

Performance of Waterborne Cu(II) Octanoate/Ethanolamine Wood Preservatives

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Summary

Various aqueous wood preservative solutions containing Cu(II) in the form of copper(II) sulphate or copper(II) octanoate, ethanolamine and in one case octanoic acid were investigated by spectrophotometry, polarography and Electron Paramagnetic Resonance (EPR) spectroscopy. Results have shown the same coordination environment around Cu(II) in all solutions with ethanolamine. Computer simulation of the EPR spectra also revealed that the coordination in the first coordination sphere of copper is the same at low concentration of ethanolamine. At 20% ethanolamine concentration, a mixture of two complexes (one with two nitrogens and the other with three) could be detected. The active compound in the investigated ethanolamine containing solutions is the same when previously synthesised copper(II) octanoate was used, or when copper(II) sulphate and octanoic acid were utilized instead. Fungicidal and leaching experiments with the treated wood resulted in the same conclusion: it is not necessary to use pre-synthesised copper(II) octanoate for the preparation of waterborne copper/ethanolamine wood preservatives. Preservative preparation time and costs can be reduced by simply dissolving copper(II) sulphate and octanoic acid in aqueous ethanolamine solutions.

Introduction

Copper naphthenates are metal complex compounds, which belong to the group of copper carboxylates. Oil borne copper naphthenate has been used as a wood preservative for almost a hundred years (Schultz *et al.* 1996; Craciun and Kamdem 1997; Zyskowski and Kamdem 1999; Petrič *et al.* 2000). However, due to increased environmental concerns, investigations in the field of wood preservation are directed towards development and introduction of new active compounds with an improved environmental profile. For example, water borne formulations, including water borne copper naphthenate wood preservatives, have the advantage of low volatile organic compound emissions (Shaw 1994; Craciun and Kamdem 1997).

While considerable efforts have been put into research on interactions between copper-amine preservative systems and wood (Cooper 1998; Zhang and Kamdem 2000a), much less attention has been focused on identifying Cu(II) species in ammoniacal copper or copper amine preservative solutions and to determining the influence of the various forms of copper complexes in solutions on performance of treated wood, such as its resistance against fungal decay or leaching. Zyskowski

and Kamdem (1999) and Kamdem *et al.* (2001) stressed that the determination of the amount of Cu in solution is not enough to understand and predict the performance of the copper based preservative. Each form of Cu may have a different degree of solubility and bio-availability, and thus a different wood protection level. For example, extensive XPS and FTIR measurements of the commercial preservative Cunapsol, containing Cu(II), naphthenic acid and 2-aminoethanol (often known as ethanolamine (EA); subsequently used in this paper) indicated the presence of copper/carboxylate/ethanolamine complex in the solution (Craciun and Kamdem 1997). This finding could be used to predict the type of copper complex in treated wood.

Sundman (1984) studied composition and performance of the “Cu/caprylic (octanoic) acid/NH₃/CO₃” wood preservative, and proposed that copper in the copper tetramine system does not form a copper caprylate (copper octanoate) complex. We have studied the synthesis and fungicidal performance of various copper carboxylates and their derivatives, including copper(II) octanoate (caprylate), Cu₂(O₂CC₇H₁₅)₄, for almost a decade (Petrič *et al.* 1993, 1998, 2000; Pohleven *et al.* 1994; Humar *et al.* 2001b), with emphasis on the investigation of waterborne copper octanoate solutions, con-

taining ammonia or ethanolamine (Petrič *et al.* 1999; Humar and Petrič 2000a, b). Some of our earlier electron paramagnetic resonance (EPR) analyses (Pohleven *et al.* 1994) show, in contrast to Sundman's data indicated, that in the Cu(II) octanoate aqueous ammonia solution, copper could form Cu(II) octanoate-ammonia complexes. So, the question of Cu(II) species in waterborne ammoniacal copper octanoate solutions remained unsolved. We also did not have any data on Cu(II) in ethanolamine containing solutions. From the production point of view it is important to know whether it is necessary to use previously synthesised Cu(II) octanoate instead of aqueous solutions containing mixtures of Cu(II) sulphate, ethanolamine and octanoic acid. If such a mixture could be prepared without a negative influence on their preservative performance, production time and costs could be substantially reduced. In order to answer these questions, we carried out various spectroscopic analyses and performed several experiments with wood treated with different copper/ethanolamine preservatives.

