

INTERACTION OF COPPER-AMINE WITH SOUTHERN PINE: RETENTION AND MIGRATION

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ABSTRACT

The retention and leachability of copper in copper-amine (Cu-EA)-treated southern pine (SP) are influenced by the formulation and the composition of copper-amine treating solutions. The sources of copper used, $\text{Cu}(\text{OH})_2$, CuCO_3 , CuSO_4 , and $\text{Cu}(\text{NO}_3)_2$, in the copper-amine complex formulation affect the leachability of copper. Data show that copper-amine from CuSO_4 - and $\text{Cu}(\text{NO}_3)_2$ -treated wood has less copper loss during laboratory water leaching than that from $\text{Cu}(\text{OH})_2$ - and CuCO_3 -treated wood. Increasing the amine-to-copper molar ratio increases the copper retention by wood, but reduces the leach resistance of copper. The nature of amine ligands, such as monoethanolamine (primary amine), 2-methylamino-ethanol (secondary amine), and N, N-dimethyl-ethanolamine (tertiary amine), has some effect on copper retention and copper leaching. As the molecular weight of amine ligands increases, copper loss during leaching decreases.

Keywords: Copper-amine, southern pine, retention, leaching, fixation, ethanolamine, ligand.

INTRODUCTION

An increasing amount of research in wood preservation has been directed toward development of environmentally benign preservative systems with low mammalian toxicity and acceptable efficacy. The copper-amine system is one of the new emerging copper-based preservatives, receiving a lot of attention. It is a primary ingredient of amine copper quat-type D (ACQ-D), copper dimethyldithiocarbamate (CDDC), and copper azole (AWPA 1998).

The fixation mechanism of copper in chromated copper arsenate (CCA) and ammoniacal wood preservative systems has been extensively studied. The effect of formulation on the efficacy and performance, the fixation chemistry, and the reaction kinetics of copper ion in CCA-treated wood have been exten-

sively examined (Fahlstrom et al. 1967; Hagar 1969; Dahlgren and Hartford 1972; Pizzi 1982). The general theory of fixation of copper in an ammoniacal system is that the cuprammonium ion is fixed through cation adsorption reactions with the wood substrate and through precipitation of copper inorganic compounds (Hulme 1979; Jin and Archer 1991). Hartford (1972) suggested that insoluble copper precipitates were formed after the evaporation of ammonia from the solvent. Lebow and Morrell (1993) proposed that the phenolic wood extractives provided reactive sites for copper fixation in ACZA-treated wood. Smith and Tascioglu (1997) investigated the differential adsorption and absorption of copper-based wood preservatives in southern pine. They reported that about 95% of the copper adsorbed from 0.5% copper monoethanolamine solutions was not leached. They

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only used monoethanolamine as the ligand and did not mention the amine to copper molar ratio of their copper-amine formulations.

While the fixation mechanisms of other copper-based wood preservatives have been widely studied, relatively little research has been done on the fixation, retention, and leaching of copper in copper-amine-treated wood. It is reasonable to presume that the copper source, the amine ligands, and the ligand-metal molar ratio influence the copper fixation in copper-amine-treated wood. In this study, the effects of copper sources (such as copper sulfate, copper nitrate, copper carbonate, and copper hydroxide), the amine ligands (such as monoethanolamine (primary amine), 2-methylamino-ethanol (secondary amine) and N, N-dimethyl-ethanolamine), and the amine-to-copper molar ratio on the retention and leaching of copper in treated wood have been investigated.

MATERIALS AND METHODS

Formulation of copper-amine (Cu-EA)-treating solution

To evaluate the effect of different copper sources on wood-copper interaction, four different copper compounds, namely, copper hydroxide, copper carbonate, copper nitrate, and copper sulfate, were used in formulating copper-amine. Copper-amine treating solutions were made up by mixing these copper compounds with an aqueous solution of monoethanolamine (MEA). The molar ratio of amine-to-copper was kept at 4.

To evaluate the effect of amine ligands on copper fixation, copper-amine-treating solutions were prepared by mixing copper hydroxide with three different ethanolamines, including a primary amine, monoethanolamine (MEA), a secondary amine, 2-methylamino-amine (MeEA), and a tertiary amine, N, N-dimethyl-ethanolamine (DMeEA). The amine-to-copper molar ratio was kept at 4.

