) procedure. The end grains of the samples were sealed with a two-component epoxy coating. Afterwards, nine specimens, treated with the same solution, were put into three vessels and positioned with a ballasting device. Three hundred grams of distilled water was added and the vessel with its content was shaken with the frequency of 55 min^{-1}. Water was replaced seven times daily. Afterwards, atomic absorption spectroscopy (AAS) analyses of the leachate were performed and percentages of leached copper were calculated. In order to compare the modified method with the standard one, specimens impregnated with Cu(II) sulphate were used as reference.

Table 1 Preservative solutions used for impregnation of the Norway spruce blocks

Abbreviation	Amine	Carboxylic acid	Boric acid	Percentage of leached copper
Cu	/	/	/	48.2 (1.5)
CuEa6O1B	Ethanolamine (1:6)	Octanoic (1:1)	(1:1)	2.0 (0.3)
CuEa6O2B	Ethanolamine (1:6)	Octanoic (1:2)	(1:1)	1.6 (0.2)
CuEa8O1B	Ethanolamine (1:8)	Octanoic (1:1)	(1:1)	2.9 (0.5)
CuEa8O2B	Ethanolamine (1:8)	Octanoic (1:2)	(1:1)	2.0 (0.1)
CuEa12O1B	Ethanolamine (1:12)	Octanoic (1:1)	(1:1)	3.3 (0.0)
CuEa12O2B	Ethanolamine (1:12)	Octanoic (1:2)	(1:1)	2.6 (0.0)
CuEa6H1B	Ethanolamine (1:6)	2-Ethylhexanoic (1:1)	(1:1)	2.4 (0.1)
CuEa6H2B	Ethanolamine (1:6)	2-Ethylhexanoic (1:2)	(1:1)	2.9 (0.1)
CuEa8H1B	Ethanolamine (1:8)	2-Ethylhexanoic (1:1)	(1:1)	2.5 (0.6)
CuEa8H2B	Ethanolamine (1:8)	2-Ethylhexanoic (1:2)	(1:1)	3.3 (0.1)
CuEa12H1B	Ethanolamine (1:12)	2-Ethylhexanoic (1:1)	(1:1)	4.1 (0.4)
CuEa12H2B	Ethanolamine (1:12)	2-Ethylhexanoic (1:2)	(1:1)	4.1 (0.1)
CuEa8C1B	Ethanolamine (1:8)	Decanoic (1:1)	(1:1)	2.0 (0.4)
CuEa12C1B	Ethanolamine (1:12)	Decanoic (1:1)	(1:1)	3.3 (0.0)
CuEa12C2B	Ethanolamine (1:12)	Decanoic (1:2)	(1:1)	3.5 (0.4)
Cu2Ea8O1B	Diethanolamine (1:8)	Octanoic (1:1)	(1:1)	6.3 (0.6)
Cu2Ea12O1B	Diethanolamine (1:12)	Octanoic (1:1)	(1:1)	7.7 (0.2)
Cu2Ea12O2B	Diethanolamine (1:12)	Octanoic (1:2)	(1:1)	7.2 (0.0)
Cu2Ea6H1B	Diethanolamine (1:6)	2-Ethylhexanoic (1:1)	(1:1)	4.8 (0.0)
Cu2Ea8H1B	Diethanolamine (1:8)	2-Ethylhexanoic (1:1)	(1:1)	7.3 (0.2)
Cu2Ea8H2B	Diethanolamine (1:8)	2-Ethylhexanoic (1:2)	(1:1)	7.4 (0.2)
Cu2Ea12H1B	Diethanolamine (1:12)	2-Ethylhexanoic (1:1)	(1:1)	9.2 (0.4)
Cu2Ea12H2B	Diethanolamine (1:12)	2-Ethylhexanoic (1:2)	(1:1)	7.2 (0.8)
Cu2Ea12C1B	Diethanolamine (1:12)	Decanoic (1:1)	(1:1)	6.9 (1.1)
Cu2Ea12C2B	Diethanolamine (1:12)	Decanoic (1:2)	(1:1)	6.5 (0.2)
Cu3Ea8H1B	Triethanolamine (1:8)	2-Ethylhexanoic (1:1)	(1:1)	6.8 (0.3)
Cu3Ea8H2B	Triethanolamine (1:8)	2-Ethylhexanoic (1:2)	(1:1)	7.2 (0.1)
Cu3Ea12H1B	Triethanolamine (1:12)	2-Ethylhexanoic (1:1)	(1:1)	8.3 (0.5)
Cu3Ea12H2B	Triethanolamine (1:12)	2-Ethylhexanoic (1:2)	(1:1)	11.6 (1.0)