Materials and Methods

Treatment solutions

The solutions analysed and used for impregnation of wood samples are shown in Table 1. Note the difference in the composition of solutions CuE and CuSEO: solution CuE contained pre-synthesized Cu(II) octanoate ($\text{Cu}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4$), as prepared by a procedure described by Petrič *et al.* (1995), and ethanolamine (EA), while solution CuSEO contained precursors (reactants) for Cu(II) octanoate in the same proportion as CuE. EA to copper molar ratio was 27:1 being equal in all formulations. Copper(II) sulphate solution was slightly acidified with sulphuric acid to improve its solubility.

Spectrophotometry and differential pulse polarography

Absorption spectra of the solutions were obtained using Milton Roy Spectronic 1201 spectrophotometer with 1-cm long absorption cells. Absorption was measured between 250 and 750 nm.

The measurements of differential pulse polarography were performed using Princeton Applied Research (PARTM) Model 174 Polarographic analyzer. It was connected to a PAR Drop Timer Assembly 174/70, equipped with a dropping mercury electrode as a working electrode, an Ag/AgCl reference electrode and a platinum wire as an auxiliary electrode. KNO_3 (0.5 M) was used as supporting electrolyte and it was purged with nitrogen for 10 min prior to the measurements. During the experiment, nitrogen was passed over the cell. The polarograms were recorded between +0.2 and -0.2 V (vs. Ag/AgCl) using a scan rate of 2 mV/s, a drop time of 2 s and a pulse amplitude fixed at 50 mV.

EPR spectroscopy

Electron Paramagnetic Resonance (EPR) measurements of impregnated wood and of preservative solutions were performed at two different temperatures, at 293 K and at 150 K. The list of examined specimens is shown in Table 1. The samples were made of Norway spruce sapwood (*Picea abies* Karst). Dimensions of the samples were $3.0 \times 1.0 \times 0.5$ cm. They were vacuum impregnated according to the standard EN 113. Afterwards, they were dried according to the same standard (EN

113): first two weeks in closed, the third week in half closed and the fourth week in open chambers. The four corners of each sample were cut off and each single corner was inserted into a resonator of the Bruker ESP-300 X-band spectrometer for EPR measurements (Microwave Frequency = 9.62 GHz, Microwave Power = 20 mW, Modulation Frequency = 100 kHz, Modulation Amplitude = 0.1 mT).

Computer simulation of EPR spectra

The computer simulated EPR spectra were calculated by COSMOS program developed by Della Lunga *et al.* (1994). The program takes into account simultaneous occurrence of the two copper(II) isotopes and also includes the contribution of the interaction of Cu(II) ion with nitrogen nucleus (superhyperfine splitting) for fast tumbling regime. The best fit of the experimental spectra was found using the Simplex and Levenberg-Marquardt optimisation procedures. The tolerance in the magnetic parameters during minimization was consistent with the estimated experimental error. Once a good simulation was obtained, input data were used to optimise magnetic parameters until the quality of the fit was invariant to further changes.

Colour analysis

The Norway spruce sapwood samples ($1 \times 3.5 \times 10$ cm) for colour analysis were impregnated and dried as described previously. Six measurements were performed per sample (three parallel samples). Surface colours of the dry samples were determined by a Colour Difference Measuring Instrument, Dr Lange MICRO COLOR (d/8° measuring geometry, 10° standard observer, D65 standard illuminant, xenon flash lamp source, CIELAB system). In the CIELAB system L^* axis represents the lightness (L^* varies from 100 (white) to zero (black)), a^* and b^* are the chromaticity coordinates. (+ a^* is for red, - a^* for green, + b^* for yellow, - b^* for blue). The obtained L^* , a^* and b^* values were used to calculate the colour changes ΔE according to equation 1 (Brock *et al.* 2000). A low ΔE value corresponds to a small colour difference.

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2} \quad (1)$$

Leaching

Leaching was performed according to the EN 1250 procedure. The specimens ($5 \times 2.5 \times 1.5$ cm) of Norway spruce wood were impregnated with four different copper based preservatives and masses of retained solutions were determined. For comparison, specimens impregnated with distilled water were also investigated. After the samples were dried and conditioned as described above, the end grains of the samples were sealed with a two-component epoxy coating. Five specimens, treated with the same solution, were then put into the vessel and positioned with a ballasting device. 500 g of distilled water were added and the vessel with its content was stirred on a magnetic stirrer. The water was replaced six times. Afterwards, AAS analyses of the water were performed and percentages of leached copper were calculated. The experiment was repeated three times.