To evaluate the effect of amine-to-copper molar ratio on copper fixation, copper-amine-treating solutions were formulated by mixing

copper hydroxide and MEA, MeEA, and DMeEA at a molar ratio of amine-to-copper varying from 3 to 8.

Treatment

Defect-free 5- by 10- by 180-cm (2- by 4-in. by 6-ft) kiln-dried sapwood boards of southern pine (SP) were used in this study. Cubes measuring 19 mm (0.75 in.) were prepared from these boards and stored in a conditioning room maintained at 65% relative humidity (RH) and 20°C (68°F) until they reached an equilibrium moisture content (EMC) of $12 \pm 3\%$. The conditioned cubes were then pressure-treated with copper-amine solutions. The elemental copper contents in the solutions were 0, 0.25, 0.5, 0.75, and 1.0% by weight. The treating procedure included an initial vacuum at 84.6 kPa for 5 min, followed by a pressure level of 690 kPa (100 psi) for 1 h, release of the pressure, recovery of the treating solution, and then a final vacuum for 10 min. Treated samples were air-dried at room temperature for 2 weeks before further testing. The copper content in treated wood samples was analyzed by using a Perkin-Elmer atomic absorption spectrometer (AAS) model 3110, following the AWPA standard A11-93 (AWPA 1998).

Leaching

After the conditioning of treated cubes, the leaching test was carried out to determine the amount of leachable copper from treated wood. Three treated wood cubes weighing about 10 grams, were placed in 200-ml flasks and immersed in 100-ml deionized water. The flasks were positioned on a horizontal-shaking tray with continuous mild shaking, and an equal amount of fresh deionized water was renewed every day for 8 days. The copper content in water leachate and in leached cubes was analyzed by AAS.

RESULTS AND DISCUSSION

Effect of copper sources

Atomic absorption spectrometer analysis indicated that the source of copper influenced

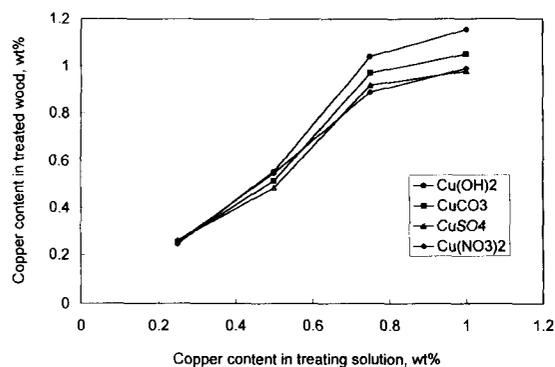


FIG. 1. Effect of copper source on copper retention. Copper-amine solutions were made by mixing monoethanolamine with different copper compounds.

the level of copper retention during the treatment of southern pine with Cu-EA (Fig. 1). At the lowest concentration of copper in solution (about 0.25%), no difference was observed for the level of copper absorbed by wood for all copper sources. As the copper concentration increased, more copper was absorbed. Solutions made from copper hydroxide and copper carbonate yielded higher copper retention level than those made from copper sulfate and copper nitrate. The pH of the treating solutions is tabulated in Table 1. It is noticed from Fig. 1 and Table 1 that the retention of copper in wood increased as the pH of treating solutions increased. High pH solution systems resulted in higher copper absorption. These findings generally agree well with a previous report (Cooper 1998). A high pH solution might increase the deionization of carboxylic, phenolic, and ester groups, which in turn might promote the retaining of copper.

Copper source also plays an important role in copper leach resistance (Fig. 2). After an 8-day water leaching of wood cubes treated with 0.5% copper solution, about 12% copper from the copper hydroxide system was lost, 10% from copper carbonate, 7% from copper sulfate, and 6% from copper nitrate (Fig. 2). The copper leach resistance showed an opposite trend to copper absorption. Copper from copper sulfate and copper nitrate is more leach-resistant than the copper from copper hydrox-

TABLE 1. pH of copper monoethanolamine treating solutions from different copper compounds, each with an amine-to-copper molar ratio of 4.

Copper compounds	Copper content in solutions (wt%)			
	0.25	0.5	0.75	1.0
Cu(OH) ₂	10.56	10.75	10.80	10.82
CuCO ₃	10.02	10.14	10.20	10.31
CuSO ₄	9.19	9.25	9.28	9.30
Cu(NO ₃) ₂	9.10	9.11	9.13	9.14

ide and copper carbonate. For copper-amine complexes, high pH solution systems led to higher copper retention and higher copper loss during leaching (Fig. 2 and Table 1).