Molar ratios between copper and respective ingredient are mentioned in parenthesis. Concentration of Cu in solution was 1%. In the last column percentages of leached copper from Norway spruce specimens impregnated with different preservative solutions as measured by AAS are shown. Standard deviations are given in parenthesis

EPR spectroscopy

Electron paramagnetic resonance (EPR) measurements of preservative solutions were performed at two different temperatures, at 293 and at 150 K (Microwave frequency = 9.62 GHz, Microwave power = 20 mW, Modulation frequency = 100 kHz, Modulation amplitude = 0.1 mT). The quartz capillaries were filled with respective solution and inserted into a resonator of the Bruker ESP-300 X-band spectrometer for EPR measurements. In order to determine the EPR spectra of the impregnated wood, four corners of the impregnated specimens were cut off from the specimens and inserted into the resonator one by one. The size of the investigated corner was 1×1×40 mm. In case the spectra consisted only of the paramagnetic centre of Cu(II) and free radicals, the magnetic parameters of the spin-Hamiltonian equation could be obtained directly from the spectrum. The $g\perp$ value was calculated from the ratio of the microwave frequency to the value of the magnetic field at the zero crossing of the spectrum, and g_{II} was measured from the ratio of the microwave frequency to the magnetic field at the centre of the four-line parallel hyperfine pattern as indicated in Fig. 1.

The value of A_{II} is given by the spacing between the components of the hyperfine pattern, measured in mT. However, the value of $A\perp$ is frequently unresolved.

Results and discussion

In order to compare the modified leaching procedure used in this experiment with the standard one, specimens treated with copper sulphate were also lea-

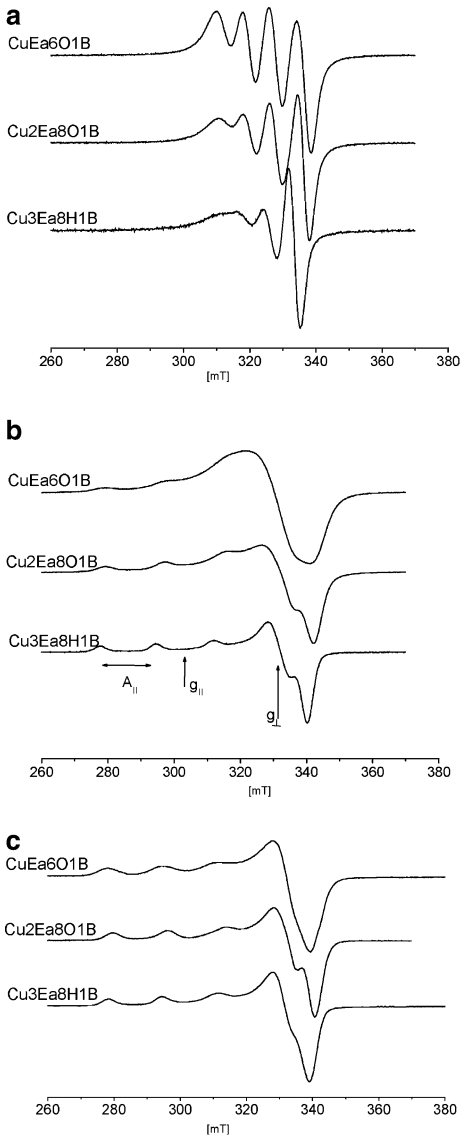

Fig. 1 EPR spectra of three different copper/amine based solutions recorded at 293 K (**a**), or at 150 K (**b**) and wood impregnated with copper/amine based solutions recorded at 293 K (**c**)

ched. Leaching of these specimens resulted in a copper loss of 48.2%, which is comparable with the results determined according to the standard procedure (Humar et al. 2003). This result confirms that modification of the method did not significantly influence the leaching rates compared to the standard procedure.