Fungicidal activity

The samples made of spruce sapwood ($0.5 \times 1 \times 3$ cm) were vacuum impregnated with the various copper based solutions according to the EN 113 procedure. The treatment resulted in a solution uptake of about 77% of the oven dry wood mass. After impregnation, samples were dried as previously described. Dried, steam sterilized samples were then exposed to wood rotting fungi.

Four fungal isolates were used: the white rot species *Trametes versicolor* (L.: Fr.) Pilát (a recently isolated strain); brown rot species *Gloeophyllum trabeum* (Pers. Ex Fr.) Murill (ZIM L017); and two isolates of *Antrodia vaillantii* (DC.: Fr) Ryv. (*A. vaillantii* 1 – P163 HUM UH) and (*A. vaillantii* 2 – ZIM L037). The first strain was kindly provided by Dr. O. Schmidt, BfH Hamburg, Germany. The cultures were maintained on agar media, which contained 3.9 % potato dextrose agar (PDA Difco). Petri dishes (glass, 9 cm diameter) with PDA medium were inoculated with small pieces of fungal mycelium. When the mycelia overgrew the nutrient medium, four samples of treated and untreated wood were introduced onto each inoculated petri dish, above plastic net. The samples were then exposed to fungal decay for 8 weeks (Temp. = 25 °C, RH = 75 %). Afterwards, mycelia were removed from the samples and mass losses determined gravimetrically. The ANOVA (Newman-Keuls multiple range test $p = 0.95$) method for statistical determination of differences between the results was used.

Results and Discussion

Spectrophotometric and polarographic measurements

Preliminary spectrophotometric and polarographic measurements of Cu(II) octanoate/ethanolamine (CuE), Cu(II) sulphate/ethanolamine (CuSEA) and Cu(II) sulphate/ethanolamine/octanoic acid (CuSEO) solutions showed the formation of complex compounds in these media. For all the solutions investigated, no distinctive differences in the shape of absorption spectra with strong absorption maxima at 590 nm were observed. The suggestion of a similar coordination environment for Cu in all solutions was also confirmed by the polarographic measurements. The polarographic reduction potentials were shifted from +0.02 V vs. Ag/AgCl which is typical for aqueous Cu solutions containing 0.5 M KNO₃ as the supporting electrolyte, to -0.16 V in the presence of all investigated ligand systems. Additionally, the shapes of the po-

larograms as well as corresponding peak heights were comparable for all the solutions.

EPR spectroscopy

The isotropic EPR spectra of various Cu based solutions recorded at 293 K are presented in Figure 1a. The values of $a_0 = 8.3$ mT and $g_0 = 2.109$ as well as the lineshapes of the spectra did not differ significantly for aqueous solutions of: Cu(II) octanoate/ethanolamine (CuE), Cu(II) sulphate/ethanolamine (CuSEA) and Cu(II) sulphate/ethanolamine/octanoic acid (CuSEO) ($c_{Cu} = 1.2 \times 10^{-1}$ mol/l). On the other hand, EPR spectra of Cu(II) sulphate in aqueous solution, without ethanolamine are completely different (Fig. 1a). The presence of the same Cu complex might be inferred. The isotropic magnetic 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; Dagarin *et al.* 1996). Similar parameters and lineshapes were also observed at lower concentrations of Cu in preservative solutions (Table 1). From the best fit of computer simulated EPR spectra, it can be seen that the spectra are broadened due to the interaction of nitrogen with copper ion, even if superhyperfine structure of copper nitrogen complex is not resolved. The spectra reported in Figure 1a were simulated using two existing Cu(II) complexes contemporarily present in the solution. One of the complexes has two nitrogens in the first coordination sphere of Cu (Fig. 1b) and the other has three nitrogens. When the ethanolamine concentration is lowered, the presence of only one species with two bound nitrogens can be detected. The number of nitrogens was obtained by comparison of the real part of the

Table 1. EPR parameters of copper containing solutions recorded at 293 K and at 150 K, and of wood impregnated with these solutions