Effect of amine ligands

The role of amine ligands in copper fixation is important because amine acts as the ligand, which can affect the stability, polarity, and solubility of copper amine complexes. Figure 3 illustrates the influence of ligands on copper absorption. As the molecular weight of amine ligands increase, less copper was absorbed. The Cu-MEA solution system showed a higher level of copper absorption than Cu-MeEA and Cu-DMeEA. This difference increased as the copper concentration of the treating solution increased.

Figure 4 shows the results of the laboratory water leaching on different copper-amine-treated wood samples. It is noted that amine ligands influence copper leachability significantly. As the molecular weight of the amine increased, the leach resistance of copper in-

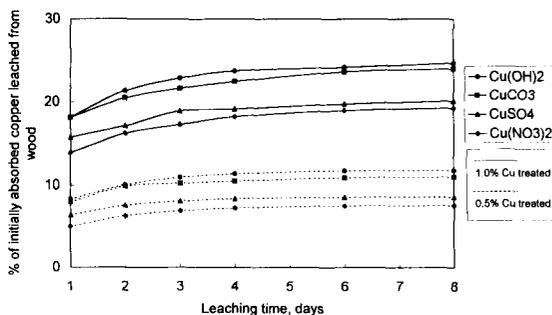


FIG. 2. Effect of copper source on copper leaching from copper-amine-treated samples.

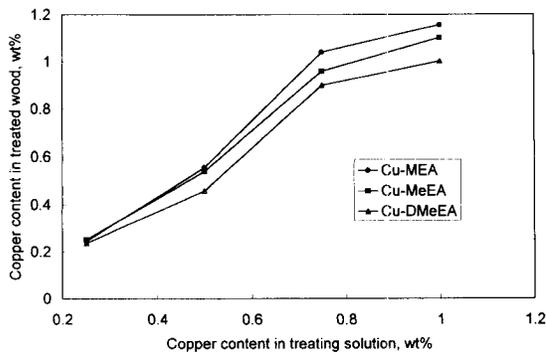


FIG. 3. Effect of amine ligand on copper retention. Copper-amine solutions were made by mixing copper hydroxide with different amines.

creased. Tertiary amine (DMeEA) systems exhibited the lowest percentage of copper loss, while the primary amine (MEA) formulation lost the most copper. After an 8-day water leaching of 0.5% copper solution-treated cubes, about 5% copper loss was obtained with wood treated in the tertiary amine (DMeEA) system, 8% in the secondary amine (MeEA), and 12% in the primary amine (MEA).

Effect of amine-to-copper molar ratio

Increasing the amine-to-copper molar ratio improves the stability of the copper amine complex (Hancock 1981), and hence increases the penetration and retention of the copper-amine complex in wood. A change in the molar ratio of amine-to-copper can alter the copper absorption and leach resistance. Figure 5 represents the copper absorption in wood pressure-treated with copper-amine solutions with amine-to-copper molar ratios varying from 3 to 8. The molar ratio of amine-to-copper affected copper absorption greatly in Cu-MeEA and Cu-DMeEA formulation systems. At an amine-to-copper molar ratio of 3, the retention of copper in wood increased substantially as the molar ratio increased to 4, and then copper absorption tended to saturate as the amine-to-copper molar ratio further increased. The influence of amine-to-copper molar ratio was not as pronounced in the Cu-MEA formulation system as in the Cu-DMeEA and Cu-MeEA

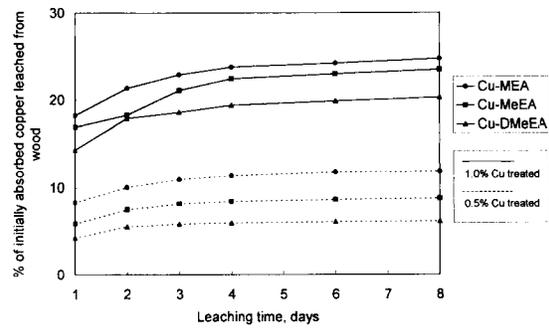


FIG. 4. Effect of amine ligand on copper leaching from copper-amine-treated samples.

formulations. An increase in amine-to-copper molar ratio from 3 to 8 in the Cu-MEA formulation caused only a slight increase of copper absorbed in wood. Increased copper absorption may be due to easier diffusion of copper in wood with the increase in amine content.