Influence of carboxylic acids

The most important contribution of the present research is the elucidation of carboxylic acid's influence on copper leaching from preserved wood (Table 1). It is reported that from the impregnated wood treated with copper/ethanolamine solution, between 15 and 22% of copper was leached (Humar et al. 2003). Addition of carboxylic acids decreased the leeching of copper from impregnated wood significantly. Among different carboxylic acids and amines, combination of octanoic acid and ethanolamine was found the most effective. From wood impregnated with preservative solution CuEa6O1B, 2.0% of copper was leached. However, if we increased the concentration of octanoic acid in preservative solution copper fixation was even better. Chemical analysis of leaching solutions revealed, that in wood treated with CuEa6O1B preservative, 98.4% of copper remained after leaching (Table 1).

The combination of octanoic acid with diethanolamine also improved the copper fixation, but not to such an extent as the specimens treated with copper/ethanolamine/octanoic acid preservatives. For example, copper was leached two times more in the solution Cu2Ea8O1B than in the similar solution (CuEa8O1B) where diethanolamine was replaced by ethanolamine (Table 1).

2-Ethylhexanoic and decanoic acids were found less effective than octanoic acid, but these acids still decreased leaching compared to the solutions of the copper/amine without carboxylic acids (Humar et al. 2003). Mazela et al. (2003) reported that from Cu-ethanolamine-quat impregnated wood, between 6.6 and 14.9% of copper is leached. Comparable leaching rates from Cu/amine treated wood were reported in the paper of Zhang and Kamdem (2000) as well.

Two types of reactions are proposed to take place between wood and copper/ethanolamine/carboxylic complex; ligand exchange and complexation. Complexation reactions are stronger and thus copper in this form is less prone to leaching. These interactions are strongly influenced by the pH value of the copper–amine complexes. At less basic pH values of the treating solution, more complexes of charged species are present. Hence, interaction between the wood and Cu/ethanolamine complex is more likely and consequently Cu leaching is reduced (Thomason and Pasek 1997; Zhang and Kamdem 2000). This is one possible explanation for the reduced copper leaching from the wood impregnated with solutions containing carboxylic acids, as preservative solutions containing carboxylic acids have lower pH values like the ones without acids. The other explanation is that carboxylic acid and particularly octanoic acid has a hydrophobic effect, or that there are certain complexes formed between octanoic acid and wood or ethanolamine, which influence copper fixation.

Influence of amines

In the described experiment, three different amines were used; ethanolamine, diethanolamine and triethanolamine (Table 1). The highest average leaching rates were determined in the specimens treated with Copper/triethanolamine and the lowest in those impregnated with copper/ethanolamine preservatives which can be easily calculated from Table 1. From the specimens treated with Cu/triethanolamine in average, 8.8% of Cu was leached, while average leaching of 2.8% was observed in specimens treated with Cu/ethanolamine aqueous solution. However, the elucidation of different amines on leaching of copper from impregnated wood was not the principal objective of this research and therefore, only the average values have been outlined. Nevertheless, this result indicates that amine significantly influences copper fixation, as amine acts like a ligand and thus affects the stability, polarity and solubility of copper amine complexes. However, these data do not evince clear evidence of amine influence on fixation, as the examined specimens were not treated with pure copper/amine solutions because of the presence of different carboxylic acids and also boron. This might explain the contradiction to the results of Zhang and Kamdem (2000). They reported the highest fixation rates in specimens treated with aqueous solutions of copper and tertiary amines like triethanolamine and the lowest ones in the specimens treated with copper/ethanolamine solutions.