	Treatment		Preservative solutions					Wood		
	c_{Cu} [mol/l]	c_{EA} [mol/l]	293 K		g_{\perp}	150 K		g_{\perp}	293 K	
		g_0	a_0 [mT]	g_{\parallel}		g_{\parallel}	A_{II} [mT]		g_{\parallel}	g_{\parallel}
Cu(II) sulphate	2×10^{-2}		2.194	13.8	/	/	/	2.079	2.360	12.4
	5×10^{-2}		2.194	13.8	/	/	/	2.079	2.367	12.3
	1.2×10^{-1}		2.194	13.8	/	/	/	2.079	2.364	12.3
Cu(II) sulphate with EA	2×10^{-2}	5.4×10^{-1}	2.107	8.6	2.057	2.238	18.2	2.061	2.259	16.9
	5×10^{-2}	1.35	2.108	8.5	2.057	2.239	18.2	2.060	2.261	16.8
	1.2×10^{-1}	3.24	2.109	8.3	2.057	2.239	18.2	2.059	2.265	16.7
Cu(II) sulphate with EA and octanoic acid	2×10^{-2}	5.4×10^{-1}	2.107	8.6	2.057	2.238	18.2	2.061	2.259	16.9
	5×10^{-2}	1.35	2.109	8.5	2.057	2.239	18.2	2.060	2.262	16.8
	1.2×10^{-1}	3.24	2.109	8.3	2.057	2.239	18.2	2.059	2.265	16.7
Cu(II) octanoate with EA	2×10^{-2}	5.4×10^{-1}	2.107	8.6	2.057	2.238	18.2	2.061	2.259	16.9
	5×10^{-2}	1.35	2.109	8.5	2.057	2.239	18.2	2.060	2.262	16.8
	1.2×10^{-1}	3.24	2.109	8.3	2.057	2.239	18.2	2.059	2.265	16.7

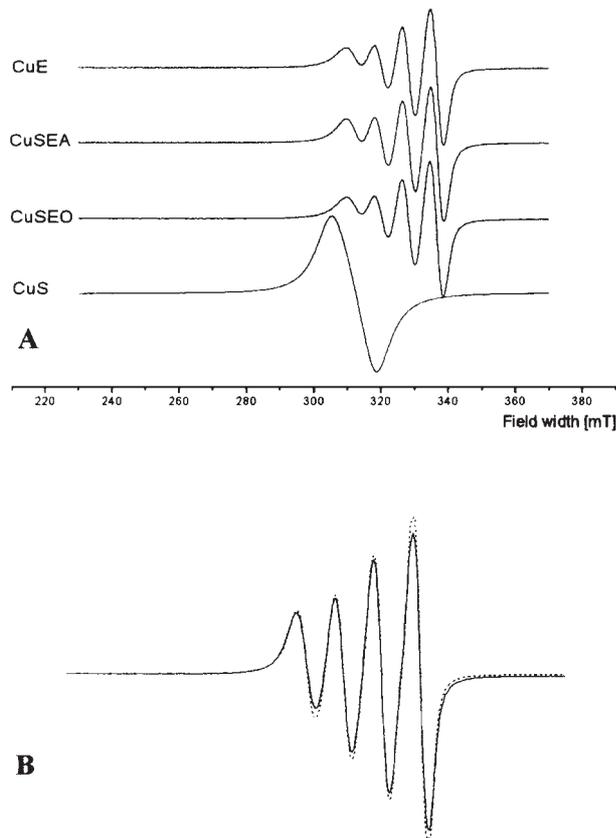


Fig. 1. A) EPR spectra of: copper(II) octanoate/ethanolamine (CuE), copper(II) sulphate/ethanolamine (CuSEA), copper(II) sulphate/ethanolamine/octanoic acid (CuSEO) and copper(II) sulphate (CuS) in aqueous solution at 293 K ($c_{\text{Cu}} = 1.2 \times 10^{-1}$ mol/l; $c_{\text{EA}} = 3.24$ mol/l) and B) comparison of experimental (Ex) and simulated (Si) EPR spectra of aqueous solution of CuE recorded at room temperature 293 K ($c_{\text{Cu}} = 2 \times 10^{-2}$ mol/l). — Ex; - - - - Si.