Figure 6 displays the percentage of copper loss after an 8-day water leaching at different amine-to-copper molar ratios. A higher molar ratio increased copper loss during leaching. The percentage of copper loss was approximately proportional to the molar ratio of ligand to copper for all the formulations. This suggests that an increase in amine-to-copper molar ratio may reduce the copper fixation in wood, therefore increasing the leaching of copper in treated samples.

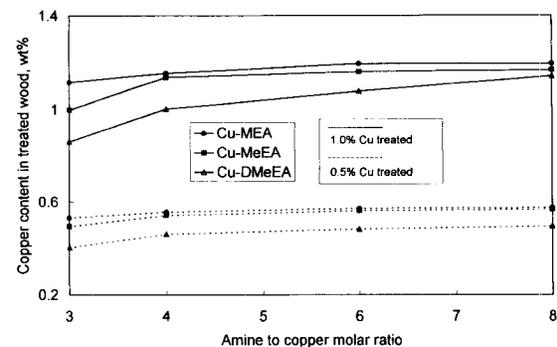


FIG. 5. Effect of amine-to-copper molar ratio on copper retention. Copper-amine solutions were made by mixing copper hydroxide with amines at different ratio.

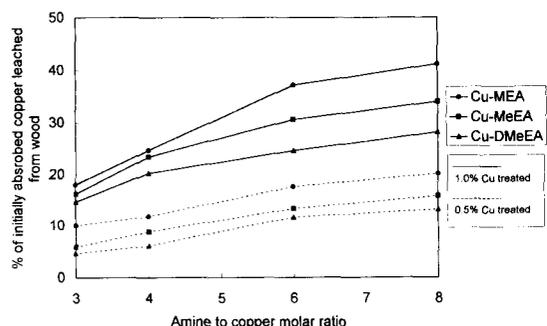


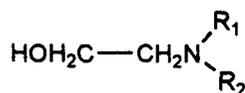
FIG. 6. Effect of amine-to-copper molar ratio on copper leaching from copper-amine-treated samples.

Copper fixation mechanism

Cupric ions are prone to form complexes with ethanolamine through amino and hydroxyl groups in aqueous solution due to the formation of a 5-member ring complex as proposed in Fig. 7 (Casassas et al. 1989). As the pH of a solution increases, deprotonation of

hydroxyl groups occurs. At neutral or low basic conditions, only one proton from hydroxyl groups of the amine ligand is released (Fig. 7B). As the pH further increases, another proton from hydroxyl groups of the amine ligand is released and the complex becomes a non-conducting species with no charge (Fig. 7C). Deprotonation enhances the stability of copper-amine complexes (Jensen 1971; Hancock 1981; Hancock and Nakani 1984 and Casassas et al., 1989). The three species of copper-amine complex maintain a dynamic equilibrium in aqueous solution. The proportion of these species varies with the pH of the solution. According to Tauler and Casassas (1986), complex B is the main species when the pH of the solution is around 8.5, and complex C becomes dominant when pH is above 10.

When wood is pressure-treated with copper-amine solutions, the copper-amine complexes penetrate into the wood substrate. The depth



Monoethanolamine: $\text{R}_1 = \text{R}_2 = \text{H}$

2-Methylamino-ethanol: $\text{R}_1 = \text{H}, \text{R}_2 = \text{CH}_3$

N, N-dimethyl-ethanolamine: $\text{R}_1 = \text{R}_2 = \text{CH}_3$

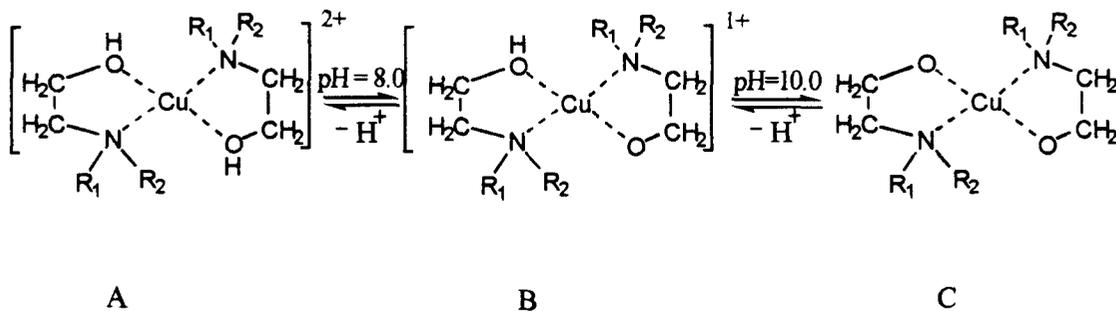


FIG. 7. Top: Amine ligands. Bottom: Copper-amine complexes.