Table 2 EPR parameters of preservative solutions and impregnated wood recorded at 150 and 293 K

Abbreviation	Preservative solution					Impregnated wood		
	293 K		150 K			293 K		
	g_0	a_0 [mT]	$g\perp$	g_{II}	A_{II}[mT]	$g\perp$	g_{II}	A_{II} [mT]
CuEa6O1B	2.111	82	2.064	2.227	18.5	2.061	2.259	16.8
CuEa6O2B	2.111	82	2.064	2.227	18.5	2.061	2.250	16.8
CuEa8O1B	2.109	83	2.059	2.228	18.8	2.060	2.252	16.8
CuEa8O2B	2.109	82	2.060	2.228	18.5	2.061	2.252	16.8
CuEa12O1B	2.109	83	2.056	2.232	18.5	2.060	2.250	16.8
CuEa12O2B	2.109	82	2.055	2.232	18.5	2.060	2.248	16.8
CuEa6H1B	2.113	79	2.065	2.229	18.7	2.061	2.253	16.8
CuEa6H2B	2.113	79	2.064	2.229	18.7	2.060	2.257	16.8
CuEa8H1B	2.109	82	2.060	2.228	18.5	2.062	2.255	16.8
CuEa8H2B	2.109	82	2.057	2.228	18.5	2.062	2.251	16.8
CuEa12H1B	2.109	83	2.056	2.320	18.5	2.060	2.250	16.8
CuEa12H2B	2.109	83	2.056	2.232	18.5	2.060	2.251	16.8
CuEa8C1B	2.109	82	2.061	2.227	18.6	2.060	2.237	16.8
CuEa12C1B	2.109	83	2.056	2.232	18.5	2.060	2.233	17.7
CuEa12C2B	2.109	82	2.056	2.232	18.5	2.060	2.237	17.7
Cu2Ea8O1B	2.109	82	2.059	2.233	17.6	2.056	2.237	16.9
Cu2Ea12O1B	2.109	83	2.051	2.233	17.6	2.057	2.240	16.7
Cu2Ea12O2B	2.109	83	2.052	2.233	17.6	2.057	2.241	16.9
Cu2Ea6H1B	2.112	83	2.062	2.233	17.6	2.058	2.243	16.7
Cu2Ea8H1B	2.112	82	2.056	2.233	17.6	2.056	2.242	16.7
Cu2Ea8H2B	2.113	82	2.056	2.237	17.6	2.056	2.242	16.7
Cu2Ea12H1B	2.111	83	2.051	2.233	17.6	2.060	2.242	16.9
Cu2Ea12H2B	2.110	83	2.051	2.233	17.6	2.056	2.237	16.9
Cu2Ea12C1B	2.108	83	2.051	2.233	17.6	2.056	2.237	17.4
Cu2Ea12C2B	2.108	83	2.051	2.233	17.6	2.057	2.239	17.4
Cu3Ea8H1B	2.121	78	2.058	2.254	17.2	2.062	2.255	16.3
Cu3Ea8H2B	2.121	78	2.057	2.253	17.3	2.063	2.253	17.0
Cu3Ea12H1B	2.118	76	2.057	2.251	17.4	2.063	2.257	16.5
Cu3Ea12H2B	2.118	76	2.057	2.251	17.3	2.063	2.257	16.2

On the other hand, there is a clear evidence that with increasing copper–amine ratio, fixation rates of copper ethanolamine solution decreases in all combinations of amines and respective carboxylic acids. For example, in specimens treated with solution CuEa12O1B where copper–amine ratio was 1:12, in average 3.3% of Cu was leached, while in specimens treated with comparable solution CuEa6O1B with copper amine ratio of 1:6, in average 2.0% of copper was lost during leaching. Similar or even more prominent leaching rates were obtained in other combinations of amines and carboxylic acids as well. Our results and cited data (Hancock 1981; Zhang and Kamdem 2000) proved that change in the molar ratio of amine-to-copper can induce copper absorption and leach resistance.