Fourier Transform sensitive to the presence of nitrogens of the experimental and simulated spectra (Della Lunga *et al.* 1994). From this comparison and data in the literature (Mahajan *et al.* 1981; Hughes *et al.* 1994), it could be concluded that coordination around Cu(II) is the same in all treatment solutions containing Cu(II) species and ethanolamine, regardless of the initial form of Cu compound in a solution. These results also indicate that octanoate in a solution of Cu(II) octanoate and ethanolamine is not bound to Cu(II); $\text{Cu}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4$ must have dissociated in the treatment solution. Similarly, for the Cu/ammonia system Sundman (1984) and Dagarin *et al.* (1996) suggested that most of the Cu in the cupriammonia system did not form copper carboxylate and hence, carboxylate has a minimal effect on the fixation of Cu(II) in wood.

EPR spectra of frozen (150 K) Cu/ethanolamine based aqueous solution are anisotropic with hyperfine splitting, typical for Cu(II) ions ($c_{\text{Cu}} = 1.2 \times 10^{-1}$ mol/l) ($g_{\perp} = 2.057$; $g_{\parallel} = 2.239$; $A_{\parallel} = 18.2$ mT) (Abragam and Bleaney 1970). These parameters were equal for all tested Cu and ethanolamine containing aqueous solutions

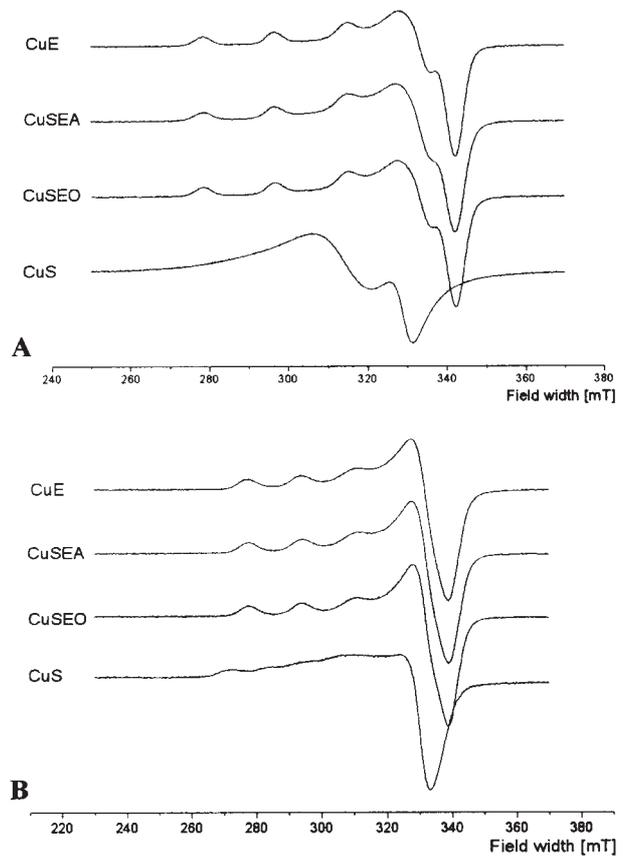


Fig. 2. A) EPR spectra of: copper(II) octanoate/ethanolamine (CuE), copper(II) sulphate/ethanolamine (CuSEA), copper(II) sulphate/ethanolamine/octanoic acid (CuSEO) and copper(II) sulphate (CuS) in aqueous solution at 150 K and B) EPR spectra of wood impregnated with these aqueous solutions ($T = 293$ K) ($c_{\text{Cu}} = 1.2 \times 10^{-1}$ mol/l; $c_{\text{EA}} = 3.24$ mol/l).

(Table 1). Furthermore, the broadening of the parallel components in the region at low field of the EPR spectra (Pogni *et al.* 1993) supports the presence of nitrogens in the first coordination sphere of copper. Therefore, the presence of ethanolamine is crucial for the formation of the Cu complex. In addition, from the low temperature measurements, we can conclude that the same copper/ethanolamine complex is present in all the studied solutions and the Cu complex is the same as that reported at room temperature. This means that the biologically active substance is the same in all solutions with ethanolamine examined. Furthermore, the EPR spectrum of frozen Cu(II) sulphate solution was substantially different from all other Cu EPR spectra (Table 1, Fig. 2a).