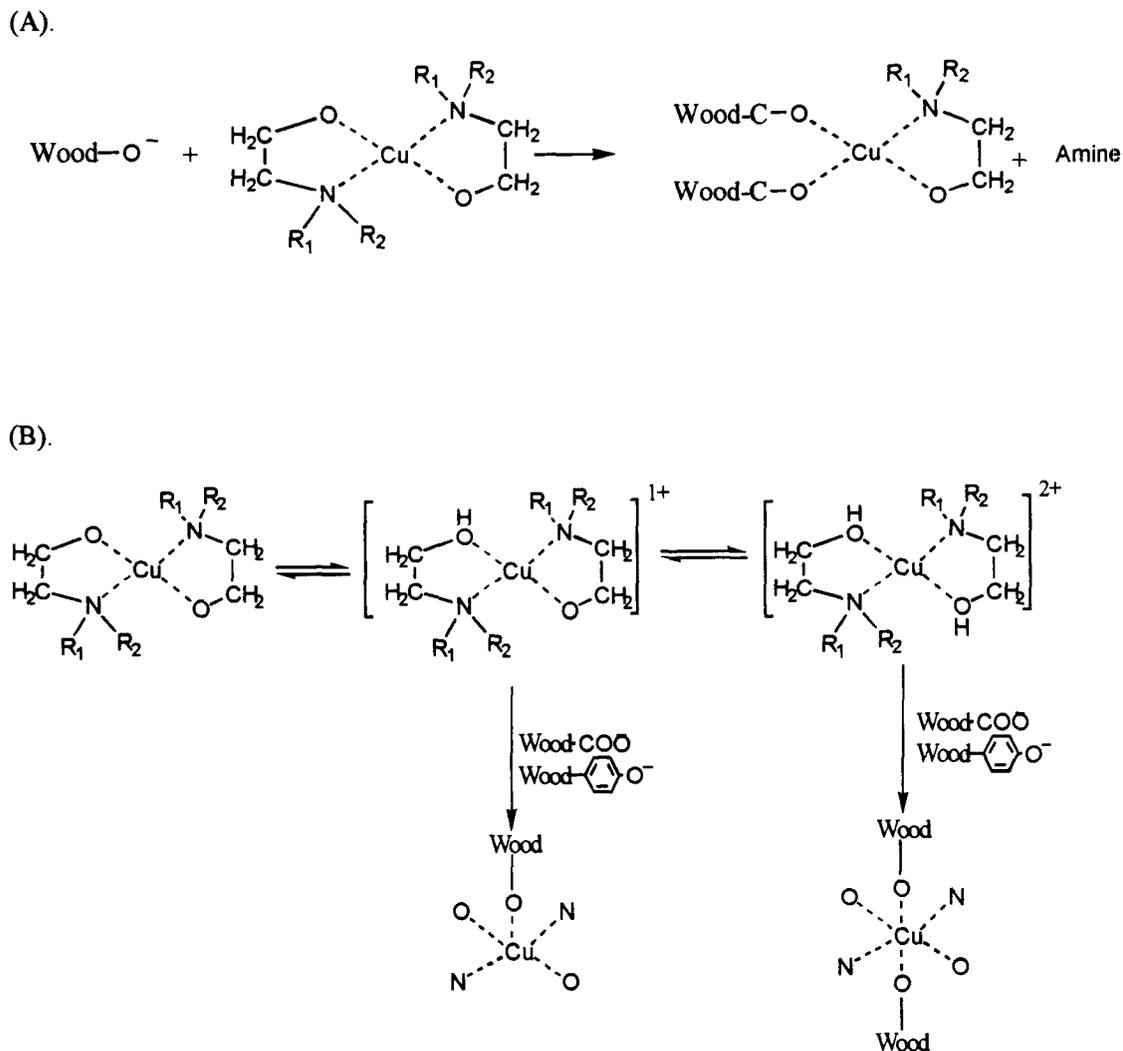


FIG. 8. Copper-amine-wood interactions. (A). Ligand exchange and (B). Complexation.

of penetration of copper into wood is related to the stability of the copper-amine complexes. A stable complex should result in deep penetration and higher absorption of copper. A less stable copper-amine complex tends to react with wood readily at the surface, which blocks further penetration of copper complexes.