EPR study

Electron paramagnetic resonance spectroscopy is a recognised method to describe the properties of copper based preservatives and impregnated wood (Pohleven et al. 1994; Hughes et al. 1994; Humar et al. 2003).

The line shapes of the EPR spectra were found dissimilar in the aqueous solutions that were investigated, and thus we believe that there are different Cu complexes present in all solutions (Fig. 1a). On the other hand, we found quite similar EPR parameters (Table 2). These parameters are similar to those of Cu(II) octanoate in aqueous ammonia (Hughes et al. 1994; Dagarin et al. 1996) and indicate the presence of mononuclear Cu species with Cu(II) in tetragonal coordination environment. This type of EPR spectra is normally found for Cu(II) species in solutions (Mahajan et al. 1981). The parameters of isotropic EPR spectra of various Cu based solutions recorded at 293 K are presented in Table 2. The values of a_0 and g_0 differ more from the type of carboxyl acid used and copper–amine molar ratio than from amine source used. With increasing Cu–amine molar ratio g_0 value is decreasing. For example, in solution CuEa6O1B a g_0 of 2.111 was determined, while in a similar formulation with Cu–amine ratio 12 g_0 of 2.109 was observed indicating that with increased ratio of amine polarity of solution increases, while ethylhexanoic acids decrease the polarity in comparison with octanoic acid. Comparable g_0 values were determined in other solutions as well, with exception of aqueous solution of copper, triethanolamine, and 2-ethylhexanoic acid (Cu3Ea8H1B) with the g_0 value of 2.121.

Electron paramagnetic resonance spectra of frozen (150 K) Cu/amine/carboxylic acid based aqueous solution are anisotropic with hyperfine splitting, typical for Cu(II) ions ($g\perp = 2.056$–2.064; $g_{II} = 2.227$–2.232; $A_{II} = 18.5$–18.8 mT) (Fig. 1b) (Abragam and Bleaney 1970). Similarly as reported for EPR spectra measured at room temperature, these spectra revealed that EPR parameters are more influenced by Cu–amine molar ratio than by the presence of carboxylic acid. Furthermore, the broadening of the parallel components in the region at low field of the EPR spectra could be the consequence of unresolved superhyperfine splitting due to the interactions with (Pogni et al. 1993), which supports the presence of nitrogens in the first coordination sphere of copper. Therefore, the presence of amines is crucial for the formation of the Cu complex. This result indicates that carboxylic acids do not affect the coordination around copper ions. Furthermore, our preliminary results indicate that presence of carboxylic acid does not affect fungistatical properties of impregnated wood as well (Humar et al. 2003).

The shapes of the EPR spectra of impregnated wood, treated with various copper based formulations, are more similar than the preservative solutions (Table 2). However, the parameters of EPR spectra of impregnated wood differ according to the amine used. For specimens impregnated with Cu/ethanolamine solutions an average EPR value $g_{\perp}$ of 2.061 was determined, for specimens treated with Cu/diethanolamine a value of 2.057 and for specimens preserved with Cu/triethanolamine a $g_{\perp}$ value of 2.063 was determined. These parameters confirm that in wood impregnated with various amines there are different complexes formed in wood (Fig. 1c). Addition of carboxylic acids to copper/amine solutions does not influence the EPR parameters of impregnated wood, with the exception of decanoic acids, which in combination with ethanolamine and diethanolamine exhibited lower g_{II} values and higher A_{II}ones (Table 2). According to the literature data of Zhang and Kamdem (2000) we presume that wood components interact with copper/amine complex perpendicularly through Cu–O interaction with a minimum to negligible displacement of the amine ligands. It seems that it is possible to replace the copper–oxygen bound in amine solution with similar copper–oxygen bound to wood components.

Conclusions

Addition of carboxylic acids to aqueous solution of copper/amine significantly decreases the leaching of copper from impregnated Norway spruce wood. Octanoic acid was found an effective agent to improve copper fixation. The lowest leaching rates were observed in specimens impregnated with a combination of copper, ethanolamine and octanoic acid.

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