The spectral parameters of treated timber are given in Table 1. The samples treated with a solution of Cu(II) sulphate gave typical anisotropic Cu EPR spectra. Hyperfine splitting of Cu^{2+} ion is not well resolved (Fig. 2b) and only g_{\perp} could be well determined ($g_{\perp} = 2.079$). The values of g_{\parallel} and A_{\parallel} are not exact values ($g_{\parallel} = 2.364$; $A_{\parallel} = 12.3$ mT) because they could not be determined

accurately from the spectrum. Hughes *et al.* (1994) observed similar parameters for Cu(II) sulphate treated pine. Nevertheless, the specimens treated with copper/ethanolamine based solution of the highest concentration exhibited a strong EPR signal with well resolved A_{II} and g_{II} EPR parameters ($g_{I} = 2.059$; $g_{II} = 2.265$ and $A_{II} = 16.7\text{mT}$). Lineshapes and parameters of spectra were the same for all specimens treated with various Cu and ethanolamine containing aqueous solutions (Fig. 2b, Table 1) The analysis of the EPR parameters showed that the Cu complex is different from that reported in Figure 2a even if nitrogens are always present in the coordination sphere of copper. Therefore, we presume that copper coordination in wood is the same, whether the octanoic component was delivered into the treatment solution as an acid or as carboxylate ligand, bound to Cu in a $\text{Cu}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4$ complex.

Colour analysis

The colour parameters of treated and untreated wood (L^* , a^* , b^* and ΔE) are presented in Table 2. It could be seen that the colour of treated samples differs significantly from that of untreated ones. The ΔE value (difference) increases with the concentration of Cu in a treatment solution. The lowest difference was at impregnation with Cu(II) sulphate containing aqueous solutions (ΔE up to 6.1). The treated wood became slightly yellowish (Δb^* up to 2.9) and greenish (Δa^* up to -2.3).

However, the described differences are low compared to the changes that appeared after treatment with copper/ethanolamine containing preservatives. With wood, treated with Cu(II) octanoate/ethanolamine, ΔE increased from initial 24.8 ($c_{\text{Cu}} = 2 \times 10^{-2} \text{ mol/l}$), to 34.7 ($c_{\text{Cu}} = 1.2 \times 10^{-1} \text{ mol/l}$). Wood, treated with the solutions of the highest concentrations of Cu(II) octanoate, be-

came significantly darker ($\Delta L^* = 34.7$) and slightly yellowish ($\Delta b^* = 1.7$), while the a^* component remained almost the same ($\Delta a^* = 0.4$). Similar changes were observed with other copper/ethanolamine treated specimens. We did not observe any colour difference between Cu(II) octanoate/ethanolamine and Cu(II) sulphate/octanoic acid/ethanolamine treated wood. But there was a slight difference in colour of the wood treated with these two systems and Cu(II) sulphate/ethanolamine preservative treated wood. However, while the a^* component after treatment with the first two systems remained almost the same or became slightly reddish and less greenish, in Cu(II) sulphate/ethanolamine preserved wood the opposite changes occurred. Treated wood became more greenish and less reddish. However, this method allowed us to observe the whole system, and not only Cu and the environment as in other chemical methods. We presume that the reason for this difference is the presence of octanoic acid in the first two systems. Octanoic acid somehow interacted with wood to give a slightly different colour as in the case of preservative without octanoic acid. This result is an additional proof that the same outcome occurs when previously synthesised Cu(II) octanoate is used or when Cu(II) sulphate and octanoic acid are used instead.

Leaching

Leaching experiments are quite often used for copper fixation studies. Our leaching results confirmed that there is no statistically significant difference between presynthesized Cu(II) octanoate with ethanolamine and a combination of Cu(II), octanoic acid and ethanolamine. In both cases, approximately 12.5 % of Cu was leached. Conversely, these results also showed an important role of octanoic acid in preserved wood. From wood, treated with a preservative solution of Cu(II) sul-

Table 2. Colour changes, caused by treatment with several copper containing solutions. L^* , a^* , b^* and ΔE values are calculated as shown in equations 1, 2, 3 and 4