If the copper-amine complex exists in wood by physical interaction, it will be leached out easily by water. To be well fixed in wood cells, the copper-amine complexes interact with wood through chemical reactions. Wood is a

weakly acidic substrate, in which functional groups, such as carboxylic groups and phenolic hydroxyl groups, are active sites for interactions with copper. Two types of reaction mechanisms, namely, ligand exchange and complexation, are proposed here. In a ligand exchange reaction mechanism, copper-amine complexes exchange ligands with wood and release one or two amine molecules (Fig. 8A). This ligand exchange mechanism is proposed because of a probable presence of the non-conducting species of copper-amine complex-

TABLE 2. *pH of copper amine treating solution made from copper hydroxide under different amine-to-copper molar ratios.**

Amine ligands	Amine-to-copper molar ratio			
	3	4	6	8
MEA	10.61	10.75	11.09	11.18
MeEA	10.68	10.82	11.20	11.34
DMeEA	10.55	10.62	10.98	11.12

* The elemental copper content in the solutions is 0.5% by weight.

es (Fig. 7C). This assumption was previously proposed by Kamdem et al. (1996) and Thomason and Pasek (1997). In the second possible reaction mechanism, noncharged species of copper-amine complexes are transformed into charged species during the treatment with wood (Fig. 8B). Functional groups, such as wood-carboxylic and wood-phenolic groups, can complex with the charged species to form a stable wood-copper-amine complex (Fig. 8B). These reactions are influenced by the stability and the pH values of copper-amine complexes. For a ligand exchange reaction, the less stable the copper-amine complex, the easier the complex disassociation will be, and therefore the reaction with wood will be driven forward. For a complexation mechanism, the lower the pH of the treating solution, the more complexes of charged species (Fig. 7A, B) will be present, and hence the interaction between wood and complex will be more likely.

The pH of the treating solution varies with the copper source (Table 1) and amine concentration (Table 2). As mentioned above, the higher the pH of the treating solution, the more stable the copper-amine complex. The complexes from copper hydroxide and copper carbonate are more stable than those from copper sulfate and copper nitrate. As a result, high retention of copper was obtained from copper hydroxide and copper carbonate. However, a stable complex resulting from high pH will not promote a good interaction between copper and wood according to the above reaction mechanism. This explains the low copper loss from copper sulfate and copper nitrate formulations.

The stability of a complex is also influenced by the amine ligand and the amine-to-copper molar ratio. A complex of copper with a primary amine is more stable than those of a secondary amine or a tertiary amine, due to the steric hindrance of methyl groups. Hancock and Nakani (1984) also pointed out that the steric effects outweigh the inductive effects when copper ion (Cu^{2+}) forms complexes with amine ligands. The high stability of a copper complex with a primary amine or with a high amine-to-copper molar ratio will lead to good penetration of the complex in wood, and hence increased retention of copper. However, the high stability is disadvantageous to the interaction between copper-amine and wood, therefore reducing copper leach resistance. Because of lower stability, a copper DMeEA complex interacts more easily with wood than a copper MEA. This explains the lower copper loss from the DMeEA system, and the high copper loss from copper MEA during the laboratory leaching tests. Increasing the molar ratio of amine-to-copper enhances the stability of the complex and increases the pH of the treating solution (Table 2), and hence improves the penetration of the complexes. At higher molar ratios, copper-amine complexes tend to exist as noncharged species and may limit the ligand exchange reaction and complexation reaction, and therefore inhibit the interaction of wood functional groups with the copper-amine complexes. This explains lower copper leach resistance at higher molar ratios of amine-to-copper.

CONCLUSIONS

The copper retention and leaching of Cu-EA-treated wood are influenced by the formulation of copper-amine complexes. A high pH formulation system results in higher copper retention in wood, but lower copper leach resistance. A higher molar ratio of amine-to-copper improved the copper penetration and the copper retention in southern pine wood. However, a high amine-to-copper ratio caused high copper loss during water leaching. At

room temperature, the pH, amine ligand, and amine to metal ratio of a copper-amine preservative can impact the retention and the penetration of copper in treated products, and the performance of copper. The biological impact of these parameters needs to be investigated.

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