	Treatment		L^*	a^*	b^*	ΔE^*
	c_{Cu} [mol/l]	c_{EA} [mol/l]				
Cu(II) sulphate	2×10^{-2}		83.6	4.9	20.9	1.6
	5×10^{-2}		81.3	2.4	22.7	5.3
	1.2×10^{-1}		80.3	2.2	22.7	6.1
Cu(II) sulphate and ethanolamine	2×10^{-2}	5.4×10^{-1}	59.2	5.0	22.7	25.6
	5×10^{-2}	1.35	54.2	4.8	21.6	30.4
	1.2×10^{-1}	3.24	50.3	4.6	20.9	34.3
Cu(II) sulphate, ethanolamine and octanoic acid	2×10^{-2}	5.4×10^{-1}	60.7	5.2	23.9	24.2
	5×10^{-2}	1.35	52.5	5.3	21.4	32.2
	1.2×10^{-1}	3.24	50.4	6.7	22.1	34.3
Cu(II) octanoate and ethanolamine	2×10^{-2}	5.4×10^{-1}	60.0	5.1	23.2	24.8
	5×10^{-2}	1.35	52.3	5.3	21.7	32.4
	1.2×10^{-1}	3.24	49.9	5.9	21.5	34.7
Control	0	0	84.6	5.5	19.8	0.0

phate and ethanolamine without octanoic acid, more than 22 % of Cu was leached. This is almost twice the amount that leached from wood impregnated with Cu based solutions with octanoic acid. Furthermore, leaching of copper from wood impregnated with aqueous solution of Cu(II) sulphate, without ethanolamine, was even higher (49.8 %). This result has confirmed that of Zhang and Kamdem (2000b) and of Hughes *et al.* (1994), that ethanolamine decreases leaching of copper from wood.

Two types of reactions are proposed to take place between wood and copper/ethanolamine complex; ligand

exchange and complexation. Complexation reactions are stronger and thus Cu in this form is less prone to leaching. These interactions are strongly influenced by the pH value of the copper-amine complexes. At lower pH values of the treatment 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 2000b). This is one possible explanation for reduced copper leaching with CuE and CuSEO treated wood, as the highest pH value was measured for solution CuSEA (12.9) compared

Table 3. Mass loss of samples impregnated with water borne copper based preparations and exposed to wood rotting fungi for 8 weeks. Where the mass loss values are in the same column, there was no statistically significant difference. The mass loss values, which are not in the same column, indicate statistically significant difference in mass loss

<i>Trametes versicolor</i>						
Treatment	2×10^{-2} mol/l		5×10^{-2} mol/l		1.2×10^{-1} mol/l	
			c_{Cu}	Mass loss [%]		
Cu(II) sulphate	4		5		3	
Cu(II) sulphate + EA		10	6			6
Cu(II) sulphate + EA + octanoic acid		8	7			5
Cu(II) octanoate + EA		9	5			6
Control		23		23		23
<i>Antrodia vaillantii</i> 1						
Treatment	2×10^{-2} mol/l		5×10^{-2} mol/l		1.2×10^{-1} mol/l	
			c_{Cu}	Mass loss [%]		
Cu(II) sulphate	14		17	12		
Cu(II) sulphate + EA	8	2			3	
Cu(II) sulphate + EA + octanoic acid	11	5	2			
Cu(II) octanoate + EA	7	2	3			
Control		28		28		28
<i>Antrodia vaillantii</i> 2						
Treatment	2×10^{-2} mol/l		5×10^{-2} mol/l		1.2×10^{-1} mol/l	
			c_{Cu}	Mass loss [%]		
Cu(II) sulphate		22		19		3
Cu(II) sulphate + EA	9		7			2
Cu(II) sulphate + EA + octanoic acid		17	7			2
Cu(II) octanoate + EA		22	6			2
Control		32		32		32
<i>Gloeophyllum trabeum</i>						
Treatment	2×10^{-2} mol/l		5×10^{-2} mol/l		1.2×10^{-1} mol/l	
			c_{Cu}	Mass loss [%]		
Cu(II) sulphate	0		1		0	
Cu(II) sulphate + EA		7	6			2
Cu(II) sulphate + EA + octanoic acid	10		6		6	
Cu(II) octanoate + EA		5	8			3
Control		37		37		37

with the preservative solution CuE (12.8) and CuSEO (12.7). The other explanation is that octanoic acid has a hydrophobic effect, or that there are certain complexes formed between octanoic acid and wood or ethanolamine which could influence Cu leaching.

Fungicidal activity

The results of the fungicidal test are presented in Table 3. It can be seen that copper-containing preservatives reduced mass loss of the samples even at the lowest concentration of Cu in all preservative solutions (2.0×10^{-2} mol/l). Only *A. vaillantii* 1 decayed the wood, protected with the lowest concentration of Cu, to almost the same extent as the untreated wood. This is not surprising, as this strain has been shown to be copper tolerant (Humar *et al.* 2001a). On the other hand, mass losses were detected, even in wood impregnated with the highest concentration of Cu ($c_{\text{Cu}} = 1.2 \times 10^{-1}$ mol/l). For instance, *T. versicolor* caused 8 % mass loss in the samples, treated with the aqueous solution of Cu(II) sulphate, ethanolamine and octanoic acid. This mass loss is still smaller than the mass loss of untreated specimens (23 %). However, compared with the other fungi, *G. trabeum* did not degrade Cu(II) sulphate treated wood.

Wood impregnated with CuS was less resistant against *A. vaillantii* 1 and *A. vaillantii* 2 than wood impregnated with copper/ethanolamine containing preservatives. This result confirms the already reported and explained finding that *A. vaillantii* or oxalic acid producing strains, cannot decay wood treated with copper containing solutions when ethanolamine is present (Humar *et al.* 2002). For example, *A. vaillantii* 1 caused more than 12 % mass loss in wood impregnated with the highest concentration of Cu(II) sulphate, but caused only 3 % mass loss in samples treated with a solution of the highest concentration of Cu(II) octanoate/ethanolamine. On the other hand, *T. versicolor* and *G. trabeum* caused less mass loss in copper/ethanolamine treated wood than in Cu(II) sulphate impregnated specimens. Preston *et al.* (1985) also reported a similar relationship between mass losses of acid CCA treated wood and alkaline Cu(II) octanoate/ammonia treated wood.

However, we did not find a statistically significant difference between the preservative efficacies of the different copper/ethanolamine containing preservatives (Table 3). Wood, impregnated with aqueous solutions of Cu(II) sulphate with ethanolamine, Cu(II) octanoate with ethanolamine or Cu(II) sulphate with ethanolamine and octanoic acid exhibited the same resistance against fungal decay. We can, therefore, conclude that fungicidal activity of pre-synthesized Cu(II) octanoate in ethanolamine containing aqueous solution does not differ from activity of an aqueous solution of Cu(II) sulphate, octanoic acid and ethanolamine. Therefore, we believe that preparation of Cu(II) octanoate for wood preservation is not necessary from a fungicidal point of view. The copper concentration in our tested solutions is quite low, as we wanted the fungi to decay the impreg-

nated wood. Concentrations of copper in commercial copper/amine based wood preservatives are at least 50 % higher than in the one we have used and, therefore, provide better efficiency against fungi (Preston *et al.* 1985). Results from both laboratory and field tests show that the performance of these amine/copper based preservatives is similar to chromated copper arsenate at the equivalent retentions of active ingredients (Sundman 1984).

Conclusions

Spectrophotometric, polarographic and EPR analysis of various aqueous wood preservative solutions, containing Cu(II) in the form of copper sulphate or copper octanoate, ethanolamine and in one case octanoic acid, showed the same coordination environment around Cu(II) in all solutions with ethanolamine. The EPR investigation additionally showed that copper in solution forms two types of complexes; one with two nitrogens in the first coordination sphere of copper, and the other with three nitrogens. The coordination around Cu(II) is the same in all solutions of Cu(II) and ethanolamine.

While the presence of the octanoic component did not have any influence on the EPR spectra of wood treated with copper ethanolamine preservatives, wood surface colour measurements indicated a possible influence of octanoate on the type of Cu(II) species in the preserved wood. This finding was supported by the reduction in leaching of copper from the treated wood, when the octanoic component was present in the formulation. However, pre-synthesis of copper(II) octanoate is not necessary since the leaching of copper was the same for wood treated with both preservatives with octanoate tested. Resistance of treated wood against *Trametes versicolor*, *Gloeophyllum trabeum* and *Antrodia vaillantii* strains was also the same for all copper/ethanolamine solutions irrespective whether it was pre-synthesised or not.

We, therefore, believe that it is not necessary to use pre-synthesised copper(II) octanoate for preparation of waterborne copper/ethanolamine wood preservatives since Cu(II) species and consequently the performance of these preservatives were the same, when copper(II) sulphate and octanoic acid were used instead. There is considerable scope for further investigation in this field, for example, water borne copper/carboxylate/amine combinations, and copper naphthenate amine preservatives should be compared.

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